LETTERS

Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites

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Carbonatite lavas are highly unusual in that they contain almost no SiO_2 and are >50 per cent carbonate minerals. Although carbonatite magmatism has occurred throughout Earth's history, Oldoinyo Lengai, in Tanzania, is the only currently active volcano producing these exotic rocks[1]. Here we show that volcanic gases captured during an eruptive episode at Oldoinyo Lengai are indistinguishable from those emitted along mid-ocean ridges, despite the fact that Oldoinyo Lengai carbonatites occur in a setting far removed from oceanic spreading centres. In contrast to lithophile trace elements, which are highly fractionated by the immiscible phase separation that produces these carbonatites, volatiles (CO_2, He, N_2 and Ar) are little affected by this process. Our results demonstrate that a globally homogenous reservoir exists in the upper mantle and supplies volatiles to both mid-ocean ridges and continental rifts. This argues against an unusually C-rich mantle being responsible for the genesis of Na-rich carbonatite and its nephelinite source magma at Oldoinyo Lengai. Rather, these carbonatites are formed in the shallow crust by immiscibility from silicate magmas (nephelinite), and are stable under eruption conditions as a result of their high Na contents.

Oldoinyo Lengai is located on the eastern branch of the East African Rift Valley, away from any influence of a deep-mantle plume[2] or subduction zone. The composite cone consists mainly of nephelinitic and phonolitic pyroclasts and lavas[1]. Although currently erupting more silicic ashes, Oldoinyo Lengai erupted large volumes of rare Na-rich (natro-) carbonatite lavas until August 2007. Such lavas are enriched in incompatible trace elements by up to four orders of magnitude relative to primitive mantle, and show extremely high ($\geq 10^3$) enrichments of light relative to heavy rare-earth elements[3]. The radiogenic isotope compositions of carbonatites, including those emitted by Oldoinyo Lengai, are typical of those that characterize mantle-derived magmas, leaving little doubt that these peculiar magmas are differentiated products of partial melts of the underlying mantle source[4]. Petrologic studies show that natro-carbonatite magma is formed by low-pressure differentiation in the shallow crust from mantle-derived nephelinites[5]. The CO_2-rich nature (~ 30 wt%; ref. 1) of carbonatite lavas raises the question of whether mantle-derived melts (for example nephelinites), which can form carbonatite liquids by differentiation, are formed from a typical mantle assemblage under specific conditions (for example extremely low partial-melt fractions[6]) or instead require unusually high C contents in the mantle source (see, for example, ref. 7). Recent experimental results have suggested that nephelinitic magmas, which were probably the Oldoinyo Lengai carbonatite parental liquids, require mantle C contents of $\sim 1,000$ p.p.m. at 1–5% partial melting [8]. Logically, a C-enriched mantle source seems necessary to produce liquids that can differentiate into carbonatite magmas.

We used exceptionally uncontaminated volcanic gases captured at Oldoinyo Lengai at the onset of a new eruptive cycle to address the issue of source C content. We note that the rate at which CO_2 is emitted at Oldoinyo Lengai ($\sim 5.5 \times 10^{10}$ mol yr^{-1}, measured in ref. 9 and by ourselves), is two orders of magnitude greater than the time-averaged solid C (carbonatite) flux (5×10^8 mol yr^{-1}; ref. 9). Therefore, the amount of C that forms carbonatite is a minor fraction only ($\sim 1\%$), in comparison with the total C released by the volcano. In this way, the volatile compositions measured in our gas samples are related to the degassing of the whole volcano, and not the volatile phase in equilibrium with carbonatite liquid at low pressure.

The gas samples were collected in July 2005, in the active crater of Oldoinyo Lengai, at the beginning of a new eruptive sequence that resulted in the emission of low-viscosity and low-temperature (550 °C) carbonatite lava flows. Sample collection followed standard protocols[10]. Gas chemistry and N isotope composition were measured by gas chromatography and isotope-ratio mass spectrometry at the University of New Mexico[11], and noble gases and C isotopes by mass spectrometry at the Scripps Institution of Oceanography[12]. All results are reported in Table 1. To determine the source characteristics of the gases, we used isotopic and elemental ratios, that is, N_2/Ar, $^3He/^4He$, $^{40}Ar/^{36}Ar$ and $N_2/^{36}Ar$, which are diagnostic of magma sources but unaffected by degassing fractionation. The effects of degassing were evaluated from gas abundance ratios (for example He/Ar and CO_2/Ar), which change upon degassing owing to solubility differences in melts.

There is overwhelming evidence to indicate that Oldoinyo Lengai gas compositions strongly resemble upper-mantle volatiles. First, the relative abundances of N_2, He and Ar (Fig. 1) overlap with volatiles emitted at mid-ocean ridges and continental rifts. Second, the $^3He/^4He$ ratios of Oldoinyo Lengai samples define a narrow range, from $6.70R_A$ to $6.86R_A$. They fall at the lower end of the MORB range and are indistinguishable from the subcontinental lithospheric mantle[13]; indeed, there is considerable overlap with well-documented examples of MORB with $^3He/^4He$ ratios below $6.5R_A$ in slow- to medium-spreading ridges (the southeast and southwest Indian ridges, the south Mid-Atlantic Ridge and the Gakkel Ridge[13]).

Third, the isotopic composition of nitrogen shows $\delta^{15}N$ values from -4.0 to $-5.1‰$ ($\delta^{15}N_{air} = 0.0‰$), similar to MORB and to continental-rift gas values ($\delta^{15}N$, $-5 \pm 3‰$; refs 14, 15). Any contribution from N-rich subducted sediments to the Oldoinyo Lengai volatile budget would shift $\delta^{15}N$ values towards $\sim +7‰$ (refs 11, 16). Fourth, plots of $N_2/^{36}Ar$ against $^{40}Ar/^{36}Ar$ for the gas samples, along with data for MORB[14], lie precisely on the mixing line between ASW and the upper mantle (Fig. 2). Although the $^{40}Ar/^{36}Ar$ ratios of the gases (950) are significantly lower than the upper-mantle end-member ($\sim 35,000$; ref. 17), they are still among the highest such ratios of any volcanic gases measured. Fifth, the $\delta^{13}C$ values (-2.36 to $-4.01‰$) are within the range of MORB[14] and subcontinental mantle gases[15].

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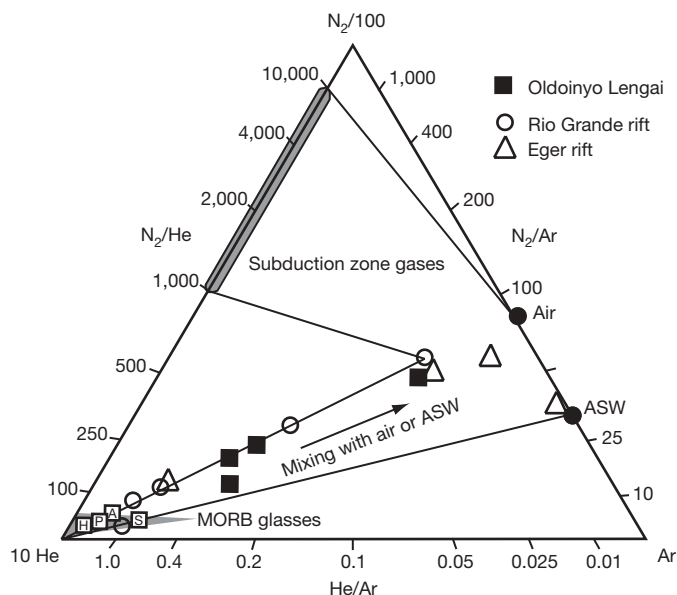
Table 1 | Composition of gas emitted from Oldoinyo Lengai crater, July 2005

	Sample					
	OLD-1	OLD-2	OLD-3	OLD-4	ASW	MORB
T (°C)	123	120	168	168	—	—
N_2/Ar	50.4	81.9	98.1	82.6	50	152 ± 58
N_2/He	177.2	261	376.2	1,558.3	150,000	48 ± 6
He/Ar	0.28	0.31	0.26	0.05	0.0005	2
$^3He/^4He$ (R/R_A)	6.73	6.86	6.68	6.7	1	8 ± 1
He/Ne (air)	4,600	6,530	2,020	2,370	0.78	235,000
$^3He/^4He$ (R_C/R_A)	6.73 ± 0.06	6.86 ± 0.06	6.68 ± 0.06	6.70 ± 0.06	—	8 ± 2
$^{40}Ar/^{36}Ar$	290.81 ± 1.67	947.83 ± 6.23	—	317.05 ± 1.01	295.5	~35,000
$^{20}Ne/^{36}Ar$	0.057	0.142	—	0.022	0.16	0.013
$CO_2/^3He$ ($\times 10^9$)	3.82 ± 0.08	4.13 ± 0.08	3.59 ± 0.08	3.80 ± 0.08	—	~1–6
$N_2/^{36}Ar$ ($\times 10^4$)	1.47	7.76	—	2.58	1.03	280
$^4He/^{40}Ar^*$	—	0.45	—	0.76	—	2
CO_2/N_2	203	152	89	23	—	85–190
$CO_2/^{40}Ar^*$	—	17,886	—	27,166	—	33,600
$\delta^{15}N$ (‰, air)	-4.0 ± 0.2	-4.1 ± 0.5	-5.1 ± 0.3	—	0	-5 ± 3
$\delta^{13}C$ (‰, PDB)	-2.36 ± 0.01	-2.40 ± 0.01	-2.37 ± 0.01	-4.01 ± 0.01	-8	-4.5 ± 2

Elemental ratios are reported on a molar basis. Errors in the N_2/Ar, N_2/He, He/Ar and CO_2/N_2 ratios are 5% (ref. 11). Errors in isotopic values are at the 1σ level. The He/Ne ratios are given relative to the He/Ne ratio of air. The He/Ne of the mid-ocean-ridge basalt (MORB) endmember was calculated from the MORB $^3He/^{22}Ne$ (10.2), $^3He/^4He$ ($8R_A$) and $^{20}Ne/^{22}Ne$ (12.5) ratios; the $^3He/^4He$ ratio is reported in R_A notation, where R_A is the $^3He/^4He$ ratio of air (1.4×10^{-6}). Using measured He/Ne ratios, the measured $^3He/^4He$ (R) value was corrected for air contamination (details in ref. 12). The $^{20}Ne/^{36}Ar$ ratio was calculated from the He/Ne, He/Ar and $^{40}Ar/^{36}Ar$ ratios. The $^{20}Ne/^{36}Ar$ ratio of air-saturated water (ASW) was measured at 20 °C (ref. 27). The $^{20}Ne/^{36}Ar$ ratio of the MORB endmember was calculated using the $^{22}Ne/^{36}Ar$ ratio of 'popping rock'[17] and the $^{20}Ne/^{22}Ne$ ratio of mantle well gases[25]. The $CO_2/^{40}Ar^*$ ratio was calculated from the $CO_2/^3He$, $^3He/^4He$ and $^4He/^{40}Ar^*$ ratios. $^{40}Ar^*$ is ^{40}Ar corrected for atmospheric Ar. MORB endmember compositions are from refs 13, 14, 16, 28, 29 and 30. $\delta^{15}N$ (‰) = $[(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1] \times 1,000$; the standard for N is air. $\delta^{13}C$ (‰) = $[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1] \times 1,000$; the standard for C is PeeDee Belemnite (PDB).
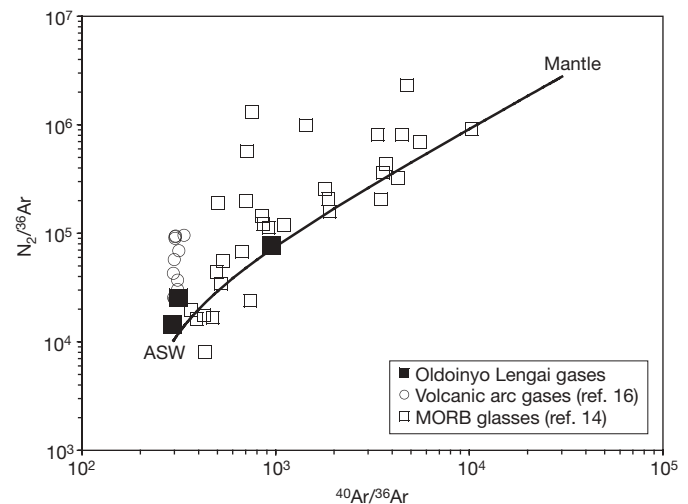
Last, and most surprisingly, $CO_2/^3He$ ratios of $(3.6–4.1) \times 10^9$ are within the range of MORB glass values $((1–6) \times 10^9$; ref. 14) and are slightly lower than ratios of subcontinental mantle gases[15,18]. The $CO_2/^3He$ ratios of Oldoinyo Lengai gases are much lower than values characteristic of gases from arc volcanoes $((11.0 \pm 3.3) \times 10^9$; ref. 19), which are the result of contributions of C-rich components in fluid released from the subducting slab to the mantle wedge.

Elemental noble gas ratios also support this conclusion. The Oldoinyo Lengai $^4He/^{40}Ar^*$ ratios (0.45–0.76; Fig. 3) are close to the mantle value ($^4He/^{40}Ar^*_{upper\ mantle} = 2$; ref. 17). This observation demonstrates that there was only very minor volatile fractionation during magmatic degassing at Oldoinyo Lengai, because He is ~10 times more soluble than Ar in both silicate and carbonatite melts[20,21] and degassing of a magma would result in large increases in the He/Ar ratio of the residual liquid. Therefore, it is reasonable to assume that the
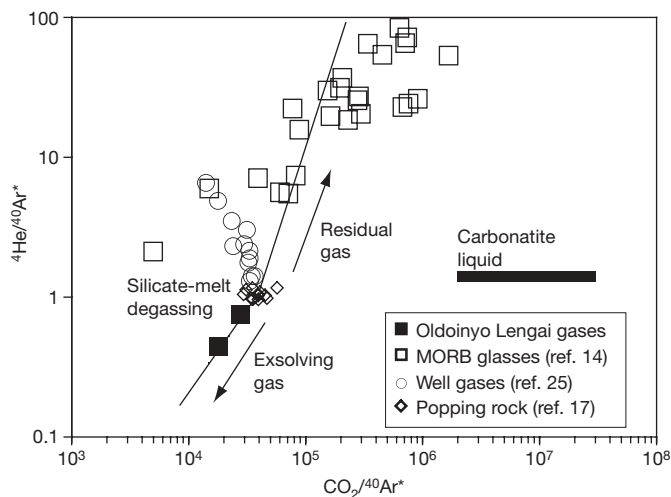
measured volatile compositions are representative of the mantle source. We note that although $^4He/^{40}Ar^*$ ratios appear unfractionated, the $CO_2/^4He$ and $CO_2/^{40}Ar^*$ compositions of the Oldoinyo Lengai gases are not consistent with compositions expected from unfractionated carbonatite liquids. The $CO_2/^4He$ and $CO_2/^{40}Ar^*$ ratios of an initial carbonatite liquid (that is, one in equilibrium with an undegassed mantle melt) can be constrained by mass balance to $\sim 1 \times 10^6$ and $\sim 2 \times 10^6$, respectively, which are two orders of magnitude greater than those measured in the gases (Supplementary Information). Thus, enormous degassing fractionation of a carbonatite source would be required to produce the $CO_2/^4He$ and $CO_2/^{40}Ar^*$ ratios observed in Oldoinyo Lengai gases, and this is not reflected in the $^4He/^{40}Ar^*$ ratio. We conclude that there is no degassing scenario from initial carbonatite compositions that could reproduce the Oldoinyo Lengai ^4He–$^{40}Ar^*$–CO_2 compositions. The gases we sampled at Oldoinyo Lengai were derived from degassing of the silicate portion of the magmatic system, as demonstrated by the fact that their compositions plot precisely on the trend predicted by open-system degassing of silicate melts (Fig. 3). This is consistent with the observation that the carbonatite lavas represent only 1% of the Oldoinyo Lengai C budget.

Figure 1 | N_2–He–Ar triangular plot. Oldoinyo Lengai gas compositions and mantle endmembers as defined by MORB glasses[14], the Rio Grande rift[31], the Eger rift (Europe)[15], popping rock (P), the Sierra Negra (S) and Alcedo (A) volcanoes (Galapagos)[32] and Halemaumau crater (H; Kilauea volcano, Hawaii) (T.P.F., unpublished observations). All samples are mixtures between the mantle endmember composition and air or ASW.

Figure 2 | $N_2/^{36}Ar$ and $^{40}Ar/^{36}Ar$ ratio diagram. Oldoinyo Lengai gases, MORB glasses[14] and arc-gas emissions[16]. All Oldoinyo Lengai samples fall on a mixing trend between ASW and a mantle endmember with $N_2/^{36}Ar = 280 \times 10^4$ and $^{40}Ar/^{36}Ar \approx 35,000$ (Table 1).

Figure 3 | $^4He/^{40}Ar^*$ and $CO_2/^{40}Ar^*$ ratios of Oldoinyo Lengai gases. New Mexico well-gas data[25] and compositions of 2IID43 popping rock are considered representative of the volatile compositions of primary mantle melts[17]. The volatile composition of a carbonatite liquid in equilibrium with such a primary melt is calculated using a mass-balance approach (Supplementary Information). Rayleigh-type degassing will fractionate the exsolved volatiles from the initial volatile compositions (defined by popping rock for silicate magmas and the calculated carbonatite pole for carbonatitic magmas), with the exsolving gases moving towards lower $^4He/^{40}Ar^*$ and $CO_2/^{40}Ar^*$ values owing to higher solubility of He (ref. 21) and CO_2 (ref. 33) relative to Ar (ref. 21) in the melt. MORB glasses[14] have compositions that represent the residual mantle gas after degassing. The models show that volatiles sampled at Oldoinyo Lengai could not have been exsolved from a carbonatite magma and instead coincide with the compositions expected from a degassing silicate magma.

Using our $CO_2/^3He$ ratios, we can constrain the concentration of C in the Oldoinyo Lengai mantle source to be no more than that of the highest C concentrations in the MORB source. The C content of the upper mantle is well constrained by three independent approaches[19,22,23] to fall between 50 and 220 p.p.m. The highest C concentration estimates in this range are found in MORB with $CO_2/^3He$ ratios identical to those of Oldoinyo Lengai (Supplementary Information); therefore, the mantle source that is generating Oldoinyo Lengai carbonatite, and its parental nephelinitic magma, contains an absolute maximum of 300 p.p.m. C (including uncertainties in the mantle C estimates). Our results argue against a C-rich mantle being the source of the unusual volcanism at Oldoinyo Lengai, including the Na-rich carbonatites.

Although the Earth's mantle contains significant amounts of C (ref. 19), all present-day volcanoes except Oldoinyo Lengai emit C exclusively as CO_2 and not carbonatite. This is because Fe, Ca and Mg carbonatite liquids are not stable at low pressure and break down to produce the CO_2 present in all volcanic emissions. Carbonatite magmas can erupt at Oldoinyo Lengai as a result of their high Na contents; unlike calcic or magnesian carbonate liquids, natro-carbonatite liquids are stable at atmospheric pressure[24]. Therefore, it is the unusual Na content of Oldoinyo Lengai magmas that permits eruption of the carbonatite lavas, not the C content of their source.

Most recent experiments on carbonatite generation use compositions that are enriched in C relative to the current best estimates of average mantle compositions, and show that either high C concentrations (of several thousand p.p.m.) and/or exceedingly small partial-melt fractions are required to produce carbonatitic primary liquids[6]. Furthermore, melting in the presence of C at low partial-melt fraction will produce nephelinitic primary liquids (higher melt fractions tend to dilute the undersaturated melts with melts of more basaltic compositions[8]), consistent with the nephelinitic lavas found at Oldoinyo Lengai. Given that the maximum C concentration of

the Oldoinyo Lengai mantle source is 300 p.p.m., the compromise between C concentration and partial-melt fraction that will still produce an undersaturated primary liquid[8] allows us to constrain the maximum partial-melt fraction at Oldoinyo Lengai to be ≤0.3%. Therefore, rather than highly unusual C-rich fluids in the mantle, or carbonated peridotite, it seems likely that the melting regime in the extensional East African Rift is what results in the low partial-melt fraction liquids of nephelinitic composition. These melts undergo further differentiation and liquid immiscibility in the shallow crust such that ~1% of the mantle C separates into a natro-carbonatite phase—into which incompatible elements preferentially partition. The remaining C degasses as CO_2, as at all other volcanoes. The source for all Oldoinyo Lengai magmas (nephelinites and carbonatites) is ultimately the upper mantle, which is indistinguishable from that under mid-ocean ridges in terms of the isotopic composition of volatiles and lithophile elements.

On a global scale, our results imply that the regions of upper mantle beneath mid-ocean ridges[17], continental North America[25] and the East African Rift are identical in their volatile abundances and isotopic compositions. Despite small differences in some trace gases (for example Xe isotopes in MORBs versus continental well gases[26]), the upper mantle appears to be a uniform and homogenous geochemical reservoir of CO_2 and other gases (N_2, He and Ar) below both continents and oceans.

METHODS SUMMARY

All gas samples were collected following methods described in ref. 10. We collected gas samples for gas chemistry and N isotopes in ~250-ml evacuated glass flasks equipped with Teflon stopcocks. Before sample collection, we filled the flasks with ~50 ml NaOH solution to absorb the acid gases (CO_2, SO_2, H_2S, HCl and HF) and inert gases (N_2, H_2, O_2, CH_4, CO and noble gases) filled the headspace. Samples for determination of He, Ar and C isotopes and $CO_2/^3He$ ratios were collected at the same time and from the same locations using evacuated alkaline-resistant-glass flasks with high-vacuum stopcocks. Samples OLD-1 and OLD-2 came from TB49, a degassing hornito (a cone several metres high made of previously erupted lava). OLD-3 and OLD -4 were collected from a nearby hole (2 m in diameter) in an old lava flow. During sampling of OLD-1, OLD-2 and OLD-3, on 4 July 2005, eruption from a vent ~50 m away was continuous and lavas were emitted at a rate of ~0.3 $m^3 s^{-1}$, flowing at a maximum speed of 2 $m s^{-1}$ over the flat crater floor. During sampling of OLD-4, on 5 July 2005, the eruption was less vigorous. The volcano was under increasing gas pressure owing to the rise of magma, and atmospheric contamination, which is always a problem when collecting volcanic gases, was limited. At the University of New Mexico, the headspaces of the gas samples were analysed by gas chromatography (using thermal-conductivity and flame-ionization detectors). From the headspace, gas aliquots were taken for N isotope analyses using an isotope-ratio mass spectrometer equipped with a gas inlet[11]. At the Scripps Institution of Oceanography, He and Ar isotopes, C isotopes on CO_2 and $CO_2/^3He$ ratios were measured by a combination of noble-gas and stable-isotope mass spectrometry, and gas manometry following ref. 12.

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