Mineralogical Magazine, August 2006, Vol. 70(4), pp. 437–444

Mineralogy of stalactites formed by subaerial weathering of natrocarbonatite hornitos at Oldoinyo Lengai, Tanzania

R. H. MITCHELL*

Department of Geology, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario, Canada P7B 5E1

ABSTRACT

Stalactites formed by the chemical weathering of natrocarbonatite lava decorate the roofs of hollow inactive hornitos at Oldoinyo Lengai, Tanzania. The stalactites are composed principally of trona with lesser and very variable amounts of nahcolite, ($NaHCO_3$), thermonatrite ($Na_2CO_3.H_2O$), aphthitalite [$(K,Na)_3Na(SO_4)_2$], kogarkoite [$Na_3(SO_4)F$], schairerite [$Na_{21}(SO_4)_7F_6Cl$], halite and sylvite. Stalactites are considered to form by the evaporation of Ca-free highly alkaline brines seeping from the altered lavas which form the roofs of the hornitos. The principal subaerial weathering products of natrocarbonatite, i.e. pirsonnite, gaylussite, shortite and calcite are not found in the stalactites and are retained in the altered lavas of the homito roof. Fluorine required for the formation of kogarkoite and schairerite is derived from the decomposition of fluorite at high pH (>10). Sulphur is derived from the decomposition of gregoryite.

KEYWORDS: natrocarbonatite, Oldoinyo Lengai, stalactites, mineralogy.

Introduction

THE volcano Oldoinyo Lengai (Tanzania) is unique with respect to the eruption of natrocarbonatite lavas (Dawson, 1989). The natrocarbonatites are composed dominantly of gregoryite [$(Na,Ca,K)_2CO_3$] and nyerereite [$Na_2Ca(CO_3)_2$] phenocrysts set in a matrix of gregoryite, nyerereite, halite-sylvite, fluorite, potassian neighborite, and a Ba-Sr-Mg-Na-Cl-F-rich carbonate known as phase X (Dawson *et al.*, 1995). 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, 2006), and Mitchell and Belton (2004).

In contrast to our knowledge of the fresh natrocarbonatite lavas, there have been few studies of the mineralogy of their alteration during subaerial weathering or of the associated fumaroles (Dawson, 1993; Dawson *et al.*, 1987; Genge *et al.*, 2001; Zaitsev and Keller, 2006). One aspect of subaerial alteration that has only been recently addressed is the formation of speleothems within cave-like extinct spatter cones (hornitos). Thus, McFarlane *et al.* (2004) have described the formation of stalactites up to 3 m long forming by thermal erosion and aqueous dissolution of natrocarbonatite hornitos. The stalactites are crystalline deposits formed by dripping meteoric water and are composed principally of trona [$Na_3(CO_3)(HCO_3).2H_2O$] with lesser amounts potassium and sodium sulphates and halides. McFarlane *et al.* (2004) did not document the textural and mineralogical character of the stalactites in any detail. Mitchell (pers. comm. in McFarlane *et al.*, 2004) reported the first occurrence of kogarkoite from stalactites at Oldoinyo Lengai but did not provide compositional data. Subsequently, Zaitsev and Keller (2006) have reported the presence of accessory kogarkoite in altered natrocarbonatite lava. The objective of this work is to document the paragenesis and origin of kogarkoite, schairereite and aphthitalite occurring in Oldoinyo Lengai speleothems.

* E-mail: rmitchel@lakeheadu.ca

DOI: 10.1180/0026461067040344

Stalactite morphology and mineralogy

Typically, the roofs of the extinct hornitos within the active north crater of Oldoinyo Lengai collapse soon after cessation of magmatic activity as a result of weakening by weathering and fumarole activity. However, the roofs of some hornitos are decorated by stalactites ranging in size from a few centimetres up to 3 m long (Fig. 1). Small stalactites (1–12 cm) are more common than the longer varieties which obviously require longer periods of roof stability for their development. There is no discernable pattern to the distribution of stalactites on the roofs of the hornitos. McFarlane *et al*. (2004) concluded that the stalactites form in the same manner as other meteoric water-derived stalactites, *i.e.* by deposition of rims of crystals around a drip to form an initial straw stalactite that is subsequently thickened into a more substantial body (Moore and Nicholas, 1964).

Oldoinyo Lengai stalactites are either simple bodies (Fig. 2*a*) consisting of a single hollow core surrounded by distinct sub-concentric layers of diverse thickness (<1 mm–0.5 cm) or complex structures with multiple cores exhibiting textural evidence for multiple episodes of solution and deposition (Fig. 2*b*,*c*). The complex stalactites are considered to result from the coalescence of several small stalactites.

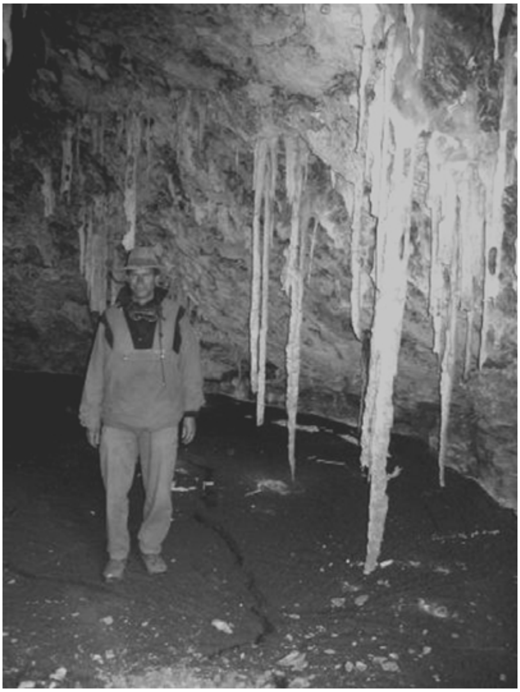

FIG. 1. Fred Belton posing with large stalactites originating from the roof of an extinct natrocarbonatite hornito. Note the absence of stalagmites.

Analytical methods

All polished thin sections of stalactites were prepared using kerosene and initially examined by standard petrographic methods and back-scattered electron (BSE) imagery. 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 spectra were processed using the LINK ISIS SEMQUANT quantitative software package with full ZAF corrections applied. The following well characterized mineral and synthetic standards were used: jadeite BM 1913-451 (Na); orthoclase (K); baryte (Ba,S); wollastonite (Ca), villiaumite (Na,F), KCl (Cl). All minerals studied were unstable in a focused electron beam and were analysed using a 20 μm × 20 μm rastered beam. Analysed areas showed no beam damage in secondary electron images.

Powder X-ray diffraction (XRD) patterns were obtained using a Philips 3710 diffractometer (Cu-$K\alpha$ radiation). Minerals present were qualitatively identified using the Bruker AXS EVA software package and the ICDD database.

Paragenesis and composition

Stalactites are very soluble in water and effervesce in 10% HCl. Powder XRD patterns of bulk stalactites indicate that they are composed principally of trona with lesser and very variable amounts nahcolite, ($NaHCO_3$), thermonatrite ($Na_2CO_3.H_2O$), aphthitalite [$(K,Na)_3Na(SO_4)_2$], kogarkoite [$Na_3(SO_4)F$], schairerite [$Na_{21}(SO_4)_7F_6Cl$], halite (NaCl) and sylvite (KCl). Petrographic study (Figs 3–5) shows that individual stalactites vary in their bulk mineralogical composition on a millimeter scale along their length and from layer to layer, thus estimation of the proportions of the phases present is not feasible or desirable. Minerals that are apparently not present include: gregoryite, nyerereite, thernardite, sulphohalite, galeite, arcanite, mirabilite, burkeite, anhydrite, gypsum, baryte, celestine, villiaumite, fluorite, sulphur and Na-Ca-phosphates. It is also notable that the common decomposition products of natrocarbonatite formed by hydration with meteoric water, i.e. pirssonite, gaylussite, shortite and calcite (Zaitsev and Keller, 2006), are also not present in the stalactites.

Figures 3–5 illustrate mineralogical modal variation transverse to the central axes of stalactites and shows that individual layers are characterized by the dominance of one or two minerals. Thus, layers can consist of Na-carbonate(s), aphthitalite, aphthitalite plus kogarkoite-schairereite, or kogarkoite-schairereite alone. The majority of the minerals form euhedral crystals which project into pore spaces (Fig. 4). In many instances the latter are filled by halides which are, on textural evidence, are the last phases of the assemblage to crystallize. Halides also commonly form distinct monomineralic layers (Fig. 5).

Individual Na carbonate minerals, which could not reliably be distinguished in terms of their composition using the EDS method employed, do not contain any other detectable (<0.3 wt.%) elements. The minerals form prismatic crystals of widely varying size and habit or massive aggregates. Comb structures, projecting into pore spaces perpendicular to the axis of the stalactite, are common (Fig. 2*a*). Na carbonates typically have crystallized after the sulphates, but in complex stalactites, deposition of subsequent generations of carbonates upon sulphates is also evident.

Aphthitalite, the most abundant of the sulphates present, occurs primarily as acicular-to-prismatic crystals of widely varying length and thickness (Figs 3–7); crystallization times can be pre- or post-kogarkoite. Table 1 indicates that the mineral is pure [$(K,Na)_3Na(SO_4)_2$].

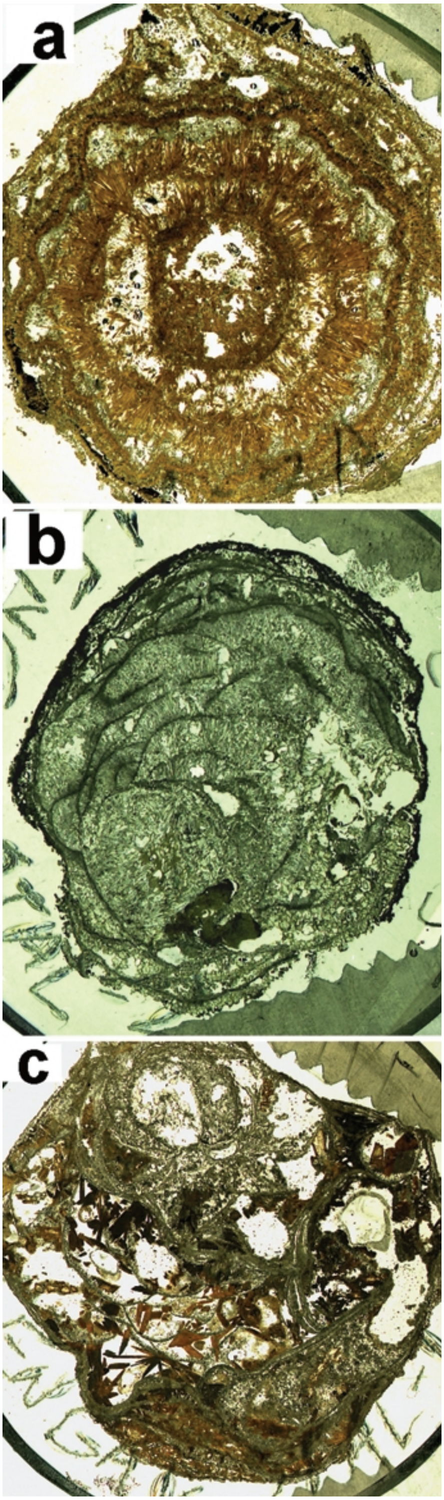

FIG. 2. (*a*) Cross-sections of 20 mm diameter single core stalactite; (*b*) 17 mm and (*c*) 22 mm diameter multiple-core stalactites. Individual growth rings and bands consist of fine-grained intergrowths of trona, nahcolite, aphthitalite, kogarkoite and schairerite. The larger brown crystals are trona (transmitted plane polarized light).

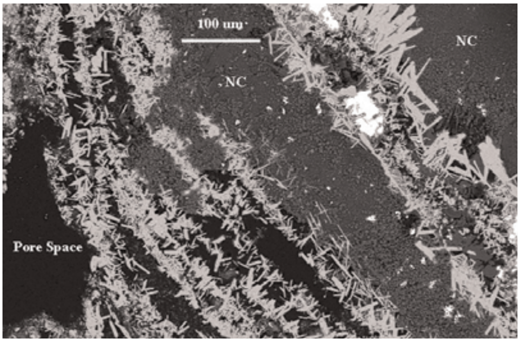

FIG. 3. BSE image of a stalactite (cut normal to the long axis) showing comb-structured bands of prismatic aphthitalite (white) and fine-grained aggregates of trona (NC).

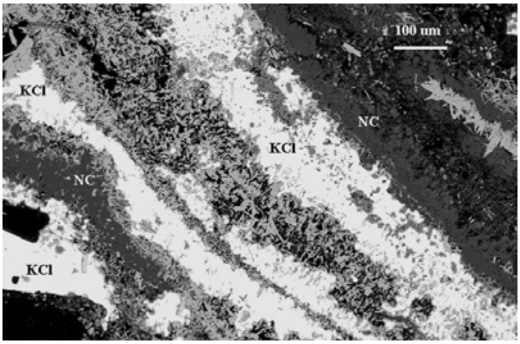

FIG. 5. BSE image of a stalactite (cut normal to the long axis) showing comb-structured bands of prismatic aphthitalite (white), bands of sylvite (KCl) and fine-grained aggregates of trona (NC).

Kogarkoite and schairereite occur as 10−60 µm euhedral single crystals (Figs 6−8). There are no obvious morphological differences between Cl-bearing and Cl-free crystals, and their habit is similar to that of synthetic [$Na_3(SO_4)F$] and natural kogarkoite from the Hortense Hot Springs described by Pabst and Sharp (1973). Crystallization times typically are prior to those of aphthitalite, sodium carbonates and halides. Compositions (Table 2) vary within and between stalactites and range from Cl-free pure kogarkoite [$Na_3(SO_4)F$] to schairerite $Na_{21}(SO_4)_7F_6Cl$ (max 3.7 wt.% Cl). Table 2 also gives the compositions of single crystals which appear to be intermediate in composition between those of kogarkoite and schairerite. Chlorine is a *bona fide* constituent of all of these minerals as none of the crystals analysed were hosted by sylvite or halite and are not intergrowths of kogarkoite and schairerite. Foote and Schairer (1930*a*,*b*), in studies of the system Na_2SO_4-NaF-NaCl-H_2O, noted that Cl can replace F in [$Na_3(SO_4)F$]. Thus, Pabst *et al.* (1963) indicated that replacement of F by Cl in [$Na_3(SO_4)F$] results in an apparent solid solution that overlaps the compositions of schairerite and galeite [$Na_{15}(SO_4)_5F_4Cl$]. However, Pabst and Sharp (1973) subsequently suggested that F in kogarkoite is not replaced by Cl and that the conclusions of Foote and Schairer (1930*a*,*b*) and Pabst *et al.* (1963) regarding solid solution of Cl

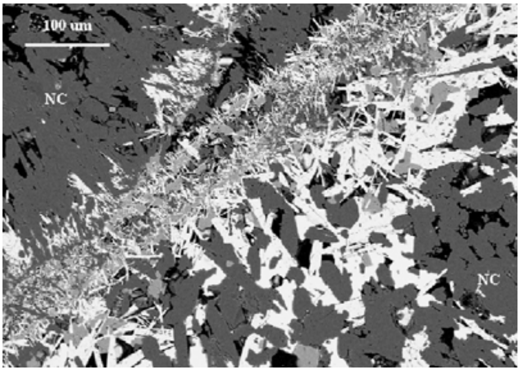

FIG. 4. BSE image of a stalactite (cut normal to the long axis) showing from upper left-to-bottom right comb-structured bands of prismatic trona (NC), fine-grained kogarkoite-schairerite (dark grey) plus aphthitalite (white), and coarse-grained intergrowth of aphthitalite (white) and trona (NC).

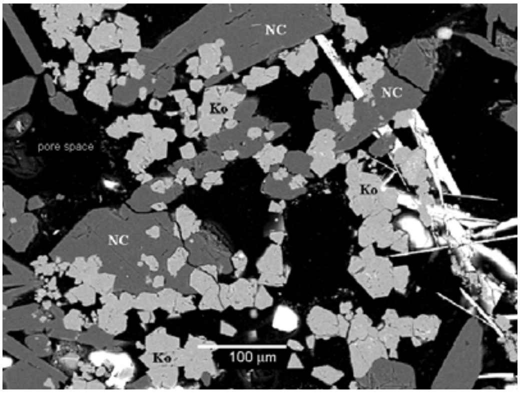

FIG. 6. BSE image of a stalactite showing prismatic trona (NC) and aphthitalite (white) together with euhedral crystals of kogarkoite-schairerite (Ko).

TABLE 1. Representative compositions of aphthitalite

Wt.%	1	2	3	4	5
Na_2O	10.39	10.69	10.97	10.63	9.32
K_2O	42.27	41.75	41.10	42.12	42.51
SO_3	47.17	48.70	48.38	47.97	48.17
F	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.83	101.14	100.45	100.72	100.00

Compositions: 1−4 aphthitalite; 5 ideal $K_3Na(SO_4)_2$
n.d. = not detected.

in kogarkoite are incorrect. That Cl-bearing kogarkoite from Oldoinyo Lengai appears to contain significant Cl apparently replacing F suggests that further work on the system Na_2SO_4-NaF-NaCl-H_2O is desirable as the original studies of Foote and Schairer (1930*a*,*b*) did not assess the effects of variations in pH or ionic strength. However, as schairerite is trigonal (*P*31*m*; Fanfani *et al.*, 1975) and kogarkoite is monoclinic pseudotrigonal ($P2_1/m$; Fanfani *et al.*, 1980), a true solid solution is unlikely to be present, and the compositional variation observed might actually represent a topotactic/polysomatic intergrowth on the unit-cell scale. Clearly, HRTEM studies of these minerals are required to resolve this question.

Sylvite and halite are typically the last minerals to form in the stalactites (Figs 7 and 8). These occur as discrete irregular aggregates of anhedral crystals filling pore spaces created by prismatic Na carbonates and aphthitalite. Sylvite is typically more abundant than halite. As expected in this low-*T* environment, both minerals have essentially pure end-member compositions with sylvite containing 0.3−0.8 wt.% Na and halite <0.3 wt.% K.

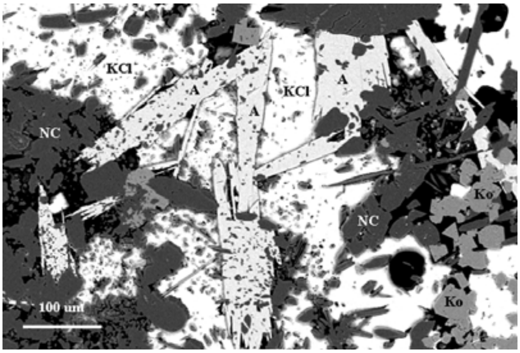

FIG. 7. BSE image of a stalactite showing prismatic trona (NC) and aphthitalite (A; white) together with euhedral crystals of kogarkoite-schairerite (Ko). Note that the interstices between the prismatic crystals of aphthitalite are filled by sylvite (KCl).

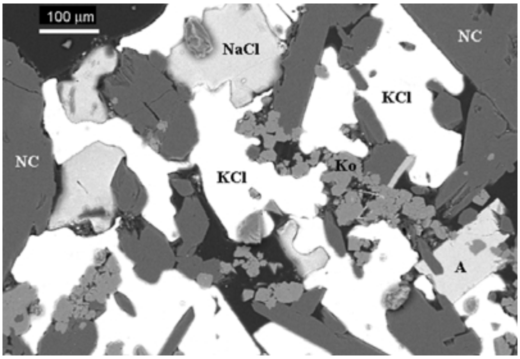

FIG. 8. BSE image of a stalactite showing prismatic trona (NC) and aphthitalite (A) together with euhedral crystals of kogarkoite-schairerite (Ko) set in a matrix of halite (NaCl) and sylvite (KCl).

Discussion

The mineralogy of the Oldoinyo Lengai stalactites is clearly different from that of their parent lavas and hence they are not endogenic lava stalactites (McFarlane *et al.*, 2004). They also differ significantly from the sub-aerial weathering products of natrocarbonatite by the absence of pirssonite, gaylussite and calcite (Zaitsev and Keller, 2006). Their mineralogy is similar to that of evaporites formed from the late crystallizing fractions of alkaline non-marine brines (Spencer, 2000), e.g. Searles Lake, Lake Magadi, Lake Natron (Spencer, 2000). Unlike many non-marine evaporites formed from such brines, gypsum and calcite are absent. The absence of gypsum implies that the solutions forming the stalactite must be an alkaline rather than a neutral or Ca-Cl brine (Spencer, 2000), and the absence of calcite reflects its low solubility in such brines.

Using the mineralogy of evaporites derived from alkaline non-marine brines as an analogy coupled with experimental studies of the solubilities of sulphates and carbonates in natural waters (Harvie *et al.*, 1984) it is possible to explain the mineralogy of the stalactites. The process begins with the alteration of natrocarbonatite by meteoric water in the roof of the hornito. As the stalactites do not contain Ca-bearing minerals, all Ca-

TABLE 2. Representative compositions (wt.%) of kogarkoite and schairerite.

	1	2	3	4	5	6	7
Na_2O	50.76	49.97	50.05	49.82	50.52	48.36	49.88
SO_3	43.35	43.65	43.12	43.24	43.50	41.64	42.95
F	10.24	8.82	8.86	8.83	10.32	4.94	8.94
Cl	n.d.	1.32	2.38	3.66	–	9.22	2.72
Total	104.35	103.76	104.41	105.55	104.34	104.16	104.49
(F=O)	4.31	3.71	3.73	3.72	4.34	2.08	3.76
(Cl=O)	–	0.30	0.54	0.83	–	2.08	0.60
Total	100.04	99.75	100.14	101.00	100.00	100.00	100.00

Compositions: 1–2 kogarkoite; 3–4 schairerite; 5 ideal $Na_3SO_4.F$; 6 ideal sulphohalite $Na_6(SO_4)_2.FCl$; 7 ideal schairerite $Na_{21}(SO_4)_7F_6Cl$.
n.d. = not detected.

bearing alteration products such pirssonite, gaylussite and calcite must be retained in these precursor roof rocks. The residual Ca-free fluids containing only highly soluble salts must separate under gravity to form droplets on the underside of the roof. Evaporation of these alkaline droplets results in the initial straw formation which acts a focus for further droplets and stalactite formation. Thus the mineralogy of the stalactite represents crystallization in the system Na-K-SO_4-Cl-F-CO_2-H_2O. The source of the Na and K are obvious as these elements are derived by the breakdown of nyerereite and gregoryite coupled with solution of halite and sylvite in the parent natrocarbonatite. The source of F is less obvious. Although fluorite is a major constituent of the groundmass of natrocarbonatite it is a relatively insoluble mineral in pure water under most sub-aerial weathering conditions, e.g. 0.22 mM kg^{-1} at pH 7 (Giguère and Campbell, 2004). However, fluorite is not stable in highly alkaline solutions and, for a pH >12.4 at any Eh, is replaced by calcite as the stable phase in the system Ca-F-CO_2-H_2O at unit molalities at 25ºC (Outokumpu HSC Chemistry, 2002). These Eh-pH conditions agree well with the thermodynamic data of Marion (2001) which indicates that trona, nahcolite and thermonatrite can crystallize at low temperatures (0–50ºC) from highly concentrated alkaline brines at a pH of 8–10. Thus, in altered natrocarbonatite, fluorite is ultimately decomposed by the alkaline brine formed by decomposition of the primary carbonates and halides into Ca^{2+} and F^- ions. The former, are reprecipitated as insoluble calcite and retained in the roof of the hornito, whereas the F^- ions concentrate in the residual alkaline brines and are available for the formation of kogarkoite and schairereite, with the sulphate ions provided by the decomposition of S-bearing gregoryite. It is also evident that some fluorine-bearing sulphate can also crystallize *in situ* in altered natrocarbonatite, as Zaitsev and Keller (2006) have noted the presence of accessory kogarkoite in such rocks.

Mineral solubility data for the system Na-K-Cl-SO_4-HCO_3-CO_3-CO_2-H_2O expressed as Jänecke diagrams (see Spencer, 2000; Harvie *et al.*, 1984; Krauskopf, 1979) show that trona, aphthitalite, sylvite and halite can all crystallize from residual fractions of alkaline brines. Innumerable crystallization paths are possible depending upon the bulk composition and HCO_3^-/SO_4^{2-} ratio of the brine. For example, formation of aphthitalite could be followed by trona plus aphthitalite and subsequently by trona plus aphthitalite plus sylvite and halite; a sequence similar to that observed for the stalactite minerals. However, the petrography of the stalactites indicates that the mineral assemblages observed are not equilibrium assemblages and thus Jänecke diagrams can only provide a qualitative description of the crystallization sequences and mineral assemblages to be expected upon evaporation of the stalactite-forming brine. Unfortunately, there are no thermodynamic or solubility data for F-bearing sulphates and their stability fields in Jänecke diagrams cannot be predicted.

Summary

The mineralogy of speleothems decorating the roofs of hornitos at Oldoinyo Lengai represents the crystallization by evaporation of a residual, highly alkaline brine formed by alteration of natrocarbonatite under sub-aerial weathering conditions. Most of the products of alteration of these lavas are retained in the roof of the hornito as insoluble pirssonite, gaylussite, shortite and calcite (Zaitsev and Keller, 2006). Highly soluble components such as Na, K, Cl and F are concentrated as residual brines which percolate to the underside of the hornito roof and upon evaporation form stalactites. Further studies of the genesis of these unusual stalactites requires collection of the stalactite-forming brines to determine their composition, Eh and pH, in conjunction with experimental studies of their crystallization.

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. Fred Belton is thanked for the photograph used as Fig. 1. Constructive reviews of the original version of this paper by A.G. Christy and J. Keller are appreciated. 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.

References

Church, A.A. and Jones, A.P. (1995) Silicate-carbonatite immiscibility at Oldoinyo Lengai. *Journal of Petrology*, **36**, 869−889.

Dawson, J.B. (1989) Sodium carbonatite extrusions from Oldoinyo Lengai, Tanzania: implications for carbonatite complex genesis. Pp. 255−277 in: *Carbonatites: Genesis and Evolution* (K.Bell, editor). Unwin Hyman, London.

Dawson, J.B. (1993) A supposed sövite from Oldoinyo Lengai: a result of extreme alteration of alkali carbonatite lava. *Mineralogical Magazine*, **57**, 93−101.

Dawson, J.B., Garson, M.S. and Roberts, B. (1987) Altered former alkalic carbonatite lava from Oldoinyo Lengai, Tanzania: inferences for calcite carbonatite lavas. *Geology*, **15**, 765−768.

Dawson, J.B., Pinkerton, H., Norton, G.E., Pyle, D.M., Browning, P., Jackson, D. and Fallick, A.E. (1995) Petrology and geochemistry of Oldoinyo Lengai lavas extruded in November 1988: magma source, ascent and crystallization. Pp. 47−69 in: *Carbonatite Volcanism* (K. Bell and J. Keller, editors). Springer-Verlag, Berlin.

Dawson, J.B., Pyle, D.M. and Pinkerton, H. (1996) Evolution of natrocarbonatite from a wollastonite nephelinite parent: evidence from the June 1993 eruption of Oldoinyo Lengai, Tanzania. *Journal of Geology*, **104**, 41−54.

Fanfani, L., Nunzi, A., Zanazzi, P.F., Zanazri, A.R. and Sabelli, C. (1975) The crystal structure of schairerite and its relationship to sulphohalite. *Mineralogical Magazine*, **40**, 131−139.

Fanfani, L., Giuseppetti, G., Tadini, C. and Zanazzi, P.F. (1980) The crystal structure of kogarkoite Na_3SO_4F. *Mineralogical Magazine*, **43**, 753−759.

Foote, H.W. and Schairer, J.F. (1930*a*) The system Na_2SO_4-NaF-NaCl-H_2O. I. The ternary systems with water and two salts. *Journal of the American Chemical Society*, **52**, 4202−4209.

Foote, H.W. and Schairer, J.F. (1930*b*) The system Na_2SO_4-NaF-NaCl-H_2O. II. The quaternary system at 25 and 35º. *Journal of the American Chemical Society*, **52**, 4210−4217.

Genge, M.J., Balme, M. And Jones, A.P. (2001) Salt-bearing fumarole deposits in the summit crater of Oldoinyo Lengai, northern Tanzania: interaction between natrocarbonatite lava and meteoric water. *Journal of Volcanology and Geothermal Research*, **106**, 111−122.

Giguère, A. and Campbell, P.G.C. (2004) Fluoride toxicity towards freshwater organisms and hardness effects − new review and reanalysis of existing data. *Revue Science Eau*, **17**, 373−393.

Harvie, C.E., Møller, N. and Weare, J. (1984) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25ºC. *Geochimica et Cosmochimica Acta*, **48**, 723−751.

Keller, J. and Krafft, M. (1990) Effusive natrocarbonatite activity at Oldoinyo Lengai, June 1988. *Bulletin Volcanologie*, **52**, 629−645.

Krauskopf, K.B. (1979) *Introduction to Geochemistry*. McGraw-Hill Book Company, New York.

Marion, G.M. (2001) Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system. *Geochimica et Cosmochimica Acta*, **65**, 1883−1896.

McFarlane, D.A., Lundberg, J. And Belton, F. (2004) An unusual lava cave from Oldoinyo Lengai, Tanzania. *Journal of Cave and Karst Studies*, **66**, 98−101.

Mitchell, R.H. (1997) Carbonate-carbonate immiscibility, neighborite and potassium iron sulphide in Oldoinyo Lengai natrocarbonatite. *Mineralogical Magazine*, **61**, 779−789.

Mitchell, R.H. (2006) Sylvite and fluorite microcrysts and fluorite-nyerereite intergrowths from natrocarbonatite, Oldoinyo Lengai, Tanzania. *Mineralogical Magazine*, **70**, 103–114.

Mitchell, R.H. and Belton, F. (2004) Niocalite-cuspidine solid solution and manganoan monticellite from natrocarbonatite, Oldoinyo Lengai, Tanzania. *Mineralogical Magazine*, **68**, 787–799.

Moore, J.G. and Nicholas, G. (1964) *Speleology – The Study of Caves*. D.C. Heath, Boston, USA.

Outokumpu HSC Chemistry (2002) *Outokumpu HSC Chemistry for Windows v. 5.0*. Outokumpu Research Oy, Pori, Finland.

Pabst, A. and Sharp, W.N. (1973) Kogarkoite, a new natural phase in the system Na_2SO_4-NaF-NaCl. *American Mineralogist*, **58**, 116–127.

Pabst, A., Sawyer, D.L. and Switzer, G. (1963) Galeite and related phases in the system Na_2SO_4-NaF-NaCl. *American Mineralogist*, **48**, 485–510.

Peterson, T.D. (1990) Petrology and genesis of natrocarbonatite. *Contributions to Mineralogy and Petrology*, **105**, 143–155.

Spencer, R.J. (2000) Sulphate minerals in evaporite deposits. Pp. 173–192 in: *Sulfate Minerals* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy & Geochemistry, **40**, Mineralogical Society of America and the Geochemical Society, Washington, D.C.

Zaitsev, A.N. and Keller, J. (2006) Mineralogical and chemical transformations of Oldoinyo Lengai natrocarbonatites, Tanzania. *Lithos*, in press.

[*Manuscript received 22 February 2006:*
revised 25 September 2006]