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Carbon Dioxide Emissions from Subaerial Volcanic Regions

Two Decades in Review

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8.1 Introduction

Volcanism and metamorphism are the principal geologic processes that drive carbon transfer from the interior of Earth to the surface reservoir.\textsuperscript{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\textsubscript{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;\textsuperscript{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).\textsuperscript{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\textsubscript{2}O), carbon dioxide (CO\textsubscript{2}), and sulfur (S), with CO\textsubscript{2} being the least soluble in silicate melts.\textsuperscript{8} For this reason, it is not only Earth’s active volcanoes that are a source of magmatic CO\textsubscript{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.\textsuperscript{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\textsubscript{2} are less obvious. CO\textsubscript{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
springs. Occasionally, older volcanic areas can also exhibit cold degassing of CO₂. CO₂ is denser than air, and therefore an asphyxiation hazard can exist in low-lying areas. Visual indicators of CO₂ release include thermally perturbed or bare ground and the odor of H₂S. Atmospheric plumes of CO₂ can also form in such areas, even if a region is not thermal, and these emissions may not be visible. Additional contributions of volcanic carbon can be found in groundwaters, 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 CO₂ 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, there is now greater global coverage of subaerial volcanic areas emitting CO₂ compared to previous efforts. CO₂ 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 emis-
sions 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 CO2 emissions (in the absence of SO2) 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 CO2: Established Techniques and
Recent Advances

The principal challenges in the measurement of CO2 from volcanic regions are related to
the detection of volcanic CO2 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 CO2 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 CO2 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 CO2 emission rates. Here, the SO2 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 measurements24,25 and the plume
speed. Indirect techniques rely on reliable and representative SO2 emissions and C/S data.
Uncertainties in the SO2 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 ($\sim$400 ppm and rising due to anthropogenic contributions) that dominate the signal of column-average measurements. Even at some of the strongest volcanic gas sources (e.g., Etna, Italy), the volcanic CO$_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 ($1.3 \times 2.3$ 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 CO₂

Quantifying global emissions of volcanic CO₂ is an area of ongoing research that will continue to evolve as more measurements become available. Some of the first estimates of global volcanic CO₂ degassing, published in the 1990s, were based on only seven to nine measurements of passive CO₂ degassing;⁶⁷,⁶⁸ our understanding of CO₂ degassing in volcanic areas has progressed greatly since then. Here, we review methodologies from recent studies quantifying global volcanic CO₂ and how our new understanding may allow us to reduce some of the uncertainties in these estimates.

Until recently, most estimates of global CO₂ emissions were determined by proxy where volcanic CO₂ was scaled globally by a tracer (e.g. SO₂ or ³He). Work focused on determining the C/S ratio of fumaroles based on level of activity⁶⁹ or on an arc-wide basis⁷⁰ and combining these data with global SO₂ 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, SO₂ 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 SO₂, thereby reducing some measurement bias. For example, recent work used Ozone Monitoring Instrument (OMI) satellite data⁷⁵ to calculate a global passive volcanic SO₂ flux of 23 ± 2 Tg SO₂/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 CO₂, but not emitting SO₂ over the satellite detection limit. Some previous global estimates of CO₂ emissions have assumed that the strongest emitters of SO₂⁵⁷ also produce the most CO₂, but the time frame of measurement is important to consider, as is the number of degassing systems. The temporal distribution of volcanic CO₂ outgassing could be very different from that of SO₂,⁷⁷ 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 CO₂ 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 revised⁸¹ 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 CO2 flux from arcs is estimated to be $22 \times 10^{11}$ mol/yr or 95 Tg CO2/yr, based on the CO2/3He ratio of volcanic gases with outlet temperatures of $>200^\circ$C, although variability in the mantle CO2/3He adds considerable uncertainty to such calculations.

A third approach has been to extrapolate CO2 data based on actual measurements. The latest budget calculation 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 CO2/yr) of the total global subaerial emission of CO2 (540 Tg CO2/yr) was estimated to come from ~150 passively degassing volcanoes, based on the average CO2 emissions measured at 33 active volcanic systems. An additional 20% was estimated by extrapolating observed diffuse emissions to the ~550 historically active volcanoes. CO2 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. suggested ~150 volcanoes were degassing today, or 10% of the ~1500 volcanoes active in the Holocene. Satellite measurements show instead that 91 systems have emitted significant amounts of SO2 (and thus CO2) 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 SO2 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 CO2 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 CO2 degassing from volcanic areas should not assume that only historically active or Holocene volcanoes are actively degassing, but also consider the 1325 Pleistocene volcanoes.

8.4 Current State of Knowledge of CO2 Degassing from Volcanoes

8.4.1 CO2 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 CO₂ compilations calculate average emissions based on all published estimates of CO₂ 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 CO₂ output.

In an attempt to reduce the above uncertainty, the average CO₂ 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 published¹⁵ for all of the major volcanic CO₂ sources (Supplemental Table 8.1). For example, recent observations of CO₂ 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–1970s¹⁵,⁸⁸). Similarly, we report a new time-averaged CO₂ flux for Miyakejima volcano in Japan (1070 t/d⁵⁷) based on nearly two decades of systematic observations. This longer data set yields one order of magnitude lower CO₂ 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 CO₂ 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 CO₂ plume has more than tripled since 2013 (33¹⁵ vs. 102), the total (cumulative) CO₂ emitted is roughly two-thirds of the previous estimate (44 Mt CO₂/yr, or Tg/yr, vs 59.7;¹⁵ Supplemental Table 8.1), largely due to the diminished estimates for the top volcanic CO₂ 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 CO₂ flux estimated from global compilations of the most active volcanoes that represent longer time frames. We utilize the 2005–2015 OMI volcanic SO₂ flux measurements⁷⁵ and combine these with CO₂/SO₂ ratios from Aiuppa et al.⁷³ and elsewhere where available to estimate CO₂ emissions from these sources (Supplemental Table 8.1). At the time of writing, 49 of the 91 volcanoes in the OMI data set⁷⁵ have their volcanic gas CO₂/SO₂ ratio signatures characterized (Supplemental Table 8.1), leaving a sizable gap in our knowledge. If only the CO₂ emissions from these 49 volcanoes are summed, the OMI-based data result in a total CO₂ emission of only 27 Tg/yr, compared to the 44 Tg/yr CO₂ by direct measurements (Supplemental Table 8.1). Overall, a reasonable correlation exists between the two data
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 CO₂ 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 SO₂ 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 SO₂ data sets for estimating global CO₂ emission rates, it is important to note that many of the “passive” degassing measurements in fact represent eruptive periods. For instance, the OMI decadal data set omits eruptive emissions using a threshold SO₂ amount, 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 with the OMI SO₂ 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 (±1.6) volcanoes experienced a non-zero SO₂ 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 SO₂ 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), with the latter approaching the length of time that the volcanic gas community has been making CO₂ 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 CO₂ Emissions during Explosive Eruptions

Our present knowledge of CO₂ 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 CO₂ emission rates during explosive eruptions has been achieved on rare occasions, either from airborne plume measurements (e.g. during the 2009 Redoubt eruption, though here the most explosive events were not captured) or by coupling real-time FTIR spectroscopy of CO₂/SO₂ ratios in eruptive gases with the UV-sensed SO₂ flux (e.g. during the 2010 Eyjafjallajökull eruption). In other cases, bulk CO₂ emissions from explosive eruptions have been estimated by combining CO₂/SO₂ data from in situ measurements with satellite-based SO₂ data or by modeling the pre-eruptive vapor-phase composition. Such techniques yield, for instance, estimates of ~10 and ~50 Mt CO₂ for the 1980 Mount St Helens and 1991 Pinatubo eruptions, respectively. These
estimates imply CO2/SO2 mass ratios of ~3–10 in the eruptive emissions, although higher ratios cannot be excluded. Indeed, mass budgets for these and other explosive eruptions of silicic magmas strongly suggest pre-eruptive accumulation of a CO2-rich vapor phase. 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. Magmatic vapor may migrate to the roof zones of reservoirs via gas transport through channelized flow in crystal-rich mush. Because of its low solubility, CO2 becomes preferentially enriched in the accumulating vapor phase. Therefore, high CO2/ SO2 ratios and high CO2 and SO2 fluxes can be expected during the initial phases of explosive eruptions that tap the gas-rich upper levels of magma reservoirs.

Measuring volcanic CO2 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, and spaceborne CO2 measurements will also be hindered by volcanic ash. However, UAV (or drone) technology and improved satellite SO2 instruments (e.g. TROPOMI) hold great promise to improve measurements of explosive volcanic CO2 emissions in the coming decade.

8.4.3 CO2 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 CO2. These volcanoes may support smaller CO2 plumes that may or may not contain SO2 derived from fumarolic emissions, or they may host large regions of diffuse degassing 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 CO2 plumes in the absence of significant SO2 emission, are more difficult to characterize for their CO2 emission rate than those that have strong SO2 plumes. Roughly 40% of the 102 direct CO2 flux measurements listed in Supplemental Table 8.1 are from volcanoes where the volcanic plume was not detected by OMI and thus fall in this category (we refer to these as “small plumes,” although some do not have low CO2 emissions). The CO2 emissions associated with these volcanoes range from 13 to nearly 1500 t/d, with an average of 300 t/d (σ = ±360) and a median of 147 t/d, excluding the large emission from Oldoinyo Lengai (Tanzania). Some of the largest CO2 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 CO₂ 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 SO₂ 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 CO₂ emissions from these “small” volcanic plumes, they amount to only 5 Tg CO₂/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 CO₂/yr. If we use the median (147 t/d) instead of the average, this results in 17 Tg CO₂/yr. This exercise suggests that the emissions from volcanoes with small plumes (or in the absence of SO₂ emission) could potentially emit a similar order of magnitude of CO₂ globally as volcanoes whose SO₂ plumes were detected by satellite. This result, if robust, would potentially stand in contrast to recent regional studies in Japan\textsuperscript{57,112} that suggest that the global volatile budget is dominated by the high SO₂-emitting volcanoes, although this study\textsuperscript{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 CO₂ emissions from volcanoes that do not emit satellite-detectable SO₂.

8.4.3.2 Diffuse Emission of CO₂: Hydrothermal Systems, Calderas, and Continental Rifts

Our understanding of the magnitude of the diffuse CO₂ 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 CO₂ 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\textsuperscript{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 CO₂ (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 CO₂ emissions for active volcanoes may simply reflect a sampling bias due to method limitations (e.g. fumarolic contributions and plumes below SO₂ 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 CO₂ 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
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,\(^9^8\) 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 8.4 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.
Unrest in caldera systems is common,\textsuperscript{124,125} and thus using unrest catalogs may allow us to understand and constrain this likely significant CO\textsubscript{2} source better. Globally, there are 446 caldera systems, of which 225 have erupted in the Quaternary and 97 in the Holocene.\textsuperscript{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,\textsuperscript{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.\textsuperscript{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.\textsuperscript{116,124,126} However, the time-averaged release of CO\textsubscript{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 CO₂ 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 SO₂-producing volcanoes in the world. For example, the CO₂ emission from Mammoth Mountain (last eruption 70 ka) 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 CO₂ 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, but our estimate does not include large-scale extrapolated values for Indonesia–Philippines and the Subaerial Pacific Rim. 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; Campi Flegrei, Italy; the TRDS and CDS, central Italy; the EAR; and the Taupo Volcanic Zone (TVZ), New Zealand), we expect several other areas will also be globally important for their CO₂ 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, 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 CO₂ 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, 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 CO2/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 CO2/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 continue to be used for global compilations and comparisons of CO2. The TVZ is an intra-arc rift zone that hosts over 20 separate hydrothermal regions with heat flux greater than 20 MW, and many of these regions are exploited for geothermal energy. Previous estimates of the CO2 output of the TVZ as a whole have been extrapolated based on the heat flux and the CO2 content of upwelling fluids. However, diffuse CO2 flux at the surface for many of these systems greatly exceeds previous CO2 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; Supplemental Table 8.3) is nearly equal to that previously estimated for the whole TVZ (~1200 t/d). To date, 7 of the 18 hydrothermal systems have been measured for CO2; 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 CO2 content of the deep hydrothermal fluids or degassing from gas reservoirs at depth. In any case, arc-scale estimates for other regions on Earth should not be based on TVZ data, and continued effort should be placed on measuring the total diffuse CO2 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. 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 CO2. Several recent studies attempted to estimate the diffuse CO2 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 CO2/yr for the EAR. A second study focused on tectonic degassing away from active volcanic centers and estimated 38–104 Tg CO2/yr for the EAR, not including focused degassing through the active centers. For our estimate, we use the midpoint of the range presented by Hunt et al. because our aim is to estimate volcanic degassing; this value is one-third of the
total CO₂ emissions from all diffuse sources in our compilation (Supplemental Table 8.3). While the estimates of EAR fault-related degassing\textsuperscript{133} are not volcanic per se, isotopic evidence suggests there exists a significant flux of mantle-derived CO₂ 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 CO₂ 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 CO₂ flux can vary on meter scales. However, it is clear the EAR is a very important region for global CO₂ emissions, and more work is needed to quantify the flux of CO₂ 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 CO₂/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 CO₂ Emissions

As our understanding of the distribution and magnitude of volcanic and magmatic CO₂ degassing evolves, so will our ability to estimate accurately the present-day global CO₂ emission from these areas. As a culmination of the DECADE program, scientists came together in May 2018 to constrain better the total global CO₂ 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 CO₂ budget (Supplemental Table 8.4). Our methods are similar – and thus comparable – to previous studies\textsuperscript{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 CO₂ flux from the volcanoes that have been measured using ground-based or airborne techniques (i.e. measured directly) that were detected by OMI\textsuperscript{75} (58 of 91 volcanoes in Supplemental Table 8.1) and apply the average emission from these volcanoes (1730 ± 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 ± 13 Tg CO₂/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 SO₂ in large enough quantities to be detected by OMI – the average CO₂ output of these volcanoes is 300 ± 68 t/d; Supplemental Table 8.4) to 324 volcanoes results in 35 ± 8 Tg CO₂/yr. The sum of these results in 88 ± 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. Of these, 28 (17%) are thought to have plumes large enough for airborne measurements, but only 8 (4%) were detected by OMI. 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 during the period of OMI measurements, only 7 were detected by OMI (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.

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 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. 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). 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), 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 CO₂ emissions to lie between ~220 and 300 Tg CO₂/yr, and between ~280 and 360 Tg CO₂/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., 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 CO₂ Emission from Active and Less Active Volcanoes

Most of what we now know about the temporal evolution of CO₂ 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 CO₂ 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.](https://www.cambridge.org/core/coremedia/10.1017/9781108677950.008)
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 CO2 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 SO2 emissions,89,149 but is mirrored by CO2 emissions where measured (e.g. Redoubt in 1989 and 2009,65 Figure 8.4a).

Over an entire arc, the dominant volcanic CO2 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 CO2 output one order of magnitude higher (22,500 ± 4900 t/d56) than previous estimates, owing to the reactivation of Turrialba Volcano, as well as an increase in CO2 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 Japan112).

Finally, large-caldera systems are thought to be underlain by silicic magma bodies, and in turn underplated by mafic magma.109 The CO2 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 CO2 output in these systems often follow a geophysical manifestation of magma movement at depth116,150 whereby the transport of the gas to the surface is buffered by the overlying crust.

### 8.6.2 Using the Temporal Variability of CO2/SO2 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 CO2 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 time-scales 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 and Kilauea 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 CO₂ only amounted to roughly 15% of the total budget, 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 SO₂ and 5.1 Mt CO₂ was emitted over the course of the eruption. The low bulk C/S ratio (0.7) compared to most high-temperature volcanic gases might imply that substantial amounts of CO₂ degassed before monitoring began. In fact, a new study discovered significant degassing from glacially covered Katla volcano (∼37 kt/d CO₂) in the absence of a visible plume, unusual geophysical unrest, or S gas emission. These studies highlight a gap in our ability to detect CO₂ 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), whereas CO₂ released from MORs and hot spots is dominated by mantle carbon. The carbon isotopic composition (δ¹³C) of the depleted MOR mantle (DMM) is −5 ± 1 and that of plumes is documented as −3.1 ± 1.9 (high-temperature fluids from Iceland) and −3.4‰ (Kilauea summit gas), whereas the subcontinental lithospheric mantle likely contains carbon of composition between −3.5‰ and −6‰. Research on CO₂ 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 C³He signature on the discharging gases. This approach, combined with CO₂ 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.

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 SO₂ scrubbing in the month prior to eruption were removed – see Ref. 141 for details.
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.\textsuperscript{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.\textsuperscript{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 \(\text{CO}_2\) 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 \(\sim 0.02\) Ra, where Ra is the \(^{3}\text{He}/^{4}\text{He}\) ratio of air at \(1.4 \times 10^{-6}\), to 29 Ra in fluids discharged from hot spot hydrothermal systems and volcanoes.\(^{176}\) In subduction-zone settings, \(^{3}\text{He}/^{4}\text{He}\) 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 \(^{3}\text{He}/^{4}\text{He}\) 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 \(^{3}\text{He}/^{4}\text{He}\) in arc gases is the contribution of \(^{4}\text{He}\) 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 \(\delta^{13}\text{C}\) and \(^{3}\text{He}/^{4}\text{He}\) 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 \(\text{CO}_2\) at arc volcanoes; (2) samples where \(^{3}\text{He}/^{4}\text{He}\) is \(7 \pm 1\) Ra have \(\delta^{13}\text{C}\) values ranging from \(+2\)‰ to \(-12\)‰, implying that if the source of \(\text{CO}_2\) is from the subducted slab, it is sourced from both carbonates and organic carbon. Alternatively, the wide \(\delta^{13}\text{C}\) 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 \(^{3}\text{He}/^{4}\text{He}\) values <7 Ra show an equally wide distribution of \(\delta^{13}\text{C}\) as those >7 Ra, implying that both carbonate and organic carbon derived from the overlying crust (as implied by low \(^{3}\text{He}/^{4}\text{He}\)) may contribute to the degassing \(\text{CO}_2\).

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 \(\delta^{13}\text{C}\) remains from -12‰ to 0‰ for both gases with \(^{3}\text{He}/^{4}\text{He}\) 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 \(\text{CO}_2\) 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% \(\text{CO}_2\). This
Figure 8.9 (a) Helium and carbon isotope signatures for volcanic and hydrothermal gas discharges and (b) data from discharges with vent temperatures \(>200^\circ\text{C}\). 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 \(^3\text{He}/^4\text{He}\) ratios measured at a given locality.

The 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 \(\text{CO}_2\) 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, 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 CO₂ 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 CO₂ 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 pCO₂ 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 CO₂ 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, and fluid addition to the subcontinental lithosphere from the convecting asthenosphere over time have led to the subcontinental lithosphere becoming a large carbon sink. 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, 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 CO₂ (reviewed further in Chapter 11).

The results of our modern-day volcanic CO₂ 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 CO₂ output and warming during the initial stages of continental breakup and providing a way for short-term tectonics and volcanism to impact climate.

8.9 Synthesis

Considerable progress has been made in the last decade in quantifying CO₂ emissions from volcanic areas worldwide. Technological advances, including widespread use of miniaturized UV spectrometer systems and Multi-GAS instruments, have resulted in a greater
number of CO\textsubscript{2} measurements. Volcanic CO\textsubscript{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\textsubscript{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\textsubscript{2} degassing in the near future. We suggest the highest 10–20 SO\textsubscript{2}-emitting volcanoes be prioritized for measurement as these volcanoes may dominate the total CO\textsubscript{2} output from active volcanoes. CO\textsubscript{2} emissions from volcanoes with SO\textsubscript{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\textsubscript{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\textsubscript{2} from inactive or dormant volcanoes rivals that of active volcanoes when considered over long timescales. Regional volcanic CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} budgets of submarine regions.

A fraction of the CO\textsubscript{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\textsubscript{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\textsubscript{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 CO₂ emissions?
2. How can we quantify the CO₂ 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 CO₂ emissions?
4. How can we improve our knowledge of how many volcanoes are emitting CO₂ in the absence of significant quantities of SO₂?
5. How significant is CO₂ degassing from magmas located at the base of the crust and how would we distinguish this from shallower magma degassing?
6. Can CO₂ degas from the mantle without the presence of magma?
List of Online Resources

- MaGa database: www.magadb.net
- EarthChem Library: www.earthchem.org/library

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