1 **LEACHING OF LAVA AND TEPHRA FROM THE**
2 **OLDOINYO LENGAI VOLCANO (TANZANIA):**
3 **REMOBILIZATION OF FLUORINE AND OTHER**
4 **POTENTIALLY TOXIC ELEMENTS INTO SURFACE**
5 **WATERS OF THE GREGORY RIFT**

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Abstract

Volcanic ash leachate studies have been conducted on various volcanoes on Earth, but few have been done on African volcanoes until now. Tephra emissions may affect the environment and the health of people living in this area, and therefore we conducted a first tephra (ash and lapilli sized) leachate study on the Oldoinyo Lengai volcano, situated in northern Tanzania. The recent explosive eruption in 2007-2008 provided us with fresh samples from the first three weeks of the eruption which were used for this study. In addition, we also used a natrocarbonatitic sample from the activity prior to the explosive eruption, as the major activity at Oldoinyo Lengai is natrocarbonatitic. To compare the leaching process affecting the natrocarbonatitic lavas and the tephtras from Oldoinyo Lengai, the 2006 natrocarbonatitic lava flow was resampled 5 years after the emplacement and compared to the initial, unaltered composition.

Special interest was given to the element fluorine (F), since it is potentially toxic to both humans and animals. A daily intake of fluoride (F^-) in drinking water of more than 1.5 mg/l can lead to dental fluorosis, and higher concentrations lead to skeletal fluorosis. For this reason, a guideline value for fluoride in drinking water was set by the WHO (2011) to 1.5 mg/l. However, surface waters and groundwaters in the Gregory Rift have elevated fluoride levels of up to 9.12 mg/l, and as a consequence, an interim guideline value for Tanzania has been set at 8 mg/l.

The total concentration of fluorine in the samples from the natrocarbonatitic lava flow is high (3.2 wt.%), whereas we observed a significant decrease of the fluorine concentration (between 1.7 and 0.5 wt.%) in the samples collected three days and three weeks after the onset of the explosive 2007-08 eruption. However, the total amount of water-extractable fluoride is lower in the natrocarbonatitic lavas (319 mg/l) than in the nephelinitic tephra (573-895 mg/l). This is due to the solubility of the different F-bearing minerals. In the natrocarbonatites, fluorine exists predominantly in fluorite (CaF_2), and in the early tephra as neighborite ($NaMgF_3$) and sellaite (MgF_2). All these three minerals have very low solubility in water (13-16 g/l). The later nephelinitic tephtras contain surface coating of villiaumite (NaF), which is highly soluble (42'200 mg/l) in water and can thus release the fluoride more readily upon contact with water.

Although there is still the need for further data and a more precise study on this topic in Tanzania, we can already draw a first conclusion that the intake of water during or directly following the deposition of the tephra is not advisable and should be avoided, whereas the release of fluoride from the lava flow has less influence on the river waters.

1 Introduction

Oldoinyo Lengai volcano in northern Tanzania is most famous for being the world's only currently active carbonatite volcano (Dawson, 1962a; Bell and Keller, 1995 and references therein). The mildly explosive to effusive activity associated with carbonatite eruptions have repeatedly been truncated by more explosive eruptions dominated by silicate magmas. Here we focus on two unique events in the recent eruptive history of the volcano, in order to constrain the effects of leaching of lavas and tephra and how different elements are redistributed into surface waters by leaching processes. These volcanic events are: (i) the large natrocarbonatitic lava flow erupted in 2006 ($9.2 \pm 3.0 \times 10^5 \text{ m}^3$; Kervyn et al., 2008), and (ii) mixed carbonatite-silicate tephra from the explosive 2007-2008 eruption (Mitchell and Dawson, 2007; Keller et al., 2010; Kervyn et al., 2010; Mattsson and Reusser, 2010; Bosshard-Stadlin et al., 2014).

It is well known that tephra generated by explosive volcanic eruptions may have a complex array of physical, chemical and biological effects on receiving environments (Ayriss and Delmelle, 2012). This especially applies to fluorine, which is a potentially toxic element at elevated dosages, and may be strongly enriched in the fine ash-fraction in many volcanic eruptions (Oskarsson, 1980; Witham et al., 2005). Tracing the interactions between water and lavas/tephras are especially interesting at Oldoinyo Lengai, because of the unusually F-rich nature of the natrocarbonatitic magmas commonly erupted at the volcano (average of 2.48 wt.% fluorine for 25 natrocarbonatitic samples, but individual lava flows may contain up to >4 wt.% F; Keller and Zaitsev, 2012).

In this study we present the first combined lava and tephra-leachate study of an African volcano, and we use the 2006 lava flow to constrain natural leaching of lava flows. This data are combined with leaching experiments on tephra samples collected between three months prior to the onset of the explosive phase and samples collected during the first weeks of eruption (i.e. on the third day and third week into the eruption). We will show that long-term leaching of lava flows have a smaller effect in redistributing fluorine into the surface waters of the Gregory Rift than the more explosive silicate-rich eruptions do. At a first glance this result is counterintuitive, as silicate magmas hold less total fluorine in comparison with the lavas, but are much more efficient in releasing the fluorine into waters during the leaching process. This feature can be explained by the different solubilities of the fluorine-bearing minerals involved, which occurs predominantly as fluorite in the lavas and as neighborite/sellaite/villiaumite on the outer surfaces of pyroclasts.

2 Background

2.1 Geology and eruptive history of Oldoinyo Lengai

Oldoinyo Lengai volcano currently stands approximately 2000 meters above the surrounding rift-plain in the Gregory Rift of northern Tanzania (Fig. 1). It is most known for being the world's only active carbonatite volcano, erupting extremely sodic magmas (i.e., natrocarbonatites with ~34 wt.% Na₂O; Dawson 1962b; Keller and Zaitsev, 2012). In despite being most famous for the natrocarbonatites, the volcanic edifice is predominantly composed of phonolitic to nephelinitic lavas and pyroclastics (i.e., ~95%; Dawson, 1962a; Klaudius and Keller, 2006). The oldest rocks from Oldoinyo Lengai can be found in debris avalanche deposits at the shore of Lake Natron and yields ⁴⁰Ar/³⁹Ar ages 793±63 ka (Sherrod et al., 2013). The first eruption to be witnessed and described occurred in 1883 A.D. (Fischer, 1884-1885). Since then, five major ash eruptions were observed in the years 1917, 1926, 1940, 1960-67 and 2007-2008, all of sub-Plinian to Plinian type (Richard, 1942; Dawson et al., 1968; Dawson et al., 1995; Dawson and Mitchell, 2007; Dawson, 2008). In the years between these explosive eruptions (i.e. in 1904, 1914, 1954, 1960-1966, 1983-2007), natrocarbonatitic lava flows were recorded (Keller and Krafft, 1990; Dawson, 2008; Kervyn et al., 2008; Mattsson and Vuorinen, 2009; Keller and Zaitsev, 2012).

The most recent explosive eruption at Oldoinyo Lengai began in the night from the 3rd to 4th September 2007 and lasted until April 2008, terminating 25 years of effusive, natrocarbonatitic activity (e.g. Keller et al., 2010; Kervyn et al., 2010). This eruption mainly deposited lapilli and ash onto the western flank of the volcano (Fig. 1a) and the rift shoulder (Fig. 1b). The initial explosions produced an approximately 3 km high ash plume drifting northwards (GVN, 2007; Vaughan et al., 2008), which deposited a 1 cm thick fallout 20 km north of Oldoinyo Lengai (Kervyn et al., 2010; Mattsson and Reusser, 2010). The intensity of the eruption varied with time over the following eight months, with a peak activity towards the end of February 2008, when a mushroom-shaped eruption plume reached up 15 km into the atmosphere (Kervyn et al., 2010). Fallout from these explosive phases was reported in the areas of Lake Eyasi and Ngorongoro caldera, which lie 100 km south-west of Oldoinyo Lengai (Kervyn et al., 2010). The first samples of the eruption (collected on September 7th; three days after the onset of the eruption) show a clear natrocarbonatitic component, and with time of the eruption, the composition of the tephra changes towards nephelinitic (Mitchell and Dawson, 2007; Keller et al., 2010; Mattsson and Reusser, 2010; Bosshard-Stadlin et al., 2014). The September 7th tephra fall has been interpreted to be from incomplete mixing of nephelinitic and natrocarbonatitic magma, with the smooth-rounded shapes of the

natrocarbonatitic droplets being an evidence for molten carbonatitic magma at the time of the eruption (Mattsson and Reusser, 2010; Bosshard-Stadlin et al., 2014). Already three weeks after the eruption started, the tephra changed to being silicate-dominated (Mitchell and Dawson, 2007). Samples collected in May 2011 (Fig. 1c and d), thus three years after the end of the eruption do not show any clear carbonatitic component (Bosshard-Stadlin et al., 2014).

2.2 Studies of volcanic ash leachates

It is well-known that fresh-erupted tephra and ash may release significant amounts of soluble elements upon contact with water (Ayriss and Delmelle; 2012 and references therein). The interaction between gas and aerosol phases and tephra particles in the cooling plume is thought to be responsible for the presence of soluble sulphate and halide salts on tephra and ash surfaces (Witham et al., 2005). Witham et al. (2005) summarized tephra leachate studies conducted prior to 2005 from a total of 27 volcanoes worldwide. Ayriss and Delmelle (2012) provide an updated review and summary of tephra leachate compositions. The most abundant soluble elements are usually Ca, Na, Cl and S, followed by Mg, F, P, K and Al. Tephra surface coatings are known to be highly variable both within and between eruptions, as well as both spatially and temporally. Factors influencing surface coating composition include magma composition and eruption style, in-plume residence time, meteorological conditions and post-eruptive processes such as precipitation leaching or contamination from surfaces deposited on. Inconsistencies between studies, particularly with respect to ash:water ratios and leaching times, have hampered direct comparisons between studies (Witham et al., 2005). To promote the collection of high-quality leachate data that may be readily compared with other studies, a leachate methods protocol has been proposed under the auspices of the International Volcanic Health Hazard Network (Stewart et al., 2013; see www.ivhnn.org).

For the Oldoinyo Lengai volcano, Dawson et al. (1968) performed a first tentative leaching experiment on natrocarbonatitic lavas from 1960 and tephra collected from the 1966 eruption. Crushed material of the samples was leached in distilled water and the insoluble residue filtered off. The results showed that 52% of the natrocarbonatitic lava and 31% of the tephra sample had been dissolved. The composition of the dissolved fraction is comparable from both the natrocarbonatite and the tephra, only chlorine stands out as it is almost doubled in the tephra-leachate compared to the lava-leachate (see Table 1 in Dawson et al., 1968), indicating that scavenging of volatiles from the eruption plume onto the outer surfaces of tephra particles may be important at Oldoinyo Lengai. Here, we extend the tentative leaching experiments of Dawson et al. (1968) and provide more detailed data on the characteristics of

certain elements in terms of their leaching behavior in both tephra and lavas from Oldoinyo Lengai.

2.3 Health hazards caused by excess fluoride

Certain inorganic ions (such as arsenic, fluoride and nitrate) may cause widespread health effects as a consequence of exposure through excessive quantities in drinking-water (WHO, 2011). Of particular interest here is fluoride (F⁻) as long-term exposure to concentrations in drinking water of over 1.5 mg/l is associated with an increased risk of dental fluorosis in children during enamel formation. Exposure to higher concentrations >4 mg/l increases the risk of skeletal fluorosis (e.g. Apambire et al., 1997; WHO, 2011). Fluoride is generally occurring in high concentrations in waters along most of the East African Rift System (e.g. Kilham and Hecky, 1973; Nanyaro et al., 1984; Gaciri and Davies, 1993; Apambire et al., 1997; Nielsen and Dahi, 2002; Reimann et al., 2003; Davies, 2008) and many studies have shown a high prevalence of both dental and skeletal fluorosis in the region (e.g. Shorter et al., 2010; Rango et al., 2012).

Based on the potential health hazards, a general recommendation of an upper limit of fluoride in drinking water has been set to 1.5 mg/l, based on a daily water consumption rate of 2 liters per day (WHO, 2011). However, the Tanzanian government has adjusted this recommendation to 8 mg/l (Ministry of Water Energy and Minerals (MAJI), 1974), because many communities only have access to drinking water with an elevated concentration of F⁻ (Shorter et al., 2010). Today, the regions in Tanzania that are most affected by fluorosis are the northern and western part of the country (Mjengera and Mkongo, 2003), and thus also the area surrounding Oldoinyo Lengai. In terms of fluoride concentrations in the rivers of the Lake Natron area, only the water samples from Peninj river (0.38-0.46 mg/l, Table 1) lie below the 1.5 mg/l guideline from WHO (2011), and the other two rivers (Engare Sero and Moïnik) are significantly higher, between 3.46 and 9.12 mg/l (Gueddari, 1984), which is already a risk for people who drink the water regularly (Table 1).

3 Methods

3.1 Sample collection and storage

For the leachate study we used five different samples (one lava flow and four tephra samples), all collected between June and September 2007 on different locations on and

around Oldoinyo Lengai (Fig. 2 and Table 2). These samples thus represent different stages just prior to the explosive eruption and the initial weeks. Sample OL-LL2 is a natrocarbonatite from the active lava lake in the crater of Oldoinyo Lengai, collected in June 2007, and kept under vacuum in dry conditions since then. Samples OL-GATE, OL-CLINIC and OL-SCHOOL are tephra samples and were collected on September 7th 2007, three days after the onset of the eruption. These samples were collected in the Maasai village Engare Sero, approximately 15 km north of Oldoinyo Lengai. Sample BD4465 (tephra) was collected by Barry Dawson on September 24th 2007 (i.e., three weeks after the eruption started), on the north-western flank of Oldoinyo Lengai. The 2006 natrocarbonatitic lava flow was resampled in May 2011, in order to compare the initial composition (provided by Kervyn et al., 2008) of the lava flow to the composition of the altered natrocarbonatites and to calculate the budget of leached fluorine.

Common for all tephra samples is that they never touched the ground during the eruption, i.e. they were falling directly onto a plastic sheet or a container placed on the ground for sampling purposes. Similarly, all samples have been stored in desiccators under vacuum since the eruption in order to minimize the effect of alteration of the natrocarbonatitic material.

3.2 Geochemical and mineralogical analyzes

All samples were milled to powder in an agate mill, homogenized with Li₂B₄O₇ in a ratio 1:5 and fused into glass pills. In order to avoid the loss of volatile elements, the powders were directly molten into glass pills without performing the loss of ignition first. The glass pills were measured by a wavelength dispersive X-Ray Fluorescence (XRF) spectrometer (Axios, PANalytical) and trace elements by Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS). The XRF measurements have been conducted with specially designed carbonatite standards which are able to account for the usually high sodium content of the natrocarbonatites. The trace elements were measured using LA-ICP-MS with a dwell time of 30-60 s, a beam size of 115 µm and a frequency of 20 Hz. In order to get a uniform number of counts, the stage was moved during the measurement. A standard reference material (NIST610) was measured for calibration, following the ablation protocol and the data reduction protocol by (Longerich et al., 1996). The minerals of the surface of the tephra grains were identified using the EDS system of a scanning electron microscope (SEM; JEOL JSM 6390LA).

3.3 Ash/tephra leaching experiments

The leaching of the tephra samples was conducted following the interim IVHHN protocol (Stewart et al., 2013). Since initial tests indicated a high soluble salt burden, leaching was carried out only at a ratio of 1:100 (g tephra to ml extractant) rather than at both 1:20 and 1:100 as recommended in the protocol. Subsamples of tephra were leached with deionized water in an end-over-end shaker for 60 min and afterwards centrifuged (3 min, 5000 rpm) and filtered (0.45 μ m), to separate the leached solution from the residual tephra sample. Samples were filtered into separate containers for analysis of anions and cations. Conductivity and pH measurements were made on the filtered samples. Fluoride determinations were made by ion selective electrode at Massey University, New Zealand. Chloride and sulphate were determined by ion chromatography at Lincoln University, New Zealand. Cation analyses were carried out by Optical Emission Spectroscopy (IPC-OES) at Lincoln University. Method blanks were run by omitting the tephra from centrifuge tubes but subjecting the extracting solution to all other processing steps. One sample was run in duplicate; duplicate samples produced results consistent to within 2-3%.

4 Results

4.1 Natural leaching of natrocarbonatitic lavas: The 2006 lava flows

The process of leaching of natrocarbonatitic lavas left to the effects of nature is well illustrated by the March-April 2006 lavas of Oldoinyo Lengai. We sampled fresh, unaltered samples of this particular lava flow in April 2006, just after the emplacement. At that time, the lava was dark-grey in color and showed no signs of alteration in hand specimen or in thin section. The petrography and geochemistry of the 2006 lava flows have been well described in previous publications (Kervyn et al., 2008; Mattsson and Vuorinen, 2009; Mitchell, 2009) and will not be reiterated here. It can be summarized as a typical natrocarbonatitic lava, with the exception of the presence of silicate spheroids, which makes the bulk-rock composition slightly enriched in SiO₂ (i.e., 1.71 wt.% compared to the normal 0.22 wt.%; Kervyn et al., 2008; Keller and Zaitsev, 2012).

In June 2011 we revisited the same lava flow to sample it once again at exactly the same location as in 2006 (Table 2). The alteration process, having operated freely for more than five years since the time of emplacement, has left significant differences in the morphology and texture of the lava flow. Moreover, white stalactites were exposed on the underside of the lava flow (see inset in Fig. 3) which were also sampled for the purpose of this study (Table 2).

Figure 3 shows a combined major-and selected trace element plot of the lava flow sampled in 2011 normalized to the unaltered samples from 2006 (see also Table 2). From this plot it is clear that elements known to be mobile during leaching are also depleted in the lava flow (i.e., Cl, S, K, Rb and Na), whereas the other elements are enriched or close to unity due to the immobile nature of those. Here it is interesting to note that the fluorine content remains close to unity (Table 2 and Fig. 3), only slightly depleted in the lava, suggesting that it is not very mobile in the leaching of natrocarbonatitic lava flows in five years' time. This is in sharp contrast to Cl, which is nearly absent in the leached lava, but heavily enriched in the stalactites underneath the lava flow (i.e., >3 times; Table 2 and Fig. 3).

4.2 Experimental leaching of tephras: The mixed carbonatite-silicate tephra of 2007-2008

4.2.1 Petrography and geochemistry of the starting material

A detailed petrological and geochemical description of all samples used for this study can be found in Mattsson and Reusser (2010) and Bosshard-Stadlin et al. (2014). The tephra samples collected on September 7th 2007 are very fine grained (around 0.5 mm in size) and display a sub-rounded shape. Two types of grains could be distinguished: (i) grains with only little ash sticking on the surface of the minerals (Fig. 4a), and (ii) grains, where the coring mineral is completely covered in a thin layer of melt and ash particles (Fig. 4b). In cross section (Fig. 4c,d), the pyroclasts typically display a single or several coring mineral, which can be either a carbonate mineral such as nyerereite and gregoryite, or a silicate mineral (i.e., nepheline, garnet, pyroxene or wollastonite). The coring mineral is coated by a thin (5-100µm) melt film. Sample BD4465, which was collected on September 24th 2007, is coarser grained than the September 7th samples (which is also consistent with the fact that this sample was collected closer to the volcano itself). The grains are in the range of 0.5-1 mm, and clearly rounded. The surface of these grains shows abundant lath-shaped, platy crystals of natrite (Na₂CO₃, Fig. 4e,f), with agglomerates of sylvite (red arrows in Fig. 4e,f). The cross section of these pyroclasts show larger silicate phenocrysts (200-400 µm; Fig. 4g,h) surrounded by fine-grained silicate minerals and adhering small ash particles on the outer surface. Nyerereite and gregoryite are absent in these late samples, however, there is still a minor amount of carbonatitic material in the outer coating of the grains, which is visible as white alteration product when left outside a desiccator.

In terms of their geochemistry, the samples show some distinct and important differences concerning their compositions (Table 3). SiO₂ shows a significant increase from 0.11 wt.% in

sample LL2 (natrocarbonatite from June 2007) to 28.22 wt.% in BD4465 (September 24th tephra). There is a negative correlation between SiO₂ and CO₂, which decreases from 31.28 to 9.28 wt.%, with time in the eruption. Only small variations can be observed in CaO (15.57 to 16.27 wt.%) and K₂O (7.98 to 4.30 wt.%). The compositional change of the samples with time indicates a mixing between a natrocarbonatitic and a nephelinitic melt (Fig. 5; Bosshard-Stadlin et al., 2014). Indeed, all tephra samples plot on a tie line between the average natrocarbonatites of Oldoinyo Lengai (Keller and Zaitsev, 2012) and the bulk-rock of silicate lavas (Klaudius and Keller, 2006).

Of special interest for the current study are the elements Cl, S and F, as these are common components of magmatic gases (as HCl, SO₂ and HF) and usually are relatively mobile during the leaching process. The concentration of chlorine is 4.80 wt.% in the natrocarbonatites, and 0.46 wt.% in the September 24th samples (BD4465). A similar decreasing trend with time can also be seen for fluorine, with 3.22 wt.% and 0.50 wt.% for the same time period. SO₃ shows smaller variations, but is also decreasing from 3.20 wt.% in LL2 to 2.07 wt.% in BD4465.

4.2.2 Geochemistry of the leachates

Leachate compositional data are shown in Tables 4a and 4b, alongside comparative global data from a recent review by Ayris and Delmelle (2012). The overall soluble salt burden is very high, and the most-abundant elements are Na, K, Cl and S. Compared to other tephra leachates, the Oldoinyo Lengai leachate composition is strikingly unusual. Concentrations of water-extractable Na, K, Cl, Li and Mo are extremely high and exceed the maximum values for tephra leachates previously reported by Ayris and Delmelle (2012). For example, samples OL-CLINIC and OL-SCHOOL contain 43 mg/kg Mo, approaching two orders of magnitude greater than the previous maximum value recorded of 0.62 mg/kg. Of the other elements, F, S (as SO₄), As and B are high in comparison to global medians but are within the previously-reported range (Tables 4a, 4b). The remaining elements measured (Ca, Mg, Al, Cu, Fe, Mn and Zn) are all low by global standards. Another striking feature is the very high alkalinity of the tephra leachate (pH 11.0); this exceeds the previous highest-reported value of pH 10.5 for fresh tephra from the 1993 eruption of Lascar volcano, Chile (Risacher and Alonso, 2001), which was attributed to the hydration of alkali and alkaline earth metal oxides formed during pyrolysis of vegetation by hot tephra. The high pH of the Oldoinyo Lengai tephra leachate is most likely due to the dissolution of natrite (Fig. 4e,f) and/or other Na-bearing carbonate phases.

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327 **5. Discussion**

328 **5.1 Atmospheric alteration and leaching of natrocarbonatitic lava flows**

329 Previous studies (Zaitsev and Keller, 2006; Zaitsev et al., 2008) have shown that subaerial
330 weathering and leaching of natrocarbonatitic lavas rapidly produce an array of secondary
331 carbonate minerals indicative of alteration/leaching (such as pirssonite $[\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}]$,
332 gaylussite $[\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}]$, shortite $[\text{Na}_2\text{Ca}_2(\text{CO}_3)_3]$, trona $[\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}]$,
333 nachtolite $[\text{NaHCO}_3]$ and thermonatrite $[\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}]$).

334 In a previous study, Mitchell (2006a) also analyzed stalactites from a hornito inside the
335 summit crater of Oldoinyo Lengai, which is consistent with the data presented here. He found
336 that the stalactite mineralogy was composed of various amounts of nachtolite and
337 thermonatrite together with aphthitalite $[(\text{K},\text{Na})_3\text{Na}(\text{SO}_4)_2]$, kogarkoite $[\text{Na}_3(\text{SO}_4)\text{F}]$, shairerite
338 $[\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}]$, halite $[\text{NaCl}]$ and sylvite $[\text{KCl}]$. This type of mineralogy, similar to that
339 found in alkaline non-marine evaporites (Spencer, 2000), fits very well with the bulk-rock
340 compositions of the stalactites underneath the leached 2006 lava flow (Table 2 and Fig. 3).
341 However, as pointed out by Mitchell (2006a), the absence of Ca-bearing phases, such as
342 gypsum, indicates that the brine from which the stalactites precipitated must have been
343 alkaline rather than neutral or a Ca-Cl brine. Mitchell (2006a) further argued that the fluorine
344 required to stabilize/saturate kogarkoite and shairerite in the stalactites was derived from
345 decomposition/dissolution of fluorite in the natrocarbonatites which also requires high pH
346 (>10 ; Mitchell, 2006a).

347 It is clear from the leaching of the 2006 lava flow that some fluorine has been removed
348 from the system, and we find it likely to be due to leaching of fluorite at high pH similar to
349 the process previously proposed by Mitchell (2006a). However, these brine-like fluids are
350 much more efficient in dissolving and transporting Cl, which is derived from the highly
351 soluble minerals halite and sylvite. Therefore, leachates derived from interactions with the
352 lava flows of Oldoinyo Lengai will have high pH values, and high contents of alkali metals
353 and chloride, but the total amount of potentially toxic elements like fluorine will be limited. A
354 simple back-of-the-envelope calculation shows that only $<13\%$ of the total fluorine in the
355 2006 lava flow has been lost in five years of leaching (Table 2). This is despite the fact that
356 the upper slopes of the volcano, where the samples were collected, receive almost twice the
357 amount of annual rainfall compared to the surrounding rift floor (i.e., 750 mm/year compared
358 to 427 mm/year; Vicens and Casanova 1987). Mangler et al. (2014) also performed three-day
359 long leaching experiments using samples from the natrocarbonatitic lava flow covering

different alteration stages and their result fits well with the results presented in this study, with the observations that after three days, only small quantities of F are dissolved from the lava flow, whereas Cl and Br are leached out in large quantities.

Although it is difficult to directly compare the leaching of a lava flow in nature with laboratory experiments on pyroclasts (mainly because of the different water:rock ratios involved), we can still make important observations on the main leaching processes of the lava. We know the total volume of lava ($9.3 \times 10^5 \text{ m}^3$; Kervyn et al. 2008) and the approximate rainfall during five years ($\sim 3750 \text{ mm}$; Vicens and Casanova, 1987). This converts into estimated water:rock ratios of approximately XX:X and X:X between the two separate sampling occasions (i.e., May 2006 and June 2011). These estimates depends how much rock the rainfall actually can be in contact with, but the 2006 lavas have an much larger open porosity compared to closed porosity (16 to 21% for open porosity and $>1\%$ for closed porosity; Mattsson and Vuorinen, 2009), which suggests that most of the rainfall can percolate through the lavas and subsequently result in significant leaching.

Based on these results, we conclude that leaching of the natrocarbonatitic lavas of Oldoinyo Lengai can contribute with fluoride and chloride to the surface waters of the Gregory Rift. However, the total quantities leached are small and in addition, the total volume of natrocarbonatitic magmas is also small compared to the overall volume of the volcanic edifice (Klaudius and Keller, 2006). Additionally, the main transport of fluoride into the surface waters will be associated with rainy seasons and thus the amount of fluoride in the overall water will be diluted during times of heavy rain. In combination, all these factors suggest that fluoride derived from passive leaching of natrocarbonatitic lava flows will not significantly affect the compositions of the surface waters in the area around the volcano as these are known to be substantially elevated normally (Edmunds and Smedley, 2013, and references therein).

5.2 Leaching of volcanic ashes

To evaluate the role of magma mixing on the resulting chemistry of the leachates, we use SiO_2 (from the bulk rock XRF analyses) as an index for the degree of magma mixing. When plotted against SiO_2 (Fig. 6), it is clear that a correlation between bulk rock chemistry and the resulting leachates can be seen in Cl^- , which is decreasing in bulk rock composition as well as in the leaching experiments ($31'003 \text{ mg/kg}$ in LL2 to 7547 mg/kg in BD4465; Fig. 6). However, for fluorine, the observed trend is the opposite and is actually decreasing in the bulk rock samples with time of the eruption, but increasing in the leaching experiments from

319 mg/kg in LL2 to 895 mg/kg in BD4465 (Fig. 6). This result is rather counterintuitive and raises the question how and where the fluorine occurs in the different rocks.

In the natrocarbonatites, the main F-bearing phase is fluorite (Peterson, 1990), and Keller and Krafft (1989) found in samples from the 1988 eruption, that fluorite is the most common phase after gregoryite and nyerereite. Neighborite has been reported in the matrix of natrocarbonatites by Mitchell (2006b). An elemental distribution map of a grain from the September 7th tephra (Fig. 7) shows fluorine enrichment in the particles adhering to the surface of the grain. Here, fluorine occurs mainly as salts such as neighborite (NaMgF_3) and sellaite (MgF_2). An analysis of the September 24th tephra shows that the fluorine predominantly occurs in the mineral villiaumite (NaF), on the outer rim of the grain. These observations and the results from the leaching experiments suggest, that the solubility of the F in the mineral increases from neighborite and fluorite to sellaite and villiaumite. This is also substantiated by Chao et al. (1961), who showed that neighborite is insoluble in water and slowly soluble in hydrochloric or nitric acid. The solubilities of fluorite, sellaite and villiaumite are 16 mg/l, 130 mg/l and 42'200 mg/l (IFA, 2014), which correlate with the observations made from the leaching experiments.

5.3 Release of fluoride into the surface waters

5.3.1 Indicative hazard assessment

Exposure via drinking water

Inputs of leachable elements from tephra fall can cause compositional changes to surface waters, which may be used as sources of drinking water. The extent of alteration depends on the catchment area, thickness and soluble salt burden of the tephra fall, the volume available for dilution and the pre-existing composition of the water body, with changes more likely to be apparent for low ionic strength waters (Stewart et al., 2006). Compositional changes in lakes and reservoirs are generally minor to indiscernible due to the large volume available for dilution. Marked changes in streams and rivers have been reported but are typically short-lived (e.g. Klein, 1984; Flaathen and Gislason, 2007; Cronin et al., 2014). For several volcanic eruptions, simple modelling has been carried out to predict composition changes to drinking water sources for a range of tephra leachate compositions (e.g. Stewart et al., 2006; Cronin et al., 2014). For eruptions studied to date, effects on drinking-water palatability (due to large increases over background levels of elements such as Fe, Al and Mn) are expected to outweigh toxicity concerns due to elements such as F or As. These predictions are supported by available data on composition of surface waters following tephra fall (Cronin et al., 2014; references in previous paragraph).

This approach is applied here to the Oldoinyo Lengai tephra. While the primary source of drinking water in this region is from the Engare Sero river or water tanks in Gelai Boma, there may be potential pathways for contamination; for example if water is stored in open tanks. Table 5a presents an indicative set of calculations showing expected concentration increases caused by a 10 mm tephra fall in a standard 227 liter (60-gallon) stock watering trough, using the leachate composition data from Tables 4a and 4b for the potentially-toxic elements F, As, Mo and B and also Na, which is not of toxic concern in water but has a threshold value set for palatability.

Drinking-water guidelines for humans (WHO) and livestock (FAO) are provided in Table 5 for comparison. Predicted increases of F, As and Mo are clearly well in excess of levels acceptable for long-term consumption of drinking water by humans; F and Mo also exceed livestock drinking water guidelines by substantial margins. However, we note that the WHO health standards for drinking-water are based on lifetime exposure and are therefore not relevant for assessing short-term exposures such as those resulting from a single tephra fall event. Cronin et al. (2014) derived approximate acute (short-term) threshold values for drinking water for the elements F and As. Values predicted to be lethal to both adults and children, and to cause the onset of short-term symptoms are also listed in Table 5b. It may be seen that for both F and As, predicted concentrations are well below lethal concentrations but may be sufficient to result in the onset of mild intoxication (in the case of F, manifested as nausea, vomiting and gastric pain), particularly in children.

While these calculations are rudimentary and do not account for the pre-existing composition of receiving waters, the potential of this tephra to contaminate shallow, open water supplies is evident. We therefore make the following recommendations in the event of a similar tephra fall in the future:

- Any open water supplies should be covered
- Water should not be drawn from streams immediately after tephra fall or after the first heavy rains following tephra fall events.

5.4 Additional sources of fluorine in the Gregory Rift

The results presented here show that a considerable amount of fluorine can be introduced into the surface waters by leaching of volcanic tephra falls, and to a lesser extent also leaching of natrocarbonatitic lava flows. However, the total effect of these tephra fall episodes or the long-time leaching of lavas is likely to have a small overall effect on the fluoride distribution within the surface waters of the Gregory Rift. In fact, considerably higher values of fluoride

have been measured in the numerous hot springs found all around the lake, although it is not clear if these waters are used as drinking water (i.e., up to 294 mg/l; Gueddari 1984). In addition to this, the local population living around Lake Natron frequently uses natural evaporite deposits (predominantly trona) as salt in the preparation of food (Nielsen and Dahi, 2002). These evaporites frequently contain fluorite which is precipitated in the evaporation process on the lake shore, and these may contain as much as 2940-6200 mg/kg in samples from Lake Natron (Adhia, 1983; Nielsen and Dahi, 2002).

6 Conclusions

The bulk rock geochemistry of the analyzed samples shows a decrease in fluorine with time of the most recent explosive eruption from 1.7 to 0.5 wt.%, whereas the ash leachates increase in fluoride (573-895 mg/l). In contrast, the natrocarbonatitic lava is high in fluorine (3.22 wt.%), but the leachates are the lowest compared to all measurements performed (319 mg/l). This difference in bulk geochemistry and leachate composition is due to differences in the solubility of the fluorine-bearing minerals. Fluorite and neighborite are the main fluorine-bearing phases in natrocarbonatitic lavas, and the neighborite is not soluble in water, whereas fluorite is slightly soluble in water. The fluorine in the later tephra is present in the minerals neighborite, sellaite and villiaumite, which are found as surface coatings on the outer surface of the pyroclasts. Especially villiaumite has a high solubility, and has thus a large impact on the fluoride concentration of the leachates. The release of fluorine from the tephra is a fast process and the river water should be safe again several hours after the tephra fall halted. However, it is not advisable to consume the river water during or hours after a tephra fall episode, as the fluoride will then be highly enriched in the water. The release of fluoride from the lava flow is a much slower process and has therefore no big impact on the water chemistry in the area.

There is still a lack of data from this area, such as the total amount of water flowing in the rivers and the residence time of fluoride in water, as well as leachate data from later in the eruption and the exact number of Maasai people living in the vicinity of the volcano. However, the main activity at Oldoinyo Lengai is natrocarbonatitic, and we could show that the release of fluoride from natrocarbonatites into the water is a slow process and does not have any significant impact on the water concentration and therefore the health of the local population.

The following key findings of this study can be summarized as follows:

- Oldoinyo Lengai tephra leachate composition is very unusual and expands the range of concentrations previously reported, particularly for the alkali metals Li, Na and K plus

Cl and Mo which are approaching two orders of magnitude higher concentrations than previously-reported global maxima

- Simple calculations show that Oldoinyo Lengai tephra fall has the potential to cause toxicity hazards (from F, As, Mo) in shallow, open water supplies, therefore the following recommendations can be made:

- Any open water supplies should be covered
- Water should not be drawn from streams immediately after tephra fall or after the first heavy rains following tephra fall.

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Fig. 1: Field photographs of the study area and studied tephra layer. a) Oldoinyo Lengai covered in tephra fallout from the 2007-2008 eruption, looking at the south-eastern flank of the volcano. Sparse vegetation is already growing back. b) View from about half-way up Oldoinyo Lengai towards the west, onto the rift shoulder of the East African Rift System, which is covered with tephra from the 2007-2008 eruption. The tephra was deposited several kilometers away on the rift escarpment, blown there by the overall wind direction coming from the east. (c) Close up of the 2007-2008 ash deposits showing die-back of vegetation. (d) Close up of the tephra on the northern flank of the volcano and the predominance of spherical pyroclasts.

Fig. 2: Topographic map of the study area. The tephra distribution is the fallout which can be seen on a satellite image, i.e., the part that destroyed the vegetation. The stars indicate the locations of all samples used for this study. Indicated are also the rift escarpment and the Lake Natron, with the main rivers flowing into the lake. Most of the rivers (except the one coming down the rift escarpment) are dry during dry season and only have water during rainy season.

Fig. 3: Leached lava flow and leachate products normalized vs. the average 2006 natrocarbonatitic composition. The photograph shows the lower surface of the 2006 natrocarbonatitic lava flow, and the stalactites, which are a product of leaching the carbonatites. In the graph, it is clearly seen that the alkalis, Cl, SO₃ and Rb are leached out of the flow, whereas the F stays relatively immobile.

Fig. 4: SEM images of different pyroclasts of the samples used for this study. a), b) September 7th 2007 samples, a) euhedral pyroxene crystal with only small amount of ash coating; b) a grain completely covered in ash; c) September 7th ash, backscattered electron image, a droplet of nyerereite (Ny) and gregoryite (G) with small nyerereite and gregoryite in between the larger minerals, the white mineral in the ground mass is sylvite; d) September 7th ash, backscattered electron image, round tephra grain with a large gregoryite crystal, surrounded by smaller gregoryite and sylvite minerals, as well as melt and small ash particles; e), f) secondary electron images of the surface of sample BD4465 (September 24th). The lath-shaped platy minerals on the surface are natrite (Na₂CO₃), and the rounded particles in between (red arrows) are sylvite grains; g) BD4465, backscattered electron image, cross

section through a grain with a large nepheline (N) and garnet (Grt) crystal, in an agglomerate of fine grained minerals and ash particles; h) BD4465, backscattered electron image, agglomerate of nepheline, pyroxene (P) and smaller minerals and ash particles.

Fig. 5: Ternary diagram projected from CO₂, showing the five samples used for this study, together with the average natrocarbonatitic composition from Oldoinyo Lengai (black point, Keller and Zaitsev, 2012) and bulk rock analyses from silicate lavas (grey field, Klaudius and Keller 2006). The natrocarbonatite sampled in June 2007 lies close to the average natrocarbonatitic composition, and the samples collected on September 7th and 24th lie exactly between the natrocarbonatite and the silicate lavas of Oldoinyo Lengai. This implicates that the sampled tephra fall results from mixing of the two endmember magmas.

Fig. 6: Comparison of XRF analyses made of the samples before leaching (left) and the analyses of the leachates (right). The elements are plotted versus SiO₂, as this oxide shows clearly the evolution of the eruption from natrocarbonatitic to nephelinitic. The most remarkable feature is the fluoride, which decreases in the bulk rock analyses with increasing SiO₂, but fluoride increases in the leaching experiment with SiO₂ (as a proxy for time during the eruption).

Fig. 7: Backscattered electron image of a September 7th tephra sample and an elemental distribution map for fluorine showing that fluorine is mainly adhered to the outer surface of the grains (occurring here as sellaite and neighborite).

35°50' E

36°00' E

- ★ Sample locations
- ☼ Tephra distribution
- Main rivers
- 2006 Lava flow
- ⊙ Summit crater
- ▤ Rift escarpment

2°20' S

2°25' S

2°30' S

2°35' S

2°40' S

2°45' S

Peninj

Moinik

Lake Natron

Engare Sero

OL-GATE, CLINIC, SCHOOL

BD4465

OL-LL2

Oldoinyo Lengai

Kilometers

5

Sample/Average 2006 lava natrocarbonatite

Bulk rock composition; wt. %

Leaching experiment; mg/kg water extractable

Table 1. Compilation of measurements of river waters in the vicinity of Oldoinyo Lengai.

Sample#	31	35	36	41	42	43	44	66	74
River	ES	ES	ES	Mo	Mo	Mo	Pe	Pe	Pe
pH	8.54	9.26	9.08	8.29	8.82	8.11	8.92	8.80	8.66
Cl (mg/l)	53.53	104.94	104.94	48.57	48.92	46.44	5.81	6.38	6.74
SO₄ (mg/l)	132.57	332.38	331.42	104.71	102.79	103.75	11.05	10.57	10.57
F (mg/l)	3.46	9.12	8.93	5.89	6.27	5.32	0.46	0.38	0.38

River names: ES: Engare Sero; Mo: Mo'inik; Pe: Peninj (see Fig. 2 for locations).

Data recalculated from Gueddari (1984).

Table 2. Major and selected trace element analyses of the 2006 lava flow before and after leaching, as well as analyses of the stalactites.

Sample	Lava 2006*	Lava 2011	Stalactites
SiO _{2SiO2}	1.71	2.22	0.35
TiO _{2TiO2}	0.04	0.06	0.00
Al ₂ O _{3Al2} O ₃	0.47	0.59	0.00
Fe ₂ O _{3Fe2} O ₃	0.58	1.41	0.00
MnO	0.4	0.54	0
MgO	0.47	0.52	0.02
CaO	16.35	25.60	0.12
SrO	1.3	1.9	0.0
BaO	1.04	1.34	0.00
Na ₂ O Na ₂ O	31.36	22.05	46.21
K ₂ O K ₂ O	7.37	3.20	12.56
P ₂ O _{5P2} O ₅	0.96	0.81	0.97
CO _{2CO2}	31.21	32.52	30.71
Cl	2.60	0.10	8.20
SO ₃	2.26	0.63	4.15
F	2.64	2.31	0.07
-O=F,Cl	1.80	1.00	2.21
Total	98.92	94.79	101.15
Rb	148	74	243
Sr	10646	16696	18
Ba	9286	12177	50
Pb	86	77	9
Th	8	11	0.3
U	12	11	2
Nb	67	103	0.3
Zr	b.d.	31	1
Y	13	15	b.d.
V	137	76	125
La	486	701	1
Ce	717	823	7
Nd	118	170	b.d.

Major elements are in wt% and traces in ppm.

Note that trace elements for the 2006 lava were analyzed by XRF and reanalyzed using LA-ICP-MS for lava and stalactites in 2011

*Average of 3 analyses from Kervyn et al., 2008

Table 3. Bulk rock composition (in wt.%) measured by XRF of all samples used for this study.

Sample	Sampling date	SiO ₂	CaO	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	Fe ₂ O ₃	Cl	SO ₃	F	CO ₂
OL-LL2	19.06.2007	0.11	15.57	33.13	7.98	0.38	0.01	0.33	4.80	3.20	3.22	31.28
OL-GATE	07.09.2007	14.25	16.16	23.04	5.79	1.17	5.03	3.83	1.52	2.05	1.32	23.12
OL-SCHOOL	07.09.2007	12.51	16.42	24.89	5.82	0.85	2.17	2.24	1.91	2.21	1.53	25.52
OL-CLINIC	07.09.2007	7.20	17.71	27.19	6.18	0.74	1.49	1.94	2.15	2.47	1.69	30.29
BD4465	24.09.2007	28.22	16.27	15.76	4.30	1.39	9.66	7.24	0.46	2.07	0.50	9.28

Table 4a. Water extractable major elements in Oldoinyo Lengai lava and tephra.

Sample	Coll. date	pH	Conductivity mS/cm	Ca	Mg	Na (mg/kg water extractable)	K	F	Cl	SO ₄ -S
<i>Oldoinyo Lengai lava</i>										
OL-L12	19.06.2007	11.3	5.34	86	49	149,020	33,467	319	31,003	8,329
<i>Oldoinyo Lengai tephra</i>										
OL-GATE	07.09.2007	10.9	3.73	93	73	77,742	14,369	573	13,301	4285
OL-CLINIC	07.09.2007	10.9	3.19	124	101	107,935	20,595	816	18,489	5982
OL-SCHOOL	07.09.2007	11.0	2.61	132	100	106,019	20,511	703	18,524	5989
BD4465	24.09.2007	10.4	0.162	1481	10	62,646	15,906	895	7,547	5278
Global median*				2,140	335	378	71	129	1,162	1,662
Global maximum*		10.5		23,590	4.24	2,560	788	3,140	11,160	17,770

*Global median and maximum values from Ayris and Delmelle (2012), and Risacher and Alfonso (2001)

Table 4b. Water extractable minor elements in Oldoinyo Lengai lava and tephra.

Sample	Coll.date	Al	As	B	Cu	Fe	Li	Mn	Mo	Zn
mg/kg water extractable										
<i>Oldoinyo Lengai lava</i>										
OL-LL2	19.06.2007	<1	8.6	10.9	0.29	<1	121	<1	72	<1
<i>Oldoinyo Lengai tephra</i>										
OL-GATE	07.09.2007	<1	4.2	2.8	0.17	<1	56	<1	33	<1
OL-CLINIC	07.09.2007	<1	5.9	4.2	0.2	<1	80	<1	43	<1
OL-SCHOOL	07.09.2007	<1	6	3.7	0.33	<1	79	<1	43	<1
BD4465	24.09.2007	<1	5.3	3	0.42	<1	25	<1	<1	1.1
Global median ¹		58	0.13	2.6	5	21	0.22	20	0.063	3.6
Global maximum ¹		1,164	9.3	7.7	95	606	1.9	144	0.62	53

¹From Ayris and Delmelle (2012).

Table Sa. Predicted concentration increases in water for Oldoinyo Lengai ashfall events.

	C_{ash}^2 mg/kg	Ash depth ³ m	Density kg/m ³	A/V ⁴ m ² /l	C_{water}^5 mg/l
F	816	0.01	700	0.0049	28
As	6	0.01	700	0.0049	0.21
Mo	43	0.01	700	0.0049	1.5
B	4.2	0.01	700	0.0049	0.14
Na	107.9	0.01	700	0.0049	3700

Table Sb. Comparatative drinking-water guidelines and indicative human toxicological thresholds for drinking-water

For long-term consumption			For short-term consumption				
Humans ⁵ (mg/l)		Livestock ⁶ (mg/l)	Lethal concentrations ⁷ (mg/l)		Concentration for onset of acute symptoms ⁷ (mg/l)		
	WHO	Tanzanian Gov.		Adult	Child	Adult	Child
F	1.5	8	2	633	258	33	8.3
As	0.01	-	0.2	20	5	0.67	0.17
Mo	0.07	-	0.15-0.5	-	-	-	-
B	0.5	-	5	-	-	-	-
Na*	200	-	-	-	-	-	-

¹Highest values used from Tables 3a and 3b

²Assuming a tephra deposit of 10 mm.

³Valid for 60 gallon trough of length 2 m width 0.66 m depth 0.38 m A/V refers to surface area divided by volume of trough

⁴ $C_{water} = C_{ash} \text{ (mg/kg)} \times \text{ash depth (m)} \times \text{density (kg/m}^3\text{)} \times A/V \text{ (m}^2\text{/L)}$ (Stewart et al., 2013). Note that these are concentration increases.

⁵Reported in Stewart et al. 2013

⁶From the Food and Agriculture Organisation of the United Nations (Avers and Westcott 1994)

⁷See Cronin et al. (2014) for derivations. Water concentrations are derived from toxicological threshold data, assumed body masses of 70 kg for an adult and 10 kg for a child and assumed water consumption rates of 2.1 L/day for an adult and 1.2 L/day for a child. Note that there are considerable uncertainties in the derived thresholds.

^{*}Not a health-based standard but the WHO advises that Na concentrations >200 mg/l may affect the taste of water

Table Sb. Comparatative drinking-water guidelines.

For long-term consumption			For short-term consumption			
Recommended humans ⁶ (mg/l)			Livestock ⁷ Lethal concentrations (mg/l)		Concentration for onset of acute symptoms (mg/l)	
WHO	Tanzania		Adult	Child	Adult	Child
F	1.5	8-2	633	258	33	8.3
As	0.01	- 0.2	20	5	0.67	0.17
Mo	0.07	- 0.15-0.5	-	-	-	-
B	0.5	- 5	-	-	-	-
Na	2008	- -	-	-	-	-

Cases:

A. Drinking-water standards (mg/l) (human)⁶

B. Drinking-water guidelines for livestock (mg/l) ⁷

C. Lethal concentration (mg/l)

D. Concentration for onset of acute symptoms (mg/L)