

Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes

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ABSTRACT

Airborne measurements of CO₂ released from Oldoinyo Lengai, the only carbonatite-erupting volcano in the world, reveal a CO₂ flux of 0.055×10^{12} mol/yr. This flux is substantially smaller than that of Mount Etna (1×10^{12} mol/yr), which accounts for over half of the global carbon flux attributed to subaerial volcanoes ($1-2 \times 10^{12}$ mol/yr). We propose that the subaerial flux distribution may be a power-law distribution (fractal) rather than Gaussian. Fitting the limited available volcanic flux data to a fractal distribution yields a power-law exponent of <1 . Although rigorous testing of the power-law nature of the flux distribution is impossible, the skewed nature of the distribution and low value of the power-law exponent suggest that simultaneous measurement of the 20 largest-flux volcanoes could yield an accurate assessment of the volcanic CO₂ flux. Summation over the power-law distribution predicts a maximum global subaerial passive volcanic flux of $2-3 \times 10^{12}$ mol/yr and $2-3 \times 10^{11}$ mol/yr for CO₂ and SO₂, respectively. Normalizing the emission flux by scaling per unit crater area (instead of per volcano) to investigate the extension of the power-law behavior to geothermal areas with lower gas fluxes yields a power-law exponent of ~ 1 and predicts a subaerial volcanic-metamorphic CO₂ flux of 6×10^{12} mol/yr.

INTRODUCTION

Over 10^4-10^5 yr time scales, the natural fluxes of CO₂ from volcanism and metamorphism balance the removal of CO₂ during silicate weathering (Berner et al., 1983; Gerlach, 1991). Many geochemical carbon models thus assume that the present-day volcanic-metamorphic CO₂ flux equals the removal of atmospheric CO₂ by silicate weathering ($6-11 \times 10^{12}$ mol/yr; Holland, 1978; Berner et

al., 1983; Berner, 1990). Direct measurements of CO₂ emission rates exist for only nine subaerial volcanoes (Table 1). Gerlach (1991) used the median value for seven fluxes and assumed 60 active volcanoes to estimate a global flux of 1.8×10^{12} mol CO₂/yr. Williams et al. (1992) calculated a similar value for the CO₂ emission, using SO₂ fluxes and CO₂/SO₂ ratios. On the basis of direct measurements, one alkalic volcano, Mount Etna, produces more than

TABLE 1. CO₂ EMISSION RATES FOR SUBAERIAL VOLCANOES

Volcano	Period observed	Method*	Rate (x 10 ¹² mol/yr)	Reference	Area of volcano# (km ²)
Mount Etna	9/84, 6/85	A	0.58 (1.0) [‡]	Allard et al. (1991); Carbonnelle et al. (1985)	2000
Oldoinyo Lengai	6/94	B	0.06	This study	170
Augustine	4/86	A	0.05	Symonds et al. (1992)	N.a.
Mount St. Helens	7/80-9/81	B	0.04	Harris et al. (1981)	90
White Island	11/83	A	0.03	Rose et al. (1986)	50
Kilauea	12/83	B	0.03	Greenland et al. (1985)	10 900
Redoubt	6/90	B	0.015	Casadevall et al. (1990)	N.a.
Grimsvotn	3/92	C	0.003	Brantley et al. (1993)	522
Vulcano	9/84	A	0.0015 (0.0017) [‡]	Carbonnelle et al. (1985); Baubron et al. (1990)	475
Lake Nyos	12/89, 9/90	C	0.00026	Evans et al. (1993)	N.a.

Note: Modified from Gerlach (1991). N.a. – information was not available.

*A–Measurement by airborne COSPEC ultraviolet spectrophotometer of SO₂ coupled with data for CO₂/SO₂ ratios of plume or fumarole gases. B–Measurement by airborne infrared spectrophotometer. C–Measurement by crater-lake mass balance or solute profile.

[‡]Includes diffuse emanations outside of crater rim.

#Area of plan view of volcanoes calculated using the crater diameters and flank widths published in Pike and Clow (1981).

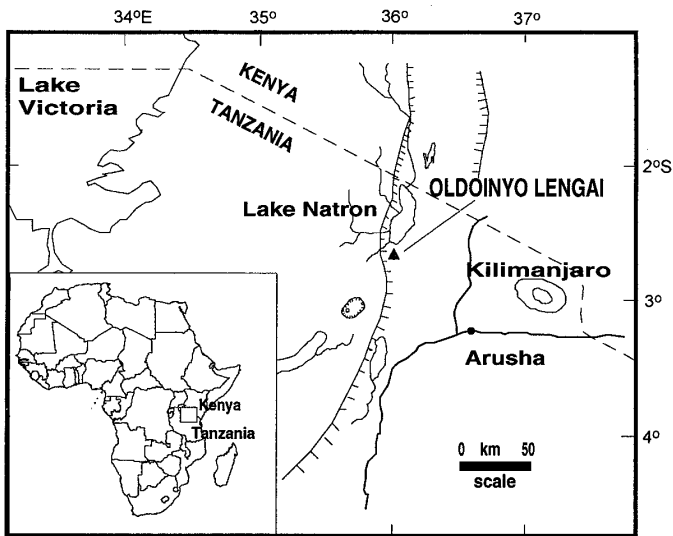


Figure 1. Location map of alkalic volcano Oldoinyo Lengai in northern Tanzania. Hachured line marks walls of eastern branch of East African rift system. Last reported lava flows at Oldoinyo Lengai occurred in June 1993; however, fumarolic activity has been observed since 1983, and there were at least 10 eruptions having volcanic explosivity index (VEI) > 2 in past century (Simkin et al., 1981).

50% of the estimated subaerial volcanic CO₂ flux to the atmosphere ($1\text{--}2 \times 10^{12}$ mol/yr, Gerlach, 1991). However, these global summations do not include emissions from any volcano in the largest alkalic volcanic region of the world, East Africa, and thus may be underestimated. We report the first estimate of C degassing at the alkalic volcano Oldoinyo Lengai, Tanzania, the world's only carbonatite-erupting volcano, and discuss the distribution of flux measurements with respect to global extrapolations.

GEOLOGIC CHARACTERISTICS

Oldoinyo Lengai is a symmetrical Neogene (0.35 Ma) strato-volcano situated in the East African Rift (Fig. 1). The 60 km³ cone consists of phonolitic and nephelinitic pyroclastic rocks (Dawson, 1989) with <1% Na-rich carbonatite (Barker, 1989). Given Dawson's (1989) estimate for the oldest known carbonatite tuff from Oldoinyo Lengai (22 ka), the mass of carbonatite lava represents a time-averaged C flux (solid products only) of 5×10^8 mol/yr. Previous analysis of fumarole gases revealed CO₂ concentrations of nearly 97% (dry gas analysis: Javoy et al., 1988), but no flux estimates have been published.

FLUX MEASUREMENTS

Two airborne spectrophotometer measurements of Oldoinyo Lengai's volcanic emissions were made one week apart in June 1994. The method was modified from Harris et al. (1981), and a Li-Cor 6262 nondispersive infrared gas analyzer, calibrated for each flight, was used. The Li-Cor 6262 has a response time of 1 s and measures the concentration of CO₂ to ± 1 ppm.

RESULTS

Emission rates of CO₂ of 0.05×10^{12} and 0.06×10^{12} mol/yr were measured at Oldoinyo Lengai 1 and 2 km downwind, respectively, of the crater (Fig. 2). This flux is similar to that of Augustine (Alaska; Table 1), which represents the second-largest measured CO₂ emission rate at a subaerial volcano. Augustine was measured subsequent to a low-level explosive event (Gerlach, 1991), whereas the Oldoinyo Lengai measurement represents passive degassing. However, Mount Etna, another alkalic volcano, produces more than 17 times the Oldoinyo Lengai flux (1×10^{12} mol/yr), half of which comes from diffuse emanations from the flanks (Allard et al., 1991). The smaller flux from Oldoinyo Lengai is presumably related to the smaller body of degassing magma or decarbonating country rock in the subsurface.

DISCUSSION

The large contribution of CO₂ emissions from one volcano indicates that the emission distribution may not be Gaussian. If the global distribution of gas fluxes, like that of ore deposits, developed as a concentration process following the so-called law of proportionate effect (West and Shlesinger, 1990), then a skewed distribution is expected. Shaw (1961) and Harris (1984) argued that the skewed distributions of ore deposit tonnage are either log normal or power law. For a wide distribution, the only difference between the log normal and power law is that the latter overestimates the frequency of small individuals (West and Shlesinger, 1990). Many geophysical phenomena—including frequency of volcanic eruptions, earthquakes, and meteorite impacts—exhibit a power-law (fractal) distribution (Turcotte, 1992). The physical argument for why ore deposits might show a power-law distribution (Turcotte, 1992) may also describe the development of the distribution of gas-flux centers.

If the distribution of volcanic emissions follows a power law, the number of volcanoes, N , with an emission rate of $\geq f$ can be described by

$$N = af^{-c}, \quad (1)$$

where a and c are constants. The total global flux, f_{tot} , can be calculated if $c < 1$ by

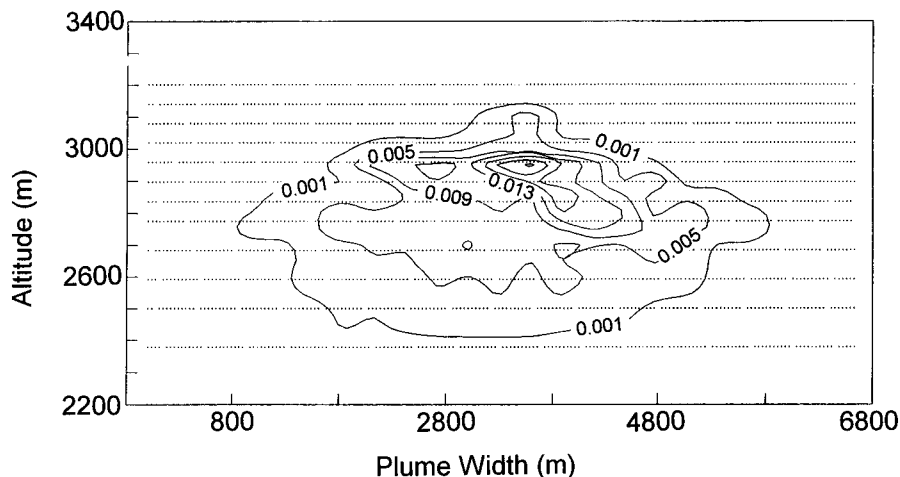


Figure 2. Spatial distribution of density of excess CO₂ (g/m³) above background in plume cross section measured June 8, 1994, 1 km downwind of crater (maximum anomalous CO₂ concentration of 60 ppm). Each plume measurement consisted of 12–14 horizontal flight paths (dotted lines) perpendicular to plume trajectory, made at constant speed (129 ± 8 km/h), and elevation (± 15 m). Average wind speed (16 ± 4 km/h) was determined as difference between ground speeds while traveling into and with wind (60° NE). Total flux estimates were computed from product of plume area, mean excess CO₂ concentration, and wind speed.

Figure 3. A: Cumulative frequency of number of volcanoes (N) emitting SO_2 flux $\geq f$. SO_2 emission data were compiled by Stoiber et al. (1987) from 101 passively degassing volcanoes over one-year period during 1981–1982. Emissions were grouped into four categories according to plume size and/or emission rate. We plotted average emission rate per volcano from each category and added SO_2 emission rate for Mount Etna (2.3×10^{12}), because it does not fit into categories assigned for other volcanoes. **B:** Cumulative frequency of number of volcanoes (N) emitting CO_2 flux $\geq f$. CO_2 emission data (Williams et al., 1992) were estimated by using data from Stoiber et al. (1987) and representative CO_2/SO_2 ratios, plus rates for Mount Etna and Oldoinyo Lengai which do not fit into assigned categories. Estimate for 1400 unmeasured volcanoes represents maximum flux for volcanoes not included in compilation (see text). **C:** Cumulative frequency plot of area (N , in square kilometres) of land surface emitting CO_2 flux $\geq f'$, where f' is area-normalized flux. Total global land area and one estimate of geothermal CO_2 flux per square kilometre (McKibben et al., 1993) are indicated.

$$f_{\text{tot}} = - \int_{f_{\text{min}}}^{f_{\text{max}}} \frac{dN(f)}{df} f df = \frac{c}{1-c} f_{\text{max}}, \quad (2)$$

where f_{max} is the largest gas flux at a volcano. For $c > 1$, the sum will only be finite if a lower limit, f_{min} (flux of the smallest-flux volcano), is specified. Marrett and Almedinger (1991) pointed out that equation 2 underestimates the summation, and they derived a better formulation:

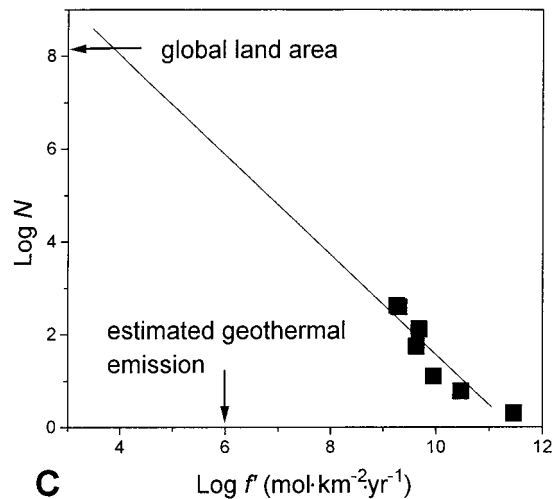
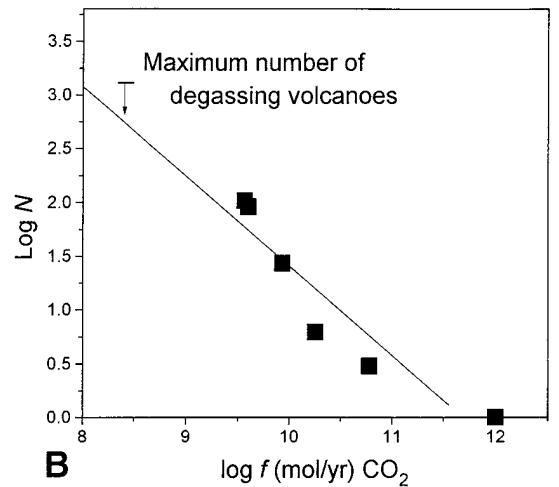
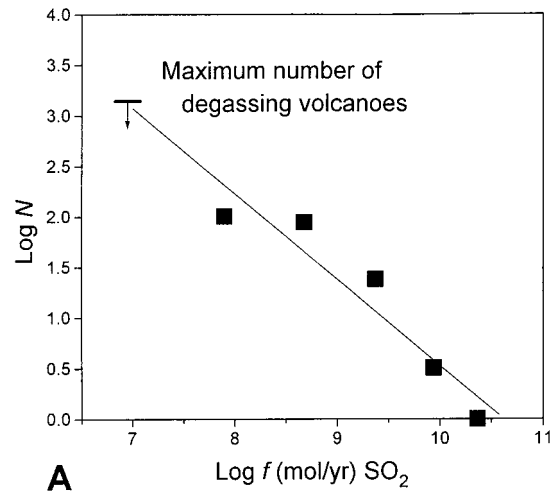
$$f_{\text{tot}} = f_1 + f_2 + f_3 + \dots + f_N \left[\frac{c}{1-c} (N+1) \left(\frac{N}{N+1} \right)^{1/c} \right], \quad (3)$$

where f_N refers to the N th-largest flux. If the distribution is not power law, but rather log normal, $c > 1$ implies that the power-law extrapolation greatly overestimates f_{tot} , whereas for $c < 1$, the extrapolation can be valid. Therefore, the value of c determines whether a global compilation—which realistically will never include all small-flux volcanoes—can accurately estimate the global flux: $c < 1$ or $c > 1$ implies that the estimate is possible or impossible, respectively. For a distribution with known f_{min} and f_{max} and $c = 1$, we can calculate

$$f_{\text{tot}} = f_{\text{max}} (\ln f_{\text{max}} - \ln f_{\text{min}}). \quad (4)$$

We examined the hypothesis of a power-law distribution for the only available simultaneous emission estimate (SO_2 data from Stoiber et al., 1987; Fig 3A). The flux data are only linear for the larger volcanoes ($\log f \geq 8.5$). The compilation includes 101 volcanoes exhibiting visible plumes; it is impossible to assess whether the distribution is power law or log normal because volcanoes with smaller plumes (smaller fluxes) may have been neglected. The distribution of CO_2 emissions calculated by using CO_2/SO_2 ratios from the same data set (Williams et al., 1992) was also fit to a power law (Fig. 3B). The power-law exponents for both SO_2 (~ 0.8) and CO_2 (~ 0.8) are < 1 , although poorly constrained by the limited data.

To determine a maximum value of c in order to ascertain whether a global summation is possible, we assumed that up to 1400 volcanoes (McClelland et al., 1989) emit a CO_2 flux $\leq 2.6 \times 10^8$ mol/yr, the anomalously high rate observed from the dormant volcano at Lake Nyos, Cameroon (see Table 1), and that very small volcanoes have a CO_2/SO_2 ratio of 29 (Williams et al., 1992). The calculated slopes of the power-law fit including these data ($c \approx 0.9$) are still < 1 . For a value of $c = 0.8\text{--}0.9$, convergence is achieved for $N \approx 20$, revealing that *even if the distribution is log normal, the global extrapolation from a few volcanoes is valid*. Maximum estimates of



global fluxes of CO_2 and SO_2 made by using the power-law distribution for subaerial, passively degassing volcanoes are therefore $2\text{--}3 \times 10^{11}$ mol/yr and $2\text{--}3 \times 10^{12}$ mol/yr ($c \approx 0.8$), respectively. Figure 3 also suggests that several high-flux volcanoes remain to be measured, if the distribution is power law.

The power-law assessment has been applied here to CO_2 flux per volcano, but CO_2 flux per unit area also represents a skewed distribution: if we assume that each of the 100+ volcanoes degasses over 10000 km^2 (the smallest area that encompasses the largest

volcano [see Table 1]), the distribution of cumulative areas of land degassing at a CO₂ flux rate of $\geq f'$ (in mol · km⁻² · yr⁻¹) still yields the same power-law exponent because the slope is unaffected.

However, if we normalize the CO₂ flux data by an average crater size of 2 km² (Mount Etna's crater is 1.7 km²) and partition the Etna flux into crater and diffuse flux (Allard et al., 1991), the slope increases to ~1, with $f'_{\min} = 5 \times 10^3$ mol · km⁻² · yr⁻¹ (Fig. 3C). The value of f'_{\min} , the minimum volcanic-metamorphic CO₂ flux per square kilometre for continental land area, is below the lowest measurement of terrestrial CO₂ flux: 10⁶ mol · km⁻² · yr⁻¹, attributed to soil respiration (Raich and Schlesinger, 1992). From equation 4, we extrapolate a maximum subaerial volcanic-metamorphic CO₂ flux of 6×10^{12} mol/yr—consistent with global estimates of CO₂ uptake due to weathering, but higher than the published estimates of worldwide volcanic degassing. A slope of ~1 implies that small and large subaerial CO₂ sources are equally important globally and that the CO₂ flux is stable to temporal variations in individual volcanic emissions. Either area-normalized distribution predicts that <1% of the land area should release ~10⁶ mol · km⁻² · yr⁻¹ of volcanic-metamorphic CO₂, consistent with estimates of worldwide high-level geothermal resources (Rowley, 1982) and geothermal degassing (McKibben et al., 1993).

CONCLUSIONS

Aerial measurements at Oldoinyo Lengai reveal a CO₂ flux that is slightly larger than fluxes at nonalkalic volcanoes, but much smaller than that of Mount Etna, which accounts for over half of the global carbon flux attributed to subaerial volcanoes. Fitting the SO₂ and CO₂ volcanic flux data to a fractal distribution yields a power-law exponent of <1, because the distribution is dominated by large-flux volcanoes. An accurate assessment of the global subaerial volcanic flux could therefore be made by simultaneous measurement at the 20 largest-flux volcanoes. Using the power-law distribution to extrapolate over all volcanoes yields a maximum global volcanic CO₂ flux at most a factor of three higher than other estimates. Normalizing the emission fluxes by scaling per unit crater area to analyze the distribution of flux per area worldwide yields a power-law exponent of ~1, suggesting that degassing areas such as geothermal zones may be as important as large volcanoes in the global distribution and that the CO₂ flux is stable to temporal variations in individual volcanic emissions.

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