

Tracing helium isotope compositions from mantle source to fumaroles at Oldoinyo Lengai volcano, Tanzania



Gaëlle Mollex^{a,*}, Evelyn Füri^a, Pete Burnard^a, Laurent Zimmermann^a, Gilles Chazot^b, Emmanuel O. Kazimoto^c, Bernard Marty^a, Lydéric France^a

^a CRPG, UMR 7358, CNRS, Université de Lorraine, 15 rue Notre Dame des Pauvres, 54501 Vandœuvre-lès-Nancy, France

^b Université de Brest, CNRS, UMR 6538 Domaines Océaniques, Institut Universitaire Européen de la Mer, Place Copernic, 29280 Plouzané, France

^c Department of Geology, University of Dar es Salaam, P. O. Box 35052, Dar es Salaam, Tanzania

ARTICLE INFO

Keywords:

Carbonatite
Neon
2007–2008 eruption
SCLM
Cognate xenoliths
Helium
Neon
Argon

ABSTRACT

Oldoinyo Lengai is the only volcano on Earth currently erupting natrocarbonatites, of which the source and genesis remain controversial. Cognate xenoliths and fumaroles were sampled at the summit of Oldoinyo Lengai, and deep crustal xenoliths from Oltatwa maar, in 2010 and 2014, after the 2007–2008 sub-Plinian eruption. The summit cognate xenoliths provide direct information on the isotopic composition of the mid-crustal magma chamber that was active during the 2007–2008 explosive eruption. Cognate xenolith-hosted pyroxenes from Oldoinyo Lengai have an average ${}^3\text{He}/{}^4\text{He} = 6.58 \pm 0.46 R_A$, similar to values from nearby silicate volcanoes ($4.95\text{--}7.30 R_A$), and reflecting a sub-continental lithospheric mantle (SCLM) signature. This similarity implies that Oldoinyo Lengai carbonatites form from a similar mantle reservoir as the nearby silicate volcanoes. We identify SCLM, metasomatized by fluids/melts derived from the depleted convective mantle, as the common source of magmas in the Arusha volcanic province. Fumarole measurements highlight that fumarolic ${}^3\text{He}/{}^4\text{He}$ values have been relatively constant since at least 1988, indicating that dramatic changes to the crater region morphology during the 2007–2008 eruption did not affect the architecture of the hydrothermal system, which is probably connected to the crustal magma chamber(s). Moreover, the similarity between ${}^3\text{He}/{}^4\text{He}$ values from the mid-crustal magma chamber ($6.58 \pm 0.46 R_A$) and fumaroles ($7.31 \pm 0.24 R_A$) of Oldoinyo Lengai attests that helium is not subjected to atmospheric contamination or crustal assimilation during transport to the surface.

1. Introduction

Carbonatite magmas are unusual as they are characterized by high concentrations of primary magmatic carbonate ($\geq 50\%$), and $< 20\%$ SiO_2 (LeMaitre, 2002). They are far less common than silicate magmas, yet have been emitted throughout Earth's history, and on all continents. The origin of carbonatite magmas remains controversial, and they are considered to represent either primary melts of a carbon-rich (metasomatized) mantle domain, or the products of liquid immiscibility, late-stage fractionation, or remobilized crustal carbonates (e.g., Jones et al., 2013, and references therein). Oldoinyo Lengai (East African Rift – EAR) is the lone volcano erupting carbonatites today, and therefore of key importance for investigation of the genesis and evolution of carbonatite melts, and the plumbing system of a carbonatite volcano.

Noble gases, particularly helium isotopes, are powerful geochemical tools for tracing mantle sources or determining the degree of crustal contamination in magmatic phenomena (Graham, 2002); they therefore

may provide constraints on the origin and evolution of carbonatite melts generated at Oldoinyo Lengai. Helium isotopic ratios (${}^3\text{He}/{}^4\text{He}$) of mantle-derived gases in the EAR and Natron valley have been well documented. In the Afar region (northern EAR), Marty et al. (1996) reported helium isotopic ratios ranging from $0.035 R_A$ (where R_A is the atmospheric ${}^3\text{He}/{}^4\text{He}$ of 1.4×10^{-6}) for low-Ti lavas, demonstrating a high degree of crustal contamination, to $19.6 R_A$ for high-Ti lavas, reflecting the surface manifestation of a primitive mantle plume. In the Kenyan and Tanzanian cratons (central EAR), Pik et al. (2006) and Barry et al. (2013) found helium isotopic compositions to be consistently mid-ocean ridge basalt (MORB)-like ($8 \pm 1 R_A$) or lower, indicating either an asthenospheric upper mantle source combined with crustal assimilation, or a sub-continental lithospheric mantle (SCLM) source. Hilton et al. (2011) measured high ${}^3\text{He}/{}^4\text{He}$ up to $15 R_A$ at the southernmost extension of the EAR within the Kenya Dome, implying the involvement of a deep mantle source. Combined He-Ne-Ar isotopic compositions of mantle-derived xenoliths and lavas are also explained

* Corresponding author.

E-mail address: gaelle.mollex@mailoo.org (G. Mollex).

<http://dx.doi.org/10.1016/j.chemgeo.2017.08.015>

Received 9 December 2016; Received in revised form 31 May 2017; Accepted 14 August 2017

Available online 15 August 2017

0009-2541/© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

by the deeply rooted African plume, which impacts the entire EAR (Halldórsson et al., 2014). However, the number of plumes below the EAR, and their influence on magmatism in the region, remain controversial.

Helium isotopic compositions of mantle xenolith-hosted minerals from small cones and maars near Oldoinyo Lengai (Porcelli et al., 1986; Hilton et al., 2011) and nearby volcanoes (Pik et al., 2006; Hilton et al., 2011; Halldórsson et al., 2014) range from 4.95–6.79 R_A , consistent with a SCLM signature ($6.1 \pm 0.9 R_A$; Gautheron and Moreira, 2002; Dunai and Porcelli, 2002, and references therein). All fumarolic $^3\text{He}/^4\text{He}$ measurements from the summit of Oldoinyo Lengai have as well been consistent with SCLM or MORB sources: a value of 7.6 R_A was first reported by Javoy et al. (1988), values of 6.32–7.02 R_A were measured prior to the 2007–2008 explosive eruption (Teague et al., 2008; Fischer et al., 2009), and two gas samples after the 2008 explosive phase yielded a value of 6.77 R_A (Barry et al., 2013). The good agreement between all previous helium measurements and SCLM or MORB helium signatures precludes the involvement of a deep, undegassed mantle source or crustal carbonates during the genesis of Oldoinyo Lengai carbonatites.

To further understand the spatio-temporal helium isotope variations at Oldoinyo Lengai, we present helium isotope compositions of fumarolic gases and xenolith-hosted minerals sampled after the 2007–2008 explosive eruption, and compare those with previously published results related to the Arusha volcanic province. These data allow us to (1) discuss the mantle source of Oldoinyo Lengai magmas, including carbonatites; (2) discuss the processes that govern the genesis and evolution of carbonatites and related alkaline magmas; and (3) provide new constraints on the architecture and evolution of the hydrothermal system following an explosive eruption that modified its surface expression.

2. Geological setting of Oldoinyo Lengai and the 2007–2008 eruption

Oldoinyo Lengai stratovolcano is located in the Natron Lake volcanic province in northern Tanzania (eastern branch of the EAR; Fig. 1A). Much of the edifice comprises phonolite and nephelinite lavas, tuffs, and agglomerates, but eruption of natrocarbonatite lava flows has been the dominant activity over the last century (Klaudius and Keller, 2006). Carbonatites of Oldoinyo Lengai are characteristically low viscosity, sodium- and potassium-rich, and strongly enriched in incompatible trace elements (Zaitsev and Keller, 2006). Oldoinyo Lengai represents a natural laboratory for the study of carbonatite genesis, as it is the only active system erupting carbonatites, and thus preserves the link between natrocarbonatite and silicate lavas.

Various models have been proposed to explain the formation of Oldoinyo Lengai natrocarbonatite magmas. Derivation from an unusually carbon-rich mantle (Morogan and Martin, 1985) is unlikely since $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, and $^3\text{He}/^4\text{He}$ values, and $\text{CO}_2/^3\text{He}$ elemental ratios of fumarolic gases are similar to MORB signatures (Fischer et al., 2009; Barry et al., 2013). Moreover, Fischer et al. (2009) estimated the Oldoinyo Lengai mantle source to contain ≤ 300 ppm C based on comparison of $\text{CO}_2/^3\text{He}$ ratios between the upper MORB mantle and Oldoinyo Lengai. Instead, a very low degree of partial melting ($\leq 0.3\%$) and extreme crustal differentiation may lead to immiscibility between silicate and carbonatite magmas. Although this hypothesis is supported by numerous studies, the origin and evolution of the Oldoinyo Lengai parental magma is still debated. Peterson and Kjarsgaard (1995) and Dawson (2012) proposed that Oldoinyo Lengai lavas are derived from intense fractionation of olivine nephelinite melts, whereas Wiedenmann et al. (2010) and Keller et al. (2006) argued for a connection between olivine melilitites and highly evolved peralkaline combeite-wollastonite nephelinites.

Eruptions at Oldoinyo Lengai alternate between effusive and explosive activity; during the last century, five major explosive eruptions

have been observed, the last of which began in September 2007. Silicate and carbonatite lavas were erupted contemporaneously during this sub-Plinian phase (Bosshard-Stadlin et al., 2014; Keller et al., 2010), in contrast to typical effusive emplacement of solely natrocarbonatite flows. Dike emplacement below Gelai and Oldoinyo Lengai volcanoes occurred before the 2007–2008 eruptions (Albaric et al., 2010). Less-evolved, recharged magma injected into the deep, still active Oldoinyo Lengai magma chamber interacted and mixed with the resident natrocarbonatite magma, thereby triggering CO_2 exsolution and the associated explosive eruption (Bosshard-Stadlin et al., 2014). The 2007–2008 eruption dramatically changed the morphology of the Oldoinyo Lengai northern summit plateau, forming a ~ 120 -m-deep, ~ 400 -m-wide crater, and destroying hornitos that had previously emitted natrocarbonatite lava flows. The hydrothermal system related to the northern crater, from which numerous fumarole measurements had been obtained, was also destroyed.

3. Samples and analytical methods

3.1. Sample descriptions

Rocks and fumaroles were sampled in 2010 and 2014, thus after the 2007–2008 explosive eruption. Samples 10TL01, 10TL05, and 10TL06 are coarse-grained xenoliths from the rim of the northeast crater, and represent the most recent products of the explosive eruption. Petrologically, the xenoliths are coarse grained (thus having crystallized at depth), display a cumulative texture, and are classified as ijolite (nepheline, clinopyroxene, and garnet main phases, with subordinated apatite, sulfides, Ti-magnetite, wollastonite, and quenched melt). The widespread occurrence of quenched interstitial melt at grain boundaries (see Fig. S1), textural relationships with surrounding minerals, and wetting angles provide evidence for a late stage melt that quenched during rapid xenolith ascent to the surface. The selected xenoliths were therefore crystallizing at depth when the eruption occurred, and can be considered as deriving from a crystal mush zone of the 2007–2008 active magma chamber. These samples are cognate xenoliths that sampled the mid-crust magma chamber (Mollex et al., 2015). Petrographic relationships (mutual inclusive relations) allow us to constrain the crystallization sequence: first clinopyroxene, then garnet, then nepheline, then apatite. As pyroxene was the first mineral to crystallize in the magma chamber, it documents the least evolved melt available; pyroxene grains were thus hand-picked and analyzed with the aim of deriving the composition of noble gases present within the magma chamber. For the Oldoinyo Lengai summit samples, ~ 300 mg of pyroxene were analyzed by vacuum crushing to extract noble gases (He, Ne, Ar) trapped in inclusions and along grain boundaries. Two to three replicate analyses were carried out per sample (Table 1).

To obtain a crustal profile of noble gases in the Oldoinyo Lengai igneous plumbing system, we sampled another cumulate at Oltatwa maar, on the eastern slope of Oldoinyo Lengai. Sample 14TG21 is a cumulate xenolith containing spinel, olivine, clinopyroxene, phlogopite, pargasite, and subordinated sulfides - a mineralogical assemblage indicating deep crustal crystallization. It has been sampled at the northern tip of the phlogopite and olivine melilitite tuffs that erupted 353 ± 65 kya (Sherrod et al., 2013). These melilitites near Oldoinyo Lengai are considered to be the most primitive magmas of the area (Keller et al., 2006), and are interpreted as having rapidly ascended from mantle or deep crustal depths (e.g., Mattsson et al., 2013). Based on its mineralogy, the presence of olivine-hosted very primitive nephelinite melt inclusions, and the composition of the host melt, we suggest that sample 14TG21 is a deep crustal cumulate, therefore documenting deep crustal processes and compositions. Olivine grains were hand-picked and analyzed for noble gas content by vacuum crushing.

In addition to the above samples that document mid- and deep-crust magmatic systems, we sampled fumaroles at the northern crater of

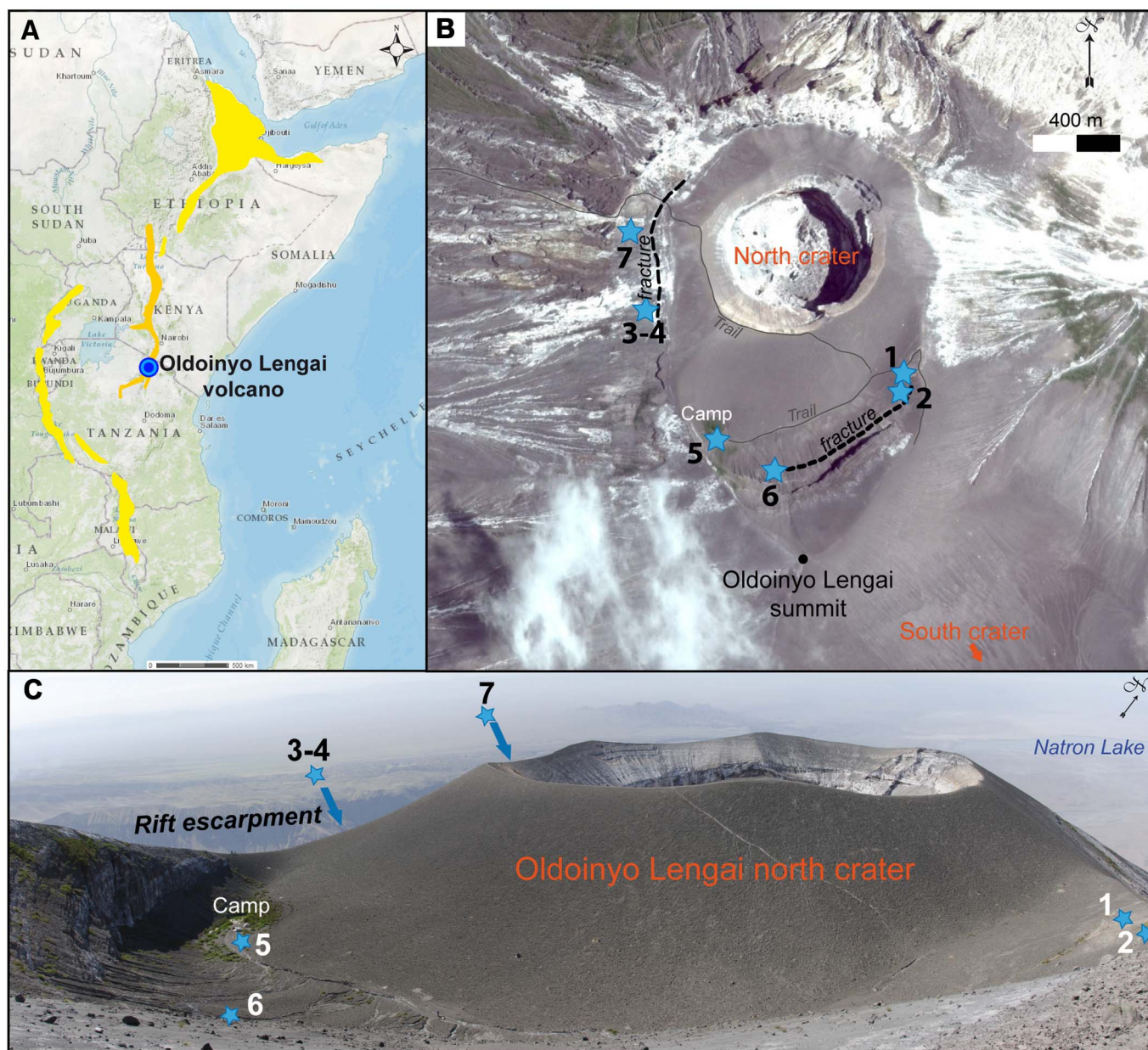


Fig. 1. A) Location of Oldoinyo Lengai in the EAR system (represented in orange). The background map is from Google Earth, with data from the Data SIO, NOAA, U.S. Navy, NGA, and GEBCO Image Landsat. Yellow represents the wider African Rift system. B) Satellite view of Oldoinyo Lengai crater. Blue stars indicate fumarole sampling locations, with location numbers corresponding to the last digit of sample numbers (e.g., sample OLD14-05 is from fumarole 5). C) An October 2014 photograph illustrating the crater morphology after the last explosive eruption and further detailing the location of the sampled fumaroles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Oldoinyo Lengai (Fig. 1B and C) to trace the complete evolution of the noble gas signature from the mantle source to the surface (Table 2). At the summit of Oldoinyo Lengai, seven fumaroles were accessible; yet, only the fumaroles with a temperature $> 50\text{ }^{\circ}\text{C}$ were selected for this study (fumaroles #1, 3, 6, and 7; Fig. 1B and C) because fumaroles of lower temperature are more likely to be contaminated by air. Gas samples were collected by two methods; two samples were collected in 300 ml evacuated glass flasks containing 50 ml of 5 N NaOH solutions (Giggenbach and Goguel, 1989), whereas the other gas samples were collected in copper tubes. Gas samples in Giggenbach bottles were immediately transferred into double-valve stainless steel samplers upon return from the field to minimize diffusive loss of helium.

3.2. Noble gas analyses

Noble gas (He-Ne-Ar) compositions were analyzed at the noble gas laboratory at CRPG, Nancy (France). Mineral separates (pyroxene and olivine) were cleaned in an ultrasonic acetone bath, placed in crushers, and baked at $80\text{ }^{\circ}\text{C}$ for 12 h to desorb any gases trapped on the grain surface. The mass of minerals analyzed for each sample is presented in Table 1. The noble gas purification and crushing methods are described in detail in Burnard et al. (2013). Helium, neon, and argon isotopic abundances and ratios were measured using a VG5400 noble gas mass spectrometer (or a Helix MC Plus for sample 10TL05). The $^{40}\text{Ar}^{++}$ contribution to ^{20}Ne was monitored and found to be negligible (i.e., ≤ 5 cps). The CO_2^{++} signal of all samples was comparable to the mass spectrometer background, and the contribution of CO_2^{++} to the ^{22}Ne signal was corrected as part of the blank. On the Helix MC Plus, we

Table 1
Noble gas (He, Ne, Ar) abundances and isotopic ratios of the 2007–2008 Oldoinyo Lengai xenoliths.

Sample	Name	mml	Weight	Helium			Neon			Argon					
				⁴ He	³ He/ ⁴ He	⁴ He/ ²⁰ Ne	²⁰ Ne	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	³⁶ Ar	⁴⁰ Ar/ ³⁶ Ar	³⁸ Ar/ ³⁶ Ar	⁴ He/ ⁴⁰ Ar ⁿ		
		mg	10 ⁻¹² mol/g	(R/R _A)	10 ⁻¹⁵ mol/g	10 ⁻³	10 ⁻¹⁴ mol/g	10 ⁻²	±	±	±	±	±	±	
10TL01	10TL01-1	cpx	342	1.30	0.13	6.68	0.62	932	1.40	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
	10TL01-2	cpx	308	3.86	0.37	2.42	0.36	760	5.08	0.07	9.89	0.10	28.8	0.6	1.065
10TL05	10TL05 ^a	cpx	334	3.31	0.06	6.60	1.14	390	8.50	0.27	9.97	0.63	30.7	2.7	2.140
	10TL05-1	cpx	314	5.19	0.50	6.62	0.40	789	6.58	0.09	9.75	0.10	30.8	0.8	1.459
	10TL05-2	cpx	322	7.35	0.71	7.24	0.44	6110	1.20	0.02	10.77	0.73	36.9	3.0	1.082
10TL06	10TL06-1	cpx	332	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.883	0.011
	10TL06-2	cpx	344	1.39	0.13	5.79	0.82	741	1.87	0.03	9.46	0.20	27.3	3.7	0.395
14TG21	14TG21	ol	330	4.20	0.40	4.89	0.72	846	4.97	0.07	9.57	0.10	30.0	0.9	n.d.

n.d. - no data due to high blank contributions (≥ 20%).

mml - analyzed minerals; cpx - clinopyroxene, and ol - olivine.

^a Sample 10TL05 was analyzed using a Helix MC Plus, whereas all other samples were analyzed using a VG5400.

corrected the ²⁰Ne signal for interference from HF⁺, assuming a constant HF⁺ signal of 0.004 V. Given the high mass resolution of the MC Plus (~1800), ⁴⁰Ar⁺⁺ is partially resolved from the peak of interest (Honda et al., 2015). The CO₂⁺ signal was monitored after each analysis, and the ²²Ne signal was corrected using a CO₂⁺⁺/CO₂⁺ ionization ratio of 0.8%.

Standard and blank analyses were performed before and after each mineral sample analysis, using the same protocol as for the samples. Notably, the standard aliquot was diluted in the purification line in order to match the ion intensities of the samples. Air was used to determine analytical sensitivity and reproducibility, except for helium, for which we used the standard HESJ of Matsuda et al. (2002) with ³He/⁴He of 20.63 ± 0.10 R_A. The reproducibility of standard measurements was on the order of 1.8% for argon, 2.6% for neon, and 9% for helium abundances, whereas the reproducibility of the isotopic ratio of the helium standard is 3.5%. Blank contributions to sample analyses were ≤ 15% for ²⁰Ne (1 × 10⁻¹⁶ mol) and ≤ 10% for ³⁶Ar (5 × 10⁻¹⁶ mol; with the exception of gas-poor sample 14TG21, for which the Ar blank represented 24%); helium blanks were below the detection limit (≤ 10⁻¹⁶ mol). Analyses with blank contributions ≥ 20% are not considered for further discussion. The uncertainty attributed to the data (1 sigma) includes both internal (i.e., counting statistics) and external (i.e., standard reproducibility) analytical uncertainties.

The helium isotopic composition and the ⁴He/²⁰Ne ratio of fumarole gases were analyzed with the Helix SFT multicollector noble gas mass spectrometer, following separation of the He-Ne fraction from the heavy noble gases using liquid nitrogen cooled activated charcoal. The standard reproducibility of the helium isotope ratio was better than 5%, and blank contributions were below the detection limit (therefore assumed to be negligible). Fumarole gas analyses were bracketed by blank and air-standard measurements. Neon isotope ratios were measured with the Helix MC Plus on a separate gas aliquot. However, the measured ratios were not corrected for possible mass interferences. Therefore, the reported ²⁰Ne/²²Ne and ²¹Ne/²²Ne ratios should be used with caution.

4. Results

4.1. Helium isotopic composition of the deep- and mid-crust magmatic system

Olivine and pyroxene separates, which are inferred to reflect, in the present study, the noble gas composition of the deep- and mid-crust magmatic system at Oldoinyo Lengai, respectively, have helium concentrations ranging from 1.30 × 10⁻¹² to 7.35 × 10⁻¹² mol/g and high ⁴He/²⁰Ne ratios of 390–6110 (Table 1). Helium isotopic compositions of pyroxenes of the three cognate xenoliths (10TL01, 10TL05, 10TL06) and olivines of the cumulate xenolith (14TG21) vary between 2.42 ± 0.36 and 7.24 ± 0.44 R_A. The lowest pyroxene helium isotope ratio (2.42 R_A) of sample 10TL01-2 is enigmatic; the high ⁴He/²⁰Ne of these pyroxenes (760) is indistinguishable from the other mineral separates, and rules out air contamination as the cause of the low ³He/⁴He. Furthermore, since all pyroxene samples are products of the same very recent eruption, post-eruptive radiogenic in-growth of ⁴He cannot have lowered the ³He/⁴He of sample 10TL01-2. Similarly, pre-eruptive in-growth of ⁴He or a significant crustal contamination appears inconsistent with the fact that the ⁴He concentration of sample 10TL01-2 agrees with that of the other samples. Given that its duplicate (10TL01-1) yields ³He/⁴He = 6.68 ± 0.62 R_A, sample 10TL01-2 is excluded from further discussion. Thus, the helium isotope compositions of the cognate xenoliths sampled at the summit of Oldoinyo Lengai vary from 5.79 ± 0.82 R_A for sample 10TL06-2 to 7.24 ± 0.44 R_A for sample 10TL05-2. These ³He/⁴He values overlap with the SCLM (5.2 to 7.0 R_A; Gautheron and Moreira, 2002) and the lower end of the MORB range (7 to 9 R_A; Graham, 2002; Fig. 2).

Table 2
Helium and neon isotopic ratios, and $^4\text{He}/^{20}\text{Ne}$ ratios, of Oldoinyo Lengai fumaroles.

Sample	Sampling	#	Temperature	$^3\text{He}/^4\text{He}$	\pm	$^4\text{He}/^{20}\text{Ne}$	\pm	$^3\text{He}/^4\text{He}$	\pm	$^{20}\text{Ne}/^{22}\text{Ne}$	\pm	$^{21}\text{Ne}/^{22}\text{Ne}$	\pm
Name	Vessel	Fumarole		(R/R _A)				R _C /R _A				10 ⁻²	
OLD14-01	Cu tube	1	79 °C	7.07	0.29	207	7	7.08	0.38	n.d.		n.d.	
OLD14-03	Cu tube	3	62 °C	6.57	0.26	3.40	0.02	7.24	0.29	n.d.		n.d.	
OLD14-04_1	Giggenbach	3	62 °C	6.91	0.28	4.72	0.02	7.41	0.30	9.87	0.02	2.99	0.027
OLD14-04_2				n.d.		n.d.		n.d.		9.83	0.03	2.88	0.031
OLD14-06	Cu tube	6	79 °C	6.70	0.27	6.48	0.08	7.05	0.30	n.d.		n.d.	
OLD14-07_1	Giggenbach	7	75 °C	7.32	0.30	228	1.3	7.33	0.30	10.00	0.04	2.76	0.038
OLD14-07_2				7.75	0.31	462	6	7.76	0.33	n.d.		n.d.	

n.d. – no data due to high blank contributions ($\geq 20\%$).

Olivines of the cumulate xenolith from Oltatwa maar (sample 14TG21) have helium isotopic compositions of $4.89 \pm 0.72 R_A$, agreeing, within error, with the $^3\text{He}/^4\text{He}$ of two of the cognate mid-crustal magma chamber xenoliths. This value is also remarkably similar to pyroxenes from mantle-derived xenoliths of Pello Hill (Hilton et al., 2011). However, given the older eruption age of sample 14TG21 (365 kya; Sherrod et al., 2013), a contribution of radiogenic ^4He from post-eruptive in-growth cannot be ruled out, so the measured isotopic ratio represents a minimum estimate. Therefore, the $^3\text{He}/^4\text{He}$ of olivines of the Oltatwa xenolith cannot be distinguished from those of the Oldoinyo Lengai pyroxenes.

4.2. Neon and argon isotopic compositions of Embalulu Oltatwa and Oldoinyo Lengai

Neon isotopic compositions of Oldoinyo Lengai pyroxenes (10TL01, 10TL05, 10TL06) and Embalulu Oltatwa olivines (14TG21) are similar to the air ratio (Fig. 3). The only exception is sample 10TL05-2, which also records the highest $^3\text{He}/^4\text{He}$ value; these pyroxenes are characterized by $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ of 10.77 ± 0.73 and 0.037 ± 0.003 , respectively. These values are in the range of the MORB line defined by Moreira et al. (1998) and Sarda et al. (1988), and the SCLM line defined by Gautheron et al. (2005), and indicate mixing of neon derived from the air with MORB or SCLM reservoirs.

Pyroxenes from the cognate xenolith samples of Oldoinyo Lengai are enriched in ^{40}Ar compared to the atmospheric ratio ($^{40}\text{Ar}/^{36}\text{Ar} = 298.56 \pm 0.31$; Lee et al., 2006), with $^{40}\text{Ar}/^{36}\text{Ar}$ varying from 332 ± 27 to 675 ± 12 (Table 1). Since the xenoliths were erupted very recently, their elevated $^{40}\text{Ar}/^{36}\text{Ar}$ values cannot result from the post-eruptive radioactive decay of ^{40}K . Instead, such elevated isotopic ratios compared to air indicate mixing between air and a mantle reservoir with a high $^{40}\text{Ar}/^{36}\text{Ar}$ value; however, the measured isotopic ratio does not permit distinction between the MORB reservoir (maximum $^{40}\text{Ar}/^{36}\text{Ar}$ of $\sim 44,000$; Moreira et al., 1998) or the deep mantle ($^{40}\text{Ar}/^{36}\text{Ar} \leq 10,000$; Mukhopadhyay, 2012).

For each mineral sample, ^{40}Ar concentrations are corrected for atmospheric argon by:

$$^{40}\text{Ar}^* = [^{36}\text{Ar}_m] \times \left[\left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_m - \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_{\text{air}} \right],$$

where $^{36}\text{Ar}_m$ and $(^{40}\text{Ar}/^{36}\text{Ar})_m$ are the measured ^{36}Ar concentration and argon isotopic ratio, respectively, and $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}}$ is the isotopic ratio of air. We assume that all ^{36}Ar is derived from the atmosphere. Our calculated $^4\text{He}/^{40}\text{Ar}^*$ ratios range from 0.41 to 5.69 (Table 1), similar to the calculated $^4\text{He}/^{40}\text{Ar}$ mantle production ratio, which is on the order of 2.9 (1.6–4.2) based on the U, Th, and K concentrations of the mantle (Jochum et al., 1983; Graham, 2002). Since equilibrium degassing leads to increased $^4\text{He}/^{40}\text{Ar}^*$ in the residual magma due to the solubility contrast between He and Ar in basaltic melts (Jambon et al., 1986), low $^4\text{He}/^{40}\text{Ar}^*$ values between 1.6 and 4.2 are generally assumed to indicate that samples have not experienced significant

degassing (e.g., Furi et al., 2010). Our calculated $^4\text{He}/^{40}\text{Ar}^*$ values are therefore consistent with their parent Oldoinyo Lengai melts being relatively undegassed. The undegassed cognate xenoliths are thus consistent with an origin as partially crystallized crystal mushes that document the mid-crustal magma chamber.

4.3. He and Ne compositions of Oldoinyo Lengai fumaroles

The measured helium isotopic compositions of Oldoinyo Lengai fumaroles sampled in 2014 range from $6.57 \pm 0.26 R_A$ to $7.75 \pm 0.31 R_A$. These helium isotope ratios were corrected for atmospheric contamination on the basis of the $^4\text{He}/^{20}\text{Ne}$ ratio measured in the gas samples (Sano and Wakita, 1985). The corrected helium isotopic ratios (R_C) agree within error, varying from $7.05 \pm 0.30 R_A$ for fumarole #6 to $7.76 \pm 0.33 R_A$ for sample 2 from fumarole #7 (Fig. 4), with an average fumarolic value of $7.31 \pm 0.24 R_A$. Notably, replicate analyses of sample OLD14-07 yielded consistent results of 7.33 ± 0.30 and $7.76 \pm 0.33 R_A$. In general, the helium isotopic compositions of the 2014 Oldoinyo Lengai fumarole samples are comparable to the lower end of the MORB range; however, uncertainties on the measurements are large enough that no clear distinction can be made between a MORB and SCLM signature.

Neon isotopic ratios of samples OLD14-07 and OLD14-04 that were collected in the Giggenbach bottles are $^{20}\text{Ne}/^{22}\text{Ne} = 9.83\text{--}10.00$ and $^{21}\text{Ne}/^{22}\text{Ne} = 0.028\text{--}0.029$, and have not been corrected for possible mass interferences. Notably, these values are similar to the isotopic signature of air (Fig. 3), indicating severe atmospheric contamination of the collected gases. Therefore, no inference can be made about the neon signature of the Oldoinyo Lengai mantle source based on the fumarolic gases.

5. Discussion

5.1. Spatial distribution of helium isotopes, and carbonatite genesis

In Fig. 2, our xenolith-hosted mineral samples are compared to other xenoliths sampled in the Arusha volcanic province within 100 km of Oldoinyo Lengai (Pik et al., 2006; Hilton et al., 2011; Halldórsson et al., 2014). The five pyroxene samples that document the active mid-crustal magma chamber have an average $^3\text{He}/^4\text{He} = 6.58 \pm 0.46 R_A$, in excellent agreement with $6.78 \pm 0.13 R_A$ previously reported for pyroxenes from the Oldoinyo Lengai summit (Hilton et al., 2011). Thus, all measurements of summit xenoliths are similar. Furthermore, olivines of a mantle peridotite xenolith at the nearby Embalulu Kirurum volcano are comparable, with $^3\text{He}/^4\text{He} = 5.91 \pm 0.12 R_A$ (Hilton et al., 2011). The deep crustal cumulative xenolith from the adventive eastern flank maar of Oldoinyo Lengai (Embalulu Oltatwa) is characterized by a slightly lower $^3\text{He}/^4\text{He}$ of $4.89 \pm 0.72 R_A$; however, post-eruptive radiogenic ingrowth may have affected this sample. Within error, both the Oltatwa (deep crustal) and Embalulu Kirurum (mantle) sources have helium isotope compositions similar to Oldoinyo

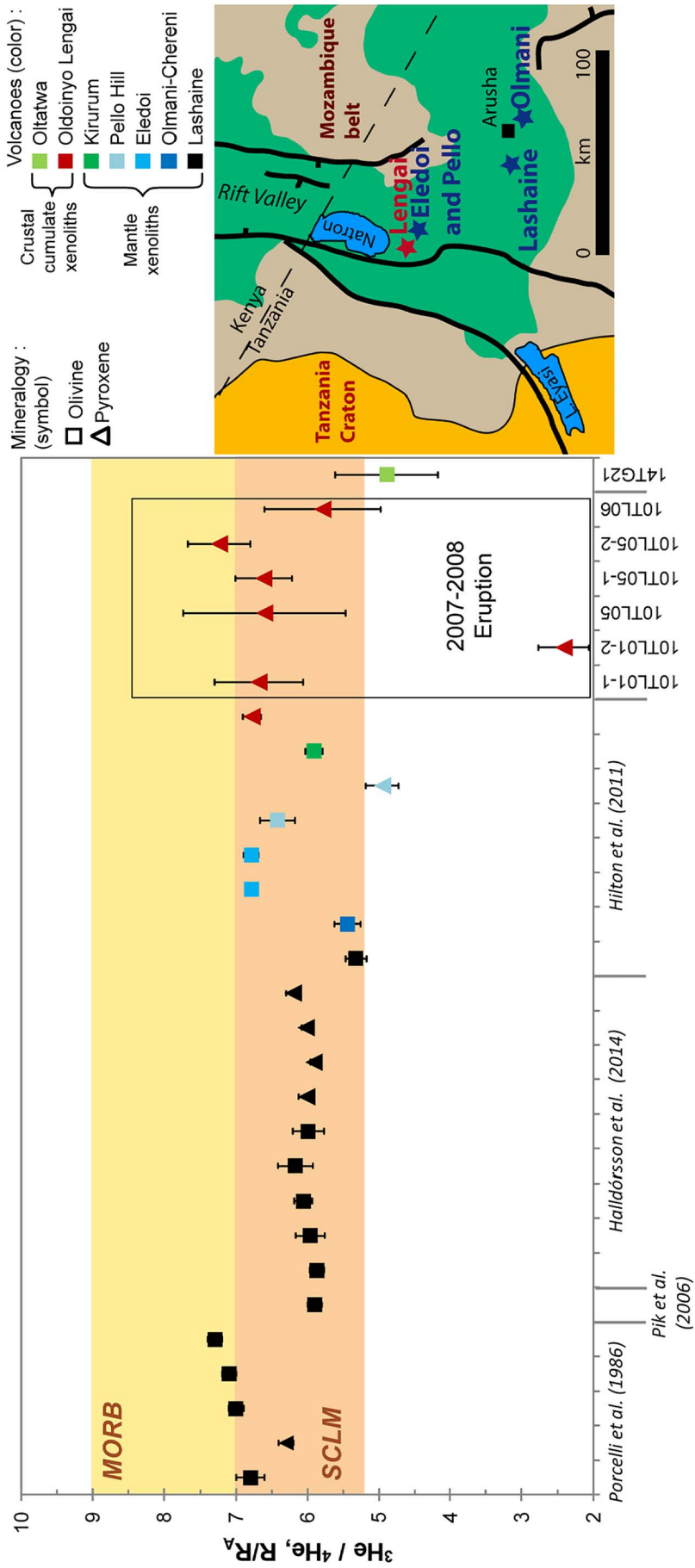


Fig. 2. Measured helium isotopic ratios (R/R_A) from in-vacuo crushing analyses of pyroxene (triangles) and olivine (squares) in xenoliths from the east branch of the EAR. Symbol colors indicate the sampled volcanoes. Oltatwa is a maar on the Eastern flank of the Oldoinyo Lengai. The typical range for the depleted mantle (MORB; 7–9 R_A ; Graham, 2002) and SCLM (5.2–7.0 R_A ; Gautheron and Moreira, 2002) are indicated in yellow and orange, respectively. The map represents a simplified geological map of the Arusha region, with volcanic rocks show in green, and sampled volcanoes indicated by stars. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

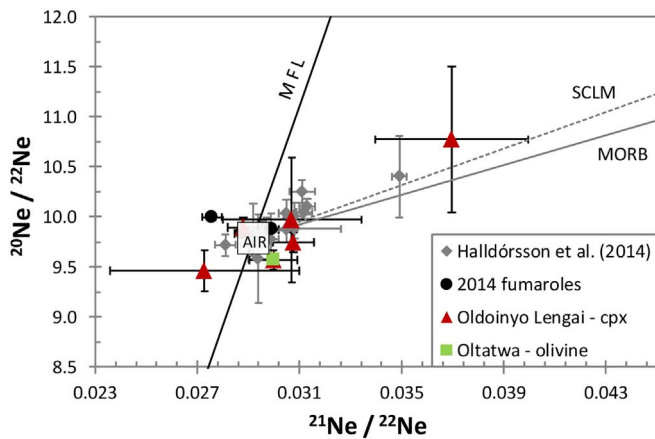


Fig. 3. Neon isotope systematics ($^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$) of minerals and fumaroles from Oldoinyo Lengai and Oltatwa maar. One clinopyroxene (cpx) sample lies on the MORB or SCLM lines (Moreira et al., 1998; Sarda et al., 1988), indicating mixing between the MORB or SCLM end-member and air. Gray data points are from northern Tanzania (Halldórsson et al., 2014). MFL is the mass fractionation line.

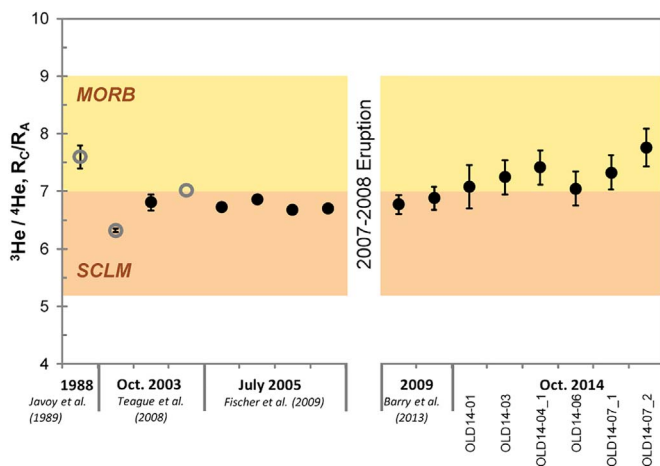


Fig. 4. Corrected helium isotopic ratios (R_C/R_A) of Oldoinyo Lengai fumaroles, where R_C is the $^3\text{He}/^4\text{He}$ ratio corrected for atmospheric contamination. Data are shown as a function of relative time, and include five fumaroles from this study and results from the literature (Javoy et al., 1988; Teague et al., 2008; Fischer et al., 2009; Barry et al., 2013). Gray data points represent uncorrected $^3\text{He}/^4\text{He}$ values (R/R_A). The typical range of the depleted mantle (MORB; 7–9 R_A ; Graham, 2002) and SCLM (5.2–7.0 R_A ; Gautheron and Moreira, 2002) are indicated in yellow and orange, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Lengai.

At about 10 km from Oldoinyo Lengai, mantle-derived olivines from the Eledoi volcano have $^3\text{He}/^4\text{He} = 6.69 \pm 0.10 R_A$ (Hilton et al., 2011), values overlapping with our crustal pyroxene and olivine measurements at Oldoinyo Lengai. Still further away, mantle xenoliths from Lashaine and Olmani-Chereni volcanoes have helium isotopic ratios of $6.02 \pm 0.10 R_A$ (based on 10 measurements) and $5.44 \pm 0.18 R_A$, respectively (Halldórsson et al., 2014). Porcelli et al. (1986) reported higher values of $6.9 \pm 0.3 R_A$ for Lashaine olivines, but their samples might have been affected by a cosmogenic ^3He contribution (Porcelli et al., 1987). Thus, although the $^3\text{He}/^4\text{He}$ of the Olmani-Chereni mantle source is slightly lower than that of Oldoinyo Lengai, Lashaine records a similar value.

Two helium isotopic measurements of Pello Hill mantle xenoliths are presented in Fig. 2; crushing of olivine produced a result of $6.42 \pm 0.25 R_A$, and crushing of pyroxene produced $4.95 \pm 0.23 R_A$ (Hilton et al., 2011). This result is consistent with the notion that pyroxene is more susceptible to diffusive helium exchange with the

crust because of its lower closure temperature (e.g., Shaw et al., 2006), implying that the helium isotope composition of olivine is a more reliable volatile source tracer. We note that at the summit of Oldoinyo Lengai, no olivine-bearing sample was found during field sampling in 2014. However, since our samples are cognate xenoliths, i.e., they were crystallizing just before transport to the surface in 2008, we expect that there was insufficient time for radiogenic ^4He production and diffusion of helium to have significantly affected their helium isotopic compositions.

Within analytical uncertainties, mantle xenoliths of the Arusha volcanic province and the deep and mid-crustal magma chambers of Oldoinyo Lengai record a SCLM helium isotope signature (Fig. 2). Hence, based on helium isotopes alone, the mantle source sampled by various silicate (basanite, nephelinite, and melilitite) volcanoes cannot be distinguished from that of the Oldoinyo Lengai carbonatitic system, indicating that carbonatite and alkaline magmas of the Arusha volcanic province do not result from melting of different mantle domains. Fischer et al. (2009) demonstrated that a low degree of partial melting of a relatively C-poor (≤ 300 ppm C) lithospheric mantle occurs below the Oldoinyo Lengai. Therefore, Mitchell and Dawson (2012) proposed a carbonatite genesis model by protracted differentiation until immiscibility between carbonate and silicate magmas. Considering our results and these studies (Fischer et al., 2009; Mitchell and Dawson, 2012), carbonatite genesis must therefore be unrelated to compositional variations of the mantle source or to melting parameters, but rather related to the extreme differentiation that occurs at Oldoinyo Lengai.

5.2. Identification of a metasomatized SCLM mantle domain

Halldórsson et al. (2014) suggested that helium and neon isotopic compositions of the EAR represent mixing between a mantle plume and either a depleted MORB mantle (DMM) or SCLM component. The presence of a mantle plume is better supported by high $^3\text{He}/^4\text{He}$ in the Afar (north) and Rungwe (south) provinces than in the central EAR (Kenya and northern Tanzania) where xenoliths record DMM or SCLM He signatures (Pik et al., 2006; Hilton et al., 2011; Barry et al., 2013) with little to negligible plume contribution. The helium isotopic compositions of crustal and mantle xenoliths from Oldoinyo Lengai and nearby volcanoes are consistent with an important contribution of a SCLM mantle source (Fig. 2). This conclusion is in agreement with petrographic, geochemical, and isotopic (Sr, Nd, and Li) investigations revealing the regional old cratonic lithospheric mantle to be heterogeneous and pervasively metasomatized by asthenospheric melts (Dawson and Smith, 1988; Rudnick et al., 1993; Aulbach et al., 2008). The Sr-Nd-Pb isotopic compositions of the various alkaline magmas from Oldoinyo Lengai similarly indicate an EM1-like lithospheric mantle source that has been metasomatized by melts/fluids with HIMU-DMM affinity (Bell and Simonetti, 1996). Based on CO_2 , He, N_2 , and Ar isotopes, Fischer et al. (2009) argued that volatiles emitted near the summit of Oldoinyo Lengai are MORB-like, indicating a volatile signature similar to that of the degassed convecting upper mantle. Altogether, those previous studies and our new results, support a model in which the source of Oldoinyo Lengai magmas is the lithospheric mantle that has been enriched and intensely metasomatized by fluids/melts that derive from the degassed upper convecting mantle (DMM-like). An alternative model with an asthenospheric mantle derived melt (DMM-like) interacting during its ascent with the metasomatized and enriched lithospheric mantle would also support the data.

5.3. Gases throughout the plumbing system to fumaroles

The exceptional cognate xenoliths of the 2007–2008 eruption allow direct access to the volatile composition of the active magma chamber. The helium isotopic composition of six mineral samples from this eruption varies from 5.79 ± 0.82 to $7.24 \pm 0.44 R_A$, with an average

value of $6.58 \pm 0.46 R_A$. This value is quite close to the average $^3\text{He}/^4\text{He}$ of $7.31 \pm 0.24 R_A$ characterizing the five fumaroles sampled in 2014. Therefore, all of the most recent helium isotope ratio measurements at Oldoinyo Lengai are similar within analytical uncertainties. Furthermore, the similarity between cognate xenolith and fumarolic values reveals that volatiles in the magma chamber are nearly identical to the fumarolic gases emanating at the surface.

The similarity of the hydrothermal fluid in the magma chamber and at the surface raises two salient points. First, no contamination or assimilation (which would decrease the $^3\text{He}/^4\text{He}$ of the gas phase en route to the surface) is evidenced by the helium isotopic compositions of either fumarolic gases or fluids trapped in minerals from the crustal magma chamber. Second, the cognate xenoliths record the primary volatile component during an explosive eruption, which is impossible to monitor from fumarolic gas emissions during explosive eruptive activity.

5.4. Temporal evolution of the Oldoinyo Lengai helium isotopic compositions

Oldoinyo Lengai fumarole samples collected in October 2014 are compared to previous gas samples collected between 1988 and 2009 (Fig. 4). The average helium isotope ratio of the fumaroles sampled in October 2014 is $7.31 \pm 0.24 R_A$, in agreement with the only other reported fumarolic sample since the 2007–2008 explosive eruption ($6.82 \pm 0.25 R_A$; Barry et al., 2013). Prior to the explosive eruption, fumarolic gas values have been reported as $6.74 \pm 0.07 R_A$ in 2005 (Fischer et al., 2009), $6.72 \pm 0.30 R_A$ in October 2003, Teague et al. (2008), and $7.6 \pm 0.2 R_A$ in 1988 (Javoy et al., 1988). Fumarole analyses pre-dating the 2007–2008 explosive eruption were sampled at the active north crater of Oldoinyo Lengai, which resembled a flat platform, marked by several hornitos formed during natrocarbonatite flow emissions (Kervyn et al., 2008; Keller and Krafft, 1990). The 2007 sub-Plinian eruption destroyed the platform, creating a deep crater (Fig. 1B and C). Although this morphology change impacted the surface location of fumaroles, and despite recharge by a less-evolved melt in the mid-crustal magma chamber (e.g., Bosshard-Stadlin et al., 2014), the helium isotopic composition of fumarolic emissions remained fairly unaffected, certifying that the deep volatile plumbing system has remained stable. The Oldoinyo Lengai hydrothermal system thus appears to have been stable since at least 1988, with a fumarolic gas source that has not significantly evolved.

6. Conclusion

Noble gas (He, Ne, Ar) measurements of various mantle and crustal xenoliths and fumaroles from Oldoinyo Lengai provide new constraints on the genesis, evolution, and architecture of the only active carbonatite system. Helium isotopic compositions of deep crustal xenoliths (deep cumulates), the mid-crustal active magma chamber, and summit fumaroles are similar. Neon and argon isotopic compositions provide constraints on the degree of degassing and the source mantle domain. Our results show that:

- Helium isotope ratios of summit fumaroles and deep- and mid-crustal magma chambers below Oldoinyo Lengai are similar to numerous mantle xenoliths from the Arusha volcanic province that indicate a SCLM mantle source.
- The mantle source is suggested to be an old, cratonic, heterogeneous, and enriched SCLM, which has suffered extensive metasomatism by fluids or melts derived from the degassed convecting mantle (MORB type), although an asthenospheric melt interacting with the heterogeneous and metasomatized SCLM may also match with the data.
- The similarity between the helium isotope compositions of carbonatite and silicate volcanoes of the Arusha volcanic province

supports a model in which carbonatites result from melting of a similar source as their silicate counterparts, but differ by following a complex liquid line of descent.

- Helium isotope compositions of fumaroles are similar to samples derived from the deep- and mid-crustal magma chambers, arguing against crustal contamination or air assimilation during magma and volatile ascent.
- Cognate xenoliths sample volatiles during brief episodes of sub-Plinian silicate magma emissions at this dominantly (over the last century) carbonatite volcano.
- Fumarolic helium isotope compositions have remained fairly constant since 1988, including during and after the sub-Plinian 2007–2008 eruption, demonstrating that the hydrothermal system is deeply rooted, with an architecture that has been stable for a minimum of 30 years.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2017.08.015>.

Acknowledgments

This contribution is dedicated to the memory of Pete Burnard with whom we loved sharing time, his knowledge and happiness during East African field trips. Clémentine Le Gentil is thanked for her help with the analytical treatment of the fumarole data. Constructive reviews by Masahiko Honda, Samuel Niedermann and an anonymous reviewer are gratefully acknowledged. We thank the Tanzania commission for science and technology (COSTECH) for the field permits. We thank all the guides and porters for their help during field work. The authors acknowledge the help of Robert Dennen for English editing. This work has been supported by the French National Research Agency through the national program “Investissements d’avenir” with the reference ANR-10-LABX-21-01/LABEX RESSOURCES21, and through the project GECO-REE (ANR-16-CE01-0003-01; P.I.: Lydéric France). This study was also supported by the Région Lorraine, and PNP and CESSUR programs from INSU-CNRS (grants to Lydéric France). This is CRPG contribution no 2531, and GECO-REE contribution no 01.

References

- Albaric, J., Perrot, J., Déverchère, J., Deschamps, A., Le Gall, B., Ferdinand, R.W., Petit, C., Tiberi, C., Sue, C., Songo, M., 2010. Contrasted seismogenic and rheological behaviours from shallow and deep earthquake sequences in the North Tanzanian Divergence, East Africa. *J. Afr. Earth Sci.* 58 (5), 799–811. <http://dx.doi.org/10.1016/j.jafrearsci.2009.09.005>.
- Aulbach, S., Rudnick, R.L., McDonough, W.F., 2008. Li-Sr-Nd isotope signatures of the plume and cratonic lithospheric mantle beneath the margin of the rifted Tanzanian craton (Labait). *Contrib. Mineral. Petrol.* 155 (1), 79–92. <http://dx.doi.org/10.1007/s00410-007-0226-4>.
- Barry, P.H., Hilton, D.R., Fischer, T.P., de Moor, J.M., Mangasini, F., Ramirez, C., 2013. Helium and carbon isotope systematics of cold “mazuku” CO₂ vents and hydrothermal gases and fluids from Rungwe Volcanic Province, southern Tanzania. *Chem. Geol.* 339, 141–156. <http://dx.doi.org/10.1016/j.chemgeo.2012.07.003>.
- Bell, K., Simonetti, A., 1996. Carbonatite magmatism and plume activity: implications from the Nd, Pb and Sr isotope systematics of Oldoinyo Lengai. *J. Petrol.* 37 (6), 1321–1339. <http://dx.doi.org/10.1093/ptrology/37.6.1321>.
- Bosshard-Stadlin, S.A., Mattsson, H.B., Keller, J., 2014. Magma mixing and forced exsolution of CO₂ during the explosive 2007–2008 eruption of Oldoinyo Lengai (Tanzania). *J. Volcanol. Geotherm. Res.* 285, 229–246. <http://dx.doi.org/10.1016/j.jvolgeores.2014.08.017>.
- Burnard, P., Zimmermann, L., Sano, Y., 2013. The noble gases as geochemical Tracers: history and background. In: Burnard, P. (Ed.), *The Noble Gases as Geochemical Tracers*. Springer, Berlin Heidelberg, pp. 1–15.
- Dawson, J.B., 2012. Nephelinite–mellilite–carbonatite relationships: evidence from Pleistocene–recent volcanism in northern Tanzania. *Lithos* 152, 3–10. <http://dx.doi.org/10.1016/j.lithos.2012.01.008>.
- Dawson, J.B., Smith, J.V., 1988. Metasomatized and veined upper-mantle xenoliths from Pello Hill, Tanzania: evidence for anomalously-light mantle beneath the Tanzanian sector of the East African Rift Valley. *Contrib. Mineral. Petrol.* 100 (4), 510–527. <http://dx.doi.org/10.1007/BF00371380>.
- Dunai, T.J., Porcelli, D., 2002. Storage and transport of noble gases in the subcontinental lithosphere. *Rev. Mineral. Geochem.* 47 (1), 371–409. <http://dx.doi.org/10.2138/rmg.2002.47.10>.

- Fischer, T.P., Burnard, P., Marty, B., Hilton, D.R., Füre, E., Palhol, F., Sharp, Z.D., Mangasini, F., 2009. Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. *Nature* 459 (7243), 77–80. <http://dx.doi.org/10.1038/nature07977>.
- Füre, E., Hilton, D.R., Halldórsson, S.A., Barry, P.H., Hahm, D., Fischer, T.P., Grönvold, K., 2010. Apparent decoupling of the He and Ne isotope systematics of the Icelandic mantle: the role of He depletion, melt mixing, degassing fractionation and air interaction. *Geochim. Cosmochim. Acta* 74, 3307–3332. <http://dx.doi.org/10.1016/j.gca.2010.03.023>.
- Gautheron, C., Moreira, M., 2002. Helium signature of the subcontinental lithospheric mantle. *Earth Planet. Sci. Lett.* 199 (1–2), 39–47. [http://dx.doi.org/10.1016/S0012-821X\(02\)00563-0](http://dx.doi.org/10.1016/S0012-821X(02)00563-0).
- Gautheron, T., Moreira, M., Alle, C., 2005. He, Ne and Ar composition of the European lithospheric mantle. *Chem. Geol.* 217 (1), 97–112. <http://dx.doi.org/10.1016/j.chemgeo.2004.12.009>.
- Giggenbach, W.F., Goguel, R.L., 1989. *Methods for the Collection and Analysis of Geothermal and Volcanic Water and Gas Samples*. Department of Scientific and Industrial Research, Chemistry Division, Petone, New Zealand.
- Graham, D.W., 2002. Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts; characterization of mantle source reservoirs. eds. D. Porcelli, C. Ballentine and R. Wieler. *Rev. Mineral. Geochem.* 47, 247–317.
- Halldórsson, S.A., Hilton, D.R., Scarsi, P., Abebe, T., Hopp, J., 2014. A common mantle plume source beneath the entire East African Rift System revealed by coupled helium-neon systematics. *Geophys. Res. Lett.* 41 (7), 2304–2311. <http://dx.doi.org/10.1002/2014GL059424>.
- Hilton, D.R., Halldórsson, S.A., Barry, P.H., Fischer, T.P., de Moor, J.M., Ramirez, C.J., Mangasini, F., Scarsi, P., 2011. Helium isotopes at Rungwe Volcanic Province, Tanzania, and the origin of East African Plateaux. *Geophys. Res. Lett.* 38 (21), 1–5. <http://dx.doi.org/10.1029/2011GL049589>.
- Honda, M., Zhang, X., Phillips, D., Hamilton, D., Deerberg, M., Schwieters, J.B., 2015. Redetermination of the ^{21}Ne relative abundance of the atmosphere, using a high resolution, multi-collector noble gas mass spectrometer (HELIX-MC Plus). *Int. J. Mass Spectrom.* 387, 1–7. <http://dx.doi.org/10.1016/j.ijms.2015.05.012>.
- Jambon, A., Weber, H., Braun, O., 1986. Solubility of He, Ne, Ar, Kr and Xe in a basalt melt in the range 1250–1600 °C. *Geochemical implications*. *Geochim. Cosmochim. Acta* 50, 401–408.
- Javoy, M., Pineau, F., Cheminee, J.L., Krafft, M., 1988. The Gas Magma Relationship in the 1988 Eruption of Oldoinyo Lengai (Tanzania) [abs.]. vol. 69. *Eos (Transactions, American Geophysical Union)*, pp. 1466.
- Jochum, K.P., Hofmann, A.W., Ito, E., Seufert, H.M., White, W.M., 1983. K, U and Th in mid-ocean ridge basalt glasses and heat production, K/U and K/Rb in the mantle. *Nature* 306 (5942), 431–436. <http://dx.doi.org/10.1038/306431a0>.
- Jones, A.P., Genge, M., Carmody, L., 2013. Carbonate melts and carbonatites. *Rev. Mineral. Geochem.* 75 (1), 289–322. <http://dx.doi.org/10.2138/rmg.2013.75.10>.
- Keller, J., Krafft, M., 1990. Effusive natrocarbonatite activity of Oldoinyo Lengai, June 1988. *Bull. Volcanol.* 52 (8), 629–645. <http://dx.doi.org/10.1007/BF00301213>.
- Keller, J., Zaitsev, A.N., Wiedenmann, D., 2006. Primary magmas at Oldoinyo Lengai: the role of olivine melilitites. *Lithos* 91 (1), 150–172. <http://dx.doi.org/10.1016/j.lithos.2006.03.014>.
- Keller, J., Klaudius, J., Kervyn, M., Ernst, G.G.J., Mattsson, H.B., 2010. Fundamental changes in the activity of the natrocarbonatite volcano Oldoinyo Lengai, Tanzania. *Bull. Volcanol.* 72 (8), 893–912. <http://dx.doi.org/10.1007/s00445-010-0371-x>.
- Kervyn, M., Ernst, G.G.J., Klaudius, J., Keller, J., Kervyn, F., Mattsson, H.B., Belton, F., Mbede, E., Jacobs, P., 2008. Voluminous lava flows at Oldoinyo Lengai in 2006: chronology of events and insights into the shallow magmatic system. *Bull. Volcanol.* 70 (9), 1069–1086. <http://dx.doi.org/10.1007/s00445-007-0190-x>.
- Klaudius, J., Keller, J., 2006. Peralkaline silicate lavas at Oldoinyo Lengai, Tanzania. *Lithos* 91 (1), 173–190. <http://dx.doi.org/10.1016/j.lithos.2006.03.017>.
- Lee, J.Y., Marti, K., Severinghaus, J.P., Kawamura, K., Yoo, H.S., Lee, J.B., Kim, J.S., 2006. A redetermination of the isotopic abundances of atmospheric Ar. *Geochim. Cosmochim. Acta* 70 (17), 4507–4512. <http://dx.doi.org/10.1016/j.gca.2006.06.1563>.
- LeMaitre, R.W. (Ed.), 2002. *Igneous Rocks. A Classification and Glossary of Terms. Recommendations of the International Union of Geological Sciences Subcommittee on the Systematics of Igneous Rocks*. Cambridge University Press, Cambridge.
- Marty, B., Pik, R., Gezahegn, Y., 1996. Helium isotopic variations in Ethiopian plume lavas: nature of magmatic sources and limit on lower mantle contribution. *Earth Planet. Sci. Lett.* 144 (1–2), 223–237. [http://dx.doi.org/10.1016/0012-821X\(96\)00158-6](http://dx.doi.org/10.1016/0012-821X(96)00158-6).
- Matsuda, J., Matsumoto, T., Sumino, H., Nagao, K., Yamamoto, J., Miura, Y., Kaneoka, I., Takahata, N., Sano, Y., 2002. The $3\text{He}/4\text{He}$ ratio of the new internal He standard of Japan (HESJ). *Geochem. J.* 36, 191–195. <http://dx.doi.org/10.2343/geochemj.36.191>.
- Mattsson, H.B., Nandedkar, R.H., Ulmer, P., 2013. Petrogenesis of the melilititic and nephelinitic rock suites in the Lake Natron-Engaruka monogenetic volcanic field, northern Tanzania. *Lithos* 179, 175–192. <http://dx.doi.org/10.1016/j.lithos.2013.07.012>.
- Mitchell, R.H., Dawson, J.B., 2012. Carbonate-silicate immiscibility and extremely peralkaline silicate glasses from Nasira cone and recent eruptions at Oldoinyo Lengai Volcano, Tanzania. *Lithos* 152, 40–46. <http://dx.doi.org/10.1016/j.lithos.2012.01.006>.
- Mollex, G., France, L., Burnard, P., Boudoire, G., 2015. Genesis and Evolution of Highly Alkaline Magmas at Oldoinyo Lengai, Tanzania. *Proceeding of the 13th*.
- Moreira, M., Kunz, J., Allègre, C., 1998. Rare gas systematics in popping rock: isotopic and elemental compositions in the upper mantle. *Science* 279 (5354), 1178–1181. <http://dx.doi.org/10.1126/science.279.5354.1178>.
- Morogan, V., Martin, R.F., 1985. Mineralogy and partial melting of fenitized crustal xenoliths in the Oldoinyo Lengai carbonatitic volcano, Tanzania. *Am. Mineral.* 70 (11–12), 1114–1126.
- Mukhopadhyay, S., 2012. Early differentiation and volatile accretion recorded in deep-mantle neon and xenon. *Nature* 486 (7401), 101–104. <http://dx.doi.org/10.1038/nature11141>.
- Peterson, T.D., Kjarsgaard, B.A., 1995. What are the parental magmas at Oldoinyo Lengai? In: Bell, K., Keller, J. (Eds.), *Carbonatite Volcanism: Oldoinyo Lengai and Petrogenesis of Natrocarbonatites*. Springer-Verlag, Berlin, pp. 148–162. http://dx.doi.org/10.1007/978-3-642-79182-6_12.
- Pik, R., Marty, B., Hilton, D.R., 2006. How many mantle plumes in Africa? The geochemical point of view. *Chem. Geol.* 226 (3–4), 100–114. <http://dx.doi.org/10.1016/j.chemgeo.2005.09.016>.
- Porcelli, D.R., O'Nions, R.K., O'Reilly, S.Y., 1986. Helium and strontium isotopes in ultramafic xenoliths. *Chem. Geol.* 54 (3–4), 237–249. [http://dx.doi.org/10.1016/0009-2541\(86\)90139-7](http://dx.doi.org/10.1016/0009-2541(86)90139-7).
- Porcelli, D.R., Stone, J.O.H., O'Nions, R.K., 1987. Enhanced $^3\text{He}/^4\text{He}$ ratios and cosmogenic helium in ultramafic xenoliths. *Chem. Geol.* 64 (1–2), 25–33. [http://dx.doi.org/10.1016/0009-2541\(87\)90149-5](http://dx.doi.org/10.1016/0009-2541(87)90149-5).
- Rudnick, R.L., McDonough, W.F., Chappell, B.W., 1993. Carbonatite metasomatism in the northern Tanzanian mantle: petrographic and geochemical characteristics. *Earth Planet. Sci. Lett.* 114 (4), 463–475. [http://dx.doi.org/10.1016/0012-821X\(93\)90076-L](http://dx.doi.org/10.1016/0012-821X(93)90076-L).
- Sano, Y., Wakita, H., 1985. Geographical distribution of $^3\text{He}/^4\text{He}$ ratios in Japan: implications for arc tectonics and incipient magmatism. *J. Geophys. Res.* 90, 8729–8741.
- Sarda, P., Staudacher, T., Allègre, C.J., 1988. Neon isotopes in submarine basalts. *Earth Planet. Sci. Lett.* 91 (1–2), 73–88. [http://dx.doi.org/10.1016/0012-821X\(88\)90152-5](http://dx.doi.org/10.1016/0012-821X(88)90152-5).
- Shaw, A.M., Hilton, D.R., Fischer, T.P., Walker, J.A., Leeuw, G.A.M., 2006. Helium isotope variations in mineral separates from Costa Rica and Nicaragua: assessing crustal contributions, timescale variations and diffusion-related mechanisms. *Chem. Geol.* 230 (1–2), 124–139. <http://dx.doi.org/10.1016/j.chemgeo.2005.12.003>.
- Sherrod, D.R., Magigita, M.M., Kwelwa, S., 2013. *Geologic map of Oldoinyo Lengai (Oldoinyo Lengai) and surroundings, Arusha Region, United Republic of Tanzania*. U.S. Geological Survey Open-File Report (No. 2013-1306).
- Teague, A.J., Seward, T.M., Harrison, D., 2008. Mantle source for Oldoinyo Lengai carbonatites: evidence from helium isotopes in fumarole gases. *J. Volcanol. Geotherm. Res.* 175 (3), 386–390. <http://dx.doi.org/10.1016/j.jvolgeores.2008.04.001>.
- Wiedenmann, D., Keller, J., Zaitsev, A.N., 2010. Melilite-group minerals at Oldoinyo Lengai, Tanzania. *Lithos* 118 (1–2), 112–118. <http://dx.doi.org/10.1016/j.lithos.2010.04.002>.
- Zaitsev, A.N., Keller, J., 2006. Mineralogical and chemical transformation of Oldoinyo Lengai natrocarbonatites, Tanzania. *Lithos* 91 (1–4), 191–207. <http://dx.doi.org/10.1016/j.lithos.2006.03.018>.