Geophysical Research Letters

RESEARCH LETTER
10.1029/2023GL107474

Large Isotopic Shift in Volcanic Plume CO_2 Prior to a Basaltic Paroxysmal Explosion

Fiona D'Arcy[1], Alessandro Aiuppa[2], Fausto Grassa[3], Andrea Luca Rizzo[4,5], and John Stix[1]

[1]Department of Earth & Planetary Sciences, McGill University, Montreal, QC, Canada, [2]Dipartimento DiSTeM, Università degli Studi di Palermo, Palermo, Italy, [3]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italy, [4]Department of Earth and Environmental Sciences, University of Milano-Bicocca, Milan, Italy, [5]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Milano, Milan, Italy

Key Points:

- Rapid collection of volcanic plume CO_2 enabled by Uncrewed Aerial Systems
- A carbon isotopic anomaly was present two weeks prior to the Stromboli 2019 paroxysm
- High CO_2 concentrations, elevated CO_2/S_t and light $\delta^{13}C\text{-}CO_2$ may precede paroxysms on timescales of months to weeks

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

F. D'Arcy,
fiona.darcy@mail.mcgill.ca

Citation:

D'Arcy, F., Aiuppa, A., Grassa, F., Rizzo, A. L., & Stix, J. (2024). Large isotopic shift in volcanic plume CO_2 prior to a basaltic paroxysmal explosion. *Geophysical Research Letters*, *51*, e2023GL107474. https://doi.org/10.1029/2023GL107474

Received 28 NOV 2023
Accepted 11 JUL 2024

Abstract Carbon dioxide is a key gas to monitor at volcanoes because its concentration and isotopic signature can indicate changes to magma supply and degassing behavior prior to eruptions, yet carbon isotopic fluctuations at volcanic summits are not well constrained. Here we present $\delta^{13}C$ results measured from plume samples collected at Stromboli volcano, Italy, by Uncrewed Aerial Systems (UAS). We found contrasting volcanic $\delta^{13}C$ signatures in 2018 during quiescence ($-0.36 \pm 0.59‰$) versus 10 days before the 3 July 2019 paroxysm ($-5.01 \pm 0.56‰$). Prior to the eruption, an influx of CO_2-rich magma began degassing at deep levels (~100 MPa) in an open-system fashion, causing strong isotopic fractionation and maintaining high CO_2/S_t ratios in the gas. This influx occurred between 10 days and several months prior to the event, meaning that isotopic changes in the gas could be detected weeks to months before unrest.

Plain Language Summary Volcanoes produce gases which change composition depending on how active the volcano is. One of these gases, carbon dioxide, is known to change in proportion to other gases before an eruption occurs, but little is known about how the isotopes of carbon change leading up to an eruption. Using drones to reach the gaseous plume of Stromboli volcano, Italy, we have captured carbon dioxide both during an inactive phase in 2018 and during the lead-up to a highly explosive eruption called a paroxysm in 2019. There is a stark difference in the carbon isotopes measured 10 days before the 3 July 2019 paroxysm as opposed to those measured in 2018. This is caused by the arrival of CO_2-rich magma which progressively degassed, leading to lighter carbon isotopes in the residual magma over time. This process could have started anywhere from 10 days to several months before the paroxysm. This provides a warning signal which can be detected weeks to months before an active period begins.

1. Introduction

Volcanoes play a significant role in the global cycle of carbon (Burton et al., 2013; Mather, 2015; Werner et al., 2019). This is because carbon is the second major species dissolved in a magma, it is transferred from the lithosphere to the atmosphere during eruption, and more significantly, during quiescence between eruptions at open-vent volcanoes (Edmonds et al., 2022). Carbon isotopes provide information complementary to gas ratios and fluxes, as the isotopes can be used to constrain degassing pathways (Barry et al., 2014; Boudoire et al., 2018; Gerlach & Taylor, 1990), distinguish magma sources (Fischer et al., 2015; Paonita et al., 2012; Troll et al., 2012), and monitor magmatic inputs to hydrothermal systems (D'Arcy et al., 2022; Federico et al., 2008, 2023).

Sampling of volcanic plumes provides a safe and fast alternative to directly collecting volcanic gases from fumarolic vents into sample bottles. The plume can be sampled at varying distances from the source vent depending on the topography and wind conditions, but it is crucial to sample CO_2 as close to the source as possible for isotopic characterization. Sampling was first done by physically entering the plume and manually collecting samples (Chiodini et al., 2011) before evolving to plume traverses in ground vehicles (Rizzo et al., 2015), helicopters (Fischer & Lopez, 2016), and use of field laboratories (Malowany et al., 2017; Schipper et al., 2017). Such sampling has entered a new era with the onset of compact sensor arrays combined with lightweight pumps for targeted sampling of volcanic plumes by Uncrewed Aerial Systems (UAS) (D'Arcy et al., 2022; Liu et al., 2020; Shingubara et al., 2021; Tsunogai et al., 2022).

Stromboli volcano is part of the Aeolian arc of volcanoes in Italy, which results from the subduction of the African plate below the European plate (e.g., Gasparini et al., 1982). It has a well-studied volcanic gas composition, with

up to ~35 mol% CO_2 during passive degassing and up to 54 mol% CO_2 during syn-explosive degassing (Aiuppa & Bertagnini et al., 2010; Aiuppa & Burton et al., 2010; Burton et al., 2007; Pering et al., 2020). The plumbing system of the volcano comprises a deep magma storage zone at ~6–8 km, from which low-porphyritic (LP) materials are erupted. The magmas here are CO_2-rich, reflected by gases at the surface with elevated CO_2/S_T exceeding values of 20. A second shallower storage zone <3 km deep produces highly porphyritic (HP) eruptive products, with associated gases depleted in CO_2 and having CO_2/S_T values less than 10–15 (Aiuppa & Bertagnini et al., 2010; Aiuppa & Burton et al., 2010; Aiuppa et al., 2021; Metrich et al., 2009). Prior to this study, carbon isotopes of CO_2 at the summit of Stromboli varied from −1.0 to −2.5‰ $\delta^{13}C$ (Capasso et al., 2005; Di Martino et al., 2021; Federico et al., 2008; Finizola et al., 2003; Rizzo et al., 2009), yet plume samples from the summit have never been captured during and immediately prior to paroxysms.

In this work, we have refined a series of custom UAS gas sampling assemblies to collect CO_2 from Stromboli for isotopic analysis. We show distinct differences in $\delta^{13}C$ of CO_2 between passive quiescent degassing versus immediately before a devastating explosive paroxysm. We relate these changes to transitions between closed-system and open-system degassing, that is, to whether the gas travels with or separates from the host melt, respectively. We demonstrate the potential utility of carbon isotopes to better understand these styles of degassing and their implications for eruption forecasting at open-vent volcanoes.

2. Materials and Methods

2.1. Sampling and Isotopic Analysis

We conducted 25 sampling flights in May 2018 and June 2019 at the summit of Stromboli. We used a series of UAS (Figures 1a and 1b) and Compact Aerial Receiver-initiated Gas-sampling Operations (CARGOs) which we developed over the course of this study, paired with ground-based plume samples, which are described in detail in Supporting Information S1 (Text S1 in Supporting Information S1). Each sampling flight collected two to ten 600 ml bags of plume gas, while individual ground-based samples of plume gas were collected with a pump and portable MultiGAS at the crater rim. Bags were closed with clamps upon landing the aircraft and immediately taken from the summit to the field lab at the end of the day for same-day $\delta^{13}C$ analysis (Text S2–S6 in Supporting Information S1).

2.2. Estimates of the Isotopic Signature of Magmatic Carbon

Volcanic plumes are a mixture of atmosphere and volcanic gas, such that:

$$\delta^{13}C_p[CO_2]_p = f * \delta^{13}C_v[CO_2]_v + (1-f) * \delta^{13}C_b[CO_2]_b \quad (1)$$

where f is the relative contribution from the volcanic source (Chiodini et al., 2011), and subscripts p, b, and v denote plume, background, and volcanic, respectively. To estimate the isotopic composition of the volcanic source of gas, isotopic results of plume samples must account for the presence of background air. A number of authors (Fischer & Lopez, 2016; Liu et al., 2020; Malowany et al., 2017; Rizzo et al., 2014, 2015; Shingubara et al., 2021; Tsunogai et al., 2022) have adopted the Keeling method (Keeling, 1958) to calculate the source $\delta^{13}C$ of volcanic plumes. This method uses linear regression to fit the observations of plume $\delta^{13}C$ against $1/CO_2$ to a line of best fit, wherein one endmember is background air and the other is the volcanic source. A linearization of Equation 1 yields the equation of a line (Equation 2) wherein the y-axis intercept represents the theoretical composition of the volcanic source, $\delta^{13}C$ (Malowany et al., 2017):

$$\delta^{13}C_p = \frac{1}{[CO_2]_p}[CO_2]_b\left[\delta^{13}C_b - \delta^{13}C_v\right] + \delta^{13}C_v \quad (2)$$

There is a simplified method adapted from Equation 1 which uses each discrete point sampled in a plume to estimate the $\delta^{13}C_v$ which takes the weighted mean of the combined estimates (Schipper et al., 2017):

$$[CO_2]_v \cdot \delta^{13}C_v = [CO_2]_p \cdot \delta^{13}C_p - [CO_2]_b \cdot \delta^{13}C_b \quad (3)$$

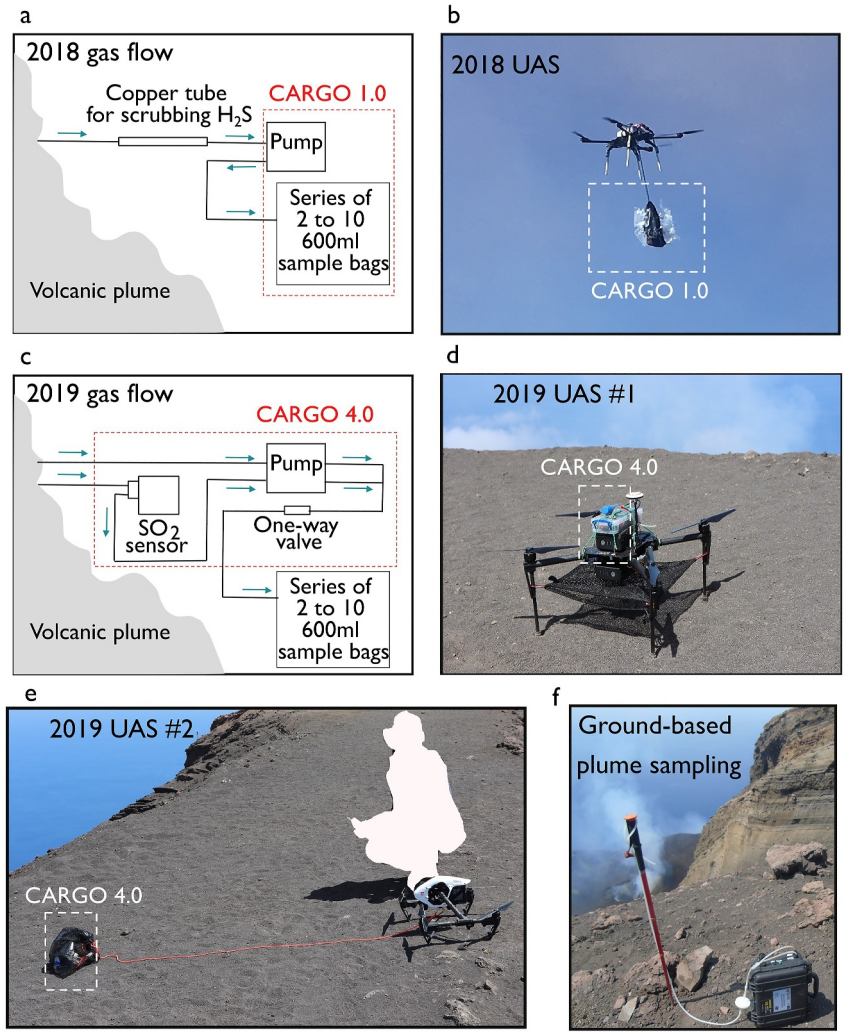

Figure 1. Sampling set-up for 2019 and 2018 samples. Gas flow schematics of the 2018 (a) and 2019 (c) compact aerial receiver-initiated gas-sampling operations (CARGOs) along with the uncrewed aerial system (UAS) used to fly them in 2018 (b) and in 2019 (d, e). In (f), the general method used for ground-based sampling is pictured.

We applied both methods to calculate the volcanic source δ^{13}C-CO_2.

3. Results and Discussion

3.1. First Aerial Samples of Volcanic CO_2 Capture an Isotopically Light Data Set

Average background from samples taken at the summit in 2018 was 401 ± 2 ppm CO_2 and −8.9 ± 0.2‰ δ^{13}C (n = 9), and 401 ± 2 ppm CO_2 and −9.9 ± 0.2‰ δ^{13}C in 2019 (n = 4). We discuss this background variation in Supporting Information S1 (Text S4 in Supporting Information S1). The concentration of CO_2 collected within the volcanic plume, during 14 flights from 12–17 May 2018, ranged from 405 to 490 ppm and δ^{13}C between −7.5 and −9.2‰ (Supporting Information Data set S1). We also collected 16 ground-based plume samples on the crater rim which varied from 410 to 463 ppm CO_2 with δ^{13}C of −7.6 to −9.0‰. During 11 flights from 17–21 June 2019, we measured CO_2 concentrations ranging from 403 to 555 ppm and δ^{13}C between −8.3 and −9.8‰ (Data Set S1). We also collected 12 ground-based plume samples on the rim ranging from 408 to 501 ppm CO_2 with δ^{13}C −7.8 to −9.7‰.

Our volcanic plume concentrations are comparable to those collected by UAS at other volcanoes. Shingubara et al. (2021) achieved 531 ppm (maximum volcanic CO_2 of 61 ppm), while Tsunogai et al. (2022) reached

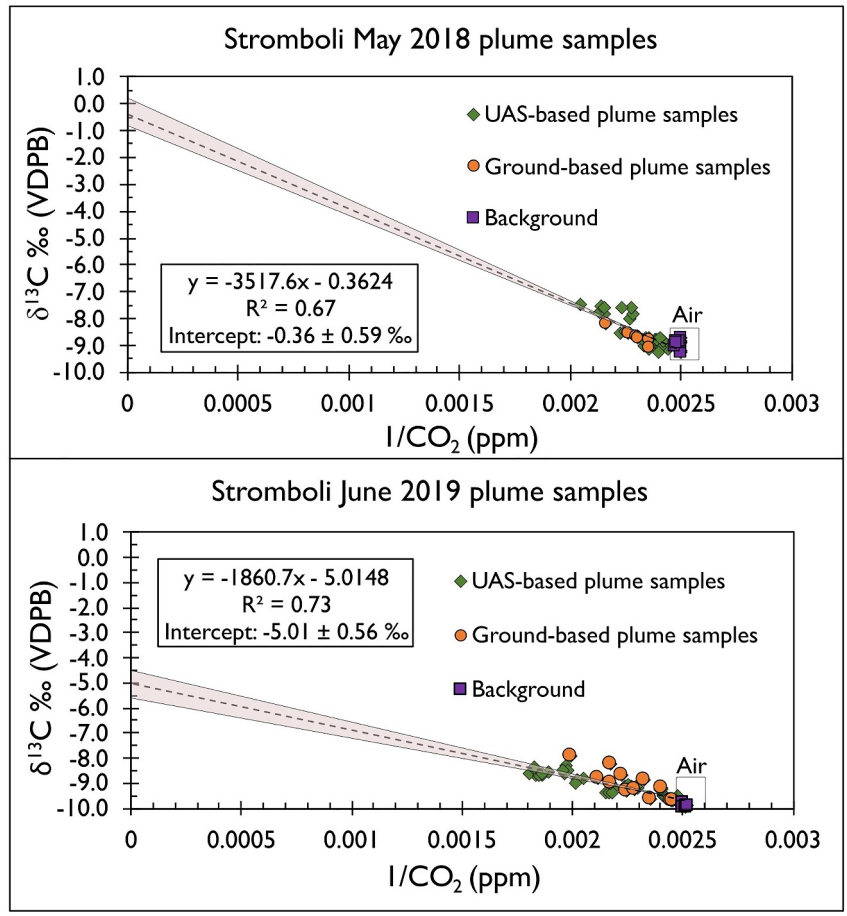

Figure 2. $\delta^{13}C$ values against inverse CO_2 concentrations of all plume samples during this study. UAS-based plume (green diamonds), ground-based plume (orange circles), and ground-based background (purple squares) samples are plotted and included in a linear regression analysis whose line of best fit (dashed line) is shown for 2018 (a) and 2019 (b). This line represents a mixing line between the volcanic source and background air which is extrapolated to the *y*-intercept in order to estimate the $\delta^{13}CO_2$ of the high concentration volcanic source.

514 ppm (maximum volcanic CO_2 of 98 ppm) at Aso volcano in Japan. At Manam volcano in Papua New Guinea, plume samples from Liu et al. (2020) ranged from 421 to 494 ppm (maximum volcanic CO_2 of 85 ppm). At Poás volcano, D'Arcy et al. (2022) reached up to 528 ppm or 120 ppm volcanic CO_2.

The $\delta^{13}C_v$ estimated from the Keeling method for May 2018 and June 2019 are $-0.36 \pm 0.59‰$ ($R^2 = 0.67$, $p = 0.05$, $n = 50$) and $-5.01 \pm 0.56‰$ ($R^2 = 0.73$, $p = 0.05$, $n = 51$), respectively. Errors are reported as the standard error of the regression multiplied by 1.96 to give $\pm 2\sigma$ (Figure 2). The estimates for the weighted mean method for 2018 and 2019 using samples with volcanic CO_2 concentration greater than 50 ppm are $-0.78 \pm 1.34‰$ and $-4.12 \pm 1.71‰$, respectively (Data Set S2).

The volcanic source $\delta^{13}C\text{-}CO_2$ composition we estimate for 2018 ($-0.36 \pm 0.59‰$) is similar to albeit slightly heavier than the range of $\delta^{13}CO_2$ measured in summit fumaroles ($-1.0‰$ to $-2.5‰$) in previous years (Figure 3). The small difference between these past fumarole measurements (Capasso et al., 2005; Di Martino et al., 2021; Rizzo et al., 2009) and that of the plume we sampled in 2018 may be due to uncertainties in estimating $\delta^{13}C$, vent-specific differences, fumarole versus dense volcanic plume differences, and/or daily variations. Even more striking, the volcanic source in 2019 ($-5.01‰ \pm 0.56‰$) is more than 2‰ lighter than the lowest $\delta^{13}C$ values usually measured at Stromboli in fumaroles (Figure 3). The large difference between the 2018 and 2019 isotopic signatures in the carbon dioxide sampled at Stromboli is a key finding, as the 2019 samples were collected two weeks prior to the July 3rd paroxysm, which was an unusually intense and fatal volcanic explosion (Andronico et al., 2021; Giordano & De Astis, 2021; Ripepe et al., 2021).

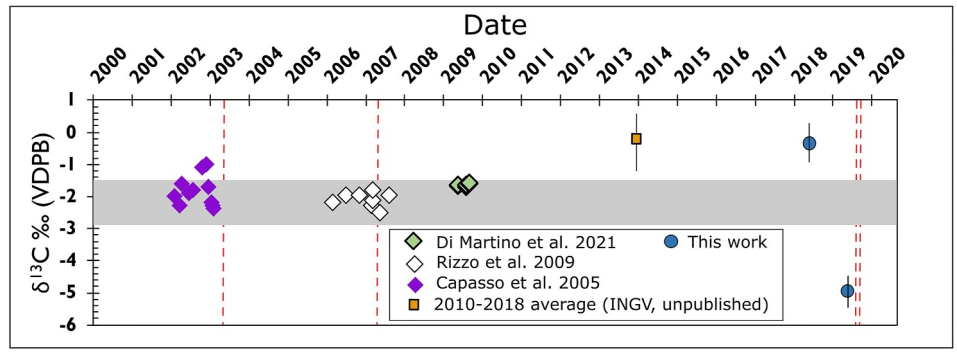

Figure 3. Carbon isotopes plotted against time on the *x*-axis, showing how 2018 and 2019 results compare with previous studies. The gray band represents the $\delta^{13}C$ range from fluid inclusions at Stromboli (Gennaro et al., 2017). The 2010–2018 average was calculated using a regression on passive gas samples taken at the summit during an 8-year period ($n = 49$) with 4 blanks as background. Vertical red dashed lines represent paroxysms.

3.2. Carbon Isotopes Reveal Change in Degassing State Prior to Paroxysmal Activity

The significant divergence in $\delta^{13}C$ of the volcanic plume between 2018 (−0.36‰) and 2019 (−5.01‰) is unprecedented at Stromboli. Such a variation in $\delta^{13}C$ has never been observed in any fumarolic or hydrothermal sample. We sampled the plume close to the vent during two fortuitous sampling windows: (a) during a quiescent period and (b) just 2 weeks before a highly energetic paroxysmal eruption. Our analytical procedures using two different instruments and employing two different statistical methods (Text S1–S6 in Supporting Information S1) demonstrate that these results represent true volcanic variations.

The well-studied magma source at Stromboli consists of a volatile-rich, deep-derived magma and a volatile-poor, shallow magma (Métrich et al., 2009). The most intuitive explanation for the nearly 5‰ difference in $\delta^{13}CO_2$ is a new magmatic source with a distinct carbon isotopic composition supplying the 2019 eruption. However, the major and trace element geochemistry of the 2019 eruptive products (Andronico et al., 2021; Métrich et al., 2021; Petrone et al., 2022) is indistinguishable from that of pyroclastic materials erupted during other recent paroxysms on Stromboli in 2003 and 2007 (Métrich et al., 2005, 2009). This indicates that all these events (2003, 2007 and 2019) were charged by compositionally similar magma sourced from the same metasomatically altered mantle source (Peccerillo & Frezzotti, 2015). Furthermore, there is no evidence for a magma source in the region with $\delta^{13}CO_2$ as light as our 2019 data (−5.01‰). Studies from fumarolic emissions of volcanoes in the Aeolian arc range from −2.5 to −1.0‰ at Stromboli (Capasso et al., 2005; Federico et al., 2008; Rizzo et al., 2009) and −3.2 to +0.7‰ at Vulcano (Capasso et al., 1997; Venturi et al., 2017). Thus, there is no evidence for the existence of a light carbon component in the mantle, both at a local scale (Gennaro et al., 2017) and regionally.

Another plausible mechanism is isotopic fractionation during degassing of the volatile-rich deep-derived magma associated with past paroxysms at Stromboli (Metrich et al., 2009). During release of gases from magma, the heavier ^{13}C isotope concentrates in the gas phase compared to the lighter ^{12}C isotope. As magma degasses, the remaining carbon in the melt becomes lighter (^{13}C-depleted), as does the gas phase released at later stages of degassing (Holloway & Blank, 1994). This depletion can occur during closed-system degassing when the melt stays in contact with the gas, or to a much greater extent during open-system degassing (Raylegh fractionation) conditions when the gas is removed from the melt (Brown et al., 1985; Rayleigh, 1896). Hence, magma degassing under open-system conditions can lower $\delta^{13}C$ of the resulting gas to levels that could explain our 2019 gas data.

3.3. Dynamic Carbon Isotopes at Arc Volcanoes

On Stromboli, as in other open-vent volcanoes (Edmonds et al., 2022), both closed- and open-system degassing conditions can occur, and even coexist. During ordinary Strombolian activity (Harris & Ripepe, 2007; Rosi et al., 2013), both quiescent and explosive degassing occur, in which the former is caused by shallow gas release from convectively circulating magma in the upper conduits, effectively acting as closed-system degassing (Allard et al., 2008). Explosive bursting at the surface reflects rapid, separate ascent of deeply sourced gas bubbles undergoing open-system degassing (Burton et al., 2007). Important in this context is that high CO_2/SO_2 ratios have typically been observed in the bulk plume (passive + explosive) before paroxysms (Aiuppa & Bertagnini

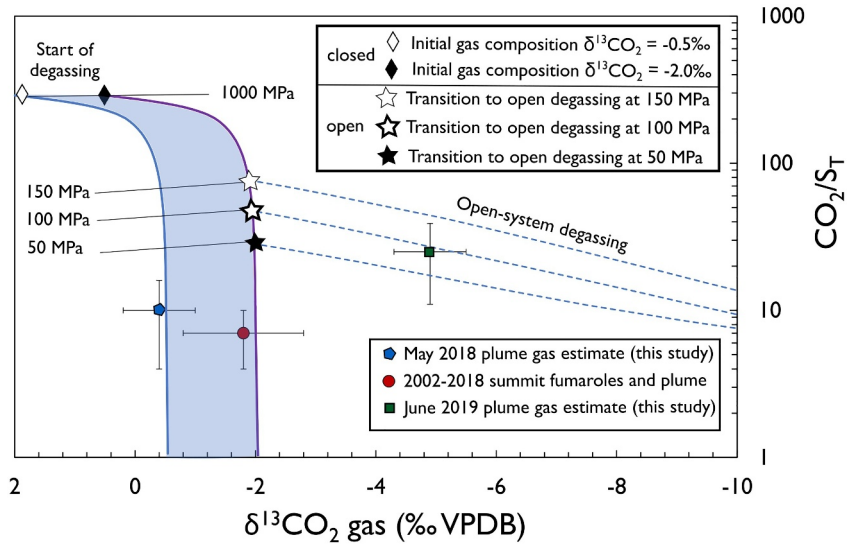

Figure 4. (a) Modeled degassing paths of magma at Stromboli, showing carbon isotopic ratios on the *x*-axis and carbon dioxide to sulfur gas ratios on the *y*-axis. The solid purple and blue lines are closed-system degassing starting from 1,000 MPa, while the dashed blue lines are open-system degassing starting from 150 to 50 MPa switchover depths from closed to open (star symbols). This corresponds to a starting f value of 0.7 at 1,000 MPa and f values of 0.03 to 0.006 at 50–150 MPa. Initial gas compositions are shown ranging from 2‰ (with a parental melt $\delta^{13}C$ of −0.5‰ (open diamond)) to 0.5‰ (with a parental melt $\delta^{13}C$ of −2‰ (solid diamond)). The green square represents June 2019 $\delta^{13}C$-CO_2 (this study) and CO_2/S (Aiuppa et al., 2021). The blue pentagon represents May 2018 $\delta^{13}C$-CO_2 (this study) and CO_2/S (Aiuppa et al., 2021). The red circle represents the average $\delta^{13}CO_2$ of 2002–2007 direct samples ($n = 25$) of summit fumaroles (Capasso et al., 2005; Di Martino et al., 2021; Rizzo et al., 2009) and the source estimate based on linear regression of 2010–2018 $\delta^{13}C$-CO_2 of summit plume gases collected from the crater rim (INGV, unpublished). The CO_2/S for the red circle is an average based on Aiuppa et al. (2011) and Aiuppa and Giudice et al., 2017) for 2006–2012.

et al., 2010; Aiuppa & Burton et al., 2010; Aiuppa et al., 2021) and major explosions (Aiuppa et al., 2011). This indicates that open-system conditions prevail in such conditions, resulting in the release of deeply sourced gas that is not in equilibrium with resident shallow conduit magma.

Geochemical and geophysical evidence indicates that a deeply derived gas was being emitted in the months prior to the July 3rd paroxysm. First, increased CO_2 concentrations and high CO_2/SO_2 ratios were noted in the plume beginning 8 months prior (Aiuppa et al., 2021), indicative of a deeply sourced magma (>4 km) due to the low solubility and deeper exsolution level of CO_2 as compared to SO_2. Second, elevated CO_2 flux from summit soil began in October 2018, accelerating to July 2019 as higher volatile input was supplied (Inguaggiato et al., 2020). Third, modeling the degassing behavior as a combination of open- and closed-system conditions has been invoked to account for the bimodal CO_2/SO_2 gas ratios observed prior to the July 3rd paroxysm (Aiuppa et al., 2021). Fourth, a seismic precursor to the July 3rd paroxysm was noted in very long period (VLP) waveforms starting at least 1 month before the eruption, thought to be caused by vigorous (deep-sourced?) gas jetting activity sustaining the Strombolian activity (Giudicepietro et al., 2020).

We now test and model if a switch from closed-system to open-system degassing conditions can explain the distinct $\delta^{13}CO_2$ plume composition in 2018 and 2019 (Figure 4). Here, we use the model of Gerlach and Taylor (1990) to simulate carbon isotope fractionation during degassing in both closed-system and open-system conditions (Supporting Information S1). In order to estimate f, the fraction of residual carbon in the melt at each step of the degassing path (see Equations 5–7 in Supporting Information S1), we use the Chosetto model (Moretti et al., 2003; Moretti & Papale, 2004) to simulate degassing upon decompression of a Stromboli-like parental melt (same initial conditions as in Aiuppa & Bertagnini et al., 2010; Aiuppa & Burton et al., 2010; see Text S7 in Supporting Information S1). The model also outputs, at each degassing step (e.g., at each pressure of the modeled decompression path), the CO_2/S_{tot} ratios in the gas coexisting with the melt. These are plotted, along with the gas carbon isotope signature, in Figure 4.

Our results indicate that the plume 2018 results, as well as the 2010–2018 fumarole data, result from degassing under closed-system conditions up to 0.1 MPa (less than 1 km) of a parental magma with $\delta^{13}C$ of −0.5 to −2.0‰ informed by melt inclusion studies (Gennaro et al., 2017) (Figure 4). This confirms that degassing of shallow convecting magma dominates the degassing budget during ordinary Strombolian activity (Aiuppa & Bertagnini et al., 2010; Aiuppa & Burton et al., 2010; Allard et al., 2008). In contrast, we see that the 2019 plume data diverge from the closed-system degassing lines due to their light (^{13}C-poor) carbon signature. Specifically, our June 2019 carbon isotopic results can be reproduced from a degassing path that switches from closed to open (Figure 4). We propose that closed-system degassing takes place as magma decompresses from 1,000 MPa (~40 km) to ~150-50 MPa (6-2 km depth). At this point, magma reaches a ponding zone (a geological or rheological discontinuity), at which point accumulating gas bubbles separate from melt (Aiuppa et al., 2021), and the system switches to open-system degassing. This "switchover depth" from closed to open-system degassing may be variable rather than constant, resulting in variable yet high CO_2/SO_2 (~20–35) observed before the July 3rd paroxysm. Vent-specific changes in CO_2/SO_2 (6.8–25.4) were noted at Stromboli during small explosive events in 2018 and attributed to differences in gas-melt separation (Pering et al., 2020). A variable switchover depth could indicate multiple levels of magma storage and/or multiple foam layers accumulating at different depths within the magma plumbing system prior to a paroxysm (Aiuppa et al., 2021). In any case, we postulate that the gas separated from the magma at 2–6 km depth then rapidly ascends toward the surface, preserving its high CO_2/SO_2 signature of 25 ± 14 (Aiuppa et al., 2021) and furthermore a strongly depleted isotopic signature in $\delta^{13}C$-CO_2 caused by fractional equilibrium degassing (open-system degassing). These are exactly the features we observe in the June 2019 plume (Figure 4).

Recent applications of carbon isotopes as monitoring tools at Stromboli assume that small increases in $\delta^{13}C$-CO_2 would indicate unrest due to injection of a fresh, CO_2-rich magma (Federico et al., 2008, 2023). By contrast, our work shows that a decrease in $\delta^{13}C$ may be indicative of gas accumulation and overpressure as a foam layer builds over time. In the same way that patterns of precursory CO_2/SO_2 increases are being documented prior to basaltic eruptions across many arcs (Werner et al., 2019), now is the time to build a similar repository for precursory $\delta^{13}C$ changes for Stromboli and other volcanic systems.

At Stromboli in 2018, the observed low CO_2/SO_2 and heavy $\delta^{13}C$ resulted from CO_2 remaining in equilibrium with the magma until shallow levels, thereby efficiently lowering the gas ratios. In 2019, high CO_2/SO_2 and light $\delta^{13}C$ were the result of the gas decoupling and separating from the deeper magma at pressures of ~100 MPa (~4 km depth). By Rayleigh fractionation, the CO_2 was depleted in ^{13}C, while CO_2/SO_2 remained high. The early onset of deep gas supply many months before the July 3rd event caused the system to pressurize, as seen in other volcanic systems host to paroxysmal activity such as Villarica (Aiuppa & Bitetto et al., 2017).

What is the "recipe" for forecasting large eruptive events at Stromboli? Based on previous work (Aiuppa et al., 2021) and ours, we propose that a combination of high CO_2 concentrations (maximum volcanic CO_2 > 50 ppm) and elevated CO_2/S_t (values > 20) as measured by Multi-GAS at the summit, combined with anomalously light $\delta^{13}C$ (e.g., less than −2 to −3‰), may indicate a heightened probability of a paroxysm. The longer the timescale of anomalous CO_2 characteristics, the greater the thickness of the foam layer(s) developing at depth (Aiuppa et al., 2021), hence the more powerful the eruption may be. Geophysical data may enhance this geochemical forecasting recipe, for example, anomalously elevated VLP seismicity on weekly to monthly timescales (Giudicepietro et al., 2020). An integrated geochemical-geophysical approach will improve our understanding of Stromboli and our ability to successfully forecast large eruptive events.

4. Conclusions

Our principal conclusions are the following:

1. Robust measurements of $\delta^{13}C$-CO_2 in volcanic plumes can be made with sampling by UAS in the plume and same-day isotopic analysis with portable spectrometers.
2. A large negative shift in plume $\delta^{13}C$-CO_2 was observed at Stromboli from quiescent degassing in May 2018 (−0.36‰ ± 0.59‰) to June 2019 (−5.01‰ ± 0.56‰), just prior to a large paroxysmal eruption.
3. We interpret this isotopic shift as a change from closed-system degassing in 2018, typical of ordinary strombolian activity, to a situation in 2019 where closed-system degassing prevailed at deep levels and transitioned to open-system degassing at 50–150 MPa (2–6 km depth). This transition allowed bubbles to separate from the melt and rise rapidly to the surface.

4. Prior to large eruptions, we hypothesize that plume gas will have high CO_2 concentrations, anomalously light $\delta^{13}C\text{-}CO_2$, and high CO_2/S_T.

We observed some potential daily variations in $\delta^{13}C\text{-}CO_2$ during our work (see Figure S9 in Supporting Information S1). Future work could examine more detailed temporal and spatial variability of $\delta^{13}C\text{-}CO_2$, for example, timescales of days to weeks and sampling of individual vents.

Data Availability Statement

The data used in the study are available for download in the Earthchem repository (D'Arcy et al., 2024). The Chosetto code used for the CO_2 modeling was downloaded from https://github.com/charlesll/chosetto and is freely available from Github (Moretti et al., 2003; Moretti & Papale, 2004).

Acknowledgments
We thank Taryn Lopez, Emma Nicholson, and Tobias Fisher for their insightful and thought-provoking reviews. We also thank Christian Huber and Kyla Lesperance for their editorial handling and flexibility during the review process. We thank Alfredo Alan for technical advice on the wiring schematics of the gas-sampling devices. FD is grateful for funding from Vanier Canada. JS is supported by funding from an NSERC Discovery grant (RGPIN-2020-04197). AA and ALR acknowledge funding from the Italian Ministero Ricerca e Università (PRIN projects 2017LMNLAW and 2022HA8XCS). AA also acknowledges funding from the RETURN Extended Partnership funded by the European Union Next-GenerationEU (National Recovery and Resilience Plan—NRRP, Mission 4, Component 2, Investment 1.3—D.D. 1243 2/8/2022, PE0000005), and from Istituto Nazionale di Geofisica e Vulcanologia under research agreement "sviluppo del sistema unico (ingv—università) di monitoraggio vulcanico e rilevamento precoce dei maremoti e delle esplosioni parossistiche di "stromboli".

References

Aiuppa, A., Bertagnini, A., Métrich, N., Moretti, R., Di Muro, A., Liuzzo, M., & Tamburello, G. (2010a). A model of degassing for Stromboli volcano. *Earth and Planetary Science Letters*, *295*(1–2), 195–204. https://doi.org/10.1016/j.epsl.2010.03.040

Aiuppa, A., Bitetto, M., Donne, D. D., la Monica, F. P., Tamburello, G., Coppola, D., et al. (2021). Volcanic CO_2 tracks the incubation period of basaltic paroxysms. *Science Advances*, *7*(38), eabh0191. https://doi.org/10.1126/sciadv.abh0191

Aiuppa, A., Bitetto, M., Francofonte, V., Velasquez, G., Parra, C. B., Giudice, G., et al. (2017a). A CO_2 - Gas precursor to the March 2015 Villarrica volcano eruption. *Geochemistry, Geophysics, Geosystems*, *18*(6), 2120–2132. https://doi.org/10.1002/2017GC006892

Aiuppa, A., Burton, M., Allard, P., Caltabiano, T., Giudice, G., Gurrieri, S., et al. (2011). First observational evidence for the CO_2-driven origin of Stromboli's major explosions. *Solid Earth*, *2*(2), 135–142. https://doi.org/10.5194/se-2-135-2011

Aiuppa, A., Burton, M., Caltabiano, T., Giudice, G., Guerrieri, S., Liuzzo, M., et al. (2010b). Unusually large magmatic CO_2 gas emissions prior to a basaltic paroxysm. *Geophysical Research Letters*, *37*(17), L17303. https://doi.org/10.1029/2010GL043837

Aiuppa, A., Giudice, G., Liuzzo, M., Burton, M., Caltabiano, T., & Salerno, G. (2017b). Volcanic gas plume data from Stromboli volcano (Italy), Version 1.0 [Dataset]. *Interdisciplinary Earth Data Alliance (IEDA)*. https://doi.org/10.1594/IEDA/100642

Allard, P., Aiuppa, A., Burton, M., Caltabiano, T., Federico, C., Salerno, G., & La Spina, A. (2008). Crater gas emissions and the magma feeding system of Stromboli volcano. In S. Calvari, S. Inguaggiato, G. Puglisi, M. Ripepe, & M. Rosi (Eds.), *The Stromboli volcano: An integrated study of the 2002–2003 eruption, geophysical monograph series* (Vol. 182, pp. 65–80). American Geophysical Union. https://doi.org/10.1029/182GM07

Andronico, D., Del Bello, E., D'Oriano, C., Landi, P., Pardini, F., Scarlato, P., et al. (2021). Uncovering the eruptive patterns of the 2019 double paroxysm eruption crisis of Stromboli volcano. *Nature Communications*, *12*(1), 1–14. https://doi.org/10.1038/s41467-021-24420-1

Barry, P. H., Hilton, D. R., Füri, E., Halldórsson, S. A., & Grönvold, K. (2014). Carbon isotope and abundance systematics of Icelandic geothermal gases, fluids and subglacial basalts with implications for mantle plume-related CO_2 fluxes. *Geochimica et Cosmochimica Acta*, *134*, 74–99. https://doi.org/10.1016/j.gca.2014.02.038

Boudoire, G., Rizzo, A. L., Di Muro, A., Grassa, F., & Liuzzo, M. (2018). Extensive CO_2 degassing in the upper mantle beneath oceanic basaltic volcanoes: First insights from Piton de la Fournaise volcano (La Réunion Island). *Geochimica et Cosmochimica Acta*, *235*, 376–401. https://doi.org/10.1016/j.gca.2018.06.004

Brown, P. E., Bowman, J. R., & Kelly, W. C. (1985). Petrologic and stable isotopic constraints on the source and evolution of skam-forming fluids at Pine Creek, California. *Economic Geology*, *80*(1), 72–95. https://doi.org/10.2113/gsecongeo.80.1.72

Burton, M. R., Allard, P., Mure, F., & La Spina, A. (2007). Magmatic gas composition reveals the source depth of slug-driven strombolian explosive activity. *Science*, *317*(5835), 227–230. https://doi.org/10.1126/science.1141900

Burton, M. R., Sawyer, G. M., & Granieri, D. (2013). Deep carbon emissions from volcanoes. In, R. M. Hazen, A. P. Jones, & J. A. Baross (Eds.), *Carbon in earth, reviews in mineralogy and geochemistry* (Vol. 75(1), pp. 323–354). : Mineralogical Society of America, Geochemical Society. https://doi.org/10.2138/rmg.2013.75.11

Capasso, G., Carapezza, M. L., Federico, C., Inguaggiato, S., & Rizzo, A. (2005). Geochemical monitoring of the 2002-2003 eruption at Stromboli volcano (Italy): Precursory changes in the carbon and helium isotopic composition of fumarole gases and thermal waters. *Bulletin of Volcanology*, *68*(2), 118–134. https://doi.org/10.1007/s00445-005-0427-5

Capasso, G., Favara, R., & Inguaggiato, S. (1997). Chemical features and isotopic composition of gaseous manifestations on Vulcano Island, Aeolian Islands, Italy: An interpretative model of fluid circulation. *Geochimica et Cosmochimica Acta*, *61*(16), 3425–3440. https://doi.org/10.1016/S0016-7037(97)00163-4

Chiodini, G., Caliro, S., Aiuppa, A., Avino, R., Granieri, D., Moretti, R., & Parello, F. (2011). First $^{13}C/^{12}C$ isotopic characterisation of volcanic plume CO_2. *Bulletin of Volcanology*, *73*(5), 531–542. https://doi.org/10.1007/s00445-010-0423-2

D'Arcy, F., Aiuppa, A., Grassa, F., Rizzo, A. L., & Stix, J. (2024). Volcanic gas plume isotopic ratios of carbon dioxide from Stromboli volcano, 2018-2019, Version 1.0 [Dataset]. *Interdisciplinary Earth Data Alliance (IEDA)*. https://doi.org/10.60520/IEDA/113060

D'Arcy, F., de Moor, J. M., Stix, J., Alan, A., Bogue, R., Corrales, E., et al. (2022). New insights into carbon isotope systematics at Poás volcano, Costa Rica. *Journal of Volcanology and Geothermal Research*, *431*, 107639. https://doi.org/10.1016/j.jvolgeores.2022.107639

Di Martino, R. M. R., Gurrieri, S., & Camarda, M. (2021). Continuous monitoring of hydrogen and carbon dioxide at Stromboli volcano (Aeolian Islands, Italy). *Italian Journal of Geosciences*, *140*(1), 79–94. https://doi.org/10.3301/IJG.2020.26

Edmonds, M., Liu, E. J., & Cashman, K. (2022). Open-vent volcanoes fuelled by depth-integrated magma degassing. *Bulletin of Volcanology*, *84*(3), 1–28. https://doi.org/10.1007/s00445-021-01522-8

Federico, C., Brusca, L., Carapezza, M. L., Cigolini, C., Inguaggiato, S., Rizzo, A., & Rouwet, D. (2008). Geochemical prediction of the 2002 – 2003 Stromboli eruption from variations in CO_2 and Rn emissions and in helium and carbon isotopes. In S. Calvari, S. Inguaggiato, G. Puglisi, M. Ripepe, & M. Rosi (Eds.), *The Stromboli volcano: An integrated study of the 2002–2003 eruption, geophysical monograph series* (Vol. 182, pp. 117–128). American Geophysical Union. https://doi.org/10.1029/182GM11

Federico, C., Inguaggiato, S., Liotta, M., Rizzo, A. L., & Vita, F. (2023). Decadal monitoring of the hydrothermal system of Stromboli volcano, Italy. *Geochemistry, Geophysics, Geosystems*, *24*(9), e2023GC010931. https://doi.org/10.1029/2023GC010931

Finizola, A., Sortino, F., Lénat, J. F., Aubert, M., Ripepe, M., & Valenza, M. (2003). The summit hydrothermal system of Stromboli. New insights from self-potential, temperature, CO_2 and fumarolic fluid measurements, with structural and monitoring implications. *Bulletin of Volcanology*, *65*(7), 486–504. https://doi.org/10.1007/s00445-003-0276-z

Fischer, T. P., & Lopez, T. M. (2016). First airborne samples of a volcanic plume for $\delta^{13}C$ of CO_2 determinations. *Geophysical Research Letters*, *43*(7), 3272–3279. https://doi.org/10.1002/2016GL068499

Fischer, T. P., Ramírez, C., Mora-Amador, R. A., Hilton, D. R., Barnes, J. D., Sharp, Z. D., et al. (2015). Temporal variations in fumarole gas chemistry at Poás volcano, Costa Rica. *Journal of Volcanology and Geothermal Research*, *294*, 56–70. https://doi.org/10.1016/j.jvolgeores.2015.02.002

Gasparini, C., Iannaccone, G., Scandone, P., & Scarpa, R. (1982). Seismotectonics of the calabrian Arc. *Tectonophysics*, *84*(2–4), 267–286. https://doi.org/10.1016/0040-1951(82)90163-9

Gennaro, M. E., Grassa, F., Martelli, M., Renzulli, A., & Rizzo, A. L. (2017). Carbon isotope composition of CO_2-rich inclusions in cumulate-forming mantle minerals from Stromboli volcano (Italy). *Journal of Volcanology and Geothermal Research*, *346*, 95–103. https://doi.org/10.1016/j.jvolgeores.2017.04.001

Gerlach, T. M., & Taylor, B. E. (1990). Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano. *Geochimica et Cosmochimica Acta*, *54*(7), 2051–2058. https://doi.org/10.1016/0016-7037(90)90270-U

Giordano, G., & De Astis, G. (2021). The summer 2019 basaltic vulcanian eruptions (paroxysms) of Stromboli. *Bulletin of Volcanology*, *83*(1), 1–27. https://doi.org/10.1007/s00445-020-01423-2

Giudicepietro, F., López, C., Macedonio, G., Alparone, S., Bianco, F., Calvari, S., et al. (2020). Geophysical precursors of the July-August 2019 paroxysmal eruptive phase and their implications for Stromboli volcano (Italy) monitoring. *Scientific Reports*, *10*(1), 1–16. https://doi.org/10.1038/s41598-020-67220-1

Harris, A., & Ripepe, M. (2007). Temperature and dynamics of degassing at Stromboli. *Journal of Geophysical Research*, *112*(B3), B03205. https://doi.org/10.1029/2006JB004393

Holloway, J. R., & Blank, J. G. (1994). Application of experimental results to C-O-H species in natural melts. In J. R. Holloway & M. R. Carroll (Eds.), *Volatiles in magmas, reviews in mineralogy and geochemistry* (Vol. 30, pp. 187–230). Mineralogical Society of America. https://doi.org/10.1515/9781501509674-012

Inguaggiato, S., Vita, F., Cangemi, M., & Calderone, L. (2020). Changes in CO_2 soil degassing style as a possible precursor to volcanic activity: The 2019 case of Stromboli paroxysmal eruptions. *Applied Sciences*, *10*(14), 4757. https://doi.org/10.3390/app10144757

Keeling, C. (1958). The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. *Geochimica et Cosmochimica Acta*, *13*(4), 322–334. https://doi.org/10.1016/0016-7037(58)90033-4

Liu, E. J., Aiuppa, A., Alan, A., Arellano, S., Bitetto, M., Bobrowski, N., et al. (2020). Aerial strategies advance volcanic gas measurements at inaccessible, strongly degassing volcanoes. *Science Advances*, *6*(44), eabb9103. https://doi.org/10.1126/sciadv.abb9103

Malowany, K., Stix, J., de Moor, J. M., Chu, K., Lacrampe-Couloume, G., & Sherwood Lollar, B. (2017). Carbon isotope systematics of Turrialba volcano, Costa Rica, using a portable cavity ring-down spectrometer. *Geochemistry, Geophysics, Geosystems*, *18*(7), 2769–2784. https://doi.org/10.1002/2017GC006856

Mather, T. A. (2015). Volcanoes and the environment: Lessons for understanding Earth's past and future from studies of present-day volcanic emissions. *Journal of Volcanology and Geothermal Research*, *304*, 160–179. https://doi.org/10.1016/j.jvolgeores.2015.08.016

Métrich, N., Bertagnini, A., & Di Muro, A. (2009). Conditions of magma storage, degassing and ascent at Stromboli: New insights into the volcano plumbing system with inferences on the eruptive dynamics. *Journal of Petrology*, *51*(3), 603–626. https://doi.org/10.1093/petrology/egp083

Métrich, N., Bertagnini, A., Landi, P., Rosi, M., & Belhadj, O. (2005). Triggering mechanism at the origin of paroxysms at Stromboli (Aeolian Archipelago, Italy): The 5 April 2003 eruption. *Geophysical Research Letters*, *32*(10), L10305. https://doi.org/10.1029/2004GL022257

Métrich, N., Bertagnini, A., & Pistolesi, M. (2021). Paroxysms at Stromboli volcano (Italy): Source, genesis and dynamics. *Frontiers in Earth Science*, *9*, 593339. https://doi.org/10.3389/feart.2021.593339

Moretti, R., & Papale, P. (2004). On the oxidation state and volatile behavior in multicomponent gas-melt equilibria. *Chemical Geology*, *213*(1–3), 265–280. https://doi.org/10.1016/j.chemgeo.2004.08.048

Moretti, R., Papale, P., & Ottonello, G. (2003). A model for the saturation of C-O-H-S fluids in silicate melts. In, C. Oppenheimer, D. M. Pyle, & J. Barclay (Eds.), *Volcanic degassing, special publication* (Vol. 213(1), pp. 81–101). : Geological Society of London. https://doi.org/10.1144/GSL.SP.2003.213.01.06

Paonita, A., Caracausi, A., Iacono-Marziano, G., Martelli, M., & Rizzo, A. (2012). Geochemical evidence for mixing between fluids exsolved at different depths in the magmatic system of Mt Etna (Italy). *Geochimica et Cosmochimica Acta*, *84*, 380–394. https://doi.org/10.1016/j.gca.2012.01.028

Peccerillo, A., & Frezzotti, M. L. (2015). Magmatism, mantle evolution and geodynamics at the converging plate margins of Italy. *Journal of the Geological Society*, *172*(4), 407–427. https://doi.org/10.1144/jgs2014-085

Pering, T. D., Liu, E. J., Wood, K., Wilkes, T. C., Richardson, T., Mcgonigle, A. J. S., et al. (2020). Combined ground and aerial measurements resolve vent-specific gas fluxes from a multi-vent volcano. *Nature Communications*, *11*(1), 3039. https://doi.org/10.1038/s41467-020-16862-w

Petrone, C. M., Mollo, S., Gertisser, R., Buret, Y., Scarlato, P., Del Bello, E., et al. (2022). Magma recharge and mush rejuvenation drive paroxysmal activity at Stromboli volcano. *Nature Communications*, *13*(1), 7717. https://doi.org/10.1038/s41467-022-35405-z

Rayleigh, J. W. S. (1896). Theoretical considerations respecting the separation of gases by diffusion and similar processes. *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science*, *42*(259), 493–498. https://doi.org/10.1080/14786449608620944

Ripepe, M., Lacanna, G., Pistolesi, M., Silengo, M. C., Aiuppa, A., Laiolo, M., et al. (2021). Ground deformation reveals the scale-invariant conduit dynamics driving explosive basaltic eruptions. *Nature Communications*, *12*(1), 1683. https://doi.org/10.1038/s41467-021-21722-2

Rizzo, A., Grassa, F., Inguaggiato, S., Liotta, M., Longo, M., Madonia, P., et al. (2009). Geochemical evaluation of observed changes in volcanic activity during the 2007 eruption at Stromboli (Italy). *Journal of Volcanology and Geothermal Research*, *182*(3–4), 246–254. https://doi.org/10.1016/j.jvolgeores.2008.08.004

Rizzo, A. L., Jost, H. J., Caracausi, A., Paonita, A., Liotta, M., & Martelli, M. (2014). Real-time measurements of the concentration and isotope composition of atmospheric and volcanic CO_2 at Mount Etna (Italy). *Geophysical Research Letters*, *41*(7), 2382–2389. https://doi.org/10.1002/2014GL059722

Rizzo, A. L., Liuzzo, M., Ancellin, M. A., & Jost, H. J. (2015). Real-time measurements of $\delta^{13}C$, CO_2 concentration, and CO_2/SO_2 in volcanic plume gases at Mount Etna, Italy, over 5 consecutive days. *Chemical Geology*, *411*, 182–191. https://doi.org/10.1016/j.chemgeo.2015.07.007

Rosi, M., Pistolesi, M., Bertagnini, A., Landi, P., Pompilio, M., & Di Roberto, A. (2013). Stromboli volcano, Aeolian Islands (Italy): Present eruptive activity and hazards. *Geological Society Memoir*, *37*(1), 473–490. https://doi.org/10.1144/M37.14

Schipper, C. I., Moussallam, Y., Curtis, A., Peters, N., Barnie, T., Bani, P., et al. (2017). Isotopically ($\delta^{13}C$ and $\delta^{18}O$) heavy volcanic plumes from central Andean volcanoes: A field study. *Bulletin of Volcanology*, *79*(8), 1–15. https://doi.org/10.1007/s00445-017-1146-4

Shingubara, R., Tsunogai, U., Ito, M., Nakagawa, F., Yoshikawa, S., Utsugi, M., & Yokoo, A. (2021). Development of a drone-borne volcanic plume sampler. *Journal of Volcanology and Geothermal Research*, *412*, 107197. https://doi.org/10.1016/j.jvolgeores.2021.107197

Troll, V. R., Hilton, D. R., Jolis, E. M., Chadwick, J. P., Blythe, L. S., Deegan, F. M., et al. (2012). Crustal CO_2 liberation during the 2006 eruption and earthquake events at Merapi volcano, Indonesia. *Geophysical Research Letters*, *39*(11), L11302. https://doi.org/10.1029/2012GL051307

Tsunogai, U., Shingubara, R., Morishita, Y., Ito, M., Nakagawa, F., Yoshikawa, S., et al. (2022). Sampling volcanic plume using a drone-borne SelPS for remotely determined stable isotopic compositions of fumarolic carbon dioxide. *Frontiers in Earth Science*, *10*, 833733. https://doi.org/10.3389/feart.2022.833733

Venturi, S., Tassi, F., Bicocchi, G., Cabassi, J., Capecchiacci, F., Capasso, G., et al. (2017). Fractionation processes affecting the stable carbon isotope signature of thermal waters from hydrothermal/volcanic systems: The examples of Campi Flegrei and Vulcano Island (southern Italy). *Journal of Volcanology and Geothermal Research*, *345*, 46–57. https://doi.org/10.1016/j.jvolgeores.2017.08.001

Werner, C., Fischer, T. P., Aiuppa, A., Edmonds, M., Cardellini, C., Carn, S., et al. (2019). Carbon dioxide emissions from subaerial volcanic regions: Two decades in review. In B. Orcutt, I. Daniel, & R. Dasgupta (Eds.), *Deep carbon: Past to present* (pp. 188–236). Cambridge University Press. https://doi.org/10.1017/9781108677950

References From the Supporting Information

Aubaud, C. (2022). Carbon stable isotope constraints on CO_2 degassing models of ridge, hotspot and arc magmas. *Chemical Geology*, *605*, 120962. https://doi.org/10.1016/j.chemgeo.2022.120962

Javoy, M., Pineau, F., & Iiyama, I. (1978). Experimental determination of the isotopic fractionation between gaseous CO_2 and carbon dissolved in tholeiitic magma – A preliminary study. *Contributions to Mineralogy and Petrology*, *67*(1), 35–39. https://doi.org/10.1007/BF00371631

Malowany, K., Stix, J., Van Pelt, A., & Lucic, G. (2015). H_2S interference on CO_2 isotopic measurements using a Picarro G1101-i cavity ring-down spectrometer. *Atmospheric Measurement Techniques*, *8*(10), 4075–4082. https://doi.org/10.5194/amt-8-4075-2015

Mattey, D. P. (1991). Carbon dioxide solubility and carbon isotope fractionation in basaltic melt. *Geochimica et Cosmochimica Acta*, *55*(11), 3467–3473. https://doi.org/10.1016/0016-7037(91)90508-3