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The origin of melanophlogite, a clathrate mineral, in natrocarbonatite lava at Oldoinyo Lengai, Tanzania.

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Abstract

We report new observations of a clathrate mineral, melanophlogite ($46SiO_2 \cdot 6(N_2,CO_2) \cdot 2(CH_4,N_2)$), as part of a tuffaceous layer within a sample of the 2006 natrocarbonatite lava, whose composition reflects the typical magma erupted passively at Oldoinyo Lengai throughout the last ~50 years. The mineral has been identified by chemical composition, micro X-ray diffraction and transmitted light optical characteristics. This is the first reported occurrence of a clathrate in an igneous carbonatite, and we conjecture that this mineral may be recognized elsewhere in alteration products of natrocarbonatite ash and in particular, combeite-bearing carbonatite lithologies. Specifically, melanophlogite is a rare polymorph of SiO_2 with guest molecules (e.g. CH_4, CO_2, SO_2, N_2, OH, Xe, and Kr) within a silicate framework. It occurs in an ash pellet-rich layer within the natrocarbonatite lava, as abundant groundmass crystals and as cores of individual ash pellets, with pseudocubic and pseudohexagonal habits, ranging from 50 to 100 μm in size, with numerous inclusions of nepheline laths aligned parallel to the crystal margins. It has high C contents (up to 2.25 wt.%) and CO_2 is considered to be the guest molecule due to crystallisation within an alkaline carbonatitic-CO_2-rich environment.

Keywords: Oldoinyo Lengai, melanophlogite, natrocarbonatite, combeite

Introduction

Oldoinyo Lengai (OL), situated in the Eastern Africa Rift Valley in NW Tanzania (Fig.1a), is the world's only active carbonatite volcano, forming a steep-sided stratocone rising to an altitude of 2960 m. Although OL is well-known for its unique natrocarbonatite lavas which have characterized activity since at least 1966, it is predominantly composed of nephelinitic and phonolitic lavas and pyroclastic deposits (Dawson, 1962, 1989, 1998). In this paper, we report the first occurrence of melanophlogite pseudomorphs after combeite, identified by electron microprobe (EMP) and confirmed by micro-Xray diffraction, from an ash pellet-rich layer within the March - April 2006 lava flows that occurred on the western flanks of OL. Melanophlogite is a very rare tetragonal (pseudocubic) polymorph of SiO_2 with structure-stabilising guest molecules (e.g. CH_4, CO_2, SO_2, N_2, OH, Xe, Kr) trapped within a clathrate-type silicate framework. This occurrence of melanophlogite is the first from Africa and the first from a carbonatite. The presence of broken melanophlogite pseudomorphs after combeite crystals requires that these pseudomorphs formed before the ash pellets were deposited. We present compositional and textural information in an attempt to understand its origin and significance at OL.

Sample location

The largest natrocarbonatite lava flow reported from OL occurred from March 25th and continued until April 5th 2006. The first effusive eruption on March 25th 2006 was associated with hornito collapse, overfilling of the summit crater, and emplacement of a 3 km long lava flow on the western flank (Kervyn et al., 2008). The lava tongue was initially confined to a deeply incised erosional gully, 15 - 20 m wide, before coming to a halt on the rift floor at an altitude of 1500 m and forming a distal lobe 150 m wide (Fig. 1b). A second effusive event occurred on April 3rd 2006, producing a flow passing through the same mid-slope gully on top of the cooled earlier lava flow (Kervyn et al., 2008). Flow morphologies are highly variable, changing considerably over a few meters, including scoriaceous, rubbly pahoehoe and blocky aa-type surfaces (Kervyn et al., 2008). The volume of lava produced during this eruptive event has been estimated at 9.2 ($\pm$3.0) x 10^5 m^3. During the period between the eruptions OL was continuously active, producing a large ash plume with ash fall observed over a wide area. In September 2007, three samples (OLD1-3) from the 2006 flows were collected from an altitude of 1850 m (Latitude 2°45'35"S; Longitude 35°53'43"E), by Mr. Colin Church.

Analytical Methods

A concentrated separate of melanophlogite crystals from the ash pellet layer was obtained by lightly crushing a subsample in a steel piston and sieving the crushed material into >850, 450 and <450μm fractions. As melanophlogite does not react readily with dilute acid, the <450 μm fraction was washed in 10% HCl to remove carbonate and to concentrate the sample. It was then rinsed with distilled water to remove acid residues and dried under heat lamps. The acid-washed material was then subdivided using 250 and 63μm sieves. The melanophlogite crystals were mostly in the concentrated >63μm fraction and were then handpicked using fine acupuncture needles and prepared as polished grain mounts for SEM, EMPA and micro-Xray diffraction analysis.

Major element mineral analyses were obtained using a Jeol JXA8100 Superprobe (WDS) and an Oxford Instruments INCA system (EDS) at UCL/Birkbeck. Analysis was carried out using an accelerating voltage of 15 kV, current of 2.5 x 10^{-8}A and a beam diameter of 1μm. The counting times were 20s on the peak and 10s each on the high and low backgrounds. Analyses were calibrated against standards of natural silicates, oxides and Spec-pure metals with the data corrected using a ZAF program. Carbon was calibrated against a synthetic moissanite (SiC) standard, using a counting time of 10s on the peak and 5s each on the high and low backgrounds and a beam diameter of 5μm. Elemental line-scans across individual melanophogite grains were obtained using an accelerating voltage of 15 kV with an acquisition time of 240s and a beam current of 1 x 10^{-8} A with a diameter of 1μm. Although, samples were carbon coated to provide electric conductivity, it was assumed the contribution of the carbon coating would be the same for across the whole surface.

Petrology of lavas

In hand specimen, lava samples OLD1 and OLD2 are light-grey, fine- to medium-grained and slightly vesiculated. Sample OLD3 is dark-grey, fine- to medium-grained with pahoehoe-like flow features on its uppermost surface and contains a conspicuous layer (1-2 cms thick) of abundant well-rounded ash pellets up to 1-2 mm in diameter (Fig. 2) similar in size and appearance to ash erupted during September 2007 (Mitchell and Dawson, 2007; Mattsson and Reusser, 2010). Previous studies of natrocarbonatite lavas have reported rounded fine-grained silicate aggregates mantling a single silicate crystal referred to as “silicate spheroids” (Kervyn et al., 2008; Mattsson and Vuorinen, 2009). They have been considered as evidence of silicate-carbonate immiscibility (Dawson et al., 1994; Church and Jones, 1995). In this study such rounded structures in sample OLD3 are referred to as “ash pellets” and “cored ash

pellets", according to the classification scheme of ash particles and accretionary lapilli proposed by Brown et al. (2010), while those in the natrocarbonatite lava samples OLD1 and OLD2 are referred to as "silicate spheroids". A polished thin section was prepared through the ash layer of OLD3. Petrographical textures of samples OLD1 and OLD2 agree with published descriptions of the same lava flow (Kervyn et al., 2008; Mattsson and Vuorinen, 2009). It is aphyric with a well-developed trachytic texture defined by subparallel alignment of microphenocrysts of nyerereite ($(Na_2Ca(CO_3)_2)$) and rounded subhedral gregoryite $(Na_2,K_2,Ca)CO_3)$, up to 2- 4 mm in diameter. The gregoryite microphenocrysts are zoned with cores containing numerous rounded inclusions of nyerereite, surrounded by clear inclusion-free rims. The interstitial groundmass consists of fine-grained nyerereite and gregoryite in close association with a skeletal network of fluorite, manganoan magnetite, galena, barite, manganoan monticellite, alabandite (MnS), REE-silica-rich-apatite, strontian witherite, rare gold and an unnamed Ba-V-Sr O-rich mineral phase. Isolated single subhedral-to-euhedral crystals of diopside, nepheline, wollastonite and rounded cored silicate spheroids (up to 2mm in diameter) are also found within the natrocarbonatite (Fig. 3). No evidence of interaction between natrocarbonatite and the silicate matrix of the ash pellets was observed. The silicate spheroids consist of single subhedral-euhedral crystal cores of nepheline, wollastonite, diopside and rare sodalite, mantled by a fine-grained aggregate of nepheline, combeite, diopside, melilite, wollastonite, titanian garnet (andradite-schorlomite) and titanian magnetite in a groundmass of Sr-rich calcite. Significantly, the combeite grains in the fine-grained aggregate of the silicate spheroid, have rectangular and hexagonal outlines, reach 100 μm in diameter and contain inclusions of nepheline laths. Combeite is also present as well-developed replacement rims around wollastonite and clinopyroxene crystal cores (Fig. 4).

The ash pellet layer in sample OLD3 is free of nyerereite and gregoryite but is dominated by abundant rounded ash pellets, cored ash pellets and silicate phenocrysts, ranging in size from 3 to 0.5 mm. The phenocrysts are subhedral - euhedral and consist of nepheline, wollastonite, melilite, titanian garnet, clinopyroxene and rare titanite. The ash pellets consist of single euhedral-subhedral crystal cores of nepheline, wollastonite, melilite and melanophlogite after combeite, mantled by finer-grained nepheline, melilite, wollastonite, clinopyroxene, titanian garnet and titanian magnetite in a matrix of Sr-bearing calcite. Similar composite crystal aggregates also occur as thin mantles around larger phenocrysts. Fluorapatite, titanian magnetite, barite, galena and Sr-rich calcite are common as groundmass phases. However, unlike the silicate spheroids in the lava samples, combeite is absent and appears to have been

replaced by melanophlogite, which occur as single pseudocubic crystal cores of the ash pellets and as abundant single pseudocubic and pseudohexagonal crystals within the fine-grained groundmass (Fig. 5). The phenocryst assemblage of nepheline, titanian garnet, melilite and wollastonite indicates that the ash pellet layer was derived from a melilite-bearing combeite-wollastonite-nephelinite magma (CWM) consistent with the description of Kervyn et al. (2008).

Mineral chemistry

Lava flow samples (OLD1 and OLD2)

Electron microprobe analyses of selected mineral phases from the lava flow samples (OLD1 and OLD2) and from the ash pellet layer (OLD3) are given in Tables 1 and 2, respectively.

Both alkali carbonates, nyerereite and gregoryite, are characterised by high Na_2O contents (ca. 23.5 wt.% and 44 wt.%, respectively) and relatively high contents of various minor elements. The nyerereite has high K_2O (6.7 - 7 wt.%) and CaO (ca. 24.8 wt.%), with subordinate SrO (2.1 - 2.3 wt.%), BaO (0.5 - 0.6 wt.%), SO_3 (1.0- 1.5 wt.%), P_2O_5 (0.37 - 0.63 wt.%) and Cl (0.16 wt.%). The gregoryite has high K_2O (2.0 - 2.4 wt.%), P_2O_5 (3.8 - 4 wt.%) and CaO (6.3 - 6.8 wt.%) contents, with subordinate amounts of SrO (1.1 - 1.3 wt.%), BaO (ca. 0.2 wt.%), SO_3 (3.7 – 4.0 wt.%) and Cl (0.14 - 0.18 wt.%). These compositions are identical to those reported in previous studies from OL natrocarbonatite (Keller and Krafft, 1990; Zaitsev et al., 2009). Manganoan monticellite occurs as very small subhedral grains (5 - 25 μm in diameter) finely dispersed within the groundmass of the lava flow samples. It contains relatively high MnO (ca. 11.5 wt.%) and has been reported from other recent natrocarbonatite lavas (Mitchell and Belton, 2004; Church and Jones, 1995). Magnetite occurs as an abundant interstitial groundmass phase containing significant amounts of MnO (12 - 13 wt.%) with subordinate amounts of TiO_2 (1.3 wt. %). An unknown Ba-V oxide occurs as an interstitial groundmass phase associated with manganoan monticellite, nepheline and apatite needles, forming subhedral-euhedral diamond-shaped crystals, up to 10-15 μm in length. It has very high BaO and V_2O_5 contents (63 wt.% and 21 wt.%, respectively) with minor SrO (3.3 wt.%), CaO (2.5 wt.%), Na_2O (1.8 wt.%) and MgO (0.87 wt.%). The presence of this Ba-V-oxide finely dispersed in the natrocarbonatite samples, is consistent with elevated whole-rock Ba and V contents obtained from effusive lavas flows from the OL summit crater during continuous activity in 1988 (Keller and Krafft, 1990). Nepheline, wollastonite, garnet, melilite and clinopyroxene occur in the cores and mantles of the silicate spheroids within the natrocarbonatite lava. They have compositions identical to those present

in the ash pellet layer sample (OLD3). Combeite was only observed in the fine-grained mantle around cored ash pellets, where it forms pseudocubic and rarer pseudohexagonal euhedral crystals, and also occurs as replacement rims around wollastonite and clinopyroxene crystal cores. Combeite is essentially a Na and Ca silicate with minor Fe, Mn and Mg contents. The Na/(Na+Ca) ratio (0.54) reveals that the combeite replacement rims have excess Na compared to the ideal value (0.50) for combeite ($Na_2Ca_2Si_3O_9$). Such excess Na is consistent with other combeite reported from silicate lavas/ash from Oldoinyo Lengai and has been attributed to crystallization from a Na_2CO_3-rich magma (Dawson, 1989). A single crystal of sodalite found in the core of a silicate spheroid, contains significant FeO (~3.2 wt.%) and K_2O (~3.5 wt.%) comparable to sodalite reported in nephelinite lava from OL (Dawson and Hill, 1998; Peterson, 1989). Titanian magnetite (7 - 8 wt. % TiO_2; 1 - 2 wt.% MnO) occurs as an abundant phase in the fine-grained silicate mantle around single crystal cores.

Ash pellet layer (OLD3)

Nepheline in the ash pellet layer has variable FeO (0.6 - 1.5 wt. %) and Na(Na/K) = 0.77 - 0.79, similar to nepheline from peralkaline nephelinite at OL (Dawson, 1998) and to the September 2007 ash eruption (Mitchell and Dawson, 2007). The garnet has variable TiO_2 (10.8 - 16.1 wt. %) and FeO (20.3 - 23.6 wt. %) with a compositional range from titanian andradite to schorlomite, comparable to garnet from older nephelinite lavas (Dawson, 1998). Clinopyroxene occurs as subhedral to euhedral phenocrysts displaying reverse zoning with rounded, partially corroded green hedenbergitic cores with high FeO (14.8 - 16.9 wt.%) and low MgO (6.5 - 8.5 wt.%) mantled by colourless diopsidic rims (8.8 - 12.2 wt.% FeO; (9.4 - 12.8 wt. % MgO) . Such zoned clinopyroxene is seen in older OL lavas including olivine melilitites (Keller et al., 2006) phonolites and nephelinites (Dawson et al., 1994; Dawson, 1998) and has been attributed to magma chamber convection and new magma injection (Dawson 1998). Melilite exhibits a narrow compositional range, with high Na_2O (5.2 - 5.4 wt. %), Al_2O_3 (5.6 - 7.1 wt.%) and FeO (7.4 - 9.6 wt.%) and subordinate MgO (3.9 - 4.7 wt. %). This melilite composition is remarkably similar to alumoåkermanite, a new mineral member of the melilite group, proposed by Wiedenmann et al. (2009). Wollastonite contains very low FeO (≈ 1 wt.%) and MnO (≈ 0.2 wt.%) similar to compositions in OL peralkaline nephelinite lavas (Dawson, 1998) and in the September 2007 ash eruption (Mitchell and Dawson, 2007). The titanian magnetite has similar composition to that in the fine-grained ash pellets in lava samples, having high TiO_2 content (ca. 8 - 9 wt/%) and lower MnO (ca. 1

wt.%).

The melanophlogite occurs as abundant single isolated groundmass crystals and as cores of individual ash pellets in the ash-rich layer in sample OLD3 (Figs. 5 and 6). The concentrated fractions of melanophlogite have predominant pseudocubic and subordinate pseudohexagonal habits (Fig.7), ranging from 50 to 100 μm in size. In thin-section, the melanophlogite is colourless in plane-polarised light, and isotropic in crossed polars. Backscattered imaging reveals numerous inclusions of nepheline laths and rarer inclusions of melilite needles and euhedral-subhedral titanian magnetite. The nepheline is predominately euhedral, up to 10 μm in length, with the C-axis preferentially orientated parallel to the melanophlogite crystal boundaries (Fig. 8). The melanophlogite displays a well-developed concentric compositional zonation usually with the outer marginal zones appearing darker in backscattered mode due to a higher concentration of the carbon-bearing guest molecule in the melanophlogite structure (Fig. 8). However, occasionally some melanophlogite crystals have intermediate growth zones with higher concentrations of the carbon-bearing guest molecule. High resolution elemental X-ray mapping of individual melanophlogite crystals reveals that the zoning corresponds to zones of carbon enrichment, especially towards the crystal margins (Fig.9). A high resolution line-scan across a zoned melanophlogite (Fig.10) confirms that carbon content increases while silica and oxygen contents decrease. A line-scan of chlorine was included to act as a control to ensure that any increase in carbon content was not due to a contribution from the carbon/chlorine based epoxy resin (Fig.10). Electron microprobe analysis of the melanophlogite reveals major Si (42 wt.%), O (56 wt.%) and C (3 wt.%) (Table 3). This melanophlogite structure was confirmed by micro X-ray diffraction at the Natural History Museum, London. The presence of minor Ca, Al, Na and K in some crystals is attributed to the presence of nepheline micro-inclusions.

Worldwide occurrence of melanophlogite

Melanophlogite (ideal formula $46SiO_2 \cdot 6(N_2,CO_2) \cdot 2(CH_4,N_2)$) is a rare tetragonal (pseudocubic) polymorph of SiO_2 with guest molecules (e.g. CH_4, CO_2, SO_2, N_2, Xe, Kr, OH) entrained within a clathrate-type silicate framework (Skinner and Appleman, 1963). It has been reported in only nine locations worldwide, being first described by Von Lasaulx (1876) from sulphur deposits in Racalmuto and Lercara, near Palermo, (Sicily). Subsequent occurrences include: Chvaletice, (Czech Republic) from metamorphosed Fe-rich rhodochrosite layers (Zak, 1967, 1972), Korozluky (Czech Republic) from fissures in tertiary

volcanic rocks (Filippi, 2002), Fortullino, (Tuscany, Italy) from a serpentinite breccia (Grassellini and Orlandi, 1972), Mount Hamilton, (Santa Clara County, California) from metamorphosed serpentine veins cutting sedimentary rocks (Cooper and Dunning, 1972), Clear Creek (San Benito County, California) from a former mercury mine (Dunning and Cooper, 2002), Lombard, (Napa Country, California) from a disused dolomite quarry (Dunning and Cooper, 2002), Tsekur-Koyash, (Ukraine) from sulphur deposits (Kopasheva and Makarov, 1975) and Parma, (Northern Appennines, Italy) from interbedded marls and volcaniclastic sediments (Adorni and Tateo, 2004 and Adorni et al., 2007). Also a report of a dredged melanophlogite-bearing pebble recovered offshore from the Oregon Coast, Pacific Ocean, from a depth of 700 m, near a methane-rich vent (Kohler et al., 1999).

Melanophlogite from Sicily and Ukraine are dominated by sulphur with minor amounts of CO_2 and OH guest molecules, consistent with association with local sulphur deposits. In contrast, that from California, from the Northern Appennines and from the Czech Republic have a mixture of CO_2 and OH guest molecules, due to the association with local carbonate-rich country rocks (Table 3). The dredged melanophlogite-bearing pebble is reported to have CH_4 as the resident guest molecule attributed to proximity to a deep-sea methane-rich fluid producing vent (Kohler et al., 1999).

Discussion

Melanophlogite in the 2006 lava flow at OL is only the tenth reported worldwide, the first from Africa and the first to be recognised as replacement after combeite in natrocarbonatite. Although the presence of a guest carbon-rich molecule in the melanophlogite framework structure was indicated by EMPA, we have not unambiguously confirmed its true molecular nature. Nonetheless, the nature of the carbon-rich guest molecule is assumed to be CO_2, by comparison with CO_2 in melanophlogite from other locations (Zak, 1972; Cooper and Dunning, 1972). In other words the melanophlogite in OL ash pellets is deemed to have significant CO_2 content (calculated 2.25 wt.% CO_2) which we attribute to crystallisation within a carbonatite-rich environment, where CO_2 is expected to be freely available (Table 3).

Pseudomorphs after combeite

Fresh combeite was observed only within silicate spheroids in natrocarbonatite lava samples (OLD1 and OLD2), where combeite crystals share distinctive textural similarity to

melanophlogite. In specimen OLD3, they have pseudocubic and pseudohexagonal outlines, an identical size range 80-100 μm and contain numerous inclusions of nepheline laths. The associated mineralogy from silicate spheroids is also identical to the mineralogy of the ash sample (OLD3) which strongly suggests that they were both derived from very similar alkali-silicate magmas. We therefore interpret melanophlogite as a pseudomorph after combeite which is inferred to have been formerly present in the ash (OLD3). In detail, the presence of broken melanophlogite crystals (Fig. 5) requires that this alteration process occurred before the incorporation of the ash layer by 2006 lava.

Misidentification of melanophologite in previous studies.

This study documents the first occurrence of melanophlogite from Oldoinyo Lengai. However, close reinspection of the literature suggests that melanophlogite may previously have been observed but not recognized, or misidentified. Hay (1989) reported an initially unidentified Na-Ca silicate mineral from the Laetoli Footprint Tuff and the nephelinite-carbonatite ash erupted in 1966, which was subsequently indentified as combeite. Significantly, we note that some published combeite has been described as cubic and hexagonal grains, up to 100μm in size, with low birefringence, concentric zoning parallel to crystal faces and containing numerous inclusions of nepheline laths (Hay, 1989). This textural description is very similar to melanophlogite in the ash pellet layer from OLD3. However, Hay (1989) also observed that some of the combeite in both the Laetoli Footprint Tuff and the 1966 ash was partly or wholly altered to an unknown mineral phase with a composition similar to "opal". We conjecture that some of the alteration products observed in Hay's (1989) study are combeite partially pseudomorphed by melanophlogite. A second example was apparently reported by Dawson (1998) in wollastonite nephelinite lavas extruded from OL in 1993. A euhedral zoned combeite phenocryst, 100μm in size, with numerous inclusions of nepheline laths, was described with partial replacement by an unidentified alteration product enriched in Si (SiO_2 79 wt.%), depleted in Ca and Na and with low analytical totals (Table 3). Dawson (1998) conjectured that the low totals for this alteration product may be due to unanalyzed elements like O, H or C. Again the low total, analysed composition and textural description is remarkably similar to microprobe analyses of melanophlogite reported in our study. A photomicrograph of the partially replaced combeite phenocryst in Dawson's 1998 paper appears to confirm the similarity to melanophlogite. Dawson (1998) also noted that the alteration of combeite enhanced symmetrical and concentric zoning, referring to the process of "skeletonization" proposed by

Bailey (1941) whereby the original crystals have been selectively leached of Ca, K and Na, without destroying the internal silica framework of the crystals. It seems likely that this "skeletonization" process refers to the secondary replacement of combeite by melanophlogite. The process of "skeletonization" could be attributed to be the secondary reaction replacing combeite with melanophlogite in the ash pellet layer. In this process, Ca, Na and K are selectively removed by leaching, from combeite, accompanied by increase in Si content. Bailey (1941) suggested that this process of "skeletonization" could be achieved by the presence of a leaching agent such as a weak acid.

Within the ash pellet-rich layer in sample OLD3, any combeite grains have been replaced by melanophlogite, suggesting that the alteration process occurred before the ash pellets were deposited on the lava surface. This is consistent with the recognition of broken melanophlogite grains occasionally present as cores of ash pellets indicating that pre-existing combeite pseudomorphs were entrained in the eruption prior to deposition of the ash layer. However, contemporaneous silicate spheroids within the natrocarbonatite, retain fresh combeite both as microphenocrysts and as replacement rims around clinopyroxene, indicating that combeite was only locally replaced by melanophlogite, and may instead constitute reworking of previous volcanic lithic materials.

Conclusions

We have documented the clathrate mineral melanophlogite as part of a tuffaceous layer within a sample of 2006 natrocarbonatite lava, whose composition reflects the "normal" magma type erupted nearly continuously at OL throughout the last ~50 years. The mineral has been characterised by chemical composition, transmitted light optical characteristics and *in-situ* micro X-ray diffraction. This is the first reported occurrence of a clathrate in a carbonatite, and is locally common. We conjecture that earlier descriptions refer to the same mineral in other carbonatite products from OL, and in regional descriptions of carbonatitic ash from the East African Rift. Therefore we can expect the occurrence of this mineral to be recognized elsewhere in alteration products of natrocarbonatite ash and in particular, combeite-bearing carbonatite lithologies. Future experiments to delineate the P-T stability of this clathrate could provide important constraints on the petrogenesis of natrocarbonatite, and add to the growing complexity of mineral pathways involved in rapid chemical weathering and distribution of alkaline salts in N Tanzania related to Lake Natron (Genge et al. 2001).

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List of Figures

Figure. 1. Schematic maps showing the a) location of Oldoinyo Lengai within the East African Rift, Northern Tanzania. b) sample location on the main lava flow on the western flank of Oldoinyo Lengai (modified from Kervyn et al., 2008).

Figure 2. The ash pellet-rich layer in sample OLD3 consisting of well-rounded ash pellets, up to 1mm in diameter, deposited on a upper surface a cooled lava flow and subsequently covered by a later lava flow.

Figure 3. Backscattered electron image (BSE) of the April 2006 natrocarbonatite lava (OLD1) with lath-shaped nyerereite (ny) and sub-rounded gregoryite (gr) with a rare silicate spheroid (ss).

Figure 4. BSE image of a combeite replacement rim (com) around a wollastonite crystal (woll) in a silicate spheroid within the natrocarbonatite lava (OLD1).

Figure 5. BSE image of melanophlogite crystal cores of ash pellets and abundant single crystals, some revealing a broken appearance in the groundmass of the ash-pellet rich layer in OLD3. Abbreviations; mel=melanophlogite, neph=nepheline, ga= garnet, and woll=wollastonite.

Figure 6. A photomicrograph of an ash pellet with a melanophlogite core displaying well - developed concentric zoning. PPL. Abbreviations; mel=melanophlogite.

Figure 7.BSE image of melanophlogite revealing both pseudocubic and pseudohexagonal outlines. Abbreviations; mel=melanophlogite.

Figure 8. BSE image of melanophlogite displaying well-developed concentric zoning with a darker C-richer rim and including numerous inclusions of subhedral nepheline laths (light grey).

Figure. 9. X-ray elemental distribution maps of a melanophlogite crystal revealing concentric zonation, with increased carbon-rich zones towards crystal boundaries. Image labeled CP is a BSE reference image (grey scale).

Figure 10. EDS elemental linescan for C, O, Si and Cl across a zoned melanophlogite revealing increased carbon content.

Tables

Table 1. A summary of electron microprobe analysis for selective major mineral phases in the natrocarbonatite lava samples (OLD 1 and OLD2) and the silicate spheroids

Table 2. A selected summary electron microprobe analysis for selective major mineral phases in the ash pellet-rich layer (OLD3).

Table 3. Electron microprobe data for melanophlogite from the ash pellet-rich layer (OLD3) compared with melanophlogites from Sicily, Italy (Von Lasaulx, 1876), Czech Republic (Zak, 1967), California, U.S.A (Cooper and Dunning, 1972) and a partially replaced combeite, Oldoinyo Lengai (Dawson, 1998).

Table 1. Electron microprobe data for major mineral phases in the natrocarbonaite lava samples (OLD 1 and OLD2) and the silicate spheroids.

Natrocarbobatite			Selected phases in natrocarbonatite groundmass										Selected silicate/oxide phases in the silicate spheroids									
	Nyerereite		Gregoryite			Mn-Mag	Unknown Ba-V-oxide		Silico-REE apatite	Manganoan monticellite				Combeite gm	Combeite gm	Combeite rim-woll	Combeite rim-woll	Neph	Woll	Mel	Garnet	Cpx	Soda	Ti-mag
Na2O	23.64	23.52	43.29	44.24	SiO2	0.68	0	SiO2	8.54	SiO2	34.91	34.86	SiO2	50.26	50.04	50.47	51.69	42.11	51.43	43.32	29.98	51.39	35.41	0.33
P2O5	0.63	0.37	3.84	4.04	TiO2	1.34	0	TiO2	0.00	FeO	3.66	4.21	TiO2	0.36	0.08	0.00	0.00	0.00	0.29	0.59	13.73	0.42	0	7.62
SO3	1.53	1.02	3.75	3.96	Al203	0.77	0	Al2O3	0.10	MnO	11.55	11.38	Al2O3	0	0	0.14	0.40	31.98	0.00	6.75	0.68	0.82	27.07	0.19
K2O	6.79	7.09	2.39	2.02	FeO	75.88	0.8	FeO	0.15	MgO	15.20	15.02	FeO	0.20	0.06	0.14	0.17	1.98	1.33	6.69	21.87	13.82	3.21	74.34
CaO	24.89	24.76	6.33	6.79	MnO	12.60	0	MnO	0.00	CaO	33.98	33.74	MnO	0.37	0.27	0.39	0.01	0.02	0.55	0.78	0.44	0.51	0.13	1.83
MnO	0.10	0.09	0.12	0.10	Cr203	0.03	0	CaO	40.12				Cr2O3	0.41	0	0.19	0.33	0	0	0	0.17	0.13	0	0.06
SrO	2.18	2.29	1.36	1.16	V2O5	n.a	20.91	MgO	0.02	Total	99.30	99.20	MgO	0.55	0.51	0.44	0.48	0.15	0.10	4.5	0.51	9.37	0.17	2.36
BaO	0.54	0.65	0.23	0.19	CaO	1.05	2.48	Na2O	0.73				CaO	27.14	27.91	28.84	28.55	0.14	46.04	30.58	32.12	21.4	0	0.93
Cl	0.16	0.17	0.14	0.18	MgO	1.64	0.87	K2O	0.50				Na2O	19.46	19.72	18.74	18.27	15.09	0.13	4.97	0	2.37	21.68	0
					Na2O	0	1.79	SrO	3.57				K2O	0.09	0.17	0.43	0.13	7.68	0	0.1	0	0	3.5	0
Total	60.46	59.96	61.44	62.68	K2O	0	0.85	P2O5	27.95				P2O5	0.59	0.76	0.28	0.00	n.a	n.a	n.a	n.a	n.a	n.a	n.a
					BaO	n.a	63.03	La2O3	6.10				SO3	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	1.7	n.a
					SrO	n.a	3.3	Ce2O3	8.42				Cl	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	6.09	n.a
					SO3	n.a	1.17	SO3	0.12															
					Cl	n.a	3.33	F	0.75				Total	99.42	99.51	100.07	100.03	99.13	99.87	98.28	99.50	100.23	98.96	87.65
								Cl	0.55															
					Total	93.99	98.53	O=F,Cl	0.44				Na/(Na+Ca)	0.54	0.54	0.53	0.52							
								Total	97.18															

Abbreviations: n.a. = not analysed, gm=groundmass, Woll = wollastonite, neph = nepheline, Mel= melilite, mag= magnetite, soda = sodalite, Cpx= clinopyroxene, Ti-mag= titanian magnetite.

Table 2. Electron microprobe data for major mineral phases in the ash pellet-rich layer (OLD3).

	Nepheline					Garnet				Melilite				Clinopyroxene						Wollastonite, titanite, apatite, magnetite				
	1	2	3	4		1	2	3		1	2	3	4	core 1	rim 1	core 2	rim2	Inclusion		Woll	Woll	Titanite	Apatite	Magnetite
SiO2	43.71	43.31	43.46	43.03		28.92	28.98	31.97		43.65	44.13	43.83	43.41	52.34	52.87	52	50.97	51.52	SiO2	50.97	51.23	30.79	0.60	0.05
TiO2	0	0	0	0		16.11	15.56	10.82		0.02	0.01	0.01	0.05	0.52	0.6	0.39	1.34	0.45	TiO2	0.04	0.06	38.35	0.00	8.46
Al2O3	31.90	31.50	32.45	33.76		0.79	0.64	0.48		7.09	6.76	6.19	5.58	0.94	0.88	0.83	2.89	2.06	Al2O3	0.00	0.03	0.39	0.01	0.68
FeO	1.28	0.62	1.54	1.29		20.35	21.09	23.57		7.4	7.4	9.5	9.64	14.88	12.21	16.9	8.89	13.01	FeO	1.04	0.99	1.35	0.09	84.11
MnO	0.05	0.24	0.01	0.00		0.36	0.32	0.50		0.2	0.23	0.26	0.32	0.52	0.43	0.56	0.22	0.48	MnO	0.43	0.43	0.1	0.01	1.11
MgO	0.04	0	0.00	0.10		0.92	1.08	0.32		3.96	4.7	4.28	4.64	7.71	9.42	6.5	12.82	9.3	MgO	0.17	0.14	0	0.01	0.48
CaO	0.35	0.20	0.18	0.19		31.56	31.61	31.62		30.36	30.81	29.66	29.94	20.65	21.9	19.82	22.16	21.47	CaO	47.15	47.11	28.54	56.47	0.49
Na2O	15.47	16.68	15.82	15.10		0.48	0.34	0.48		5.39	5.36	5.39	5.3	2.13	1.57	2.55	1.07	1.63	Na2O	0.04	0.05	0.1	0.01	0.05
K2O	6.84	6.85	6.48	6.58		0	0	0		0.09	0.09	0.14	0.17	0	0	0	0	0	K2O	0.01	0.00	0	0.07	0.03
																			P2O5	n.a	n.a	n.a	40.96	n.a
Total	99.64	99.40	99.94	100.06		99.49	99.62	99.77		98.17	99.49	99.26	99.06	99.69	99.88	99.55	100.36	99.92	F	n.a	n.a	n.a	1.74	n.a
																			Cl	n.a	n.a	n.a	0.01	n.a
Na=(Na/K)	0.77	0.79	0.79	0.78	Py	2.12	2.47	0.76	mg#	48.86	53.08	44.55	46.17	0.52	0.58	0.47	0.8	0.63						
					And	26.33	27.1	31.46											Total	99.84	100.05	99.62	99.96	95.45
					Scho	18.75	17.98	12.99																
					Gro	52.31	52.08	54.07																
					Sp	0.47	0.42	0.68																
					Uv	0.02	0	0.04																

Abbreviations: n.a. = not analysed, Woll = wollastonite, Py = pyrope, And= andradite, Scho=schorlomite, Gro= grosssular, Sp=spessartine, Uv= Uvarovite, mg#= $Mg/(Mg+Fe^{2+})$.

Table 3. Electron microprobe data for melanophlogite from the ash pellet-rich layer (OLD3) compared with melanophlogites from Sicily, Italy (Von Lasaulx, 1876), The Czech Republic (Zak, 1967), California, U.S.A (Cooper and Dunning, 1972) and a partially replaced combeite, Oldoinyo Lengai (Dawson, 1998).

	n=10 Oldoinyo Lengai Tanzania	Racalmuto Sicily Italy	Chvaletice The Czech Republic	Mt. Hamilton California U.S.A	Partially replaced combeite (from Dawson, 1998)	
wt.%						
Si	41.35	43.21	44.23	44.97	Si	36.51
S	n.d	2.28	0.1	0.01	S	0
O	55.9	52.61	52.97	53.44	O	45.36
C	2.25	1.2	0.9	0.84	Fe	1.13
H	n.a	0.81	0.6	0.79	Mg	1.27
					Ca	3.5
Total	99.5	100.11	98.8	100.05	Na	0.29
					K	0.59
					Total	88.65

Abbreviations: n.d = not detected: n.a.= not analysed.

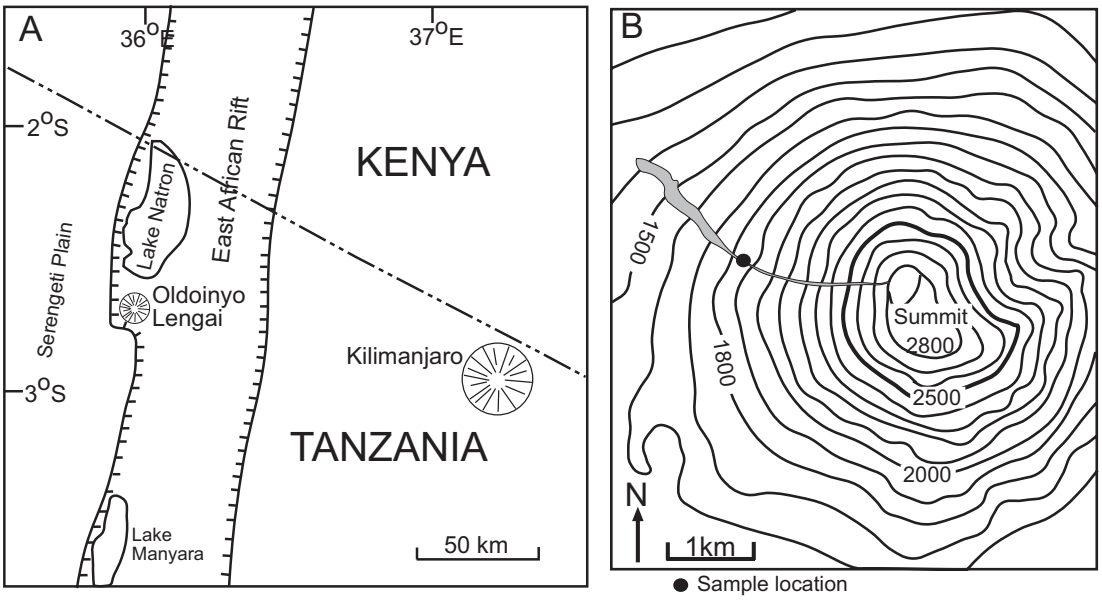
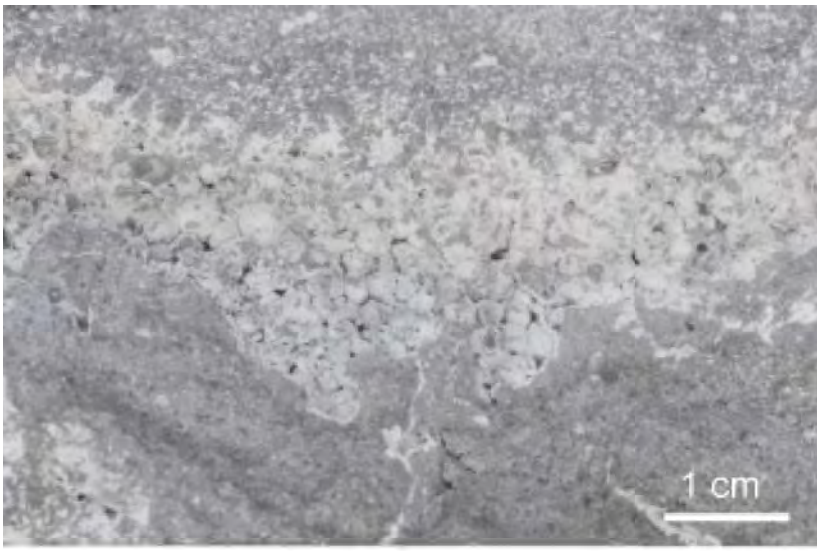

A
36°E
37°E
2°S
3°S
KENYA
TANZANIA
East African Rift
Lake Natron
Serengeti Plain
Oldoinyo Lengai
Kilimanjaro
Lake Manyara
50 km
B
1500
1800
2000
2500
2800
Summit
N
1km
Sample location

Figure 1



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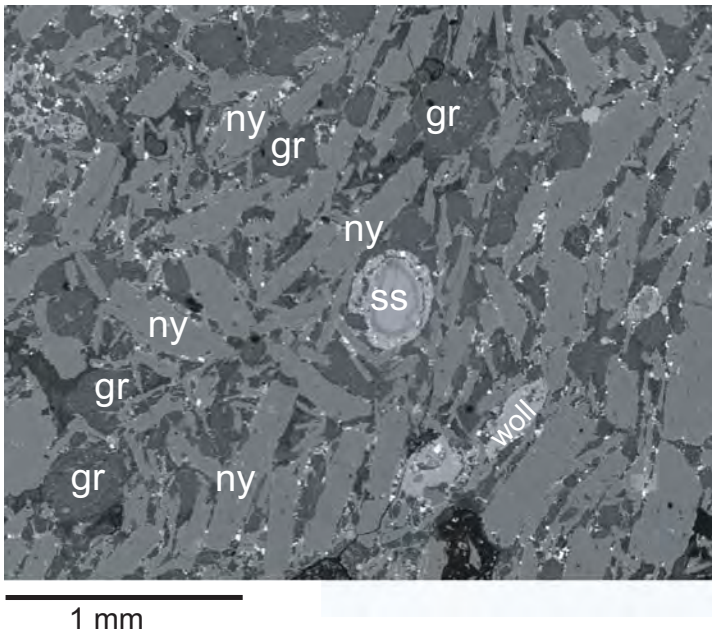

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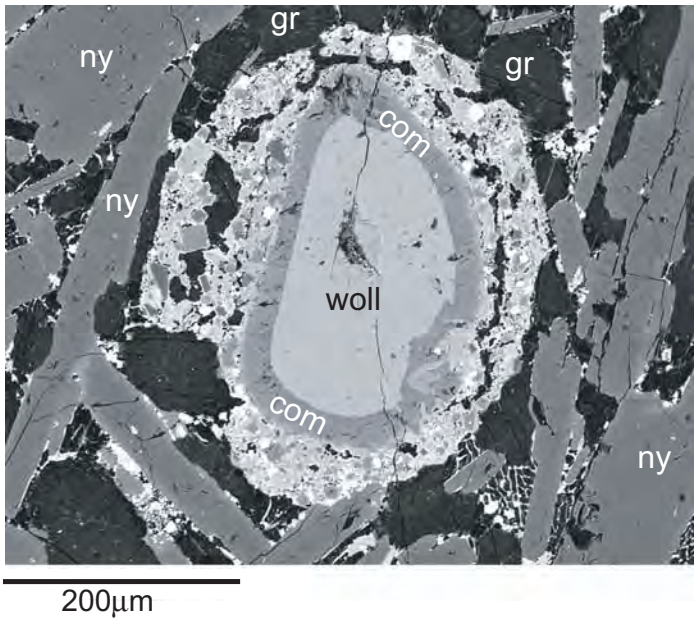

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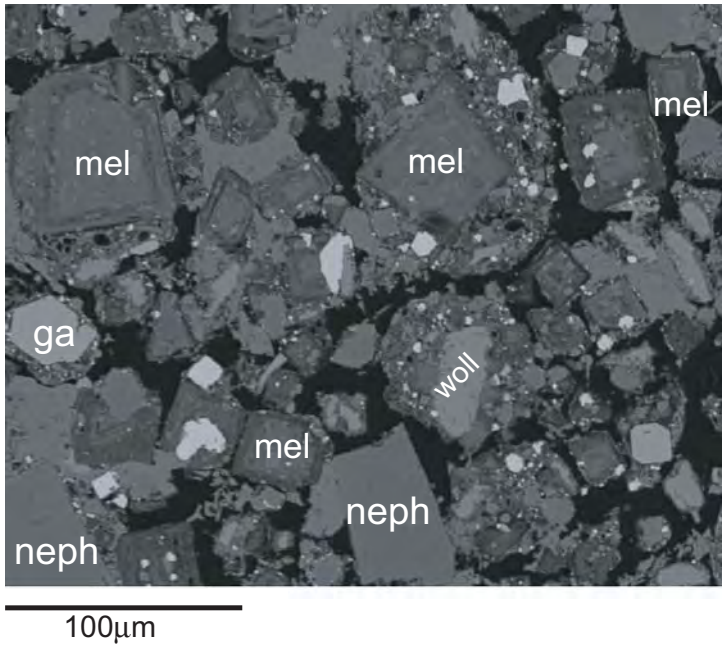

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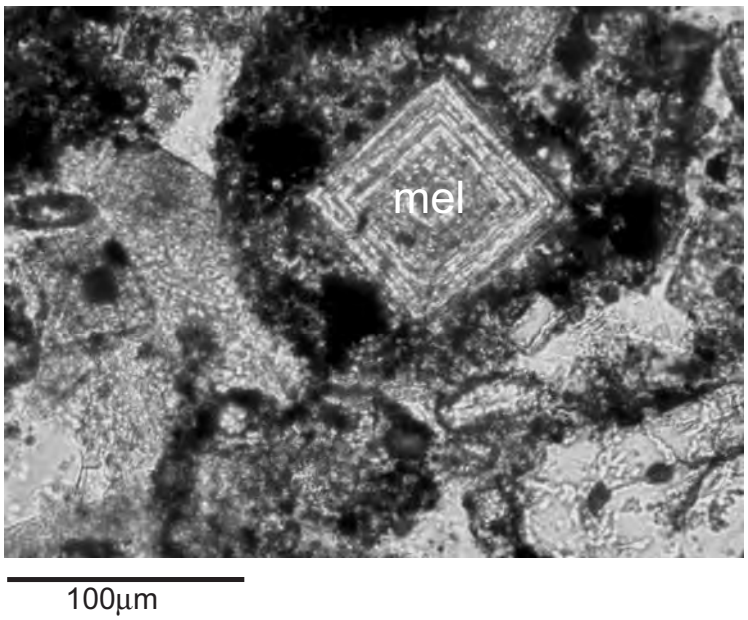

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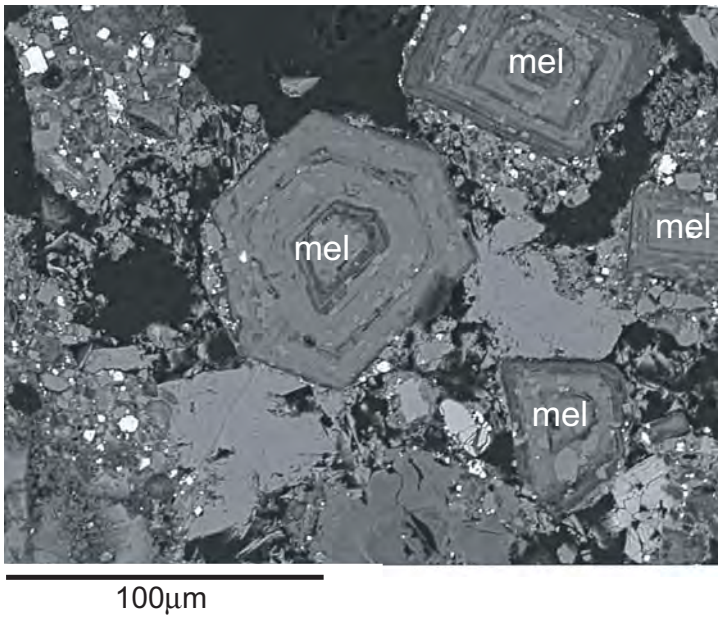

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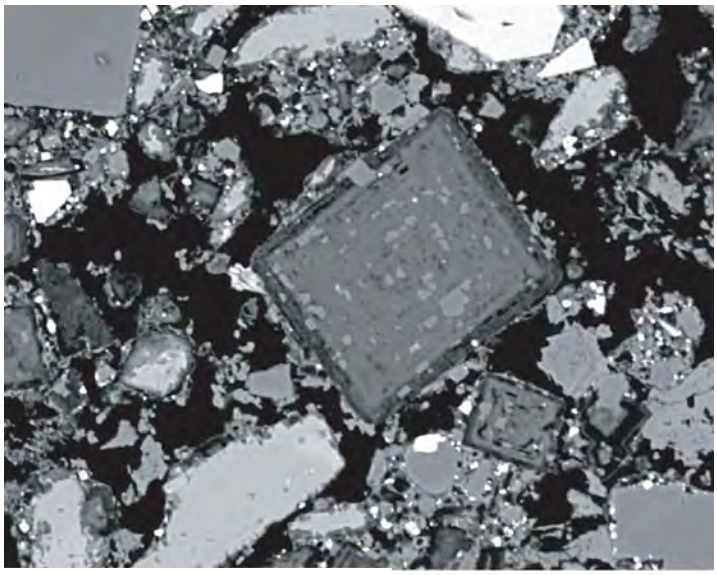

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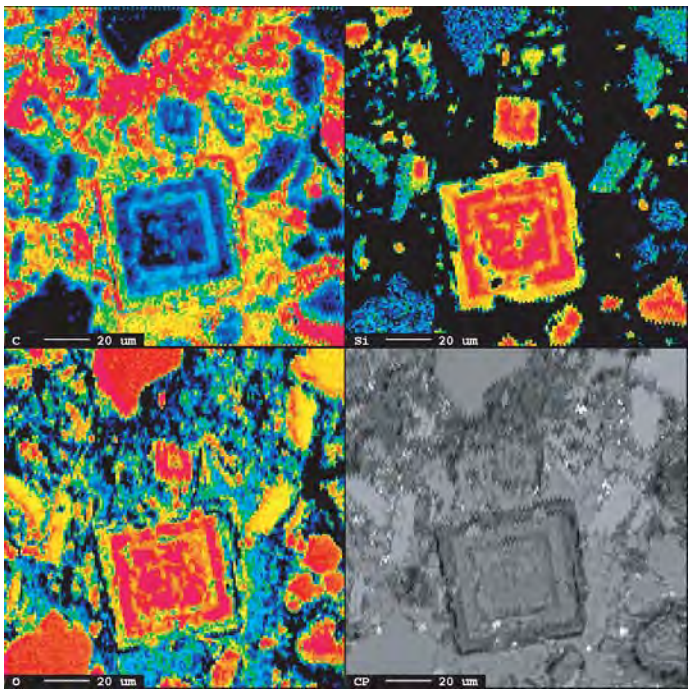

Figure 9

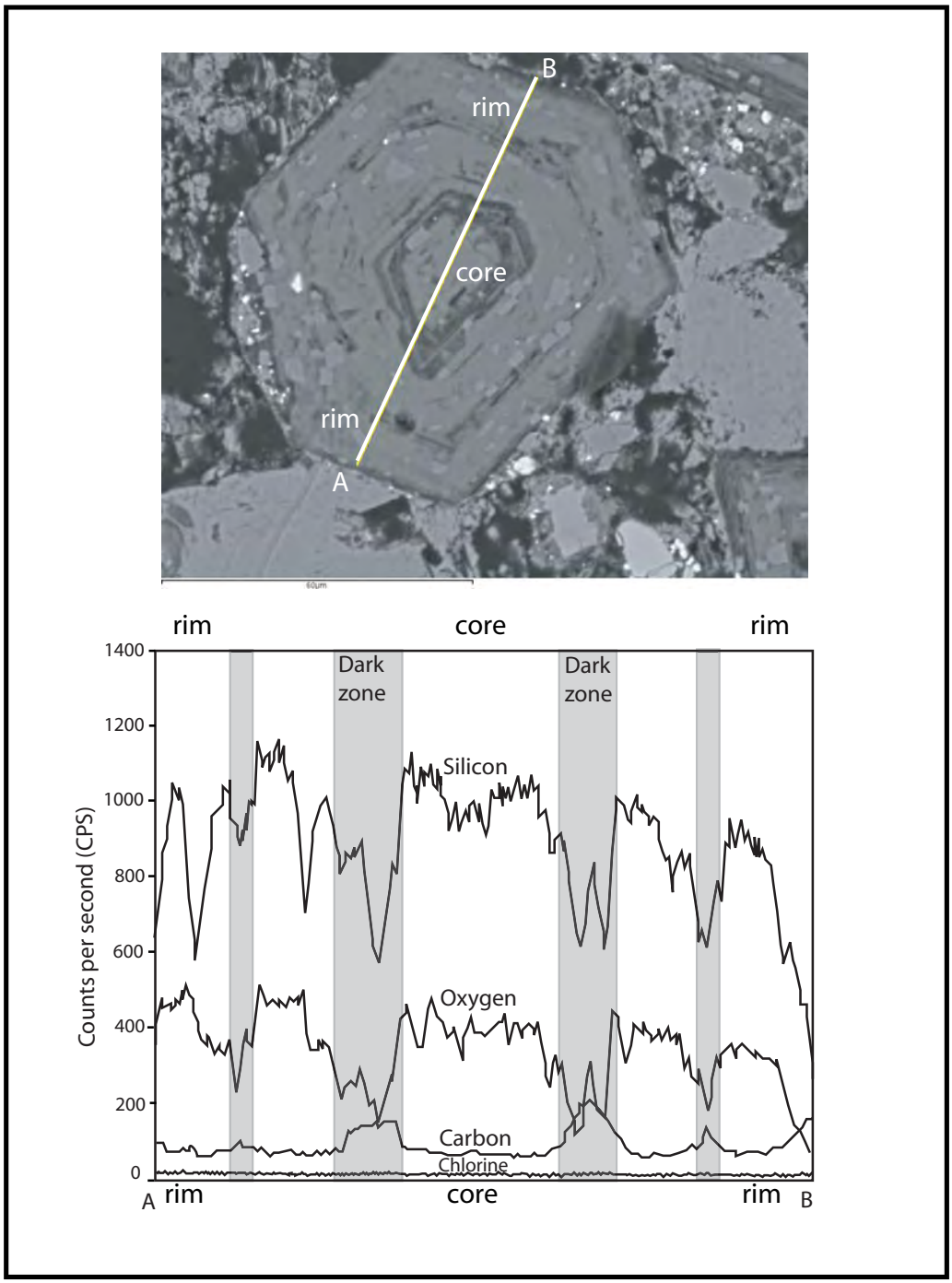
B
rim
core
rim
A
rim
core
rim
1400
1200
1000
800
600
400
200
0
Counts per second (CPS)
Dark zone
Dark zone
Silicon
Oxygen
Carbon
Chlorine
A
rim
core
rim
B

Figure 10