



# Leaching of lava and tephra from the Oldoinyo Lengai volcano (Tanzania): Remobilization of fluorine and other potentially toxic elements into surface 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<sup>-</sup>) in drinking water of >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<sub>2</sub>), and in the early tephra as Na-Mg bearing salts such as neighborite (NaMgF<sub>3</sub>) and sellaite (MgF<sub>2</sub>). All these three minerals have very low solubility in water (16–130 mg/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.

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## 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 tephtras 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 tephtras 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).

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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 (Ayris 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 addition to this, natrocarbonatitic material (lavas and pyroclastics) are unstable under atmospheric conditions and rapidly break down to form an array of secondary minerals (Dawson et al., 1987; Zaitsev and Keller, 2006).

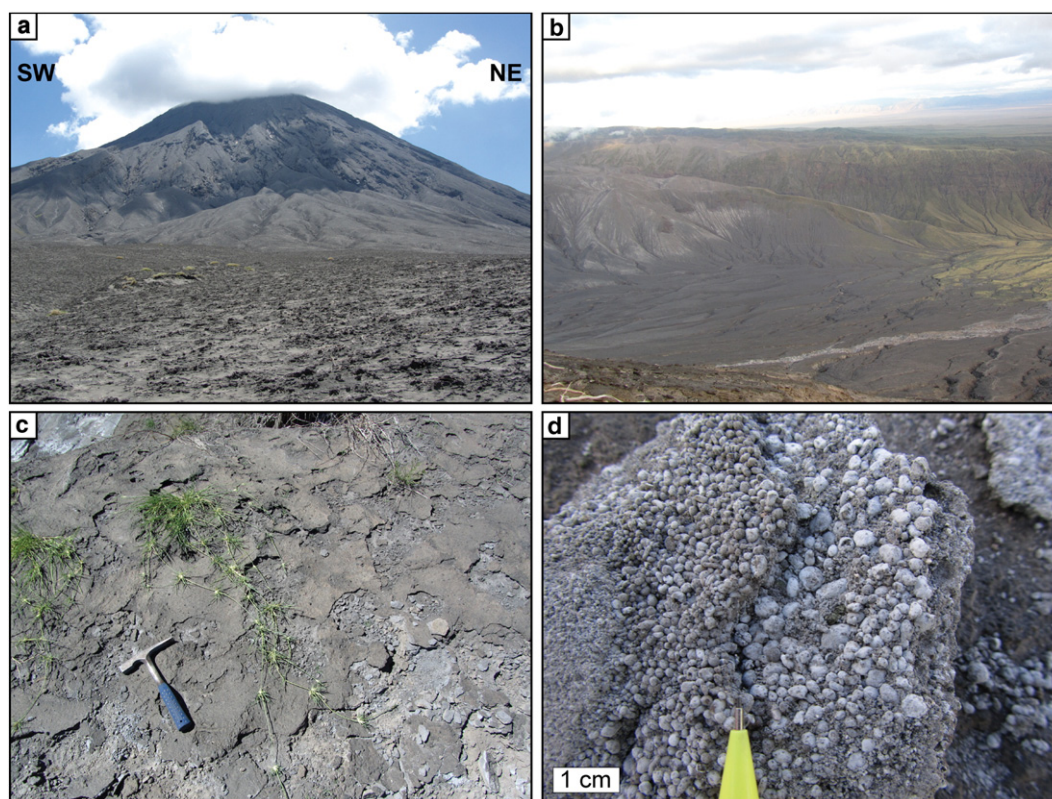
## 2. Background

### 2.1. Geology and eruptive history of Oldoinyo Lengai

Oldoinyo Lengai volcano currently stands approximately 2000 m 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% Na<sub>2</sub>O; 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 <sup>40</sup>Ar/<sup>39</sup>Ar 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, 1995a; Dawson and Mitchell, 2007; Dawson, 2008). In the years between these explosive eruptions (i.e. in 1904, 1914, 1954, 1960–1966, 1983–2007), mildly explosive eruptions and emplacement of natrocarbonatitic lava flows were recorded (Keller and Krafft, 1990; Church and Jones, 1994; 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 (75% and 25%, respectively), with the smooth-rounded shapes of the natrocarbonatitic



**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.

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