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Carbon Dioxide Emissions from Subaerial Volcanic Regions

Two Decades in Review

CYNTHIA WERNER, TOBIAS P. FISCHER, ALESSANDRO AIUPPA, MARIE EDMONDS, CARLO CARDELLINI, SIMON CARN, GIOVANNI CHIODINI, ELIZABETH COTTRELL, MIKE BURTON, HIROSHI SHINOHARA, AND PATRICK ALLARD

8.1 Introduction

Volcanism and metamorphism are the principal geologic processes that drive carbon transfer from the interior of Earth to the surface reservoir.[1–4] Input of carbon to the surface reservoir through volcanic degassing is balanced by removal through silicate weathering and the subduction of carbon-bearing marine deposits over million-year timescales. The magnitude of the volcanic carbon flux is thus of fundamental importance for stabilization of atmospheric CO_2 and for long-term climate. It is likely that the "deep" carbon reservoir far exceeds the size of the surface reservoir in terms of mass;[5,6] more than 99% of Earth's carbon may reside in the core, mantle, and crust. The relatively high flux of volcanic carbon to the surface reservoir, combined with the reservoir's small size, results in a short residence time for carbon in the ocean–atmosphere–biosphere system (~200 ka).[7] The implication is that changes in the flux of volcanic carbon can affect the climate and ultimately the habitability of the planet on geologic timescales. In order to understand this delicate balance, we must first quantify the current volcanic flux of carbon to the atmosphere and understand the factors that control this flux.

The three most abundant magmatic volatiles are water (H_2O), carbon dioxide (CO_2), and sulfur (S), with CO_2 being the least soluble in silicate melts.[8] For this reason, it is not only Earth's active volcanoes that are a source of magmatic CO_2, but also numerous inactive volcanoes with magma bodies present at depth in the crust that contribute to the carbon emissions (Figure 8.1). Emissions from active volcanoes are released through crater fumaroles and open vents to form visible volcanic plumes, but diffuse degassing and degassing through springs on the volcano flanks also contribute to the total flux of carbon from a volcano. Plume gas emissions typically dominate over flank gas emissions and are highest during periods of eruptive activity.[9] Due to the hazard associated with eruptions and the value of volcanic gas monitoring to aid in eruption forecasting, much of our knowledge about the degassing of volcanic systems comes from active volcanoes, and typically during periods of unrest.

At less active and dormant (i.e. inactive) volcanoes, magmatic emissions of CO_2 are less obvious. CO_2 emissions are typically highest in thermal areas where gases are emitted through small fumaroles, soils, and fractures as diffuse degassing and through hot and cold

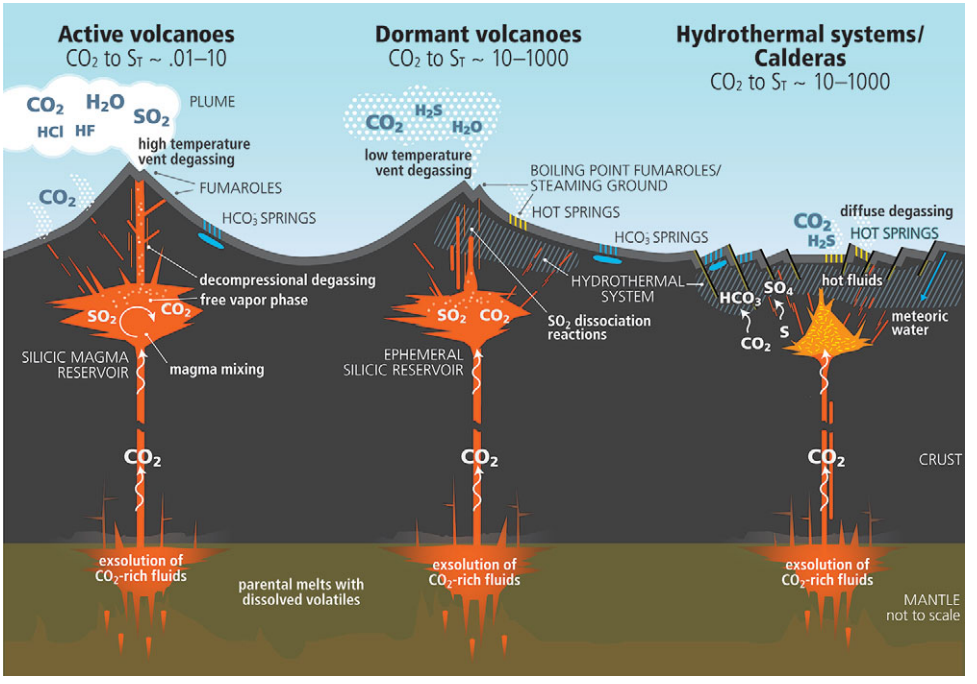

Figure 8.1 Conceptual models showing typical CO_2 emission patterns from volcanic and magmatic systems. CO_2 may be sourced from magma bodies deep in the crust, whereas other volatiles may remain largely dissolved in magma until much shallower depths. Visible plumes are typical for active volcanoes, whereas CO_2 degassing from dormant/inactive volcanoes and hydrothermal systems is less obvious. Low-temperature degassing may or may not result in a visible plume even when CO_2 is present. Significant quantities of CO_2 are emitted from areas of diffuse degassing, and CO_2 also reacts with groundwater.

springs. Occasionally, older volcanic areas can also exhibit cold degassing of CO_2.[10] CO_2 is denser than air, and therefore an asphyxiation hazard can exist in low-lying areas. Visual indicators of CO_2 release include thermally perturbed or bare ground and the odor of H_2S. Atmospheric plumes of CO_2 can also form in such areas, even if a region is not thermal,[11] and these emissions may not be visible. Additional contributions of volcanic carbon can be found in groundwaters,[12,13] but globally this contribution is less well studied compared to gas emissions.

In this chapter, we review recent advances in our understanding of the flux of CO_2 emitted in subaerial volcanic areas and how these emissions vary in space and time. Carbon released through mid-ocean ridges (MORs) and other oceanic environments is reviewed in Chapter 9. Through the focused efforts funded by the Deep Carbon Observatory and the Deep Earth CArbon DEgassing (DECADE) research initiative,[14] there is now greater global coverage of subaerial volcanic areas emitting CO_2 compared to previous efforts.[15] CO_2 emission rates have now been quantified for many of the most active volcanoes, and

some in real time. New observations reveal how the volcanic carbon flux varies through time and between different volcanic settings. Here, we discuss the nature of these emissions in terms of their magnitude, relationship to eruptive activity, and temporal variability, as well as how such measurements may enhance our ability to forecast eruptive activity.

Techniques to quantify diffuse and plume CO_2 emissions (in the absence of SO_2) were only developed in the mid-to-late 1990s;[16,17] we are now approaching two decades of routine measurements for some of the world's volcanic areas. Where monitoring has been frequent, data allow decadal-scale evaluations of the output from a number of the most prolific carbon-emitting volcanic regions. We discuss the magnitude of emissions from some of the largest diffuse degassing regions and the challenges in extrapolating diffuse measurements globally.

We review the advances in understanding the sources of carbon outgassing from volcanoes, showing how the isotopic signature of carbon and other species has allowed distinction of the carbon contribution from subducting slabs, the crust, and mantle sources on arc scales. These insights into magmatic–tectonic controls on carbon outgassing then allow us to begin to link the modern volcanic carbon outgassing picture to that which might have existed in the geological past.

8.2 Methods for Measuring Volcanic CO_2: Established Techniques and Recent Advances

The principal challenges in the measurement of CO_2 from volcanic regions are related to the detection of volcanic CO_2 over the atmospheric background, logistical difficulties associated with accessing gas plumes, and technical issues that accompany deployment of instruments in the field. Techniques to measure CO_2 emission rates from different types of sources and the related uncertainties in these measurements have been reviewed previously.[15] Here, we expand on aspects of these methods as they pertain to information presented here and review emerging techniques and measurement biases.

8.2.1 Measurements of CO_2 Emissions in Volcanic Plumes

Volcanoes that are most active display persistent gas emissions during either frequent eruptions or as "passive" degassing of shallow magma bodies.[18] These volcanoes typically produce a volcanic plume, measurable with either direct or indirect techniques. The *indirect* or *ratio* technique underpins much of the recent progress in the measurement of volcanic CO_2 emission rates. Here, the SO_2 emission rate is measured using ultraviolet (UV) spectroscopy either from the ground,[19] airborne,[20,21] or space-based platforms,[22] and then multiplied by the C/S mass ratio determined by fumarole sampling,[8] Fourier-transform infrared (FTIR) spectroscopy,[23] or Multi-GAS measurements[24,25] and the plume speed. Indirect techniques rely on reliable and representative SO_2 emissions and C/S data. Uncertainties in the SO_2 flux (e.g. due to in-plume light scattering) can produce a bias to

lower SO_2 fluxes by a factor of two or more.[26,27] Uncertainties in the C/S ratio of the gas arise from calibration of the Multi-GAS at a different altitude from the measurements, variable sensor response times to CO_2 and SO_2,[28–30] low plume concentrations (close to detection limits), and poorly mixed plumes.[31]

Direct measurements of CO_2 plumes use an airborne platform to measure the vertical profile of CO_2 concentration in the atmosphere downwind of the volcanic vent. The volcanic CO_2 (in excess of atmospheric background) is multiplied by the plume speed to derive an emission rate.[17,32,33] Uncertainties in plume speed affect both measurement types and vary greatly depending on whether the speed is estimated from radiosonde or weather models or is measured on site. Direct CO_2 measurement is the only option for the quantification of plume emissions where SO_2 is not present.[34] In-plume concentrations of 2–5 ppm above background are typically needed, depending on the CO_2 analyzer used, and ~10-50 t/d is a reasonable detection limit for airborne measurements depending on the aircraft, plume speed, and distance from the vent. Emissions less than this range or in areas where airborne measurements are not feasible are challenging to quantify and represent a recognized gap in current budgets. Future approaches to such challenging field measurements will include use of miniaturized IR (and other) sensors on drones[35–37] and ground-based light detection and ranging (LIDAR).[38,39]

8.2.2 Diffuse CO_2 Emissions and Groundwater Contributions

Many volcanic systems support areas of diffuse degassing often associated with hydrothermal activity due to magmatic intrusions at depth. A common method of quantifying diffuse emissions through soils is the accumulation chamber technique,[16,40] where a chamber is set on the ground and the concentration of the accumulated CO_2 is measured with time. Here, point measurements of the flux of CO_2 are made over an area of interest and total emissions are quantified by applying geostatistical techniques (see Refs. 16, 41 and references therein). The same chamber technique can be applied to lakes.[42,43] Eddy covariance (EC) is an aboveground technique that has been used successfully to measure the flux of CO_2 derived from diffuse, fumarole, and pool sources in regions with relatively low topographic relief.[44–47] The EC footprint (the source area on the ground contributing to the measured EC CO_2 flux) varies with atmospheric conditions such as wind speed and direction and is typically smaller than most degassing regions. Thus, to determine the CO_2 emission rate from a region of interest requires assumptions about the representativeness of the average EC flux to the larger area.[48] Alternatively, months-long deployments and inverse modeling have also been used to determine emission rates,[47,49] though such models also have inherent uncertainty. While promising for long-term hazard monitoring, more work is needed for utilizing the full potential of EC for determining emission rates.

In volcanic areas, CO_2 also dissolves into groundwaters and can emit through springs as a dissolved constituent. This flux can be quantified through chemical sampling and stream gauging,[12,50] or through mass balance of the aquifer (i.e. coupling hydrogeological and

hydrogeochemical data). For instance, using this technique, the amount of CO_2 transported by Vesuvio groundwaters was estimated at about 150 t/d, or in the same order of magnitude as the diffuse emission of CO_2 in the crater area.[13]

8.2.3 Significant Recent Advances: Continuous and Remote Techniques

One major advance toward producing robust long-term records of volcanic CO_2 emissions has arisen from the advent of autonomous Multi-GAS instruments.[51] When combined with independent SO_2 flux time series,[52] measurements from these instruments have refined the CO_2 output for several volcanoes, characterizing the variability of emissions on temporal scales of days to years for the first time.[53–57] Multi-GAS stations are being adapted for deployment at high-latitude volcanoes[28,30,58] and can perform automated calibrations for improved accuracy.[28,48] Multi-GAS has recently been used on manned airborne missions and on unmanned aerial vehicles (UAVs).[35,37,59] Overall, these measurements are fundamentally changing the way volcanic hazard is evaluated at active volcanoes.

Techniques to quantify CO_2 remotely and from smaller features have also developed in recent years. Tunable diode laser spectrometer[60–62] measurements have shown that the CO_2 output from fumaroles is significant (hundreds of t/d) at some volcanoes, illustrating a nontrivial contribution to the volcanic CO_2 flux from this largely unquantified source at a global scale. In addition, LIDAR, specifically differential absorption LIDAR,[38,63] the smaller CO_2 differential absorption LIDAR,[39] and miniaturized light laser sensing spectrometers,[64] have been used to determine path-integrated CO_2 concentrations over kilometer scales. While these studies offer new prospects for quantifying CO_2 flux, further work is required to standardize and widen their potential applications.

Advances have been made with satellite remote sensing of CO_2, although CO_2 is among the most challenging volcanic gases to detect due to high atmospheric concentrations (~400 ppm and rising due to anthropogenic contributions) that dominate the signal of column-average measurements. Even at some of the strongest volcanic gas sources (e.g. Etna, Italy), the volcanic CO_2 signal may be only up to tens of ppm above background,[21,65] requiring high precision and accuracy for detection from space. NASA's Orbiting Carbon Observatory 2 (OCO-2), with a small footprint size (1.3×2.3 km) and $<0.2\%$ accuracy, permitted the first reported satellite detection of volcanic CO_2 emissions at Yasur volcano in 2015.[66] However, neither OCO-2 nor the Japanese Greenhouse Gases Observing Satellite (GOSAT) provide sufficient temporal resolution or spatial coverage to be effective volcano monitoring tools. The future of volcanic CO_2 monitoring from space is inextricably linked to the politics of greenhouse gas measurements and climate change. Several planned or proposed satellite missions (NASA's OCO-3, JAXA's GOSAT-2, and ESA's CarbonSat) offer the potential for volcanic CO_2 detection, but it is unlikely to ever become as routine as volcanic SO_2 measurements, and will likely be restricted to "spot" measurements of the strongest persistent volcanic CO_2 sources.

8.3 Estimating Global Emission Rates of CO_2

Quantifying global emissions of volcanic CO_2 is an area of ongoing research that will continue to evolve as more measurements become available. Some of the first estimates of global volcanic CO_2 degassing, published in the 1990s, were based on only seven to nine measurements of passive CO_2 degassing;[67,68] our understanding of CO_2 degassing in volcanic areas has progressed greatly since then. Here, we review methodologies from recent studies quantifying global volcanic CO_2 and how our new understanding may allow us to reduce some of the uncertainties in these estimates.

Until recently, most estimates of global CO_2 emissions were determined by proxy where volcanic CO_2 was scaled globally by a tracer (e.g. SO_2 or ^3He). Work focused on determining the C/S ratio of fumaroles based on level of activity[69] or on an arc-wide basis[70] and combining these data with global SO_2 emission rate compilations.[71,72] While seemingly straightforward, numerous uncertainties exist in these methods. First, C/S is not constant in time, and it is challenging to discern whether variations in C/S reflect changing mixtures of sources (magmatic vs hydrothermal) or progressive degassing of a single magmatic source due to gas loss or decompression (Figure 8.1).[73,74] Second, SO_2 emission rate data are skewed toward easily accessible locations and volcanoes experiencing unrest. Progress has been made with satellite remote sensing data that, when averaged over long time periods, are sensitive enough to measure lower emission rates of SO_2, thereby reducing some measurement bias. For example, recent work used Ozone Monitoring Instrument (OMI) satellite data[75] to calculate a global passive volcanic SO_2 flux of 23 ± 2 Tg SO_2/yr during the decade 2005–2015 from 91 volcanoes, half of which also have the C/S ratio measured. However, 91 volcanoes only represents 16% of the 570 volcanoes active in historic time, and 6% of the volcanoes active in the Holocene,[76] many of which might be passively degassing CO_2, but not emitting SO_2 over the satellite detection limit. Some previous global estimates of CO_2 emissions have assumed that the strongest emitters of SO_2[57] also produce the most CO_2, but the time frame of measurement is important to consider, as is the number of degassing systems. The temporal distribution of volcanic CO_2 outgassing could be very different from that of SO_2,[77] which is dominated by a relatively small number of erupting and persistently degassing volcanoes. Further clarity on this issue may be provided in the near future with the recently launched Tropospheric Ozone Monitoring Instrument (TROPOMI) sensor (www.tropomi.eu), which has 12-times higher spatial resolution than the earlier OMI sensor, and may reveal weaker plumes.

Global ^3He fluxes have also been used to estimate global arc CO_2 fluxes.[78,79] The estimated ^3He flux from arcs is based on the well-constrained ^3He flux from MORs and the assumption that 80% of volcanic activity on Earth is associated with MORs and the remainder mainly from volcanic arcs.[80] Intra-oceanic arc magma fluxes were revised[81] and show a factor of approximately two times higher rates compared to the early studies.[80,82] While MOR ^3He fluxes appear to be quite well constrained within a factor of approximately two,[83] work on global arc-magma production rates is still sparse, and therefore arc ^3He fluxes are likely associated with uncertainties that remain challenging to

quantify. The most recent volcanic CO_2 flux from arcs is estimated to be 22×10^{11} mol/yr or 95 Tg CO_2/yr,[84] based on the $CO_2/^3He$ ratio of volcanic gases with outlet temperatures of >200°C, although variability in the mantle $CO_2/^3He$ adds considerable uncertainty to such calculations.

A third approach has been to extrapolate CO_2 data based on actual measurements.[15,57] The latest budget calculation[15] separated emissions based on the source (plume degassing, diffuse degassing from historically active volcanoes, hydrothermal and inactive areas, volcanic lakes, and MORs) and extrapolated them based on the number of similar systems globally. Roughly 50% (271 Tg CO_2/yr) of the total global subaerial emission of CO_2 (540 Tg CO_2/yr) was estimated to come from ~150 passively degassing volcanoes, based on the average CO_2 emissions measured at 33 active volcanic systems. An additional 20% was estimated by extrapolating observed diffuse emissions to the ~550 historically active volcanoes. CO_2 emissions from hydrothermal systems were treated separately, as were volcanic lakes and MORs.

The two main quantification challenges in extrapolating empirical data include the determination of a representative flux and the estimation of the total number of degassing volcanoes. The Global Volcanism Program (GVP) Volcanoes of the World catalog has been used to assess the number of volcanoes degassing globally, but it is important to note that the catalog quantifies the number of degassing volcanoes (i.e. "fumarolic" volcanoes) only where there has been "no (other) explicit evidence for Holocene eruptive activity." Thus, of the 1545 volcanoes with known or inferred eruptive activity in the Holocene, it is unclear how many are degassing other than those defined as "fumarolic" or "solfataric." In the latest volume, this category has been reduced from over 100 to 64 as more systems now have other data indicating Holocene activity.

Burton et al.[15] suggested ~150 volcanoes were degassing today, or 10% of the ~1500 volcanoes active in the Holocene.[85] Satellite measurements show[16] instead that 91 systems have emitted significant amounts of SO_2 (and thus CO_2) between 2005 and 2015, yet these data are representative of eruptive periods only, as higher-altitude plumes are more readily detected from space. As satellite surveillance of SO_2 emissions improves, the number of degassing sources measurable from space will likely increase. Our compilation shows there are now 201 Holocene volcanic systems associated with some form of CO_2 degassing observations (Supplemental Tables 8.1 and 8.2) and an additional 22 where the last eruptive activity was in the Pleistocene (Supplemental Table 8.3). Thus, future attempts to estimate global CO_2 degassing from volcanic areas should not assume that only historically active or Holocene volcanoes are actively degassing, but also consider the 1325 Pleistocene volcanoes.[76]

8.4 Current State of Knowledge of CO_2 Degassing from Volcanoes

8.4.1 CO_2 Emissions from Earth's Most Active Volcanoes

Earth's most active volcanoes are those that are best studied due to the hazards they pose. Over decadal timescales, many of the most active volcanoes alternate between periods of

strong degassing, typically associated with periods of eruptive activity, and phases of reduced (or arrested) degassing, with the former preferentially targeted by observations. Global CO_2 compilations calculate average emissions based on all published estimates of CO_2 flux,[15,67] yet many of these are spot measurements acquired during periods of heightened activity that may span decades. It is therefore likely that combining sparse measurements collected over several decades may lead to an overestimation of the real time-averaged global volcanic CO_2 output.

In an attempt to reduce the above uncertainty, the average CO_2 fluxes for some volcanoes in Burton et al.[15] were revised (Supplemental Table 8.1) using more recent observations that have been obtained in the last decade (2005–2017) where available, and including both eruptive and quiescent periods whenever possible. Our revised average fluxes are lower than previously published[15] for all of the major volcanic CO_2 sources (Supplemental Table 8.1). For example, recent observations of CO_2 emissions from Nyiragongo volcano are lower by approximately a factor of ten (i.e. ~9300 t/d,[86,87] compared to ~95,000 t/d collected during the 1950s–1970s[15,88]). Similarly, we report a new time-averaged CO_2 flux for Miyakejima volcano in Japan (1070 t/d[57]) based on nearly two decades of systematic observations. This longer data set yields one order of magnitude lower CO_2 emissions than implied by the intense degassing unrest of early 2000.[89,90] Likewise, emission rates from Augustine and Mount Spurr volcanoes are considerably lower than previously estimated when quiescent periods are considered as well as the unrest/eruptive periods that occurred between 2005 and 2015 (Supplemental Table 8.1).[65,91–93]

Our compilation also includes new results for more than 50 volcanoes whose volcanic CO_2 fluxes have been quantified for the first time since 2013 (Supplemental Table 8.1), mostly due to the DECADE initiative.[14] While the number of volcanoes with a measured CO_2 plume has more than tripled since 2013 (33[15] vs. 102), the total (cumulative) CO_2 emitted is roughly two-thirds of the previous estimate (44 Mt CO_2/yr, or Tg/yr, vs 59.7;[15] Supplemental Table 8.1), largely due to the diminished estimates for the top volcanic CO_2 emitters by including inter-eruptive periods.

Given that our data set, by necessity, includes a number of spot measurements, the relative contribution of the most active volcanoes might continue to diminish as longer records are obtained at more volcanoes. As a first-order test, we compare the data set from direct measurements (many of which are spot measurements) with the CO_2 flux estimated from global compilations of the most active volcanoes that represent longer time frames. We utilize the 2005–2015 OMI volcanic SO_2 flux measurements[75] and combine these with CO_2/SO_2 ratios from Aiuppa et al.[73] and elsewhere where available to estimate CO_2 emissions from these sources (Supplemental Table 8.1). At the time of writing, 49 of the 91 volcanoes in the OMI data set[75] have their volcanic gas CO_2/SO_2 ratio signatures characterized (Supplemental Table 8.1), leaving a sizable gap in our knowledge. If only the CO_2 emissions from these 49 volcanoes are summed, the OMI-based data result in a total CO_2 emission of only 27 Tg/yr, compared to the 44 Tg/yr CO_2 by direct measurements (Supplemental Table 8.1). Overall, a reasonable correlation exists between the two data

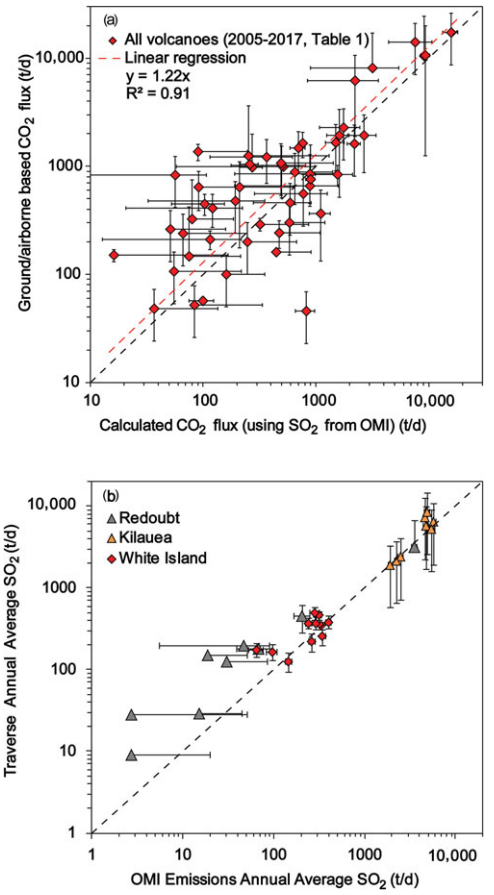

Figure 8.2 (a) Decadal average of CO_2 emissions from direct measurements for the period 2005–2017 (as available; see Supplemental Table 8.1) compared to that calculated from decadal average SO_2 emission from OMI and C/S ratio estimates. (b) Annual average SO_2 measurements from direct measurements for the years 2005–2015 when available (Redoubt,[65,91,93] White Island,[33,94,95] and Kilauea[96] compared to annual OMI estimates[75]). Error bars show one standard deviation over the period of observations in both (a) and (b), and uncertainties in OMI-derived values are propagated. Note that annual variability is low at open-system volcanoes.

sets, with scatter about the 1:1 line (Figure 8.2a), but each data set is associated with significant variability over the decadal period. The variability in the decadal average CO_2 flux is mirrored by the spread of the SO_2 annual averages over a decadal period (Figure 8.2b), pointing to inherently large temporal variability in the emission rates from active volcanoes over multiyear periods (see also Section 8.6.1) and suggesting that the spread in CO_2 data could be related to different observation periods. This lies in contrast to variability in SO_2 emission on an annual basis from the open-vent volcanoes; where frequent measurements have been made, variability is low and data cluster around the

1:1 line. This suggests that OMI-derived estimates of CO_2 emissions are accurate when the C/S ratios of volcanic gases are measured frequently. Future work should focus on a rigorous, systematic inter-comparison study between satellite and ground-based SO_2 flux data sets and on capturing the temporal variability in volcanic gas chemistry.

Given the importance and potential further use of the long-term OMI SO_2 data sets[75,77] for estimating global CO_2 emission rates, it is important to note that many of the "passive" degassing measurements[75] in fact represent eruptive periods. For instance, the OMI decadal data set omits eruptive emissions using a threshold SO_2 amount,[75] which excludes large-scale explosive emissions, but here we show that the data set includes emissions from eruptive and inter-eruptive periods. If we consider passive degassing to be degassing in the absence of eruption, we can compare the GVP volcanic eruption database[97] with the OMI SO_2 degassing data set. On an annual basis, 10 of the 91 volcanoes (11%) reflect true passive degassing such that the volcanoes did not experience an eruption between 2005 and 2015. Furthermore, 24% of the volcanoes erupted at least once every year; and, in any given year, at least half of the volcanoes experienced an eruption during this decade (the minimum number was 45 volcanoes erupted in a given year). For comparison, on average of 83 ($\pm$1.6) volcanoes experienced a non-zero SO_2 flux in a given year, suggesting that roughly half of the volcanoes might be considered to be passively degassing on an annual basis.

It is also important to note that the OMI SO_2 data set almost exclusively represents volcanoes with predominantly basaltic or basaltic–andesite compositions and is thus not globally representative of Earth's more silicic systems. Basaltic systems have been shown to have the shortest repose periods (averaging $<$1 year), whereas basaltic–andesite systems can show much longer periods of repose (averaging roughly 20 years),[98] with the latter approaching the length of time that the volcanic gas community has been making CO_2 emission rate measurements. Thus, we suggest that future work should also focus on analyzing time series data that span eruptive cycles at the more silicic of this set of dominantly mafic volcanoes to understand how emissions vary over multi-decadal time periods that include both periods of repose and open-vent degassing.

8.4.2 CO_2 Emissions during Explosive Eruptions

Our present knowledge of CO_2 emissions from large, explosive eruptions is limited owing to both proximal hazards and instrumental challenges in measuring volcanic gases during such events. Direct assessment of CO_2 emission rates during explosive eruptions has been achieved on rare occasions, either from airborne plume measurements (e.g. during the 2009 Redoubt eruption,[65] though here the most explosive events were not captured) or by coupling real-time FTIR spectroscopy of CO_2/SO_2 ratios in eruptive gases with the UV-sensed SO_2 flux (e.g. during the 2010 Eyjafjallajökull eruption[99]). In other cases, bulk CO_2 emissions from explosive eruptions have been estimated by combining CO_2/SO_2 data from *in situ* measurements with satellite-based SO_2 data or by modeling the pre-eruptive vapor-phase composition.[100–102] Such techniques yield, for instance, estimates of ~10 and ~50 Mt CO_2 for the 1980 Mount St Helens and 1991 Pinatubo eruptions, respectively.[103] These

estimates imply CO_2/SO_2 mass ratios of ~3–10 in the eruptive emissions, although higher ratios cannot be excluded.[100] Indeed, mass budgets for these and other explosive eruptions of silicic magmas strongly suggest pre-eruptive accumulation of a CO_2-rich vapor phase.[100,104] Gas accumulation in silicic magma reservoirs between eruptions can result from the second boiling of vapor-saturated crystallizing magma and/or volatile supply from basalt underplating.[105] Magmatic vapor may migrate to the roof zones of reservoirs via gas transport through channelized flow in crystal-rich mush.[106] Because of its low solubility, CO_2 becomes preferentially enriched in the accumulating vapor phase. Therefore, high CO_2/SO_2 ratios[107] and high CO_2 and SO_2 fluxes[108,109] can be expected during the initial phases of explosive eruptions that tap the gas-rich upper levels of magma reservoirs.

Measuring volcanic CO_2 emissions during explosive eruptions will continue to be challenging regardless of whether one is using *in situ* or satellite techniques. *In situ* measurements of explosive eruption plumes are hampered by proximal volcanic hazards and high atmospheric ash loadings,[101] and spaceborne CO_2 measurements will also be hindered by volcanic ash. However, UAV (or drone) technology and improved satellite SO_2 instruments (e.g. TROPOMI) hold great promise to improve measurements of explosive volcanic CO_2 emissions in the coming decade.

8.4.3 CO_2 Emissions from Dormant Volcanoes

It has been recognized for some time that volcanoes that are dormant (defined here as not erupting but likely to erupt again) emit significant amounts of CO_2.[110,111] These volcanoes may support smaller CO_2 plumes that may or may not contain SO_2 derived from fumarolic emissions, or they may host large regions of diffuse degassing (Supplemental Table 8.3) related to silicic volcanism that have long repose times typical of caldera settings. Below we review each source separately.

8.4.3.1 Small Volcanic Plumes: Fumarolic Contributions

Volcanoes that produce small plumes, or CO_2 plumes in the absence of significant SO_2 emission, are more difficult to characterize for their CO_2 emission rate than those that have strong SO_2 plumes. Roughly 40%[44] of the 102 direct CO_2 flux measurements listed in Supplemental Table 8.1 are from volcanoes where the volcanic plume was not detected by OMI[75] and thus fall in this category (we refer to these as "small plumes," although some do not have low CO_2 emissions). The CO_2 emissions associated with these volcanoes range from 13 to nearly 1500 t/d, with an average of 300 t/d ($1\sigma = \pm 360$) and a median of 147 t/d, excluding the large emission from Oldoinyo Lengai (Tanzania). Some of the largest CO_2 emissions are from active volcanoes that host crater lakes (e.g. Taal and Pinatubo, Philippines; Ruapehu, New Zealand; Supplemental Table 8.1) and from better-studied sections of arcs in the United States (Cascades and Alaska), Central and South America, and Indonesia (Supplemental Table 8.1). Where airborne methods and easy access have allowed for measurements, the data show that such emissions are common and are likely widespread in many arcs globally (Figure 8.3a).

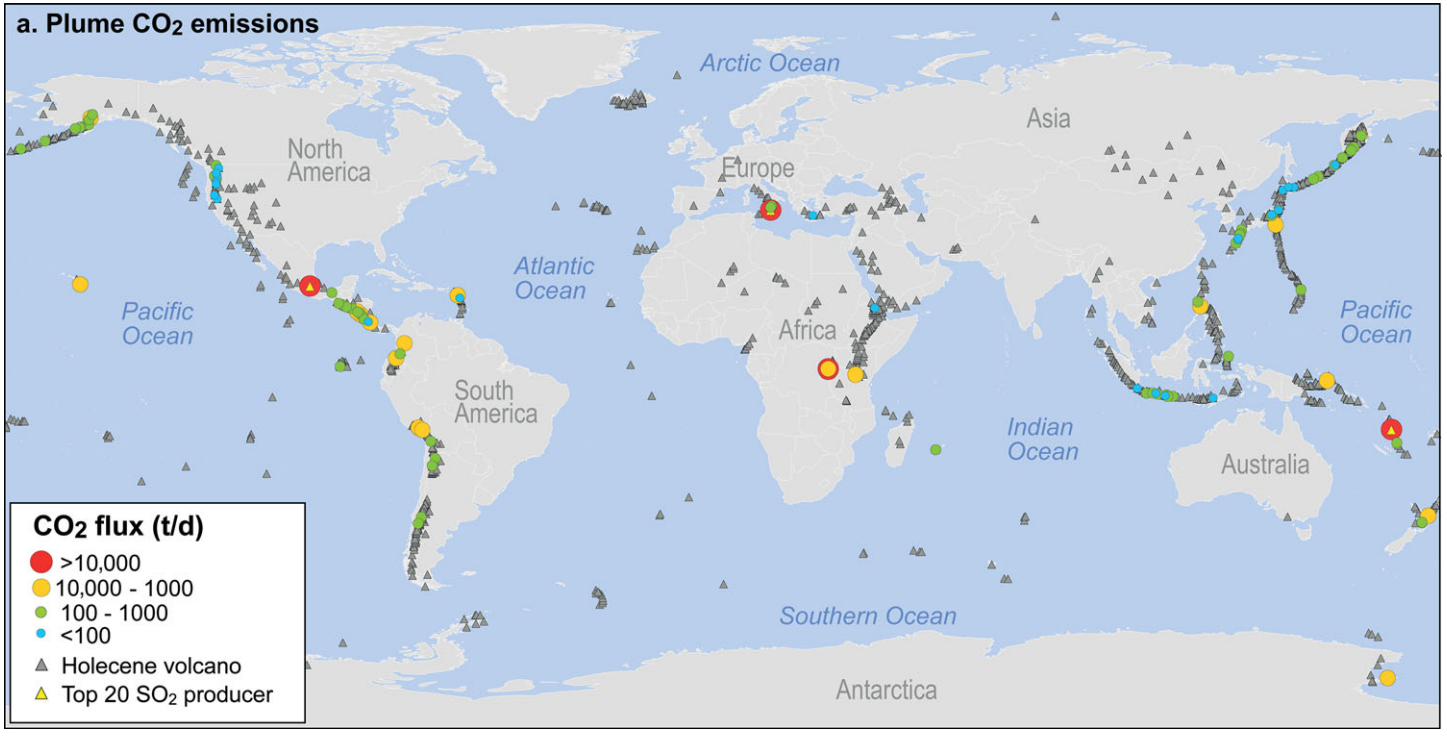

Figure 8.3 Measured CO_2 emissions from (a) active volcanoes (plume emissions; Supplemental Table 8.1) and (b) diffuse degassing sources (Supplemental Table 8.2). All plume emissions are from Holocene volcanoes. Diffuse emissions are from volcanic sources with a broader period of activity; hydrothermal locations are often colocated with active volcanoes (i.e. Holocene volcanoes). Volcano locations from Ref. 97, top 20 SO_2 producers from Ref. 75, and hydrothermal system locations from a modified version of the database from Ref. 113.

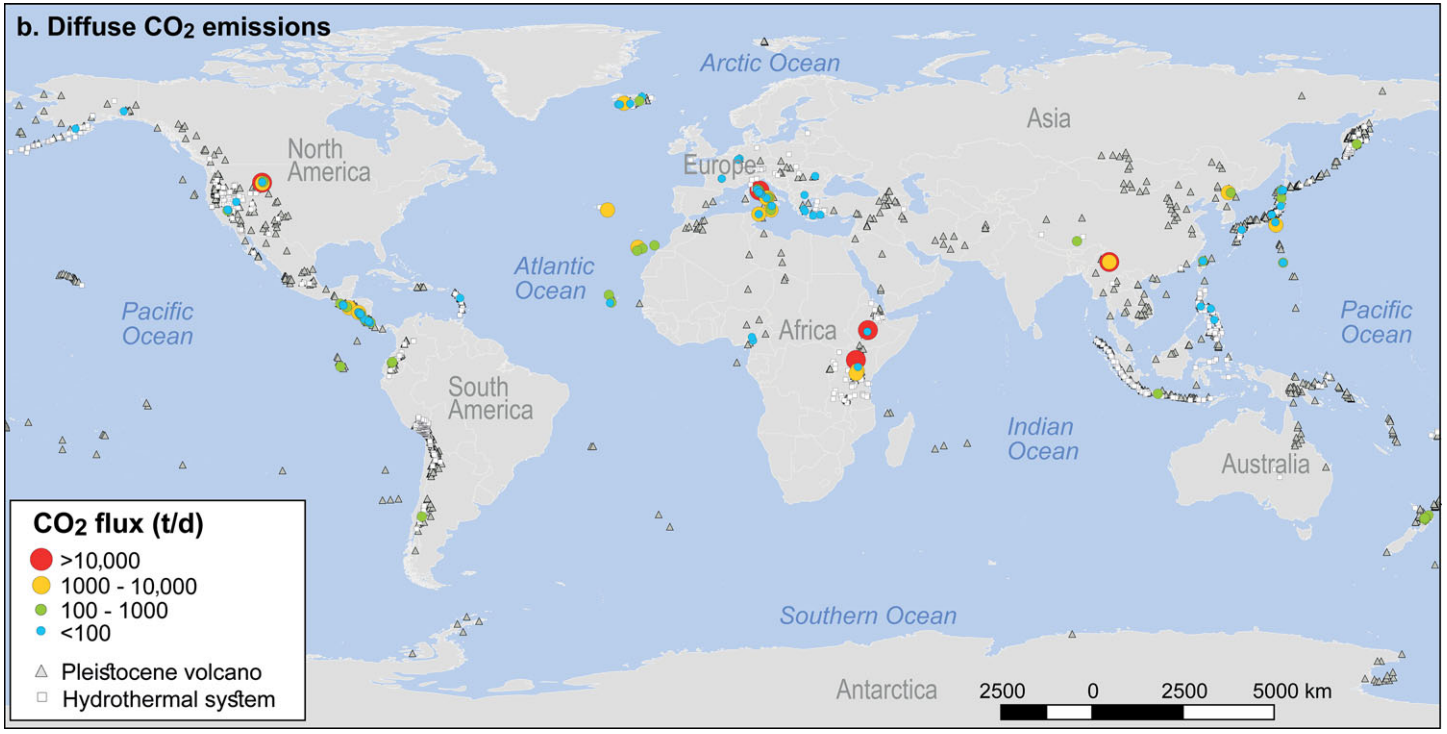

Figure 8.3 (*cont.*)

If we simply sum the CO_2 emissions from these "small" volcanic plumes, they amount to only 5 Tg CO_2/yr of the ~44 Tg/year in Supplemental Table 8.1, demonstrating the dominance of strongly emitting volcanoes in the data set. However, if we take the volcanoes that have erupted in the last 100 years (n = 407) minus the 83 volcanoes that are shown to be degassing each year (Section 8.4.1), resulting in 324 volcanoes globally, and assume that each outputs on average 300 t/d, this equates to ~35 Tg CO_2/yr. If we use the median (147 t/d) instead of the average, this results in 17 Tg CO_2/yr. This exercise suggests that the emissions from volcanoes with small plumes (or in the absence of SO_2 emission) could potentially emit a similar order of magnitude of CO_2 globally as volcanoes whose SO_2 plumes were detected by satellite. This result, if robust, would potentially stand in contrast to recent regional studies in Japan[57,112] that suggest that the global volatile budget is dominated by the high SO_2-emitting volcanoes, although this study[57] recognized that the data set lacked comprehensive measurements for the less active, diffusely degassing volcanoes. While challenging, more work is needed to verify the global contribution of CO_2 emissions from volcanoes that do not emit satellite-detectable SO_2.

8.4.3.2 Diffuse Emission of CO_2: Hydrothermal Systems, Calderas, and Continental Rifts

Our understanding of the magnitude of the diffuse CO_2 flux from volcanic and magmatically active regions on Earth continues to evolve with each year of new measurements, and we now understand this to be a significant outgassing source. What we show here is that diffuse CO_2 outgassing from calderas and dormant volcanic regions can rival outgassing from actively erupting volcanoes (Figures 8.3, 8.4, and 8.5). Quantification of such fluxes on global scales, however, remains a great challenge. Available flux data for diffuse gas emissions have been gathered, together with data from active volcanoes, into a database (the MaGa web database: www.magadb.net[114]). The data show that there are large regions where measurements have not yet been made (e.g. South America, Kamchatka, and Southeast Asia; Figure 8.3b). As new discoveries of large emission sources have been made in the last 10 years in areas with large magmatic intrusions and concentrations of hydrothermal systems (e.g. the East African Rift (EAR) and the Technong volcanic province, China), we expect that additional important areas will be located in the future.

If we compare the distribution of measured diffuse emissions of CO_2 (Figure 8.5a and Supplemental Table 8.3) with plume emissions from active volcanoes (Supplemental Table 8.1), we find significant overlap and similarity in the emission rates, especially at higher rates. The diffuse emission data tend to be bimodal, with a larger population at low emission rates (Figure 8.5a), but the lack of measurements at low CO_2 emissions for active volcanoes may simply reflect a sampling bias due to method limitations (e.g. fumarolic contributions and plumes below SO_2 satellite detection limits). Volcanic systems that have diffuse emission rates between 100 and 500 t/d are most common, representing 30% of the data, with an additional 20% falling between 500 and 5000 t/d. The highest CO_2 emission rates are for large magmatic systems (e.g. Yellowstone in the United States, the Tengchong Volcanic Field in China, the Tuscan Roman degassing structure (TRDS) and Campanian degassing structure (CDS), and the EAR system; Supplemental Table 8.3). Although

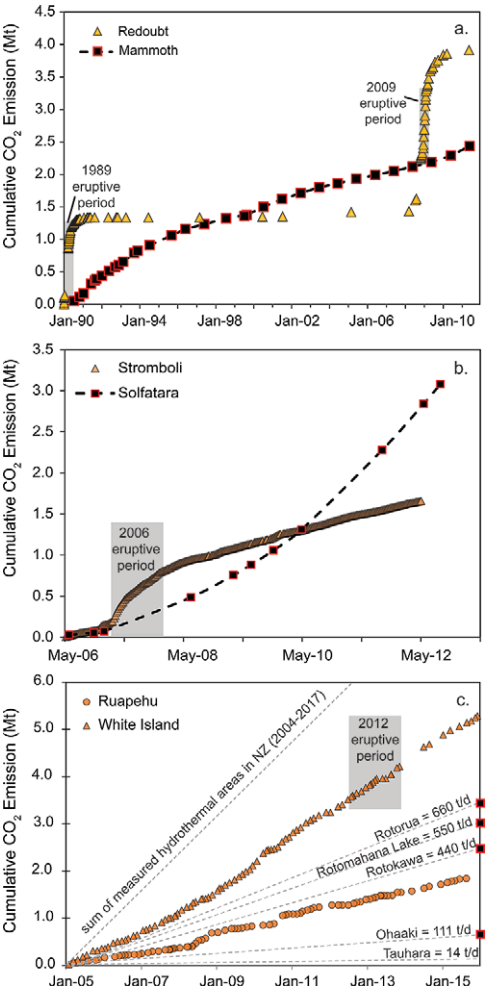

Figure 8.4 Cumulative CO_2 emissions for some of the best-studied volcanoes in the world showing the comparison of vent emissions (triangles) to diffuse emissions (squares and dotted lines). (a) Emissions from Redoubt volcano and those of Mammoth mountain are roughly equal over 20-year time frames. Redoubt data from Refs. 65, 91, 93, and 115 and Mammoth data from Ref. 116. (b) Solfatara data from Ref. 117, Stromboli data from Ref. 118. (c) White Island data from Refs. 33 and 119, Ruapehu data from Refs. 32, 94, and 95, Taupo Volcanic Zone diffuse degassing data from Refs. 120–123.

estimates for these systems have large uncertainties, high emission rates are consistent with high heat fluxes and voluminous magmatism. As run-up time, or period of unrest prior to an eruption, is positively correlated with the repose period between eruptions,[98] it should not be surprising that some of the largest and longest-lived volcanic systems (e.g. silicic calderas systems) can produce some of the largest CO_2 emissions globally (e.g. Yellowstone, Campi Flegrei, and Rotorua; Supplemental Table 8.3).

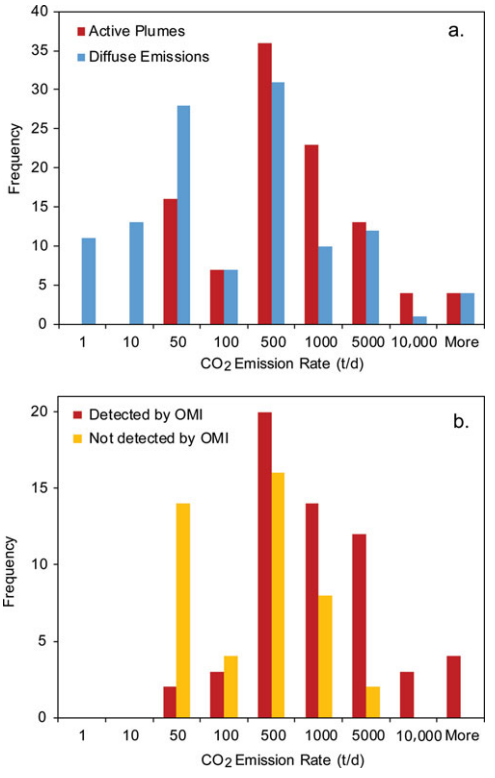

Figure 8.5 Distribution of CO_2 emission rate data for (a) active volcanic plumes (Supplemental Table 8.1) and diffuse emissions (Supplemental Table 8.2) and (b) the active volcano plumes that were detected for passive degassing by OMI[75] and those volcanoes that were not.

Unrest in caldera systems is common,[124,125] and thus using unrest catalogs may allow us to understand and constrain this likely significant CO_2 source better. Globally, there are 446 caldera systems, of which 225 have erupted in the Quaternary and 97 in the Holocene.[124,125] At caldera systems, unrest is understood to be driven by the influx of mafic, volatile-rich magma to the base of relatively shallow reservoirs containing vapor-saturated magma (Figure 8.1). In a recent study of the best-monitored caldera systems in the world, such episodes of magma intrusion were found to be the fundamental driver of unrest,[124] and 71% exhibited changes in degassing with unrest. At mafic calderas, unrest often proceeded to eruption, whereas felsic systems were thought to have a higher capacity to accommodate magmatic intrusions without leading to an eruption.[124] The hydrothermal systems and gas reservoirs that often lie above such intrusions act as buffers, such that changes in gas emission at the surface are often delayed by some time (sometimes years) from the time when fresh magma is intruded.[116,124,126] However, the time-averaged release of CO_2 from these systems is roughly similar to that of many active volcanoes (Figure 8.4). The main difference may then be the contrast in available pathways for gas release: active

(and often mafic) volcanoes maintain open conduits with high permeability (Supplemental Table 8.1) and dormant (often silicic) volcanoes and caldera systems release gas along faults and fracture networks with lower permeability than open conduits, resulting in regions of diffuse emissions (Supplemental Table 8.3).

Here, for the first time, we show that net release of CO_2 over time (decades) from areas of diffuse degassing for several well-studied systems that have not erupted in recent history (e.g. Mammoth Mountain, USA; Solfatara, Italy; Rotorua, New Zealand) can rival that of active volcanoes that have experienced an eruption recently (Etna and Stromboli, Italy; Redoubt, USA; White Island, New Zealand). The active volcanoes are all on the list of top SO_2-producing volcanoes in the world.[75] For example, the CO_2 emission from Mammoth Mountain (last eruption 70 ka[116]) over ~20-year timescales is similar to that of Redoubt Volcano (Figure 8.4a). In this case, the long-term average emission is fundamentally controlled by the period of observation (e.g. note that the 2005–2015 average emission is an order of magnitude higher in Supplemental Table 8.1 than the average over two decades portrayed in Figure 8.4a). Another example is the long-term cumulative emission from Solfatara in Campi Flegrei, Italy, which exceeds that of Stromboli Volcano (Figure 8.4b). And finally, the emission from White Island is dwarfed by the sum of the cumulative CO_2 emissions from dormant volcanoes in New Zealand (Figure 8.4c).

It is not known how many hydrothermal systems exist on Earth, but the majority are associated with areas of either present or past volcanism. Our current summation of the extent of diffuse degassing from dormant volcanoes is ~64 Tg/yr (Supplemental Table 8.3), which is similar to that published previously,[15] but our estimate does not include large-scale extrapolated values for Indonesia–Philippines and the Subaerial Pacific Rim.[127] Our data highlight the importance of several large regions of localized hydrothermal activity. While work in several areas has already begun and has yielded valuable initial data (Yellowstone, USA;[128,129] Campi Flegrei, Italy;[117,130] the TRDS and CDS, central Italy;[131,132] the EAR;[133,134] and the Taupo Volcanic Zone (TVZ), New Zealand[120,122,123]), we expect several other areas will also be globally important for their CO_2 emissions. Guidance for where these areas might be located can be gleaned from global assessments of geothermal energy reserve. In a 2016 review by the World Energy Council,[135] the five nations with the highest potential geothermal generating capacity were the USA, the Philippines, Indonesia, Mexico, and New Zealand. Several of these countries have had very few CO_2 surveys to date. On the other hand, countries such as Italy and Japan (ranked 6th and 10th, respectively, on the list of top nations) have had considerably more studies.

Here, we attempt to estimate the number of hydrothermal areas worldwide by building on a list of geothermal systems capable of power production,[113] adding in hydrothermal areas located in Alaska, Kamchatka, and Peru. This results in ~670 hydrothermal regions worldwide (Figure 8.2). The average of all diffuse emissions from localities that have not experienced eruptive activity since 2000 is 340 ± 628 t/d, demonstrating a positive skew in the population. We omitted hydrothermal areas on volcanoes with eruptions since 2000 because we did not want to include anomalous data due to recent volcanism. This average also does not include large-scale magmatic emission estimates (Supplemental

Table 8.4) because these areas are also anomalous on a global scale and are not representative of individual hydrothermal regions. While admittedly simplistic, applying this average to the 670 hydrothermal regions worldwide would result in 83 Tg CO_2/year, or an additional 30% over the current summation of the diffuse data. We consider it likely that this estimate is conservative given: (1) that our data only represent ~135 of 670 localities; (2) these data largely do not include groundwater contributions that may be similar in magnitude to diffuse emissions (see Ref. 57 and references therein); and (3) the discovery of other large systems globally (such as Yellowstone) could add significantly to the budget (currently, large magmatic provinces sum to 75 Tg CO_2/yr; Supplemental Tables 8.3 and 8.4).

The TVZ is a region that deserves extra attention given its unique tectonic setting and high heat flow and because arc-scale extrapolations based on studies from the TVZ[127] continue to be used for global compilations and comparisons of CO_2.[15,134] The TVZ is an intra-arc rift zone that hosts over 20 separate hydrothermal regions with heat flux greater than 20 MW,[136] and many of these regions are exploited for geothermal energy. Previous estimates of the CO_2 output of the TVZ as a whole have been extrapolated based on the heat flux and the CO_2 content of upwelling fluids. However, diffuse CO_2 flux at the surface[120,122,123] for many of these systems greatly exceeds previous CO_2 emission estimates for these areas, without including fumarolic contributions. As an example, the emission rate estimated for the Rotorua hydrothermal system alone (estimated at ~1000 t/d, including sub-lacustrine degassing;[123] Supplemental Table 8.3) is nearly equal to that previously estimated for the whole TVZ (~1200 t/d[127]). To date, 7 of the 18 hydrothermal systems have been measured for CO_2; together, they equal a total of ~2000 t/d. Further investigation is required to determine why the previous estimates for the TVZ hydrothermal systems were low, but likely this results from underestimating the CO_2 content of the deep hydrothermal fluids or degassing from gas reservoirs at depth.[117,137] In any case, arc-scale estimates for other regions on Earth should not be based on TVZ data,[127] and continued effort should be placed on measuring the total diffuse CO_2 output from typical arcs and high-heat-flow regions around the world.

The EAR, also deserving of extra attention due to its high global output, is a series of rift valleys that extend 4000 km from the Afar region in the north to Beira in Mozambique in the south.[138] The system is split into an eastern branch, which hosts the Main Ethiopian Rift (MER) in the north and the Kenyan rift in the south. In these two sectors alone, there exist 36 volcanoes and 28 hydrothermal areas. The western branch of the EAR is characterized by a lack of recent volcanism relative to the eastern branch, but still hosts a number of geothermal prospects as well as Nyiragongo, a major emitter of CO_2. Several recent studies attempted to estimate the diffuse CO_2 flux from the EAR. One study focused on the centers of volcanic activity in the MER and extrapolated that to between 3.9 and 33 Tg CO_2/yr for the EAR.[134] A second study focused on tectonic degassing away from active volcanic centers and estimated 38–104 Tg CO_2/yr for the EAR, not including focused degassing through the active centers.[133] For our estimate, we use the midpoint of the range presented by Hunt et al.[134] because our aim is to estimate volcanic degassing; this value is one-third of the

total CO_2 emissions from all diffuse sources in our compilation (Supplemental Table 8.3). While the estimates of EAR fault-related degassing[133] are not volcanic per se, isotopic evidence suggests there exists a significant flux of mantle-derived CO_2 to the atmosphere through these structures, and using these data would increase significantly the global contribution of the EAR. We caution that both studies found relatively few measurements of modest to high CO_2 flux in faulted or hydrothermal areas and that these results were then extrapolated over extensive regions. Significant uncertainty is associated with such large-scale extrapolations, particularly when diffuse CO_2 flux can vary on meter scales. However, it is clear the EAR is a very important region for global CO_2 emissions, and more work is needed to quantify the flux of CO_2 from this and other areas of continental rifting/extension that support volcanism and hydrothermal activity, such as the Rio Grande Rift in New Mexico and the Rhine Graben and the Eger Rift in Central Europe. Such areas could potentially add 30–40 Tg CO_2/yr (or 8–11 Tg C/yr) to global budgets, and potentially be on the same order as global arc fluxes.

8.5 The Next Iteration of Global Volcanic CO_2 Emissions

As our understanding of the distribution and magnitude of volcanic and magmatic CO_2 degassing evolves, so will our ability to estimate accurately the present-day global CO_2 emission from these areas. As a culmination of the DECADE program, scientists came together in May 2018 to constrain better the total global CO_2 flux from volcanic regions, as well as corresponding uncertainties. Here, we follow simple methods based on the extrapolation of measured data to determine a global subaerial volcanic CO_2 budget (Supplemental Table 8.4). Our methods are similar – and thus comparable – to previous studies,[15,57] but future work should focus on a rigorous statistical analysis of the data and more complex extrapolation procedures that lie beyond the scope of this chapter.

We break down the subaerial volcanic budget into three main categories: (1) passive degassing for active volcanoes, dividing these into those that have been detected by OMI and those that have not; (2) diffuse emissions from both active and dormant volcanoes, with groundwater contributions (not estimated) and large degassing provinces as separate categories; and (3) eruptive emissions. We first calculate the average of the measurements of CO_2 flux from the volcanoes that have been measured using ground-based or airborne techniques (i.e. measured directly) that were detected by OMI[75] (58 of 91 volcanoes in Supplemental Table 8.1) and apply the average emission from these volcanoes (1730 $\pm$ 440 t/d, mean and standard error) to the 83 volcanoes (Section 8.4.1) that were degassing and detected by OMI globally on an annual basis between 2005 and 2015, yielding 52 $\pm$ 13 Tg CO_2/yr (Supplemental Table 8.4) for this set of volcanoes. Multiplying the average of the remaining 33 volcanoes from Supplemental Table 8.1 (i.e. those that do not emit SO_2 in large enough quantities to be detected by OMI – the average CO_2 output of these volcanoes is 300 $\pm$ 68 t/d; Supplemental Table 8.4) to 324 volcanoes results in 35 $\pm$ 8 Tg CO_2/yr. The sum of these results in 88 $\pm$ 21 for passive degassing from active volcanoes (Supplemental Table 8.4). How the value of 324 volcanoes was determined is discussed in

Section 8.4.3. The uncertainty in this number is difficult to quantify without global arc-wide assessments of the numbers of expected degassing volcanoes that have not been detected by OMI. To put this number in context, there are 169 active volcanoes in the United States, and 81 (47%) have notable degassing as determined through visual surveys.[139] Of these, 28 (17%) are thought to have plumes large enough for airborne measurements, but only 8 (4%) were detected by OMI.[75] Thus, 90% of the US volcanoes that emit CO_2 and 71% of the US volcanoes that have plumes large enough for airborne surveying were not detected for passive degassing of SO_2 by OMI. Similarly, of the 19 persistently degassing volcanoes in Japan[112] during the period of OMI measurements, only 7 were detected by OMI[75] (i.e. 63% were not detected by OMI). If this relationship were to hold globally (i.e. that 63–71% of volcanoes with significant CO_2 emissions are not detected by OMI), this would suggest that 245–313 volcanoes with notable plume emissions worldwide remain undetected by OMI, which is similar to the value we used. We suggest that completing a global assessment of which volcanoes are degassing, and the nature of that degassing, based on visual assessment and documented activity in the GVP database would lead to a much more accurate estimate of the number of degassing volcanoes globally than the methods used here. However, it must be considered that additional invisible or nearly invisible emissions of CO_2 may also exist.[140–142]

As discussed above, the CO_2 contribution from explosive eruptions is poorly constrained. Here, we estimate eruptive emissions of CO_2 (Supplemental Table 8.2) by combining recent decadal-scale (2005–2018) SO_2 fluxes derived from satellite measurements of eruptions[143] with the most representative CO_2/SO_2 ratios measured at corresponding volcanoes, and separate these data into explosive and effusive events (Supplemental Table 8.2). In previous estimates, CO_2/SO_2 ratios were assumed to have uniformly high values of 10 and 7 in the pre-eruptive vapors of silicic and basaltic magmas, respectively.[57] Such an assumption is reasonable for initial phases, but is not necessarily valid for the whole eruption length. The figure we obtain by using measured ratios (0.6 Tg/yr; Supplemental Table 8.2) is much lower than previously estimated based on theoretical ratios (7 Tg/yr[57]). We anticipate that our value is likely underestimated and that the true answer may lie between these two values. Regardless, the estimates show that explosive emissions are minimal compared to the passive degassing estimates. CO_2 emissions from effusive eruptions in the same period (Supplemental Table 8.2) are inferred by subtracting explosive CO_2 emissions from the total CO_2 load from all eruptions. In this case, the calculated contribution is similar to previous estimates (1.3 compared to 1 Tg/yr CO_2 for effusive eruptions[57]), and again the contribution is a small fraction of the total subaerial budget.

Our calculations suggest that diffuse degassing of CO_2 from volcanoes is only slightly lower than that from active volcanic vent emissions, with diffuse emissions estimated at 83 ± 15 Tg/yr. However, combined contribution of 170 Tg/yr CO_2 from diffuse degassing from all volcanic–hydrothermal systems, including groundwater contributions and degassing related to large regions of intrusive magmatic activity is higher (Supplemental Table 8.4). This value is likely an underestimate given that fumarolic contributions (focused venting/small fumaroles) in regions of diffuse degassing are often not quantified as part of the estimation of degassing across such regions, and because groundwater contributions

are largely unquantified. Furthermore, we anticipate the discovery of additional large emission sources as many of the countries with the highest potential for geothermal power generation have few measurements.

In total, we conservatively estimate global subaerial volcanic CO_2 emissions to lie between ~220 and 300 Tg CO_2/yr, and between ~280 and 360 Tg CO_2/yr including the contribution of MOR (Supplemental Table 8.4), based on currently known sources. Our estimates are lower than those published by Burton et al.,[15] but higher than previous estimates for global subaerial sources.[111,144]

8.6 Temporal Variability of Volcanic Degassing

8.6.1 Comparison of the Temporal Variability of CO_2 Emission from Active and Less Active Volcanoes

Most of what we now know about the temporal evolution of CO_2 emissions from volcanoes has been learned in the last two decades. Advances in instrumental techniques now permit continuous, real-time monitoring.[51,56,145] The trends emerging from these data show that emissions vary dramatically with volcanic setting (Figure 8.1) and that timescales of observation are important for understanding the relative contributions from different systems. Active volcanoes with open-vent degassing such as Stromboli and Mount Etna (Italy) show orders of magnitude variability over very short time frames (Figure 8.6) correlating with magma supply and eruptive activity.[53,54,146] In such active, often mafic systems, volatiles reach the atmosphere via magma convection, permeable gas flow, or bubble rise through low-viscosity melts.[18,147] Despite short-term variability, the long-term average output at these volcanoes stays relatively constant over multiyear periods (Figure 8.4). In some cases, paroxysmal-type activity will increase emissions for over a year before returning to the long-term average (see Stromboli, 2006; Figures 8.4b and 8.6). Minor eruptive activity, on the other hand, can be difficult to discern in long-term

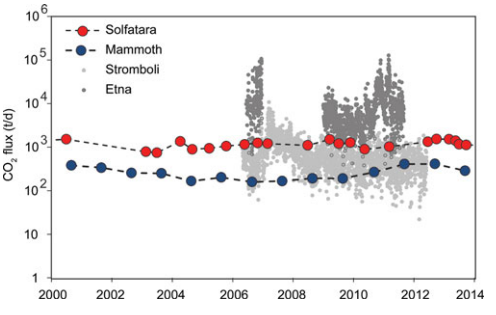

Figure 8.6 Temporal variability of CO_2 emissions from some of the best-studied volcanoes in the world. Emissions from open-vent volcanoes vary dramatically in time, whereas diffuse emissions are buffered and show less variability. Solfatara data from Ref. 117, Mammoth data from Ref. 116, Stromboli data from Ref. 118, and Etna data from Ref. 148.

trends. For instance, White Island and Ruapehu (New Zealand) demonstrate steady emissions over decadal periods during which eruptive activity is barely detectable (Figure 8.4c).

Closed-system volcanoes, or volcanoes that oscillate between closed- and open-vent degassing, can show dramatic variability in emissions over periods of years related to magma intrusion and variations in conduit permeability. Increases in CO_2 emission rates are typically associated with eruptive activity (Redoubt; Figure 8.4a) and sometimes when intrusions occur without eruption.[92] Periods of unrest can last months to years and are often accompanied by increases in emissions that then decrease exponentially following eruptive activity. Such behavior has been better documented for SO_2 emissions,[89,149] but is mirrored by CO_2 emissions where measured (e.g. Redoubt in 1989 and 2009;[65] Figure 8.4a).

Over an entire arc, the dominant volcanic CO_2 producers may vary over decadal timescales, with some volcanoes becoming more or less active. A recent compilation of data for the Central American Arc estimated an arc-scale CO_2 output one order of magnitude higher ($22{,}500 \pm 4900$ t/d[56]) than previous estimates, owing to the reactivation of Turrialba Volcano, as well as an increase in CO_2 flux from Momotombo and Masaya volcanoes over the previous decade. Other arc segments have had similar changes to the overall degassing budget due to the reactivation of particular volcanoes (e.g. Miyakajima in Japan[112]).

Finally, large-caldera systems are thought to be underlain by silicic magma bodies, and in turn underplated by mafic magma.[109] The CO_2 emissions from such volcanoes, often modulated by large hydrothermal systems, show much less variability over annual or even decadal scales than emissions from active volcanoes (Figures 8.4 and 8.6). Where long-term measurements are available, small variations in the CO_2 output in these systems often follow a geophysical manifestation of magma movement at depth[116,150] whereby the transport of the gas to the surface is buffered by the overlying crust.

8.6.2 Using the Temporal Variability of CO_2/SO_2 in Volcanic Gas for Eruption Forecasting

It has been shown that the relative proportions of C and S change prior to and during eruptive activity.[151,152] Owing to the low solubility of CO_2 in silicate melts,[153] the magmatic vapor phase typically has a high molar C/S ratio at depths of >~5 km in the crust,[102] and then C/S decreases with magma ascent as more S exsolves from the magma.[141,146] With more frequent monitoring of pre-eruptive volcanic gas using Multi-GAS, we now know that an elevated C/S in gas emissions is common prior to the onset of eruptions.[51,55,154] In Figure 8.7a, we show variability of C/S over various timescales for 12 episodes at 7 volcanoes. One can observe that C/S ratios increased to between 15 and 43 in the months to hours preceding eruption at five well-monitored basaltic volcanoes, whereas the long-term C/S signature of shallow degassing at these volcanoes typically lies between 2 and 7 (Figure 8.7a to j). Such trends are often interpreted as the migration of deeply sourced gas bubbles prior to magma ascent.[53,155]

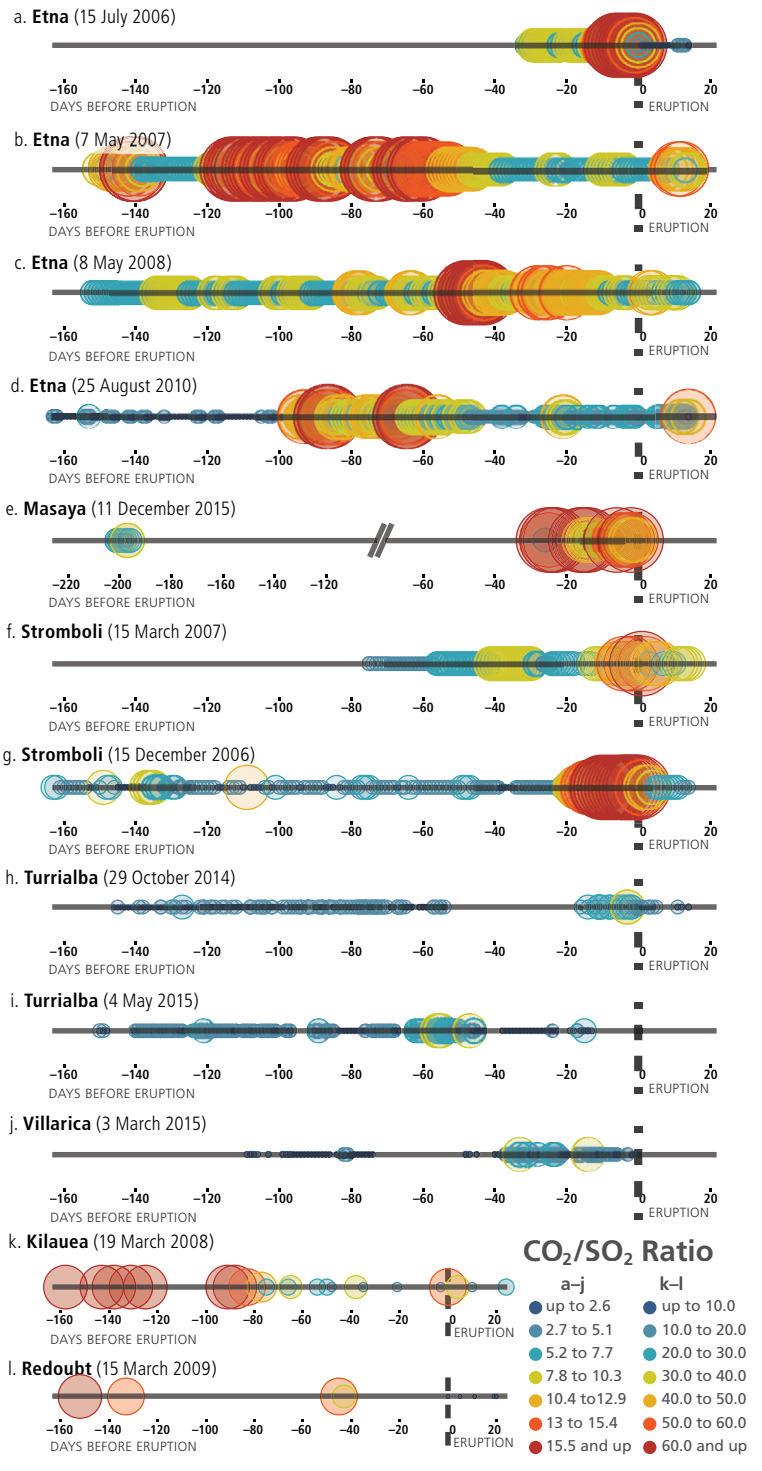

Figure 8.7 (a to j) Trends in C/S ratio observed at basaltic volcanoes monitored with Multi-GAS instruments, with elevated C/S documented in the months to hours prior to eruption. (k and l)

A second set of C/S ratio observations has been made over somewhat longer timescales and is related to degassing of deep-seated magmas prior to ascent (Figures 8.7k and l). Months- to years-long trends in C/S were observed at both Redoubt[141] and Kilauea[140] volcanoes prior to eruption (Figure 8.7b). In both cases, the C/S ratio was very high compared to the data observed at the other volcanoes, reaching values between 80 and 200, and both were associated with no visible plume (Figure 8.8). Documentation of this type of degassing is rare, but the occurrence is likely not rare. In the case of Redoubt, the pre-eruptive degassing of CO_2 only amounted to roughly 15% of the total budget,[65] but for Kilauea nearly 30 Mt of gas escaped prior to eruption. Similar patterns of pre-eruptive gas release might be inferred, for instance, from the Holuhraun/Bárðarbunga eruption, where a total of 9.6 Mt SO_2 and 5.1 Mt CO_2 was emitted over the course of the eruption.[157] The low bulk C/S ratio (0.7) compared to most high-temperature volcanic gases[73] might imply that substantial amounts of CO_2 degassed before monitoring began. In fact, a new study discovered significant degassing from glacially covered Katla volcano (~37 kt/d CO_2) in the absence of a visible plume, unusual geophysical unrest, or S gas emission.[142] These studies highlight a gap in our ability to detect CO_2 degassing from volcanoes without dedicated airborne surveys downwind of potentially degassing volcanoes.

8.7 Sources of Carbon Outgassed from Volcanoes

Carbon outgassed at subduction zone volcanoes is sourced from the mantle, the subducted slab, and the overlying lithosphere (including the crust),[158–162] whereas CO_2 released from MORs and hot spots is dominated by mantle carbon.[144,161] The carbon isotopic composition ($\delta^{13}C$) of the depleted MOR mantle (DMM) is -5 ± 1[163,164] and that of plumes is documented as -3.1 ± 1.9 (high-temperature fluids from Iceland[165]) and –3.4‰ (Kilauea summit gas[166]), whereas the subcontinental lithospheric mantle likely contains carbon of composition between –3.5‰[133,167] and –6‰.[168] Research on CO_2 sources in subduction-zone volcanic gases has emphasized the role of carbon release from subducted sediments and carbonates and has shown that the type of material subducted imprints a carbon isotopic and $C/^3He$ signature on the discharging gases. This approach, combined with CO_2 fluxes from volcanoes, led to the development of volatile budgets in subduction zones and implies that more carbon is subducted than what is currently released by volcanoes, leading to the transfer of carbon into the deeper mantle and beyond the zones of arc magma generation.[70,79,169,170] Accumulation of subducted carbon below the arc crust or

Figure 8.7 (*cont.*) Observations of elevated high C/S ratios in the years prior to eruption. Decreasing trends in C/S ratios were observed in the last 100 days prior to eruption. Both the symbol size and color scale with C/S ratio, with larger and warmer symbols relating to higher C/S ratios. Data from Refs. 118, 140, 141, 148, 155, and 156. At Masaya, the volcano (e) did not erupt, but rather experienced the opening of a new lava lake. At Redoubt, three values in excess of 80 related to a period of SO_2 scrubbing in the month prior to eruption were removed – see Ref. 141 for details.

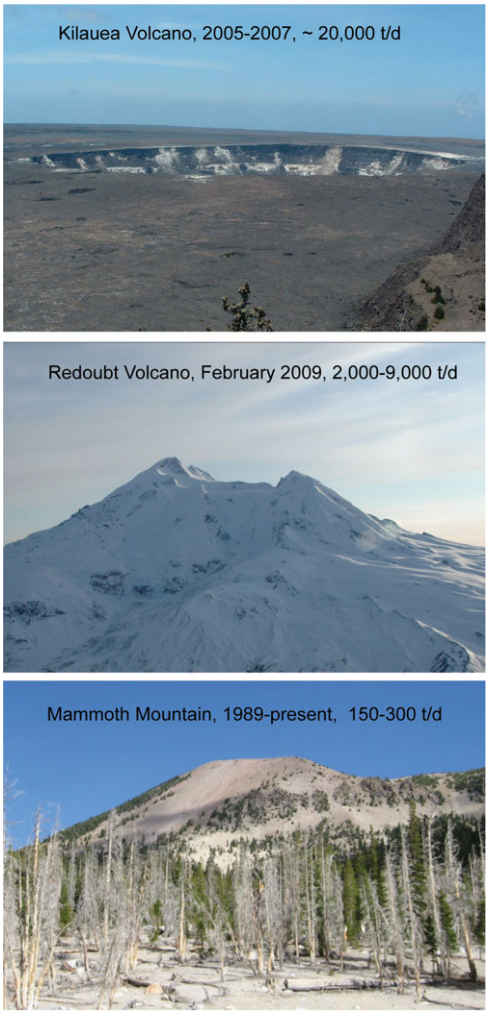

Figure 8.8 Images of volcanoes emitting significant quantities of volcanic CO_2 in the absence of a visible plume.

continental lithosphere has been suggested as a mechanism for long-term carbon storage, removing the requirement for carbon subduction into the deeper mantle to balance the input versus output budgets at arcs.[171] The extent to which this process occurs globally is poorly constrained, but it could significantly affect the carbon isotope composition of the mantle wedge and therefore the mantle component sampled by arc volcanic gases. Recently, researchers have highlighted, in addition to the subducted carbon source, the potential significance of carbon assimilation from the overlying crust in continental arc magmas as a major source of CO_2 degassing from volcanoes, both today and in the geologic past.[4,172,173] In particular, this crustally sourced carbon can have profound effects

on the generation of arc magmas,[174] the explosive activity of a volcano,[173,175] and long-term climate change resulting from CO_2 release into the atmosphere.[172]

The approach most commonly taken when assessing the contribution of volatiles from the crust is to use helium isotopes, which range widely in volcanic gases from values that approach pure crustal sources of ~0.02 Ra, where Ra is the $^3He/^4He$ ratio of air at 1.4×10^{-6}, to 29 Ra in fluids discharged from hot spot hydrothermal systems and volcanoes.[176] In subduction-zone settings, $^3He/^4He$ ratios of gas discharges range from the crustal value to 10 Ra,[176] with an unweighted average of 5.4 Ra.[70] A recent compilation of maximum $^3He/^4He$ ratios of arc gases shows a global average of 7.4 ± 1.5 Ra,[176] overlapping with the mid-ocean ridge basalt (MORB) value (Figure 8.9). The main process that lowers $^3He/^4He$ in arc gases is the contribution of ^4He from crustal sources through either magma assimilation of crustal rocks or interaction of magmatic fluids with crustal fluids at shallow depths.[176] Such processes may also affect the carbon isotopic signature. Plotting the $\delta^{13}C$ and $^3He/^4He$ of arc gases shows that: (1) very few samples plot in the DMM range for both helium and carbon, implying that subducted and/or crustal carbon affects the isotopic composition and the amount of CO_2 at arc volcanoes; (2) samples where $^3He/^4He$ is 7 ± 1 Ra have $\delta^{13}C$ values ranging from +2‰ to −12‰, implying that if the source of CO_2 is from the subducted slab, it is sourced from both carbonates and organic carbon. Alternatively, the wide $\delta^{13}C$ range for samples with Ra > 7 could be the result of modification of the mantle beneath arc volcanoes due to prior subduction events that affected carbon, but not helium; and (3) gases with $^3He/^4He$ values <7 Ra show an equally wide distribution of $\delta^{13}C$ as those >7 Ra, implying that both carbonate and organic carbon derived from the overlying crust (as implied by low $^3He/^4He$) may contribute to the degassing CO_2.

Most helium and carbon isotope data are from low-temperature (<100°C) bubbling springs and fumaroles, which can be affected by low-temperature carbon isotope fractionation in the crust and shallow hydrothermal systems.[177,178] If we only consider >200°C gases (Figure 8.9b), which are more likely to reflect their source, the range in $\delta^{13}C$ remains from −12‰ to 0‰ for both gases with $^3He/^4He$ values >7 and <7 Ra, with the same implications as stated above.

Recently, a different approach has been used to evaluate the sources of carbon in volcanic emissions, using the C/S ratio of volcanic gases in crater plumes and high-temperature (>450°C) fumaroles.[73] Selection of only high-temperature samples ensures that secondary hydrothermal processes do not affect the data set. The advantage of this approach is that many more data are available for C/S ratios than for isotope systematics, allowing for a more complete global coverage. Correlations with petrologic indicators of slab-derived fluids such as the Ba/La ratios of erupted materials allows distinction between emissions that have predominantly crustally derived CO_2 and emissions that show a strong subducted slab carbon component.[73] This global data set further reveals that only some gases with high C/S ratios (>4) are from locations where volcanoes sit on upper-plate carbonates. The data set further shows that volcanoes with low C/S ratios (<2) are in locations where the subducting sediments contain only <10% CO_2. This

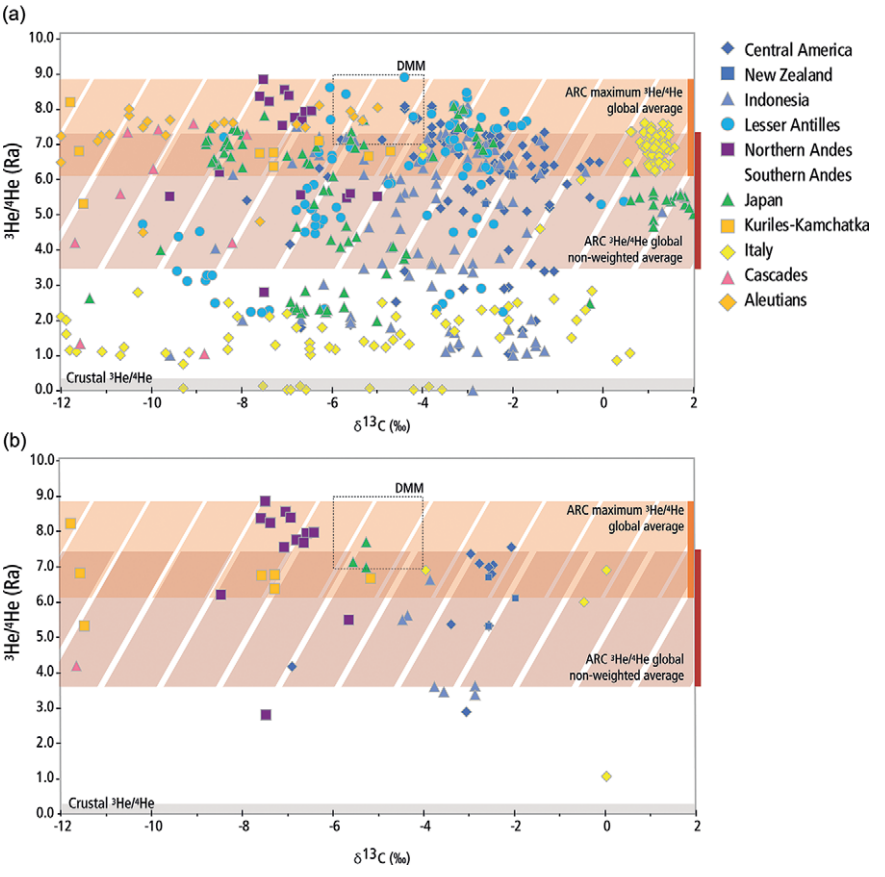

Figure 8.9 (a) Helium and carbon isotope signatures for volcanic and hydrothermal gas discharges and (b) data from discharges with vent temperatures >200°C. Data from Refs. 70 and 179–182. The field for DMM is from Refs. 162 and 163. The global data for arcs are from Ref. 70 and represent a non-weighted global average. The maximum global average for arcs is from Ref. 176 and represents the average of the maximum $^{3}He/^{4}He$ ratios measured at a given locality.

study shows that the carbon contribution from assimilation in the overriding crust may be significant in some localities (Italy, Indonesia, Central America, Lesser Antilles), but an important factor affecting the C/S ratio and CO_2 source in arc volcanoes is the subducting slab. As with the isotope approach, more work is needed since the C/S ratio in volcanic gas discharges is also significantly affected by volcanic activity, the presence of accumulated carbon-rich exsolved vapor in magma reservoirs,[107] and degassing processes. Long-term records are thus needed to constrain the average and representative C/S ratio of a particular volcano.

8.8 Volcanic Release of CO_2 over Geologic Time

The modern-day volcanic carbon flux is a snapshot in time. We have shown that the modern-day flux of volcanic carbon could be dominated by the diffuse degassing of volcanic regions and large calderas (Figure 8.3b). Equally important for the global volcanic flux are a number of large volcanic point sources that represent Earth's most active volcanoes (Figure 8.3a); these volcanoes are in a range of geologic settings (arc, ocean island/mantle plume, continental rift).

Over 1-Ma timescales, the flux of volcanic carbon to Earth's surface is counteracted by the drawdown of CO_2 by silicate weathering and the associated precipitation of marine carbonates, as well as the burial of organic carbon. Perturbations to carbon outgassing are compensated for by changes in the rate of silicate weathering (which is enhanced under conditions of high pCO_2 and atmosphere temperature), keeping the surface reservoir approximately in balance. There have been periods through Earth history, however, when volcanism has been enhanced, causing perturbations to atmospheric CO_2 that have persisted for a range of timescales. Although our study of modern volcanic carbon fluxes tells us little about the carbon cycle response to such perturbations in Earth's past, there are insights to be gained from modern observations of the magnitude of the flux from individual volcanoes and from larger regions, the nature of the flux (direct or diffuse), and its variability with time.

The processes of subduction, deep carbonated eclogite melting,[5] and fluid addition to the subcontinental lithosphere from the convecting asthenosphere over time have led to the subcontinental lithosphere becoming a large carbon sink.[183] Over Earth's past, supercontinents have accreted and broken apart. It has been recognized that periods of greenhouse climate correlate with supercontinents in the geological record,[133,184] and this has been attributed to the prevalence of high-flux continental arc volcanoes, which may capture carbon not only from the downgoing slabs, but also from the devolatilization of carbonate platforms in the overlying continental crust. In the Cretaceous, for example, Gondwana's breakup led to the closure of the Tethys Ocean, accretion and subduction of marine carbonate platforms and the formation of a long subduction zone that may have been an important source of global volcanic CO_2[4,172,185] (reviewed further in Chapter 11).

The results of our modern-day volcanic CO_2 studies have shown, however, that the continental rifts themselves may also be important sources of carbon outgassing, which may in fact be larger than the surrounding continental arcs, certainly enhancing CO_2 output and warming during the initial stages of continental breakup and providing a way for short-term tectonics and volcanism to impact climate.[183]

8.9 Synthesis

Considerable progress has been made in the last decade in quantifying CO_2 emissions from volcanic areas worldwide. Technological advances, including widespread use of miniturized UV spectometer systems and Multi-GAS instruments, have resulted in a greater

number of CO_2 measurements. Volcanic CO_2 emissions have been measured for a few decades, which is short in terms of the eruptive cycles at many of Earth's volcanoes. Measurements are heavily biased toward eruptive periods, and average emissions for some active volcanoes are decreasing as longer records become available. Global satellite studies of decadal-scale SO_2 emission from Earth's most active volcanoes, when combined with a complete C/S data set, will allow for an accurate estimate of persistent CO_2 degassing in the near future. We suggest the highest 10–20 SO_2-emitting volcanoes be prioritized for measurement as these volcanoes may dominate the total CO_2 output from active volcanoes. CO_2 emissions from volcanoes with SO_2 output below satellite detection limits are not as well quantified, yet the emissions from these sources could be significant at a global scale. More work is needed to determine both the magnitude of these emissions and how widespread these volcanoes are globally.

Our knowledge of diffuse degassing at active and dormant volcanoes continues to improve. The distribution of diffuse fluxes is similar to the distribution of CO_2 emissions from active volcanoes, and there are several areas worldwide with large, intrusive magma bodies where the diffuse fluxes are globally significant. More effort is needed to quantify emissions in these vast regions, as well as in the biggest 10–20 hydrothermal areas globally.

We summarize two decades of measurements at some well-studied volcanic systems that demonstrate that the slow release of CO_2 from inactive or dormant volcanoes rivals that of active volcanoes when considered over long timescales. Regional volcanic CO_2 fluxes are heavily influenced by individual volcanoes becoming more or less active, and thus measurements must be maintained over decadal scales to assess this variability quantitatively.

Vent emissions from active volcanoes vary by orders of magnitude over short (days to years) timescales, whereas diffuse emissions are largely buffered and show steadier rates through time. This variability is largely controlled by the plumbing of the volcanic systems. Active mafic volcanoes often host an open vent (with a free magma surface or lava lake) and volatiles are delivered rapidly to the surface, allowing for rapid variability. Larger silicic magmatic systems, sustained by the underplating of basaltic magmas, are characterized by steady diffuse outgassing over time.

Continuous Multi-GAS monitoring has improved eruption forecasting potential by showing that eruptions at mafic volcanoes are often preceded by an increase in the C/S gas ratio in the days to months prior to eruption. Long-term monitoring of some volcanoes shows months-long changes in the C/S ratio prior to eruption, and sometimes in the absence of eruption, which may accompany decompression of magma as it migrates from the lower to the upper crust. These later cases were often accompanied by the lack of a visible plume or SO_2 emission, and thus more work is needed to identify when such plumes exist.

A fundamental challenge in carbon science is to constrain the deep global carbon budget and how much of the surface-derived carbon is recycled back into the mantle. In arc

volcanoes, the source of volcanic CO_2 is a combination of mantle and slab-derived C with a potentially significant crustal component, at least in some locations. A more complete understanding of the carbon balance at subduction zones requires quantification of the amount of carbon in the subducted lithologies. The pathways and fate of subducted carbon beyond the zones of arc magma generation determine where this carbon is ultimately stored and how it could potentially affect processes in different tectonic settings through time. While great progress has been made in terms of the quantification of carbon emissions from volcanic regions, more work is needed to constrain our understanding of the balance between surface and deep carbon through geologic time.

8.10 Limits to Knowledge of Volcanic Carbon

For all of the new data and understanding, significant gaps remain in our knowledge. Some of these gaps may persist, limited by technology or the logistics of measurement. The first gap in knowledge is caused by the lack of data for key volcanic systems. These include important point sources of volcanic SO_2, such as Bagana, Tavurvur, and Manam (Papua New Guinea), as well as Aoba/Ambae (Vanuatu). Longer records are needed at most volcanoes globally to assess variability over decadal scales in relation to eruptive cycles and periods of repose. Better quantification of hydrothermal diffuse degassing is needed in areas already identified to be large CO_2 emitters, such as Yellowstone (USA), the EAR (Africa), and the TVZ (New Zealand), and more measurements are needed in the vast regions of Southeast Asia and South America, where large hydrothermal systems exist. Further measurements are also needed in rifts such as the Eger Rift (Germany) and the Basin and Range (USA). Many of these targets are accessible, but require dedicated efforts over many years, and they would benefit from further technological development and improved measurement strategies. In this category we include global MORs and submarine back-arcs, for which only limited data exist. These measurements are logistically challenging, and it is unlikely that significant progress can be made without considerable effort and expense. More tractable approaches use primary melt geochemistry (Chapter 9) and geodynamic models to reconstruct CO_2 budgets of submarine regions.

A fraction of the CO_2 released from the degassing of silicate melts and directly from the mantle or crust may be dissolved into groundwaters and transported through aquifers, delivered to the surface via cold springs. This source of CO_2 has not been quantified in most volcanic regions. Studies from central Italy have shown that significant quantities of inorganic carbon are dissolved in aquifers, derived from a mixture of biological sources, carbonate dissolution, and deep carbon sources.

Using the DECADE results thus far, it is possible to relate slab inputs at arc volcanoes to volcanic gas C/S signatures and to identify arcs and individual volcanoes where CO_2-rich crustal fluids play a significant role. However, much work remains to be done in linking magma geochemistry to the composition of outgassing fluids and for understanding the fate of devolatilized carbon in the mantle wedge and the behavior and dynamics of

magma- and crust-derived fluids in vertically protracted, complex magma reservoirs in the crust. These studies require a range of approaches, including thermodynamic and analog modeling and building detailed databases of magma geochemistry and volcanic gas composition for detailed empirical comparisons. Understanding the amount of carbon returned to the deep mantle is of fundamental importance to the carbon budget of Earth through time. Linking our understanding of the present-day volcanic carbon budget to studies of plate tectonic reconstructions is an aim for the future and is explored further by Lee et al. in Chapter 11 of this book.

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Questions for the Classroom

1 How can we improve our estimates of volcanic CO_2 emissions?
2 How can we quantify the CO_2 contribution to the atmosphere from magmatic intrusions that do not lead to eruption and how can we better combine geophysical and geochemical studies to identify when such emissions occur?
3 What methods can advance our estimation of hydrothermal CO_2 emissions?
4 How can we improve our knowledge of how many volcanoes are emitting CO_2 in the absence of significant quantities of SO_2?
5 How significant is CO_2 degassing from magmas located at the base of the crust and how would we distinguish this from shallower magma degassing?
6 Can CO_2 degas from the mantle without the presence of magma?

List of Online Resources

- Eruptions, Earthquakes & Emissions Application Citation: Global Volcanism Program, 2016. Eruptions, Earthquakes & Emissions, v. 1.0 (Mobile application software). Smithsonian Institution. Accessed March 2018, retrieved from http://volcano.si.axismaps.io
- Carn, S. A., Fioletov, V. E., McLinden, C. A., Li, C. & Krotkov, N. A. A decade of global volcanic SO_2 emissions measured from space. *Scientific Reports* 7, 44095 (2017). Direct link: www.nature.com/articles/srep44095#supplementary-information
- MaGa database: www.magadb.net
- EarthChem Library: www.earthchem.org/library

References

1. Kump, L. R. & Barley, M. E. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature* **448**, 1033–1036 (2007).
2. Berner, R. A. *The Phanerozoic Carbon Cycle: CO_2 and O_2* (Oxford University Press, 2004).
3. Dasgupta, R. Ingassing, storage, and outgassing of terrestrial carbon through geologic time. In: *Carbon in Earth, Vol. 75: Reviews in Mineralogy & Geochemistry* (eds. R. M. Hazen, A. P. Jones & J. A. Baross), 183–229 (Mineralogical Society of America, 2013).
4. Mason, E., Edmonds, M. & Turchyn, A. V. Remobilization of crustal carbon may dominate volcanic arc emissions. *Science* **357**, 290–294 (2017).
5. Dasgupta, R. & Hirschmann, M. M. The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters* **298**, 1–13 (2010).
6. Wood, B. J. Carbon in the core. *Earth and Planetary Science Letters* **117**, 593–607 (1993).
7. Berner, R. A. Atmospheric carbon dioxide levels over Phanerozoic time. *Science* **249**, 1382–1386 (1990).
8. Symonds, R. B., Rose, W. I., Bluth, G. S. & Gerlach, T. M. Volcanic gas studies: methods, results, and applications. In: *Volatiles in Magmas, Vol. 30* (eds. M. R. Carroll and J. R. Holloway), 1–60 (Mineralogical Society of America, 1994).
9. McCormick, B. T., Edmonds, M., Mather, T. A. & Carn, S. A. First synoptic analysis of volcanic degassing in Papua New Guinea. *Geochemistry, Geophysics, Geosystems* **13**, 3 (2012).
10. Gal, F., Leconte, S. & Gadalia, A. The "Escarot" gas seep, French Massif Central: CO_2 discharge from a quiescent volcanic system – characterization and quantification of gas emissions. *Journal of Volcanology and Geothermal Research* **353**, 68–82 (2018).
11. Gerlach, T. M., Doukas, M. P., McGee, K. A. & Kessler, R. Airborne detection of diffuse carbon dioxide emissions at Mammoth Mountains, California. *Geophysical Research Letters* **26**, 3661–3664 (1999).
12. James, E. R., Manga, M. & Rose, T. P. CO_2 degassing in the Oregon cascades. *Geology* 27, 823–826 (1999).
13. Caliro, S., Chiodini, G., Avino, R., Cardellini, C. & Frondini, F. Volcanic degassing at Somma-Vesuvio (Italy) inferred by chemical and isotopic signatures of groundwater. *Applied Geochemistry* **20**, 1060–1076 (2005).

14. Fischer, T. P. DEep CArbon DEgassing: the Deep Carbon Observatory DECADE Initiative. *Mineralogical Magazine* **77**, 1089 (2013).
15. Burton, M., Sawyer, G. M. & Granieri, D. Deep carbon emissions from volcanoes. In: *Carbon in Earth. Reviews in Mineralogy and Geochemistry* (eds. R. M. Hazen, A. P. Jones & J. A. Baross), 323–354 (Mineralogical Society of America, 2013).
16. Chiodini, G., Cioni, R., Guidi, M., Raco, B. & Marini, L. Soil CO_2 flux measurements in volcanic and geothermal areas. *Applied Geochemistry* **13**, 543–552 (1998).
17. Gerlach, T. M. et al. Application of the LI-COR CO_2 analyzer to volcanic plumes: a case study, volcan Popocatepetl, Mexico, June 7 and 10, 1995. *Journal of Geophysical Research* **102**, 8005–8019 (1997).
18. Shinohara, H. Excess degassing from volcanoes and its role on eruptive and intrusive activity. *Reviews of Geophysics* **46**, RG4005 (2008).
19. McGonigle, A. J. S., Oppenheimer, C., Galle, B., Mather, T. A. & Pyle, D. M. Walking traverse and scanning DOAS measurements of volcanic gas emission rates. *Geophysical Research Letters* **29**, 1985 (2002).
20. Galle, B. et al. A miniaturised ultraviolet spectrometer for remote sensing of SO_2 fluxes: a new tool for volcano surveillance. *Journal of Volcanology and Geothermal Research* **119**, 241–254 (2003).
21. Allard, P. et al. Eruptive and diffuse emissions of CO_2 from Mount Etna. *Nature* 351, 387–391 (1991).
22. Carn, S. A. & Bluth, G. J. S. Prodigious sulfur dioxide emissions from Nyamuragira volcano, DR Congo. *Geophysical Research Letters* **30**, 2211 (2003).
23. Allard, P., Burton, M., Sawyer, G. & Bani, P. Degassing dynamics of basaltic lava lake at a top-ranking volatile emitter: Ambrym volcano, Vanuatu arc. *Earth and Planetary Science Letters* **448**, 69–80 (2016).
24. Shinohara, H. A new technique to estimate volcanic gas composition; plume measurements with a portable multi-sensor system. *Journal of Volcanology and Geothermal Research* **143**, 319–333 (2005).
25. Aiuppa, A., Federico, C., Giudice, G. & Gurrieri, S. Chemical mapping of a fumarolic field: La Fossa Crater, Vulcano Island (Aeolian Islands, Italy). *Geophysical Research Letters* **32**, 4 (2005).
26. Kern, C., Werner, C., Elias, T., Sutton, A. J. & Lübcke, P. Applying UV cameras for SO_2 detection to distant or optically thick volcanic plumes. *Journal of Volcanology and Geothermal Research* **262**, 80–89 (2013).
27. Mori, T. et al. Effect of UV scattering on SO_2 emission rate measurements. *Geophysical Research Letters* **33**, L17315 (2006).
28. Kelly, P. J. et al. Long-term autonomous volcanic gas monitoring with Multi-GAS at Mount St. Helens, Washington, and Augustine Volcano. *Alaska AGU Fall Meeting Abstracts*, V23B-3095 (2015).
29. Kelly, P. J. et al. Rapid chemical evolution of tropospheric volcanic emissions from Redoubt Volcano, Alaska, based on observations of ozone and halogen-containing gases. *Journal of Volcanology and Geothermal Research* **259**, 317–333 (2013).
30. Moussallam, Y. et al. Hydrogen emissions from Erebus volcano, Antarctica. *Bulletin of Volcanology* **74**, 2109–2120 (2012).
31. Gerlach, T. M., McGee, K. A., Elias, T., Sutton, A. J. & Doukas, M. P. Carbon dioxide emission rate of Kilauea Volcano: implications for primary magma and the summit reservoir. *Journal of Geophysical Research: Solid Earth* **107**, 2189 (2002).
32. Werner, C., Christenson, B. W., Hagerty, M. & Britten, K. Variability of volcanic gas emissions during a crater lake heating cycle at Ruapehu Volcano, New Zealand. *Journal of Volcanology and Geothermal Research* **154**, 291–302 (2006).

33. Werner, C. et al. Variability of passive gas emissions, seismicity, and deformation during crater lake growth at White Island Volcano, New Zealand, 2002–2006. *Journal of Geophysical Research: Solid Earth* **113**, B01204 (2008).
34. Werner, C., Evans, W. C., Poland, M., Tucker, D. S. & Doukas, M. P. Long-term changes in quiescent degassing at Mount Baker Volcano, Washington, USA; evidence for a stalled intrusion in 1975 and connection to a deep magma source. *Journal of Volcanology and Geothermal Research* **186**, 379–386 (2009).
35. McGonigle, A. J. S. et al. Unmanned aerial vehicle measurements of volcanic carbon dioxide fluxes. *Geophysical Research Letters* **35**, L06303 (2008).
36. Mori, T. et al. Volcanic plume measurements using a UAV for the 2014 Mt. Ontake eruption. *Earth Planets and Space* **68**, 49 (2016).
37. Shinohara, H. Composition of volcanic gases emitted during repeating Vulcanian eruption stage of Shinmoedake, Kirishima volcano, Japan. *Earth Planets and Space* **65**, 667–675 (2013).
38. Aiuppa, A. et al. New ground-based lidar enables volcanic CO_2 flux measurements. *Scientific Reports* **5**, 13614 (2015).
39. Queisser, M., Granieri, D. & Burton, M. A new frontier in CO_2 flux measurements using a highly portable DIAL laser system. *Scientific Reports* **6**, 33834 (2016).
40. Werner, C., Brantley, S. L. & Boomer, K. CO_2 Emissions related to the Yellowstone volcanic system 2. Statistical sampling, total degassing, and transport mechanisms. *Journal of Geophysical Research* **105**, 10831-10846 (2000).
41. Cardellini, C., Chiodini, G. & Frondini, F. Application of stochastic simulation to CO_2 flux from soil: mapping and quantification of gas release. *Journal of Geophysical Research: Solid Earth* **108**, 2425 (2003).
42. Mazot, A. & Bernard, A. CO_2 degassing from volcanic lakes. In: *Volcanic Lakes* (eds. D. Rouwet, B. Christenson, F. Tassi & J. Vandemeulebrouck), 341–354 (Springer, 2015).
43. Pérez, N. M. et al. Global CO_2 emission from volcanic lakes. *Geology* **39**, 235–238 (2011).
44. Werner, C. et al. Monitoring volcanic hazard using eddy covariance at Solfatara volcano, Naples, Italy. *Earth and Planetary Science Letters* **210**, 561–577 (2003).
45. Werner, C., Wyngaard, J. C. & Brantley, S. Eddy-correlation measurement of hydrothermal gases. *Geophysical Research Letters* **27**, 2925–2929 (2000).
46. Lewicki, J., Fischer, M. L. & Hilley, G. E. Six-week time series of eddy covariance CO_2 flux at Mammoth Mountain, California: performance evaluation and role of meteorological forcing. *Journal of Volcanology and Geothermal Research* **171**, 178–190 (2008).
47. Lewicki, J. L., Hilley, G. E., Dobeck, L. & Marino, B. D. V. Eddy covariance imaging of diffuse volcanic CO_2 emissions at Mammoth Mountain, CA, USA. *Bulletin of Volcanology* **74**, 135–141 (2012).
48. Lewicki, J. L., Kelly, P. J., Bergfeld, D., Vaughan, R. G. & Lowenstern, J. B. Monitoring gas and heat emissions at Norris Geyser Basin, Yellowstone National Park, USA based on a combined eddy covariance and Multi-GAS approach. *Journal of Volcanology and Geothermal Research* **347**, 312–326 (2017).
49. Lewicki, J. L. & Hilley, G. E. Multi-scale observations of the variability of magmatic CO_2 emissions, Mammoth Mountain, CA, USA. *Journal of Volcanology and Geothermal Research* **284**, 1–15 (2014).
50. Rose, T. P., Lee Davisson, M. & Criss, R. E. Isotope hydrology of voluminous cold springs in fractured rock from an active volcanic region, northeastern California. *Journal of Hydrology* **179**, 207–236 (1996).

51. Aiuppa, A. et al. Forecasting Etna eruptions by real-time observation of volcanic gas composition. *Geology* **35**, 1115–1118 (2007).
52. Galle, B. et al. Network for Observation of Volcanic and Atmospheric Change (NOVAC) – a global network for volcanic gas monitoring: network layout and instrument description. *Journal of Geophysical Research –Atmospheres* **115**, D05304 (2010).
53. Aiuppa, A. et al. Unusually large magmatic CO_2 gas emissions prior to a basaltic paroxysm. *Geophysical Research Letters* **37**, L17303 (2010).
54. Aiuppa, A. et al. Total volatile flux from Mount Etna. *Geophysical Research Letters* **35**, L24302 (2008).
55. de Moor, J. M. et al. Short-period volcanic gas precursors to phreatic eruptions: insights from Poás Volcano, Costa Rica. *Earth and Planetary Science Letters* **442**, 218–227 (2016).
56. de Moor, J. M. et al. A new sulfur and carbon degassing inventory for the Southern Central American volcanic arc: the importance of accurate time-series datasets and possible tectonic processes responsible for temporal variations in arc-scale volatile emissions. *Geochemistry, Geophysics, Geosystems* **18**, 4437–4468 (2017).
57. Shinohara, H. Volatile flux from subduction zone volcanoes: Insights from a detailed evaluation of the fluxes from volcanoes in Japan. *Journal of Volcanology and Geothermal Research* **268**, 46–63 (2013).
58. Ilyinskaya, E. et al. Degassing regime of Hekla volcano 2012–2013. *Geochimica et Cosmochimica Acta* **159**, 80–99 (2015).
59. Werner, C. et al. Magmatic degassing, lava dome extrusion, and explosions from Mount Cleveland volcano, Alaska, 2011–2015: insight into the continuous nature of volcanic activity over multi-year timescales. *Journal of Volcanology and Geothermal Research* **337**, 98–110 (2017).
60. Pedone, M. et al. Volcanic CO_2 flux measurement at Campi Flegrei by tunable diode laser absorption spectroscopy. *Bulletin of Volcanology* **76**, 13 (2014).
61. Pedone, M. et al. Tunable diode laser measurements of hydrothermal/volcanic CO_2 and implications for the global CO_2 budget. *Solid Earth* **5**, 1209–1221 (2014).
62. Pedone, M. et al. Total (fumarolic plus diffuse soil) CO_2 output from Furnas volcano. *Earth Planets and Space* **67**, 12 (2015).
63. Fiorani, L. et al. Early detection of volcanic hazard by lidar measurement of carbon dioxide. *Natural Hazards* **83**, S21–S29 (2016).
64. Queisser, M., Burton, M., Allan, G. R. & Chiarugi, A. Portable laser spectrometer for airborne and ground-based remote sensing of geological CO_2 emissions. *Optics Letters* **42**, 2782–2785 (2017).
65. Werner, C. et al. Degassing of CO_2, SO_2, and H_2S associated with the 2009 eruption of Redoubt Volcano, Alaska. *Journal of Volcanology and Geothermal Research* **259**, 270–284 (2013).
66. Schwandner, F. M. et al. Spaceborne detection of localized carbon dioxide sources. *Science* **358**, eaam5782 (2017).
67. Gerlach, T. M. Present-day carbon dioxide emissions from volcanos. *Earth in Space* **4**, 5 (1991).
68. Brantley, S. L. & Koepenick, K. W. Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes. *Geology* **23**, 933–936 (1995).
69. Williams, S. N., Schaefer, S. J., Calvache, V. M. L. & Lopez, D. Global carbon dioxide emission to the atmosphere by volcanoes. *Geochimica et Cosmochimica Acta* **56**, 1765–1770 (1992).

70. Hilton, D. R., Fischer, T. & Marty, B. Noble gases and volatile recycling at subduction zones. *Reviews in Mineralogy and Geochemistry* **47**, 319–370 (2002).
71. Andres, R. J. et al. A summary of sulfur-dioxide emission rate measurements from Guatemalan volcanos. *Bulletin of Volcanology* 55, 379–388 (1993).
72. Stoiber, R. E., Williams, S. N. & Huebert, B. Annual contribution of sulfur dioxide to the atmosphere by volcanoes. *Journal of Volcanology and Geothermal Research* **33**, 1–8 (1987).
73. Aiuppa, A., Fischer, T. P., Plank, T., Robidoux, P. & Di Napoli, R. Along-arc, inter-arc and arc-to-arc variations in volcanic gas CO_2/S-T ratios reveal dual source of carbon in arc volcanism. *Earth Science Reviews* **168**, 24–47 (2017).
74. Fischer, T. P. Fluxes of volatiles (H_2O, CO_2, N_2, Cl, F) from arc volcanoes. *Geochemical Journal* **42**, 21–38 (2008).
75. Carn, S. A., Fioletov, V. E., McLinden, C. A., Li, C. & Krotkov, N. A. A decade of global volcanic SO_2 emissions measured from space. *Scientific Reports* **7**, 44095 (2017).
76. Siebert, L., Simkin, T. & Kimberly, P. *Volcanoes of the World*, 3rd edn. (University of California Press, 2010). https://doi.org/10.5479/si.GVP.VOTW4-2013.
77. Carn, S. A., Clarisse, L. & Prata, A. J. Multi-decadal satellite measurements of global volcanic degassing. *Journal of Volcanology and Geothermal Research* **311**, 99–134 (2016).
78. Torgersen, T. Terrestrial helium degassing fluxes and the atmospheric helium budget: Implications with respect to the degassing processes of continental crust. *Chemical Geology: Isotope Geoscience Section* **79**, 1–14 (1989).
79. Sano, Y. & Williams, S. N. Fluxes of mantle and subducted carbon along convergent plate boundaries. *Geophysical Research Letters* **23**, 2749–2752 (1996).
80. Crisp, J. A. Rates of magma emplacement and volcanic output. *Journal of Volcanology and Geothermal Research* **20**, 177–211 (1984).
81. Dimalanta, C., Taira, A., Yumul, G. P., Tokuyama, H. & Mochizuki, K. New rates of western Pacific island arc magmatism from seismic and gravity data. *Earth and Planetary Science Letters* **202**, 105–115 (2002).
82. Reymer, A. & Schubert, G. Phanerozoic addition rates to the continental crust and crustal growth. *Tectonics* **3**, 63–77 (1984).
83. Bianchi, D. et al. Low helium flux from the mantle inferred from simulations of oceanic helium isotope data. *Earth and Planetary Science Letters* **297**, 379–386 (2010).
84. Kagoshima, T. et al. Sulphur geodynamic cycle. *Scientific Reports* **5**, 8330 (2015).
85. Siebert, L. & Simkin, T. Volcanoes of the world: an illustrated catalog of holocene volcanoes and their eruptions. *Smithsonian Institution. Global volcanism program digital information series, GVP-3* (https://doi.org/10.5479/si.GVP.VOTW4-2013) (2002).
86. Bobrowski, N. et al. Multi-component gas emission measurements of the active lava lake of Nyiragongo, DR Congo. *Journal of African Earth Sciences* **134**, 856–865 (2017).
87. Sawyer, G. M., Carn, S. A., Tsanev, V. I., Oppenheimer, C. & Burton, M. Investigation into magma degassing at Nyiragongo volcano, Democratic Republic of the Congo. *Geochemistry, Geophysics, Geosystems* **9**, Q02017 (2008).
88. Le Guern, F. Mechanism of energy-transfer in the lava lake of Niragongo (Zaire), 1959–1977. *Journal of Volcanology and Geothermal Research* **31**, 17–31 (1987).
89. Kazahaya, K. et al. Gigantic SO_2 emission from Miyakejima volcano, Japan, caused by caldera collapse. *Geology* **32**, 425–428 (2004).

90. Shinohara, H., Kazahaya, K., Saito, G., Fukui, K. & Odai, M. Variation of CO_2–SO_2 ratio in volcanic plumes of Miyakejima; stable degassing deduced from heliborne measurements. *Geophysical Research Letters* **30**, 4 (2003).
91. Doukas, M. P. & McGee, K. A. *A Compilation of Gas Emission-Rate Data from Volcanoes of Cook Inlet (Spurr, Crater Peak, Redoubt, Iliamna, and Augustine) and Alaska Peninsula (Douglas, Fourpeaked, Griggs, Mageik, Martin, Peulik, Ukinrek Maars, and Veniaminof), Alaska, from 1995–2006*. Open File Report, report number 2007-1400 (US Geological Survey, 2007).
92. Werner, C. A., Doukas, M. P. & Kelly, P. J. Gas emissions from failed and actual eruptions from Cook Inlet Volcanoes, Alaska, 1989–2006. *Bulletin of Volcanology* **73**, 155–173 (2011).
93. Kelly, P., Werner, C., Kem, C., Clor, L. E. & Doukas, M. A compilation of airborne gas emissions data from Alaskan volcanoes. *USGS Data Release* (2019).
94. Christenson, B. W. et al. Cyclic processes and factors leading to phreatic eruption events: insights from the 25 September 2007 eruption through Ruapehu Crater Lake, New Zealand. *Journal of Volcanology and Geothermal Research* **191**, 15–32 (2010).
95. Kilgour, G. N. et al. Timescales of magmatic processes at Ruapehu volcano from diffusion chronometry and their comparison to monitoring data. *Journal of Volcanology and Geothermal Research* **288**, 62–75 (2014).
96. Elias, T. & Sutton, A. J. *Volcanic Air Pollution Hazards in Hawaii. Fact Sheet No. 2017-3017* (US Geological Survey, 2017).
97. Global Volcanism Program. *Volcanoes of the World, v. 4.7.7* (Smithsonian Institution, 2013). https://doi.org/10.5479/si.GVP.VOTW4-2013.
98. Passarelli, L. & Brodsky, E. E. The correlation between run-up and repose times of volcanic eruptions. *Geophysical Journal International* **188**, 1025–1045 (2012).
99. Allard, P., Burton, M., Oskarsson, N., Michel, A. & Polacci, M. Chemistry and fluxes of magmatic gases driving the explosive trachyandesitic phase of Eyjafjallajökull 2010 eruption: constraints on degassing magma volumes and processes. In: *AGU Fall Meeting*, V53F-07 (AGU, 2010).
100. Gerlach, T. M., Westrich, H. R. & Symonds, R. B. Preeruption vapor in magma of the climactic Mount Pinatubo eruption: source of the giant stratospheric sulfur dioxide cloud. In: *Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines* (eds. C. G. Newhall & R. S. Punongbayan), 415–434 (University of Washington Press, 1996).
101. Hobbs, P. V., Tuell, J. P., Hegg, D. A., Radke, L. F. & Eltgroth, M. W. Particles and gases in the emissions from the 1980–1981 volcanic eruptions of Mt. St. Helens. *Journal of Geophysical Research* **87**, 11062–11086 (1982).
102. Scaillet, B. & Pichavant, M. Experimental constraints on volatile abundances in arc magmas and their implications for degassing processes. *Geological Society Special Publications* **213**, 23–52 (2003).
103. Gerlach, T. M. Volcanic versus anthropogenic carbon dioxide. *EOS Transactions* **92**, 201–208 (2011).
104. Holloway, J. R. Fluids in the evolution of granitic magma: consequences of finite CO_2 solubility. *Geological Society of America Bulletin* **87**, 1513–1518 (1976).
105. Christopher, T. E. et al. Crustal-scale degassing due to magma system destabilization and magma-gas decoupling at Soufriere Hills Volcano, Montserrat. *Geochemistry, Geophysics, Geosystems* **16**, 2797–2811 (2015).
106. Parmigiani, A., Faroughi, S., Huber, C., Bachmann, O. & Su, Y. Bubble accumulation and its role in the evolution of magma reservoirs in the upper crust. *Nature* **532**, 492–495 (2016).

107. Burgisser, A., Alletti, M. & Scaillet, B. Simulating the behavior of volatiles belonging to the C–O–H–S system in silicate melts under magmatic conditions with the software D-Compress. *Computers & Geosciences* **79**, 1–14 (2015).
108. Kilbride, B. M., Edmonds, M. & Biggs, J. Observing eruptions of gas-rich compressible magmas from space. *Nature Communications* **7**, 13744 (2016).
109. Wallace, P. J. Volcanic SO_2 emissions and the abundance and distribution of exsolved gas in magma bodies. *Journal of Volcanology and Geothermal Research* **108**, 85–106 (2001).
110. Kerrick, D. M. Present and past non-anthropogenic CO_2 degassing from the solid Earth. *Reviews of Geophysics* **39**, 565–585 (2001).
111. Morner, N. A. & Etiope, G. Carbon degassing from the lithosphere. *Global and Planetary Change* **33**, 185–203 (2002).
112. Mori, T. et al. Time-averaged SO_2 fluxes of subduction-zone volcanoes: example of a 32-year exhaustive survey for Japanese volcanoes. *Journal of Geophysical Research – Atmospheres* **118**, 8662–8674 (2013).
113. Stimac, J., Goff, F. & Goff, C. J. Intrusion-related geothermal systems. In: *The Encyclopedia of Volcanoes*, 2nd edn. (eds. H. Sigurdsson, B. Houghton, S. McNutt, H. Rymer & J. Stix), 799–822 (Academic Press, 2015).
114. Cardellini, C. et al. MAGA, a new database of gas natural emissions: a collaborative webenvironment for collecting data. *Geophysical Research Abstracts* **16**, EGU2014-13715 (2014).
115. Casadevall, T. J., Doukas, M. P., Neal, C. A., McGimsey, R. G. & Gardner, C. A. Emission rates of sulfur dioxide and carbon dioxide from Redoubt Volcano, Alaska during the 1989-1990 eruptions. *Journal of Volcanology and Geothermal Research* **62**, 519–530 (1994).
116. Werner, C. et al. Decadal-scale variability of diffuse CO_2 emissions and seismicity revealed from long-term monitoring (1995-2013) at Mammoth Mountain, California, USA. *Journal of Volcanology and Geothermal Research* **289**, 51–63 (2014).
117. Cardellini, C. et al. Monitoring diffuse volcanic degassing during volcanic unrests: the case of Campi Flegrei (Italy). *Scientific Reports* **7**, 15 (2017).
118. Aiuppa, A. et al. Volcanic gas plume data from Stromboli Volcano (Italy). Interdisciplinary Earth Data Alliance (IEDA). doi:10.1594/IEDA/100643.
119. Christenson, B. W., White, S., Britten, K. & Scott, B. J. Hydrological evolution and chemical structure of a hyper-acidic spring-lake system on Whakaari/White Island, NZ. *Journal of Volcanology and Geothermal Research* **346**, 180–211 (2017).
120. Bloomberg, S. et al. Soil CO_2 emissions as a proxy for heat and mass flow assessment, Taupō Volcanic Zone, New Zealand. *Geochemistry, Geophysics, Geosystems* **15**, 4885–4904 (2014).
121. Mazot, A. et al. CO_2 discharge from the bottom of volcanic Lake Rotomahana, New Zealand. *Geochemistry, Geophysics, Geosystems* **15**, 577–588 (2014).
122. Rissmann, C. et al. Surface heat flow and CO_2 emissions within the Ohaaki hydrothermal field, Taupo Volcanic Zone, New Zealand. *Applied Geochemistry* **27**, 223–239 (2012).
123. Werner, C. & Cardellini, C. Comparison of carbon dioxide emissions with fluid upflow, chemistry, and geologic structures at the Rotorua geothermal system, New Zealand. *Geothermics* **35**, 221–238 (2006).
124. Acocella, V., Di Lorenzo, R., Newhall, C. & Scandone, R. An overview of recent (1988 to 2014) caldera unrest: knowledge and perspectives. *Reviews of Geophysics* **53**, 896–955 (2015).

125. Newhall, C. G. & Dzurisin, D. *Historical Unrest at Large Calderas of the World. USGS Bulletin No. 1855* (USGS, 1988).
126. Chiodini, G. et al. Magmas near the critical degassing pressure drive volcanic unrest towards a critical state. *Nature Communications* **7**, 13712 (2016).
127. Seward, T. M. & Kerrick, D. M. Hydrothermal CO_2 emission from the Taupo volcanic zone, New Zealand. *Earth and Planetary Science Letters* **139**, 105–113 (1996).
128. Werner, C. & Brantley, S. CO_2 emissions from the Yellowstone volcanic system. *Geochemistry, Geophysics, Geosystems* **4**, 1061 (2003).
129. Hurwitz, S. & Lowenstern, J. B. Dynamics of the Yellowstone hydrothermal system. *Reviews of Geophysics* **52**, 375–411 (2014).
130. Chiodini, G. et al. CO_2 degassing and energy release at Solfatara volcano, Campi Flegrei, Italy. *Journal of Geophysical Research: Solid Earth* **106**, 16213–16221 (2001).
131. Chiodini, G. et al. Carbon dioxide Earth degassing and seismogenesis in central and southern Italy. *Geophysical Research Letters* **31**, L07615 (2004).
132. Frondini, F. et al. Measurement of CO_2 fluxes at regional scale: the case of Apennines, Italy. *Journal of the Geological Society* **176**, 408–416 (2019).
133. Lee, H. et al. Massive and prolonged deep carbon emissions associated with continental rifting. *Nature Geoscience* **9**, 145–149 (2016).
134. Hunt, J. A., Zafu, A., Mather, T. A., Pyle, D. M. & Barry, P. H. Spatially variable CO_2 degassing in the Main Ethiopian Rift: implications for magma storage, volatile transport, and rift-related emissions. *Geochemistry, Geophysics, Geosystems* **18**, 3714–3737 (2017).
135. World Energy Council. World Energy Resources 2016. www.worldenergy.org/wp-content/uploads/2016/10/World-Energy-Resources-Full-report-2016.10.03.pdf (2016).
136. Bibby, H., Caldwell, T. G., Davey, F. J. & Webb, T. H. Geophysical evidence on the structure of the Taupo Volcanic Zone and its hydrothermal circulation. *Journal of Volcanology and Geothermal Research* **68**, 29–58 (1995).
137. Chiodini, G. et al. Carbon dioxide diffuse emission and thermal energy release from hydrothermal systems at Copahue–Caviahue Volcanic Complex (Argentina). *Journal of Volcanology and Geothermal Research* **304**, 294–303 (2015).
138. Omenda, P. A. The geothermal activity of the East African Rift, in *Short Course IV on Exploration for Geothermal Resources, organized by UNU-GTP, KenGen and GDC* (ed. UNU-GTP). https://orkustofnun.is/gogn/unu-gtp-sc/UNU-GTP-SC-10-0204.pdf.
139. Moran, S. C. et al. *Instrumentation Recommendations for Volcano Monitoring at U.S. Volcanoes Under the National Volcano Early Warning System. US Geological Survey Scientific Investigations Report No. 2008-5114* (USGS, 2008).
140. Poland, M. P., Miklius, A., Jeff Sutton, A. & Thornber, C. R. A mantle-driven surge in magma supply to Kīlauea Volcano during 2003–2007. *Nature Geoscience* **5**, 295 (2012).
141. Werner, C. et al. Deep magmatic degassing versus scrubbing: elevated CO_2 emissions and C/S in the lead-up to the 2009 eruption of Redoubt Volcano, Alaska. *Geochemistry, Geophysics, Geosystems* **13**, Q03015 (2012).
142. Ilyinskaya, E. et al. Globally significant CO_2 emissions From Katla, a subglacial volcano in Iceland. *Geophysical Research Letters* **45**, 10332–10341 (2018).
143. Carn, S. A. Multi-Satellite Volcanic Sulfur Dioxide L4 Long-Term Global Database V2. doi:10.5067/MEASURES/SO2/DATA402.

144. Marty, B. & Tolstikhin, I. N. CO_2 fluxes from mid-ocean ridges, arcs and plumes. *Chemical Geology* 145, 233–248 (1998).
145. Aiuppa, A. et al. The 2007 eruption of Stromboli volcano: Insights from real-time measurement of the volcanic gas plume CO_2/SO_2 ratio. *Journal of Volcanology and Geothermal Research* **182**, 221–230 (2009).
146. Aiuppa, A. et al. A model of degassing for Stromboli Volcano. *Earth and Planetary Science Letters* **295**, 195–204 (2010).
147. Kazahaya, K., Shinohara, H. & Saito, G. Excessive degassing of Izu-Oshima Volcano; magma convection in a conduit. *Bulletin of Volcanology* **56**, 207–216 (1994).
148. Aiuppa, A. et al. Volcanic gas plume data from Etna Volcano (Italy). Interdisciplinary Earth Data Alliance (IEDA). doi:10.1594/IEDA/100643.
149. McGee, K. A. The structure, dynamics, and chemical composition of noneruptive plumes from Mount St. Helens, 1980–1988. *Journal of Volcanology and Geothermal Research* **51**, 269–282 (1992).
150. Chiodini, G. et al. Magma degassing as a trigger of bradyseismic events: the case of Phlegrean Fields (Italy). *Geophysical Research Letters* **30**, 1434 (2003).
151. Giggenbach, W. Variations in the carbon, sulfur and chlorine contents of volcanic gas discharges from White Island, New Zealand. *Bulletin of Volcanology* **39**, 15–27 (1975).
152. Fischer, T. P., Arehart, G. B., Sturchio, N. C. & Williams, S. N. The relationship between fumarole gas composition and eruptive activity at Galeras volcano, Colombia. *Geology* **24**, 531–534 (1996).
153. Dixon, J. E. & Stolper, E. M. An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. 2. Applications to degassing. *Journal of Petrology* **36**, 1633–1646 (1995).
154. Aiuppa, A. et al. Tracking Formation of a Lava Lake From Ground and Space: Masaya Volcano (Nicaragua), 2014–2017. *Geochemistry, Geophysics, Geosystems* **19**, 496–515 (2018).
155. Aiuppa, A. et al. A CO_2-gas precursor to the March 2015 Villarrica volcano eruption. *Geochemistry, Geophysics, Geosystems* **18**, 2120–2132 (2017).
156. de Moor, J. M. et al. Turmoil at Turrialba Volcano (Costa Rica): degassing and eruptive processes inferred from high-frequency gas monitoring. *Journal of Geophysical Research: Solid Earth* **121**, 5761–5775 (2016).
157. Pfeffer, M. et al. Ground-Based Measurements of the 2014–2015 Holuhraun Volcanic Cloud (Iceland). *Geosciences* **8**, 29 (2018).
158. Allard, P. Composition isotopique du carbonne dans les gas d'un volcan d'arc: le Momotombo (Nicaragua). *Comptes rendus de l'Académie des Sciences* **290**, 1525–1528 (1980).
159. Allard, P. Stable isotope composition of hydrogen, carbon and sulphur in magmatic gases from rift and island arc volcanoes. *Bulletin of Volcanology* **45**, 269–271 (1982).
160. Allard, P. The origin of hydrogen, carbon, sulfur, nitrogen and rare gases in volcanic exhalations: evidence from isotope geochemistry. In: *Forecasting Volcanic Events*, Vol. 1 (eds. H. Tazieff & J. Sabroux), 337–386 (Elsevier, 1983).
161. Marty, B. & Jambon, A. $C/^3He$ in volatile fluxes from the solid Earth; implications for carbon geodynamics. *Earth and Planetary Science Letters* **83**, 16–26 (1987).
162. Marty, B., Jambon, A. & Sano, Y. Helium isotopes and CO_2 in volcanic gases of Japan. *Chemical Geology* **76**, 25-40 (1989).
163. Cartigny, P., Jendrzejewski, N., Pineau, F., Petit, E. & Javoy, M. Volatile (C, N, Ar) variability in MORB and the respective roles of mantle source heterogeneity and

degassing: the case of the Southwest Indian Ridge. *Earth and Planetary Science Letters* **194**, 241–257 (2001).
164. Marty, B. & Zimmermann, L. Volatiles (He, C, N, Ar) in mid-ocean ridge basalts: assesment of shallow-level fractionation and characterization of source composition. *Geochimica et Cosmochimica Acta* **63**, 3619–3633 (1999).
165. Barry, P. H., Hilton, D. R., Füri, E., Halldórsson, S. A. & Grönvold, K. 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 (2014).
166. Gerlach, T. M. & Taylor, B. E. Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano. *Geochemica et Cosmochimica Acta* **54**, 2051–2058 (1990).
167. Fischer, T. P. et al. Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. *Nature* **459**, 77–80 (2009).
168. Barry, P. H. et al. Helium and carbon isotope systematics of cold "mazuku" CO_2 vents and hydrothermal gases and fluids from Rungwe Volcanic Province, southern Tanzania. *Chemical Geology* **339**, 141–156 (2013).
169. de Leeuw, G. A. M., Hilton, D. R., Fischer, T. P. & Walker, J. A. The He–CO_2 isotope and relative abundance characteristics of geothermal fluids in El Salvador and Honduras: new constraints on volatile mass balance of the Central American Volcanic Arc. *Earth and Planetary Science Letters* **258**, 132–146 (2007).
170. Shaw, A. M., Hilton, D. R., Fischer, T. P., Walker, J. A. & Alvarado, G. E. Contrasting He–C relationships in Nicaragua and Costa Rica: insights into C cycling through subduction zones. *Earth and Planetary Science Letters* **214**, 499–513 (2003).
171. Kelemen, P. B. & Manning, C. E. Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Sciences of the United States of America* **112**, E3997–E4006 (2015).
172. Lee, C. T. A. et al. Continental arc-island arc fluctuations, growth of crustal carbonates, and long-term climate change. *Geosphere* **9**, 21–36 (2013).
173. Troll, V. R. et al. Crustal CO_2 liberation during the 2006 eruption and earthquake events at Merapi volcano, Indonesia. *Geophysical Research Letters* **39**, L11302 (2012).
174. Carter, L. B. & Dasgupta, R. Effect of melt composition on crustal carbonate assimilation: implications for the transition from calcite consumption to skarnification and associated CO_2 degassing. *Geochemistry, Geophysics, Geosystems* **17**, 3893–3916 (2016).
175. Deegan, F. M. et al. Magma-carbonate interaction processes and associated CO_2 release at Merapi volcano, Indonesia: insights from experimental petrology. *Journal of Petrology* **51**, 1027–1051 (2010).
176. Sano, Y. & Fischer, T. P. The analysis and interpretation of noble gases in modern hydrothermal systems. In: *Noble Gases as Geochemical Tracers* (ed. P. Burnard), 249–317 (Springer Verlag, 2013).
177. Ray, M. C., Hilton, D. R., Munoz, J., Fischer, T. P. & Shaw, A. M. The effects of volatile recycling, degassing and crustal contamination on the helium and carbon geochemistry of hydrothermal fluids from the Southern Volcanic Zone of Chile. *Chemical Geology* **266**, 38–49 (2009).
178. van Soest, M. C., Hilton, D. R. & Kreulen, R. Tracing crustal and slab contributions to arc magmatism in the Lesser Antilles island arc using helium and carbon relationships in geothermal fluids. *Geochim.Cosmochim. Acta* **62**, 3323–3335 (1998).

179. Evans, W. C. et al. *Aleutian Arc Geothermal Fluids: Chemical Analyses of Waters and Gases. US Geological Survey Data release* (USGS, 2015).
180. Motyka, R. J., Liss, S. A., Nye, C. J. & Moorman, M. A. *Geothermal Resources of the Aleutian Arc* (Alaska Division of Geological & Geophysical Surveys, 1994).
181. Oppenheimer, C., Fischer, T. P. & Scaillet, B. Volcanic degassing: process and impact. In: *Treatise on Geochemistry*, 2nd edn. (ed. K. K. Turekian), 111–179 (Elsevier, 2014).
182. Symonds, R. B. et al. *Scrubbing Masks Magmatic Degassing during Repose at Cascade-Range and Aleutian-Arc Volcanoes. Open-File Report 2003-435* (USGS, 2003).
183. Foley, S. F. & Fischer, T. P. An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nature Geoscience* **10**, 897–902 (2017).
184. McKenzie, N. R. et al. Continental arc volcanism as the principal driver of icehouse-greenhouse variability. *Science* **352**, 444–447 (2016).
185. Lee, C. T. A., Thurner, S., Paterson, S. & Cao, W. R. The rise and fall of continental arcs: interplays between magmatism, uplift, weathering, and climate. *Earth and Planetary Science Letters* **425**, 105–119 (2015).
186. Allard, P. et al. Prodigious emission rates and magma degassing budget of major, trace and radioactive volatile species from Ambrym basaltic volcano, Vanuatu island Arc. *Journal of Volcanology and Geothermal Research* **322**, 119–143 (2016).
187. Mailik, N. Temperature and gas composition of the Avachinsky volcano fumaroles (Kamchatka) in 2013–2017. In: *13th CCVG-IAVCEI Gas Workshop* (CCVG-IAV-CEI, 2017).
188. Burton, M. et al. New constraints on volcanic CO_2 emissions from Java, Indonesia. *Geophysical Research Abstracts* **20**, EGU2018-15195 (2018).
189. Taran, Y. et al. Gas emissions from volcanoes of the Kuril Island Arc (NW Pacific): geochemistry and fluxes. *Geochemistry, Geophysics, Geosystems* **19**, 1859–1880 (2018).
190. Aiuppa, A. et al. First determination of magma-derived gas emissions from Bromo volcano, eastern Java (Indonesia). *Journal of Volcanology and Geothermal Research* **304**, 206–213 (2015).
191. Tamburello, G. et al. Intense magmatic degassing through the lake of Copahue volcano, 2013–2014. *Journal of Geophysical Research: Solid Earth* **120**, 6071–6084 (2015).
192. Bani, P. et al. Dukono, the predominant source of volcanic degassing in Indonesia, sustained by a depleted Indian-MORB. *Bulletin of Volcanology* **80**, 5 (2017).
193. Battaglia, A. et al. The magmatic gas signature of Pacaya volcano, with implications for the volcanic CO_2 flux from Guatemala. *Geochemistry, Geophysics, Geosystems* **19**, 667–692 (2018).
194. Gerlach, T. M., McGee, K. A. & Doukas, M. P. Emission rates of CO_2, SO_2, and H_2S, scrubbing, and preeruption excess volatiles at Mount St. Helens, 2004–2005. In: *A Volcano Rekindled: The Renewed Eruption of Mount St. Helens, 2004–2006* (eds. W. E. Scott, D. R. Sherrod & P. H. Stauffer), 554–571 (2008).
195. Aiuppa, A. et al. First volatile inventory for Gorely volcano, Kamchatka. *Geophysical Research Letters* **39**, L06307 (2012).
196. Gunawan, H. et al. New insights into Kawah Ijen's volcanic system from the wet volcano workshop experiment. *Geological Society, London, Special Publications* **437**, 35 (2016).
197. Sutton, A. J. & Elias, T. One hundred volatile years of volcanic gas studies at the Hawaiian Volcano Observatory. In: *Characteristics of Hawaiian Volcanoes. US*

Geological Survey Professional Paper 1801 (eds. M. P. Poland, T. J. Takahashi & C. M. Landowski), 295–320 (USGS, 2014).
198. Allard, P. *Isotope Geochemistry and Origins of Water, Carbon and Sulfur in Volcanic Gases: Rift Zones, Continental Margins and Island Arcs* (Paris VII University, 1986).
199. Bani, P. et al. First measurement of the volcanic gas output from Anak Krakatau, Indonesia. *Journal of Volcanology and Geothermal Research* **302**, 237–241 (2015).
200. Lopez, T. et al. Geochemical constraints on volatile sources and subsurface conditions at Mount Martin, Mount Mageik, and Trident Volcanoes, Katmai Volcanic Cluster, Alaska. *Journal of Volcanology and Geothermal Research* **347**, 64–81 (2017).
201. Burton, M. R., Oppenheimer, C., Horrocks, L. A. & Francis, P. W. Remote sensing of CO_2 and H_2O emission rates from Masaya volcano, Nicaragua. *Geology* **28**, 915–918 (2000).
202. Martin, R. S. et al. A total volatile inventory for Masaya Volcano, Nicaragua. *Journal of Geophysical Research* **115**, 1–12 (2010).
203. Allard, P., Metrich, N. & Sabroux, J. C. Volatile and magma supply to standard eruptive activity at Merapi volcano, Indonesia. In: *EGU General Assembly 2011*, Vol. 13, EGU2011-13522 (EGU, 2011).
204. Dzurisin, D. et al. The 2004–2008 dome-building eruption at Mount St. Helens, Washington: epilogue. *Bulletin of Volcanology* **77**, 17 (2015).
205. Taran, Y. A. Geochemistry of volcanic and hydrothermal fluids and volatile budget of the Kamchatka–Kuril subduction zone. *Geochimica et Cosmochimica Acta* **73**, 1067–1094 (2009).
206. Lages J. et al. Volcanic CO_2 and SO_2 emissions along the Colombia Arc Segment (Northern Volcanic Zone). In: *Geophysical Research Abstracts*, Vol. 20, EGU2018-1301 (2018).
207. Bobrowski, N. et al. Plume composition and volatile flux of Nyamulagira volcano, Democratic Republic of Congo, during birth and evolution of the lava lake, 2014–2015. *Bulletin of Volcanology* **79**, 90 (2017).
208. Lyons, J. J. et al. Long period seismicity and very long period infrasound driven by shallow magmatic degassing at Mount Pagan, Mariana Islands. *Journal of Geophysical Research: Solid Earth* **121**, 188–209 (2016).
209. Tulet, P. et al. First results of the Piton de la Fournaise STRAP 2015 experiment: multidisciplinary tracking of a volcanic gas and aerosol plume. *Atmospheric Chemistry and Physics* **17**, 5355–5378 (2017).
210. Aiuppa, A. et al. Gas measurements from the Costa Rica–Nicaragua volcanic segment suggest possible along-arc variations in volcanic gas chemistry. *Earth and Planetary Science Letters* **407**, 134-147 (2014).
211. Maldonado, L. F. M., Inguaggiato, S., Jaramillo, M. T., Valencia, G. G. & Mazot, A. Volatiles and energy released by Puracé volcano. *Bulletin of Volcanology* **79**, 84 (2017).
212. D'Aleo, R. et al. Preliminary results of a multi-parametric characterization of gas manifestations from volcanoes in west Papua New Guinea. Presented at: *Conferenze Nationale Rittmann Giovani Ricercatori*, Bari, Italy, 2016.
213. Moussallam, Y. et al. Volcanic gas emissions and degassing dynamics at Ubinas and Sabancaya volcanoes; implications for the volatile budget of the central volcanic zone. *Journal of Volcanology and Geothermal Research* **343**, 181–191 (2017).
214. Granieri, D. et al. Emission of gas and atmospheric dispersion of SO_2 during the December 2013 eruption at San Miguel volcano (El Salvador, Central America). *Geophysical Research Letters* **42**, 5847–5854 (2015).

215. Bani, P. et al. First study of the heat and gas budget for Sirung volcano, Indonesia. *Bulletin of Volcanology* **79**, 60 (2017).
216. Edmonds, M. et al. Excess volatiles supplied by mingling of mafic magma at an andesite arc volcano. *Geochemistry, Geophysics, Geosystems* **11**, Q04005 (2010).
217. Allard, P. et al. Steam and gas emission rate from La Soufriere volcano, Guadeloupe (Lesser Antilles): implications for the magmatic supply during degassing unrest. *Chemical Geology* **384**, 76–93 (2014).
218. GeoNet Database. www.geonet.org.nz (2018).
219. Campion, R. et al. Space- and ground-based measurements of sulphur dioxide emissions from Turrialba Volcano (Costa Rica). *Bulletin of Volcanology* **74**, 1757–1770 (2012).
220. Conde, V. et al. SO_2 degassing from Turrialba Volcano linked to seismic signatures during the period 2008–2012. *International Journal of Earth Sciences* **103**, 1983–1998 (2014).
221. Epiard, M. et al. Relationship between diffuse CO_2 degassing and volcanic activity. Case study of the Poás, Irazú, and Turrialba Volcanoes, Costa Rica. *Frontiers in Earth Science* **5** (2017).
222. Martini, F. et al. Geophysical, geochemical and geodetical signals of reawakening at Turrialba volcano (Costa Rica) after almost 150 years of quiescence. *Journal of Volcanology and Geothermal Research* **198**, 416–432 (2010).
223. Vaselli, O. et al. Evolution of fluid geochemistry at the Turrialba volcano (Costa Rica) from 1998 to 2008. *Bulletin of Volcanology* **72**, 397–410 (2010).
224. McGee, K. A., Doukas, M. P., McGimsey, R. G., Wessels, R. L. & Neal, C. A. Gas emissions from Augustine Volcano, Alaska 1995–2006. *EOS Transactions* **87**, 1687 (2006).
225. López, T. et al. Constraints on magma processes, subsurface conditions, and total volatile flux at Bezymianny Volcano in 2007–2010 from direct and remote volcanic gas measurements. *Journal of Volcanology and Geothermal Research* **263**, 92–107 (2013).
226. Varley, N. R. & Taran, Y. Degassing processes of Popocatepetl and Volcan de Colima, Mexico. *Geological Society Special Publications* **213**, 263–280 (2003).
227. Hidalgo, S. et al. Evolution of the 2015 Cotopaxi eruption revealed by combined geochemical and seismic observations. *Geochemistry Geophysics Geosystems* **19**, 2087-2108 (2018).
228. Fischer, T. P. et al. The chemical and isotopic composition of fumarolic gases and spring discharges from Galeras Volcano, Colombia. *Journal of Volcanology and Geothermal Research* **77**, 229–253 (1997).
229. Tamburello, G., Hansteen, T. H., Bredemeyer, S., Aiuppa, A. & Tassi, F. Gas emissions from five volcanoes in northern Chile and implications for the volatiles budget of the Central Volcanic Zone. *Geophysical Research Letters* **41**, 4961–4969 (2014).
230. Menyailov, I. A., Nikitina, L. P., Shapar, V. N. & Pilipenko, V. P. Temperature increase and chemical change of fumarolic gases at Momotombo Volcano, Nicaragua, in 1982–1985 – are these indicators of possible eruption *Journal of Geophysical Research – Solid Earth and Planets* **91**, 2199–2214 (1986).
231. Hammouya, G. et al. Pre- and syn-eruptive geochemistry of volcanic gases from Soufriere Hills of Montserrat, West Indies. *Geophysical Research Letters* **25**, 3685–3688 (1998).
232. Kusakabe, M. et al. Evolution of CO_2 in Lakes Monoun and Nyos, Cameroon, before and during controlled degassing. *Geochemical Journal* **42**, 93–118 (2008).

233. Dionis, S. M. et al. Diffuse CO_2 degassing and volcanic activity at Cape Verde islands, West Africa. *Earth, Planets and Space* **67**, 48 (2015).
234. Zhang, L., Guo, Z., Zhang, M. & Cheng, Z. Study on soil micro-seepage gas flux in the high temperature geothermal area: an example from the Yangbajing geothermal field, South Tibet. *Acta Petrologica Sinica* **30**, 3612–3626 (2014).
235. Zhang, M. L. et al. Magma-derived CO_2 emissions in the Tengchong volcanic field, SE Tibet: implications for deep carbon cycle at intra-continent subduction zone. *Journal of Asian Earth Sciences* **127**, 76–90 (2016).
236. Cheng, Z., Guo, Z., Zhang, M. & Zhang, L. CO_2 flux estimations of hot springs in the Tengchong Cenozoic volcanic field, Yunnan Province, SW China. *Acta Petrologica Sinica* **28**, 1217–1224 (2012).
237. Cheng, Z., Guo, Z., Zhang, M. & Zhang, L. Carbon dioxide emissions from Tengchong Cenozoic volcanic field, Yunnan Province, SW China. *Acta Petrologica Sinica* **30**, 3657–3670 (2014).
238. Guo, Z., Zhang, M., Cheng, Z., Zhang, L. & Liu, J. Fluxes and genesis of greenhouse gases emissions from typical volcanic fields in China. *Acta Petrologica Sinica* **30**, 3467-3480 (2014).
239. Zhang, M. et al. Greenhouse gases flux estimation of hot springs in Changbaishan volcanic field, NE China. *Acta Petrologica Sinica* **24**, 2898–2904 (2011).
240. Sun, Y. & Guo, Z. CO_2 diffuse emission from maar lake: an example in Changbai volcanic field, NE China. *Journal of Volcanology and Geothermal Research* **349**, 146–162 (2017).
241. Galindo, I. et al. Emision difusa de dioxido de carbono en el volcan Irazu, Costa Rica. Carbon dioxide emissions at Irazu Volcano, Costa Rica. *Revista Geologica de America Central* **30**, 157–165 (2004).
242. Liegler, A. *Diffuse CO_2 Degassing and the Origin of Volcabic Gas Variability from Rincon de la Vieja, Miravalles and Tenorio Volcanoes*, Master of Science in Geology thesis, Michigan Technological University (2016).
243. Melián, G. V. et al. Emisión difusa de CO_2 y actividad volcánica en el volcán Poás, Costa Rica. *Revista Geológica de América Central* **43**, 147–170 (2010).
244. Padron, E. et al. Diffuse CO_2 emission rate from Pululahua and the lake-filled Cuicocha calderas, Ecuador. *Journal of Volcanology and Geothermal Research* **176**, 163–169 (2008).
245. Padron, E. et al. Fumarole/plume and diffuse CO_2 emission from Sierra Negra *caldera, Galapagos archipelago*. *Bulletin of Volcanology* **74**, 1509–1519 (2012).
246. Salazar, J. M. L. et al. Spatial and temporal variations of diffuse CO_2 degassing at the Santa Ana-Izalco-Coatepeque volcanic complex, *El Salvador, Central America*. *Special Paper – Geological Society of America* **375**, 135–146 (2004).
247. López, D. L., Ransom, L., Pérez, N. M., Hernández, P. A. & Monterrosa, J. Dynamics of diffuse degassing at Ilopango Caldera, El Salvador. In: *Special Paper of the Geological Society of America*, Vol. 375 (eds. W. I. Rose et al.), 191–202 (Geological Society of America, 2004).
248. Hutchison, W., Mather, T. A., Pyle, D. M., Biggs, J. & Yirgu, G. Structural controls on fluid pathways in an active rift system: a case study of the Aluto volcanic complex. *Geosphere* **11**, 542–562 (2015).
249. Brombach, T., Hunziker, J. C., Chiodini, G., Cardellini, C. & Marini, L. Soil diffuse degassing and thermal energy fluxes from the southern Lakki plain, Nisyros (Greece). *Geophysical Research Letters* **28**, 69–72 (2001).

250. Caliro, S. et al. Recent activity of Nisyros volcano (Greece) inferred from structural, geochemical and seismological data. *Bulletin of Volcanology* **67**, 358–369 (2005).
251. D'Alessandro, W. et al. Diffuse and focused carbon dioxide and methane emissions from the Sousaki geothermal system, Greece. *Geophysical Research Letters* **33**, 5 (2006).
252. Parks, M. M. et al. Distinguishing contributions to diffuse CO_2 emissions in volcanic areas from magmatic degassing and thermal decarbonation using soil gas Rn-222-delta C-13 systematics: application to Santorini volcano, Greece. *Earth and Planetary Science Letters* **377**, 180–190 (2013).
253. D'Alessandro, W., Brusca, L., Kyriakopouios, K., Michas, G. & Papadakis, G. Methana, the westernmost active volcanic system of the south Aegean arc (Greece): insight from fluids geochemistry. *Journal of Volcanology and Geothermal Research* **178**, 818–828 (2008).
254. Fridriksson, T. et al. CO_2 emissions and heat flow through soil, fumaroles, and steam heated mud pools at the Reykjanes geothermal area, SW Iceland. *Applied Geochemistry* **21**, 1551–1569 (2006).
255. Hernandez, P. et al. Diffuse volcanic degassing and thermal energy release from Hengill volcanic system, Iceland. *Bulletin of Volcanology* **74**, 2435–2448 (2012).
256. Toutain, J. P. et al. Structure and CO_2 budget of Merapi volcano during inter-eruptive periods. *Bulletin of Volcanology* **71**, 815–826 (2009).
257. Carapezza, M. L. et al. Diffuse CO_2 soil degassing and CO_2 and H_2S concentrations in air and related hazards at Vulcano Island (Aeolian arc, Italy). *Journal of Volcanology and Geothermal Research* **207**, 130–144 (2011).
258. Chiodini, G., Frondini, F. & Raco, B. Diffuse emission of CO_2 from the Fossa Crater, Vulcano Island (Italy). *Bulletin of Volcanology* **58**, 41–50 (1996).
259. Inguaggiato, S. et al. Total CO_2 output from Vulcano island (Aeolian Islands, Italy). *Geochemistry, Geophysics, Geosystems* **13**, Q02012 (2012).
260. Granieri, D. et al. Correlated increase in CO_2 fumarolic content and diffuse emission from La Fossa crater (Vulcano, Italy): evidence of volcanic unrest or increasing gas release from a stationary deep magma body? *Geophysical Research Letters* **33**, L13316 (2006).
261. D' Alessandro, W. et al. Chemical and isotopic characterization of the gases of Mount Etna (Italy). *Journal of Volcanology and Geothermal Research* **78**, 65–76 (1997).
262. Giammanco, S., Bellotti, F., Groppelli, G. & Pinton, A. Statistical analysis reveals spatial and temporal anomalies of soil CO_2 efflux on Mount Etna volcano (Italy). *Journal of Volcanology and Geothermal Research* **194**, 1–14 (2010).
263. Camarda, M., De Gregorio, S. & Gurrieri, S. Magma-ascent processes during 2005–2009 at Mt Etna inferred by soil CO_2 emissions in peripheral areas of the volcano. *Chemical Geology* **330**, 218–227 (2012).
264. De Gregorio, S. & Camarda, M. A novel approach to estimate the eruptive potential and probability in open conduit volcanoes. *Scientific Reports* **6**, 30471 (2016).
265. Melian, G. et al. Diffuse and visible emission of CO_2 from Etna Volcano, Italy. American Geophysical Union, Fall Meeting #V21D-202 (2009).
266. Inguaggiato, S. et al. CO_2 output discharged from Stromboli Island (Italy). *Chemical Geology* **339**, 52–60 (2013).
267. Granieri, D., Chiodini, G., Avino, R. & Caliro, S. Carbon dioxide emission and heat release estimation for Pantelleria Island (Sicily, Italy). *Journal of Volcanology and Geothermal Research* **275**, 22–33 (2014).

268. Favara, R., Giammanco, S., Inguaggiato, S. & Pecoraino, G. Preliminary estimate of CO_2 output from Pantelleria Island volcano (Sicily, Italy): evidence of active mantle degassing. *Applied Geochemistry* **16**, 883–894 (2001).
269. Frondini, F. et al. Diffuse CO_2 degassing at Vesuvio, Italy. *Bulletin of Volcanology* **66**, 642–651 (2004).
270. Granieri, D. et al. Level of carbon dioxide diffuse degassing from the ground of Vesuvio: comparison between extensive surveys and inferences on the gas source. *Annals of Geophysics* **56**, doi:10.4401/ag-6455 (2013).
271. Aiuppa, A. et al. First observations of the fumarolic gas output from a restless caldera: implications for the current period of unrest (2005–2013) at Campi Flegrei. *Geochemistry Geophysics Geosystems* **14**, 4153–4169 (2013).
272. Pecoraino, G. et al. Total CO_2 output from Ischia Island volcano (Italy). *Geochemical Journal* **39**, 451–458 (2005).
273. Chiodini, G. et al. Fumarolic and diffuse soil degassing west of Mount Epomeo, Ischia, Italy. *Journal of Volcanology and Geothermal Research* **133**, 291–309 (2004).
274. Rogie, J. D., Kerrick, D. M., Chiodini, G. & Frondini, F. Flux measurements of non-volcanic CO2 emission from some vents in central Italy. *Journal of Geohysical Research: Solid Earth* **105**, 8435–8445 (2000).
275. Chiodini, G. et al. Geochemical evidence for and characterization of CO_2 rich gas sources in the epicentral area of the Abruzzo 2009 earthquakes. *Earth and Planetary Science Letters* **304**, 389–398 (2011).
276. Frondini, F., Caliro, S., Cardellini, C., Chiodini, G. & Morgantini, N. Carbon dioxide degassing and thermal energy release in the Monte Amiata volcanic-geothermal area (Italy). *Applied Geochemistry* **24**, 860–875 (2009).
277. Costa, A. et al. A shallow-layer model for heavy gas dispersion from natural sources: application and hazard assessment at Caldara di Manziana, Italy. *Geochemistry, Geophysics, Geosystems* **9**, Q03002 (2008).
278. Quattrocchi, F. et al. Continuous/discrete geochemical monitoring of CO_2 natural analogues and of diffuse degassing structures (DDS): hints for CO_2 storage sites geochemical monitoring protocol. In: *Greenhouse Gas Control Technologies 9, Vol. 1 Energy Procedia* (eds. J. Gale, H. Herzog & J. Braitsch), 2135–2142 (Elsevier, 2009).
279. Hernandez, P. A. et al. Diffuse emission of CO_2 from Miyakejima volcano, Japan. *Chemical Geology* **177**, 175–185 (2001).
280. Hernandez, P. A. et al. Diffuse emission of CO_2 from Showa-Shinzan, Hokkaido, Japan; a sign of volcanic dome degassing. *Pure and Applied Geophysics* **163**, 869–881 (2006).
281. Hernandez, P. A. et al. Carbon dioxide degassing by advective flow from Usu volcano, Japan. *Science* **292**, 83–86 (2001).
282. Hirabayashi, J. & Mizuhashi, M. The discharge rate of volatiles from Kusatsu-Shirane volcano, Japan. Report of 4th Joint Observation of Kusatsu-Shirane Volcano, 167–174 (2004).
283. Shimoike, Y., Kazahaya, K. & Shinohara, H. Soil gas emission of volcanic CO_2 at Satsuma-Iwojima Volcano, Japan. *Earth, Planets and Space* **54**, 239–247 (2002).
284. Saito, M., Matsushima, T., Matsuwo, N. & Shimizu, H. Observation SO_2 and CO_2 fluxes in and around the active crater of Aso Nakadake Volcano. In: *Science Reports of the Kyushu University, Department of Earth and Planetary Sciences*, Vol. 22 (2007).
285. Notsu, K., Mori, T., Do Vale, S. C., Kagi, H. & Ito, T. Monitoring quiescent volcanoes by diffuse CO_2 degassing; case study of Mt. Fuji, Japan. *Pure and Applied Geophysics* **163**, 825–835 (2006).

286. Hernandez, P. A., Mori, T., Padron, E., Sumino, H. & Perez, N. Carbon dioxide emission from Katanuma volcanic lake, Japan. *Earth, Planets and Space* **63**, 1151–1156 (2011).
287. Notsu, K. et al. Diffuse CO_2 efflux from Iwojima Volcano, Izu-Ogasawara Arc, Japan. *Journal of Volcanology and Geothermal Research* **139**, 147–161 (2005).
288. Robertson, E. et al. Diffuse degassing at Longonot volcano, Kenya: implications for CO_2 flux in continental rifts. *Journal of Volcanology and Geothermal Research* **327**, 208–222 (2016).
289. Werner, C., Christenson, B., Scott, B., Britten, K. & Kilgour, G. Monitoring CO2 emissions at White Island volcano, New Zealand: evidence for total decreases in magmatic mass and heat output. In: *Water Rock Interaction, Eleventh Symposium* (eds. R. Wanty, & R. R. Seal), 223–226 (A.A. Balkema Publishers, 2004).
290. Harvey, M. C. et al. Heat flux from magmatic hydrothermal systems related to availability of fluid recharge. *Journal of Volcanology and Geothermal Research* **302**, 225–236 (2015).
291. Salazar, J. M. L. et al. Diffuse emission of carbon dioxide from Cerro Negro Volcano, Nicaragua, Central America. *Geophysical Research Letters* **28**, 4275–4278 (2001).
292. Harvey, M. C., White, P. J., Kenzie, K. M. & Lovelock, B. G. Results from soil CO_2 flux and shallow temeperature survey at the San Jacinto-Tizate geothermal power project. In: *Nicaragua in New Zealand Geothermal Workshop 2011*, 1–8 (University of Auckland, 2011).
293. Lewicki, J. L. et al. Comparative soil CO_2 flux measurements and geostatistical estimation methods on Masaya volcano, Nicaragua. *Bulletin of Volcanology* **68**, 76–90 (2005).
294. Arpa, M. C. et al. Geochemical evidence of magma intrusion inferred from diffuse CO_2 emissions and fumarole plume chemistry: the 2010-2011 volcanic unrest at Taal Volcano, Philippines. *Bulletin of Volcanology* **75**, 747 (2013).
295. Viveiros, F. et al. Soil CO_2 emissions at Furnas volcano, Sao Miguel Island, Azores archipelago: Volcano monitoring perspectives, geomorphologic studies, and land use planning application. *Journal of Geophysical Research: Solid Earth* **115**, B12208 (2010).
296. Andrade, C., Viveiros, F., Cruz, J. V., Coutinho, R. & Silva, C. Estimation of the CO_2 flux from Furnas volcanic Lake (São Miguel, Azores). *Journal of Volcanology and Geothermal Research* **315**, 51–64 (2016).
297. Frunzeti, N. *Geogenic Emissions of Greenhouse Gases in the Southern Part of the Eastern Carpathians*. PhD thesis (Babeș-Bolyai University, 2013).
298. Frunzeti, N. & Baciu, C. Diffuse CO_2 emission at Santa Ana lake-filled crater (Eastern Carpathians, Romania). *Procedia Environmental Sciences,* **14**, 188–194 (2012).
299. Inguaggiato, S., Cardellini, C., Taran, Y. & Kalacheva, E. The CO_2 flux from hydrothermal systems of the Karymsky volcanic Centre, Kamchatka. *Journal of Volcanology and Geothermal Research* **346**, 1–9 (2017).
300. Hernandez, P. A. et al. Analysis of long- and short-term temporal variations of the diffuse CO_2 emission from Timanfaya volcano, Lanzarote, Canary Islands. *Applied Geochemistry* **27**, 2486–2499 (2012).
301. Perez, P. H. et al. Carbon dioxide emissions from soils at Hakkoda, north Japan. *Journal of Geophysical Research* **108**, 9 (2003).
302. Melian, G. et al. A magmatic source for fumaroles and diffuse degassing from the summit crater of Teide Volcano (Tenerife, Canary Islands): a geochemical evidence for the 2004–2005 seismic-volcanic crisis. *Bulletin of Volcanology* **74**, 1465–1483 (2012).

303. Hernandez, P. A. et al. Geochemical evidences of seismo-volcanic unrests at the NW rift zone of Tenerife, Canary Islands, inferred from diffuse CO_2 emission. *Bulletin of Volcanology* **79**, 30 (2017).
304. Melian, G. et al. Spatial and temporal variations of diffuse CO_2 degassing at El Hierro volcanic system: relation to the 2011-2012 submarine eruption. *Journal of Geophysical Research: Solid Earth* **119**, 6976–6991 (2014).
305. Padron, E. et al. Dynamics of diffuse carbon dioxide emissions from Cumbre Vieja volcano, La Palma, Canary Islands. *Bulletin of Volcanology* **77**, 28 (2015).
306. Lan, T. F. et al. Compositions and flux of soil gas in Liu-Huang-Ku hydrothermal area, northern Taiwan. *Journal of Volcanology and Geothermal Research* **165**, 32–45 (2007).
307. Wen, H.-Y. et al. Soil CO_2 flux in hydrothermal areas of the Tatun Volcano Group, Northern Taiwan. *Journal of Volcanology and Geothermal Research* **321**, 114-124 (2016).
308. Nisi, B., Vaselli, O., Marchev, P. & Tassi, F. Diffuse CO_2 soil flux measurements at the youngest volcanic system in Bulgaria: the 12.2 Ma old Kozhuh cryptodome. *Acta Vulcanologica* **25**, 169–178 (2013).
309. Bergfeld, D., Goff, F. & Janik, C. J. Elevated carbon dioxide flux at the Dixie Valley geothermal field, Nevada; relations between surface phenomena and the geothermal reservoir. *Chemical Geology* **177**, 43–66 (2001).
310. Bergfeld, D., Evans, W. C., Howle, J. F. & Farrar, C. D. Carbon dioxide emissions from vegetation-kill zones around the resurgent dome of Long Valley caldera, eastern California, USA. *Journal of Volcanology and Geothermal Research* **152**, 140–156 (2006).
311. Bergfeld, D., Evans, W. C., Howle, J. F. & Hunt, A. G. Magmatic gas emissions at Holocene volcanic features near Mono Lake, California, and their relation to regional magmatism. *Journal of Volcanology and Geothermal Research* **292**, 70–83 (2015).
312. Evans, W. C., Bergfeld, D., McGimsey, R. G. & Hunt, A. G. Diffuse gas emissions at the Ukinrek Maars, Alaska: implications for magmatic degassing and volcanic monitoring. *Applied Geochemistry* **24**, 527–535 (2009).
313. Sorey, M. L., Werner, C., McGimsey, R. G. & Evans, W. C. *Hydrothermal Activity and Carbon Dioxide Discharge at Shrub and Upper Klawasi Mud Volcanoes, Wrangell Mountains, Alaska. Water-Resources Investigations Report 00-4207* (USGS, 2000).
314. Werner, C. et al. Volatile emissions and gas geochemistry of Hot Spring Basin, Yellowstone National Park, USA. *Journal of Volcanology and Geothermal Research* **178**, 751–762 (2008).
315. Bergfeld, D., Evans, W. C., Lowenstern, J. B. & Hurwitz, S. Carbon dioxide and hydrogen sulfide degassing and cryptic thermal input to Brimstone Basin, Yellowstone National Park, Wyoming. *Chemical Geology* **330**, 233–243 (2012).
316. Lin, P., Deering, C. D., Werner, C. & Torres, C. Origin and quantification of diffuse CO_2 and H_2S emissions at Crater Hills, Yellowstone National Park. *Journal of Volcanology and Geothermal Research*, **377**, 117–130 (2019).
317. Marty, B., Alexander, C. M. O. & Raymond, S. N. Primordial origins of Earth's carbon. In: *Reviews in Mineralogy and Geochemistry, Vol. 75*, 149–181 (Mineralogical Society of America, 2013).