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AGU Centennial Grand Challenge: Volcanoes and Deep Carbon Global CO_2 Emissions From Subaerial Volcanism—Recent Progress and Future Challenges

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Abstract Quantifying the global volcanic CO_2 output from subaerial volcanism is key for a better understanding of rates and mechanisms of carbon cycling in and out of our planet and their consequences for the long-term evolution of Earth's climate over geological timescales. Although having been the focus of intense research since the early 1990s, and in spite of recent progress, the global volcanic CO_2 output remains inaccurately known. Here we review past developments and recent progress and examine limits and caveats of our current understanding and challenges for future research. We show that CO_2 flux measurements are today only available for ~100 volcanoes (cumulative measured flux, 44 Tg CO_2/year), implying that extrapolation is required to account for the emissions of the several hundred degassing volcanoes worldwide. Recent extrapolation attempts converge to indicate that persistent degassing through active crater fumaroles and plumes releases ~53–88 Tg CO_2/year, about half of which is released from the 125 most actively degassing subaerial volcanoes (36.4 ± 2.4 Tg CO_2/year from strong volcanic gas emitters, S_{vge}). The global CO_2 output sustained by diffuse degassing via soils, volcanic lakes, and volcanic aquifers is even less well characterized but could be as high as 83 to 93 Tg CO_2/year, rivaling that from the far more manifest crater emissions. Extrapolating these current fluxes to the past geological history of the planet is challenging and will require a new generation of models linking subduction parameters to magma and volatile (CO_2) fluxes.

Key Points:
- Progress in determining subaerial volcanic CO_2 flux has been significant
- Challenges remain with regard to extrapolations through time and global coverage of measurements and with regard to diffuse tectonic degassing and dynamic nature of volcanic degassing
- Volcanic and tectonic contributions are <2% of current anthropogenic contributions

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1. Introduction and Motivation for the Study

Carbon dioxide (CO_2) is the second most abundant volcanic gas after water (W.F. Giggenbach, 1996). It has characteristic carbon isotope composition (Allard, 1980), and due to its low solubility in natural melts (Holloway, 1976), it degasses in significant quantities from volcanoes and hydrothermal systems (Williams et al., 1992). While these characteristics of magmatic CO_2 have long been known, the accurate quantification of volcanic and tectonic CO_2 emissions remains challenging. However, there is clear consensus from all the data assembled to date that current global volcanic, hydrothermal, and tectonic CO_2 emissions from subaerial and submarine sources is only a small fraction (<2%; Burton et al., 2013) of the global anthropogenic CO_2 produced by burning of fossil fuel energy sources (9.9 ± 0.5 Gt C/year for 2015; le Quere et al., 2016). However, quantifying current global volcanic CO_2 emissions remains central to reconstructing the preindustrial geological carbon cycle (Berner, 2004) and its role in climate evolution over geological time (Sleep & Zahnle, 2001). It is in fact believed that volcanic CO_2 degassing has taken place at a much faster rate at times during the geological history of the planet (Dasgupta, 2013), thus acting as a key regulator of climate and eventually leading to periods of long-term global warming. For example, it has been proposed that during the Cretaceous to the early Paleogene (150–50 Ma) elevated atmospheric CO_2 concentrations (4–8 times higher than present-day values; Royer, 2014) were the result of enhanced volcanic activity at mid-ocean ridges (MORs), the higher frequency of large igneous provinces eruptions, the increased release of crustal CO_2 from arc magmas (C-T A Lee et al., 2013), or the effect of CO_2 release from continental rifts (Brune et al., 2017; Foley & Fischer, 2017; H. Lee et al., 2016). In order to achieve these concentrations that are 4–8 times higher than present-day values in atmospheric CO_2, a minimum of approximately three times increase in CO_2 output into the exosphere would be required (C-T A Lee et al., 2013). During the particularly well-constrained time from 56 to 53 Ma, when Earth was in the Early Eocene Climatic Optimum with much warmer subtropical Arctic and midlatitude climates than today (Bijl et al., 2009), a three times increase in

current volcanic CO_2 emissions would imply a volcanic flux of only about 6% of anthropogenic emissions due to burning of fossil fuel energy sources. Extrapolation of our current understating of volcanic and tectonic CO_2 emissions to the geologic past is a critical area of future research that links volcano to climate and paleoclimate science. Of key importance here is to have better constraints on the CO_2 contents of undegassed melts, which would allow magma production and eruption rates through time to be linked more accurately to CO_2 emission rates. In this regard, recent work has shown the significance of plutonic degassing at arcs through geologic time, reconciling some of the high atmospheric CO_2 contents during the Jurassic and Cretaceous (Ratschbacher et al., 2019; Wong et al., 2019).

The low solubility of CO_2 in silicate melts, first recognized by Holloway (1976), makes this gas a powerful forecaster of magma moving toward the surface. While changes in gas chemistry leading to eruption have been recognized a long time ago (Menyailov et al., 1986), it was really the technological developments of in situ gas sensing (Aiuppa et al., 2005; Shinohara, 2005) that revolutionized our ability to fully utilize gases of different solubilities such as CO_2 and SO_2 to advance our understanding of chemical precursors to volcanic eruptions. These developments, combined with more portable ways to measure SO_2 fluxes from the ground (Galle et al., 2002) and the launching of ever improving satellite-based gas sensors (Carn et al., 2015), have enabled global initiatives focused on volcanic degassing research such as the Deep Carbon Observatory-Deep Earth Carbon Degassing (DECADE) project (Fischer, 2013) to make rapid progress toward better understanding of volcanic degassing.

Much progress has been made in the realm of better understanding of present-day volcanic and tectonic CO_2 emissions, yet several grand challenges remain. These are the focus of this review.

2. History and Development of the Field

One of the major challenges in accurately quantifying the global volcanic CO_2 output stands in the large variety of emission forms that include crater degassing via plumes and fumaroles, diffuse degassing via soils, steaming ground, faults and fractures, and volcanic aquifers. This, combined with technical challenges, has made progress in the field slow and problematic. In the following sections, the main achievements in the field over the years are summarized.

2.1. Crater Degassing

The most evident mechanism of CO_2 release from subaerial volcanoes is from their crater plumes and fumaroles. Efforts to estimate the global CO_2 flux from volcanic crater degassing started early in the 1990s, when volcanic gas data sets of increasing quality and completeness started to emerge. Traditionally, volcanic CO_2 emissions have been derived indirectly by using a proxy, because direct CO_2 flux measurements are challenging (Werner et al., 2009). In most cases and certainly when global estimates are the goal, volcanic CO_2 fluxes are computed by using ratios of CO_2 to a gas for which the flux has been estimated. Most commonly, this gas is SO_2 because it is relatively easy to measure by ground- and satellite-based remote sensing techniques.

One of the first attempts to estimate the global volcanic SO_2 flux was that of Stoiber et al. (1987), who proposed a total global SO_2 flux of 18.7 Tg/year using measurements from Central American volcanoes and a global extrapolation. The SO_2 flux data set that has been historically and most widely utilized for this purpose is that of Andres and Kasgnoc (1998) and includes the time-averaged SO_2 flux of 49 passively degassing arc volcanoes during the time period from the early 1970s to 1997. The Andres and Kasgnoc evaluation uses 49 measured volcanoes, which sum to 9.66 Tg SO_2/year, plus the SO_2 flux from 55 volcanoes with eruptions that were detected by Total Ozone Mapping Spectrometer (TOMS) over a 14-year time frame (3.7 Tg SO_2/year; Bluth et al., 1997). This data set results in a combined (eruptive and passive degassing) SO_2 flux of 13.4 Tg/year. Brantley and Koepenick (1995) recognized that not all degassing volcanoes can feasibly be measured and suggested that the distribution of volcanic SO_2 fluxes can be approximated by a power law function in the form of

$$N = af^{-c}, \tag{1}$$

where N is the number of volcanoes with SO_2 fluxes (f) that are $\geq f$, and a and c are constants. Using this approach for the fluxes of the 49 measured volcanoes, one obtains an additional 1.85 Tg/year of SO_2. This would result in a total passive volcanic flux of 11.5 Tg SO_2/year (Andres & Kasgnoc, 1998).

Satellite remote sensing, now sensitive enough to measure even low-emission passive degassing, offers an attractive alternative to overcome the issue of extrapolation, and the recent work by Carn et al. (2017) shows that global passive volcanic SO_2 flux during the decade from 2005 to 2015 was 23 ± 2 Tg SO_2/year, or 11.5 Tg S/year (or 3.6×10^{11} mol/year). This most recent SO_2 flux estimate is based on data from over 90 volcanoes, including measurements from previously poorly constrained emitters in Indonesia, Papua New Guinea, the Aleutians, the Kuriles, and Kamchatka.

New important clues have also recently emerged from regional volcanic SO_2 flux inventories. New ground-based SO_2 flux measurements of volcanoes from the Southern Central American Volcanic Arc obtained from 2015 to 2016 by de Moor et al. (2017) show that during this time period the fluxes are significantly higher than what was obtained for the same section of the arc by Andres and Kasgnoc (2,147 versus 6,240 ± 1,150 t SO_2/day). de Moor et al. (2017) also pointed out that as is the case for volcanoes degassing along the Japanese volcanic arcs (ARCs) (Mori et al., 2013), the SO_2 flux distribution does not follow a power law distribution. The volcanoes measured by satellite-based remote sensing for the Southern Central American Volcanic Arc (2005–2015) sum up to only 2,239 t SO_2/day (Carn et al., 2017). These comparisons emphasize the variability of SO_2 fluxes from volcanoes and the need for continuous measurements as well as the need for satellite- and ground-based comparisons over longer time spans as is currently the case.

Given the progress in higher temporal and spatial resolution of SO_2 measurements, for determining volcanic CO_2 fluxes, research leans heavily on SO_2 fluxes. Volcanic SO_2 fluxes combined with CO_2/SO_2 ratios obtained from fumaroles (e.g., Hilton et al., 2002; Williams et al., 1992) or only high-temperature (>305 °C) fumaroles (e.g., Fischer, 2008) have thus been used in many of the past global volcanic CO_2 flux estimates, reviewed in Figure 1. These initial studies (from the early 1990s to the early 2000s) have assessed the magnitude of global volcanic CO_2 flux at 34 to 110 Tg CO_2/year (Table 1 and Figure 1).

An alternative approach is to use either global ^{3}He fluxes, which are estimated using global magma fluxes (Marty & Tolstikhin, 1998), or the ^{3}He flux calculated by Torgersen (1989), as in Sano and Williams (1996). The estimated ^{3}He flux from arcs essentially uses the well-constrained ^{3}He flux from MORs and is based on the assumption that 80% of volcanic activity on Earth is associated with MORs and the remainder mainly from ARCs (Crisp, 1984). Dimalanta et al. (2002) revised the intraoceanic arc magma fluxes, and their calculations show a factor of approximately 2 higher rates compared to the early studies of Reymer and Schubert (1984) and Crisp (1984). While MOR ^{3}He fluxes appear to be quite well constrained within a factor of ~2 (Bianchi et al., 2010), work on global arc magma production rates is still sparse, and therefore, arc ^{3}He fluxes are likely associated with uncertainties that remain challenging to quantify. Using the ARC ^{3}He flux of 110 ± 20 mol/year, and average molar S/^{3}He ratio of 6.5×10^9 obtained from high-temperature (>200 °C) fumarole gases, Kagoshima et al. (2015) calculated an ARC S flux of 720×10^9 mol/year, or 23 Tg S/year. This value is a factor of 2 higher than the 11.5 Tg S computed by Carn et al. (2017) based on measured satellite emissions from 2005 to 2015.

The approach of using the $CO_2/^3$He ratio to estimate the CO_2 flux benefits from the fact that the issue of differential volatile degassing is minor for helium and CO_2. CO_2 solubility in natural melts is strongly pressure dependent and constrained around 0.5 ppm/bar (VolatileCalc), similarly to helium solubility. Helium solubility in silicate melts degassing a mixed COH fluid is well constrained at $2–9 \times 10^{-3}$ cc (STP)/g bar, or 0.36–1.6 ppm/bar, for compositions ranging from basalts to rhyolites (Paonita et al., 2000). Therefore, $CO_2/^3$He ratios are not expected to vary as dramatically as, for instance, S/^{3}He ratios, due to degassing. However, CO_2 contents in source melt compositions are likely 3,000 ppm or even higher (Fischer & Marty, 2005; Wallace, 2005), which would imply that CO_2 degassing starts at about 5 kbar or 15-km depth or even deeper. At this depth helium is still well below its solubility limit, and $CO_2/^3$He ratios of discharging gases would be very high until much of the CO_2 has degassed or the magma reaches shallower levels. At that point, the $CO_2/^3$He ratios would then be within the range that has been observed, that is, 1×10^9 to $1{,}000 \times 10^9$ (Oppenheimer et al., 2014). While $CO_2/^3$He ratios are strongly affected by carbon source (Marty & Jambon, 1987), described degassing processes likely affect this ratio, and flux calculations using it may be biased toward lower fluxes because the early degassing CO_2 is not captured by the approach of scaling to ^{3}He flux and magma emplacement rates.

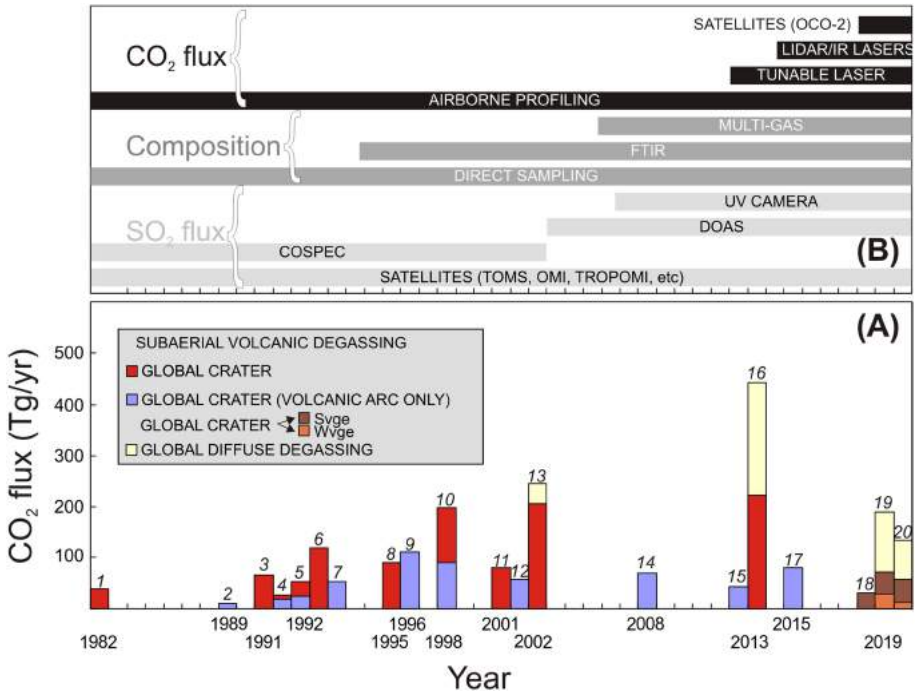

Figure 1. Overview of the technological developments in the field of volcanic SO_2 and CO_2 flux as well as gas compositions. (a) The timeline of flux measurements and the overall fluxes from volcanic craters and diffuse degassing. Numbers (in italics) above bars refer to identification numbers (ID) in Table 1. (b) The developments of technology that provided information for quantification of CO_2, SO_2 fluxes, and gas compositions. Reviews on historical development of the volcanic gas techniques can be found in Oppenheimer et al. (2014), Carn et al. (2015), and Saccorotti et al. (2015).

Table 1
Time Line of Global Volcanic CO_2 Flux Estimates in the Literature

ID[a]	Publication year	Global arc CO_2 subaerial flux (crater degassing)		Global CO_2 subaerial flux (crater degassing)		Global CO_2 subaerial flux (crater + diffuse degassing)		Reference
		10^{12} mol/year	Tg/year	10^{12} mol/year	Tg/year	10^{12} mol/year	Tg/year	
1	1982	—	—	1.1	48	—	—	Le Guern (1982)
2	1989	0.3	13.2	—	—	—	—	Marty et al. (1989)
3	1991	—	—	1.8	79	—	—	Gerlach (1991)
4	1992	0.5	22	0.8	34	—	—	Williams et al. (1992)
5	1992	0.7	31	1.5	66	—	—	Allard (1992)
6	1992	—	—	3.3	145	—	—	Marty and LeCloarec (1992)
7	1992	1.5	66	—	—	—	—	Varekamp et al. (1992)
8	1995	—	—	2.5	110	—	—	Brantley and Koepenick (1995)
9	1996	3.1	136	—	—	—	—	Sano and Williams (1996)
10	1998	2.5	110	5.5	242	—	—	Marty and Tolstikhin (1998)
11	2001	—	—	2.2	99	—	—	Kerrick (2001)
12	2002	1.6	70	—	—	—	—	Hilton et al. (2002)
13	2002	—	—	—	250	6.8	300	Möerner and Etiope (2002)
14	2008	1.9	85	—	—	—	—	Fischer (2008)
15	2013	1.2	53	—	—	—	—	Shinohara (2013)
16	2013	—	—	6.2	271	12.3	541	Burton et al. (2013)
17	2015	2.2	97	—	—	—	—	Kagoshima et al. (2015)
18	2019	—	—	0.8	38.7[b]	—	—	Aiuppa et al. (2019)
19	2019	—	—	2.0	88 (35[c])	5.27	232[d] (83[f])	Werner et al. (2019)
20	2019	1.1	49	1.2	51.3 (15.3[c])	3.28	144.3[e] (93[f])	Fischer et al. (2019)

Note. The same data are illustrated in Figure 1.
[a]Identification number, same as in Figure 1. [b]Includes only the contribution of strong volcanic gas emitters (S_{vge}). [c]Output from weak volcanic gas emitters (W_{vge}). [d]Sum of crater degassing (87 Tg/year), diffuse degassing (83 Tg/year), volcanic aquifers (12 Tg/year), and large regional degassing structures (50 Tg/year), including the East African Rift. [e]Sum of crater degassing (71.4 Tg/year) and diffuse degassing (93 Tg/year). [f]Diffuse degassing (83 and 93 Tg/year).

Using the $CO_2/^3He$ ratio of volcanic gases with outlet temperatures of >200 °C only, the most recent ARC CO_2 flux is estimated to be 22×10^{11} mol/year, or 97 Tg CO_2/year (Kagoshima et al., 2015) (Figure 1). Referring to the above most recent S flux of 3.6×10^{11} mol/year from Carn et al. (2017), which also includes large degassers that are not ARCs (Kilauea and Niragongo), the molar average C/S ratio would be about 6, which is only a factor of 2 higher than the average C/S ratio compiled to date from high-temperatures gases (Aiuppa, Fischer, et al., 2017). This gives some confidence that the two different approaches yield S and C fluxes that are quite consistent with magmatic C/S ratios expected for degassing volcanoes. The fact that both approaches roughly agree implies that both satellite remote SO_2 sensing and ^3He fluxes are primarily tracking a magmatic volatile source, consistent with the notion that SO_2 and ^3He are magmatic gases and not influenced by crustal or hydrothermal processes (Oppenheimer et al., 2014; Sano & Fischer, 2013). The observation that this derived global volcanic C/S ratio is a factor of 2 higher than that measured at high-temperature plumes/fumaroles (Aiuppa et al., 2019; Aiuppa, Fischer, et al., 2017) suggests that the average $CO_2/^3He$ ratio used in Kagoshima et al. (2015) includes $CO_2/^3He$ values from volcanoes that sample crustal CO_2 in addition to magmatic CO_2, a notion that Aiuppa, Fischer, et al. (2017) determined to be significant only in a few locations but that Mason et al. (2017) proposed to be pervasive. Crustal contamination is traditionally tracked by the $^3He/^4He$ ratios of the samples used in the Kagoshima et al. (2015) compilation, which has an average of 6.1 Ra and is somewhat lower than the accepted ratio of the upper mantle (8 ± 1 Ra). Eliminating the samples that have $^3He/^4He$ ratios <6.1 Ra results in an average $CO_2/^3He$ of 14×10^9, somewhat lower than the ratio (19×10^9) used in the arc CO_2 flux calculation of Kagoshima et al. (2015). The arc CO_2 flux calculated using this lower $CO_2/^3He$ ratio would be approximately 69.6 Tg CO_2/year (16×10^{11} mol/year). The resulting global C/S molar ratio then becomes 4.4, which is less than twice the ratio of the worldwide average of high-temperature volcanic fumaroles and plumes. This analysis shows that satellite-based SO_2 flux measurements and CO_2 fluxes computed using magmatic $CO_2/^3He$ ratios track gas emissions that originate primarily from the magmatic part of the volcanoes but still contain a contribution from hydrothermal or crustal emissions. It also implies that these approaches capture shallow degassing of CO_2, that is, at levels shallow enough where CO_2, S, and helium are degassing in proportions that are consistent with C/S and $C/^3He$ ratios commonly measured at volcanoes and therefore representing the majority of degassing flux. We note that uncertainties in the estimated arc ^3He flux remain a major source of error in the computation of volatile fluxes from arc volcanoes that use the noble gas approach. These are generally encouraging observations in light of understanding the C and S sources in volcanic systems and what global compilations represent. The caveat is that CO_2 is also contributed from sources that are not directly from the magma and therefore cannot be accurately estimated using the approaches described above. Estimating such fluxes requires additional data from diffuse degassing, hydrothermal degassing, and emissions that are captured by groundwater and springs.

A recent compilation by Burton et al. (2013) uses a different approach that takes into account the CO_2 contribution from sources that are not directly tracked by magmatic fluxes of SO_2 and ^3He. They compile all data from volcanoes that have measured CO_2 fluxes acquired either by directly measuring the CO_2 flux using direct (airborne) CO_2 flux measurements determined by LiCOR or by using C/S ratios measured at the same time as the SO_2 fluxes. In this way, temporal variations between SO_2 flux measurements and utilized C/S ratios are minimized. At the time of the Burton compilation, only 33 volcanoes, over the entire modern history of volcanic gas measurements, which spans almost five decades, had been quantified in this way and yield a total CO_2 flux of 59.7 Tg/year (or 16 Tg C/year). The average flux per volcano is then 1.8 Tg CO_2/year. The 33 measured volcanoes represent only 22% of the approximately 150 plume-emitting volcanoes, and Burton et al. (2013) therefore use a linear extrapolation that yields a global volcanic flux of 271 Tg CO_2/year, or 74 Tg C/year (Figure 1), obtained by 150 × 1.8 Tg CO_2/year. This flux is almost three times as high as the 97 Tg CO_2/year of Kagoshima et al. (2015). Based on the discussion above, it is implied that the volcanic flux of Burton et al. includes CO_2 fluxes that are sourced not only from the magmatic part of the volcanic system but also from a hydrothermal component or may include fluxes of CO_2 from sources that do not degas measurable S and helium. This flux is also much higher (Figure 1) than the CO_2 flux estimate of Shinohara (2013) that computes a

total ARC flux of 53 Tg CO_2/year (or 15 Tg C/year) and includes both the volcanic and hydrothermal as well as diffuse degassing fluxes based on detailed surveys of the Japan arc and a global extrapolation to all arcs. The extrapolation of the measured flux of only 33 volcanoes to 150 plume-creating volcanoes assumes that (a) the nonmeasured volcanoes have similar levels of emissions (on average 1.8 Tg CO_2/year) and that (b) there are 150 such volcanoes globally with plumes (Burton et al., 2013). The volcano number 150 is from the Volcanoes of the World catalog, which lists all recorded eruptions of the last 10,000 years (Siebert & Simkin, 2002). However, this database is based on the hard-copy edition of Simkin and Siebert (1994) and does not indicate whether volcanoes have persistently degassing plumes; rather, it only indicates whether a given eruption had fumarolic activity. Therefore, applying this database to estimate the total number of degassing volcanoes may be problematic at best and the resulting number is likely poorly constrained and unknown at worst. If we use the Carn et al. (2017) most recent compilation of SO_2 fluxes of 91 volcanoes that have a detectable SO_2 flux of 80 t/day, it would imply that the remaining 59 volcanoes are currently degassing at a level of <80 t/day and are not detected by satellite. If these volcanoes emit on average 1.8 Tg CO_2/year, or about 5,000 t/day, as proposed by Burton et al., then the C/S molar ratio of these volcanoes would be >90. Such high ratios are typical of hydrothermal gases that have been extensively affected by gas-water reactions resulting in the removal of most of the magmatic sulfur (Giggenbach, 1987; Symonds et al., 2001) and are therefore not included in the evaluations of the magmatic source characteristics of volcanic emissions (Aiuppa, Fischer, et al., 2017). Clearly, the question of how many volcanoes degas CO_2 without detectable SO_2 by satellite/ground is an important one when attempting to obtain the most accurate global volcanic CO_2 emission estimate. Burton et al. do not specifically address this issue but approach it by the extrapolation to 150 volcanoes, assuming an average flux of 1.8 Tg CO_2/year per volcano. While Aiuppa, Fischer, et al. (2017) emphasize the need for using only high-temperature fumarole gases or plume gases for the C/S ratio to extrapolate to global CO_2 fluxes, the approach of Hilton et al. (2002) is to use the global SO_2 flux data based on Andres and Kasgnoc (1998), divide it up by the measured volcanoes in each arc, and then use all available C/S ratios of fumarole gases to estimate a CO_2 flux on an arc-by-arc basis, recognizing the fact that arcs have variable C/S ratios and that these ratios will vary over time depending on volcanic activity. This approach, therefore, includes the nonmagmatic, that is, not derived from high-temperature or plume C/S ratios, CO_2 flux. However, the global average C/S ratio of this compilation is 5 and a factor of 2 higher than what would be expected for a purely magmatic ratio (Aiuppa, Fischer, et al., 2017). On the other hand, using such higher ratio captures some of the low-temperature, hydrothermally degassing volcanoes resulting in a total ARC CO_2 flux of 1.6×10^{12} mol/year, or 70 Tg CO_2/year (Hilton et al., 2002). This is similar to that of Shinohara (2013) with 53 Tg CO_2/year and lower than the 97 Tg CO_2/year of Kagoshima et al. (2015) that is based on $CO_2/^3He$ ratios and magma emplacement rates (Figure 1). Another aspect related to the high flux estimates of Burton et al. (2013) is that the data used are often biased toward measurements obtained during periods of high volcanic activity when CO_2 fluxes are high. The recent compilation by Werner et al. (2019) and Fischer et al. (2019) use longer-term satellite-based SO_2 flux averages that result in overall lower fluxes as discussed in detail below.

2.2. Volcano-Related Diffuse CO_2 Emissions

In addition to crater plumes and fumaroles, other volcanic sources of degassing include volcanic lakes (Pérez et al., 2011) and more subtle "diffuse" emissions from soils and groundwater systems. While much work has been done in terms of quantifying volcanic fluxes, that is, fluxes associated with volcanic vents or craters, much less is known about the global diffusive flux of CO_2, and the first global estimates (Kerrick, 2001; Möerner & Etiope, 2002) are hampered by the sparse and fragmentary data set available. Detailed and comprehensive results only exist for limited regions, for example, Kamchatka (Taran & Kalacheva, 2019) and Japan (Shinohara, 2013).

Seward and Kerrick (1996) estimate about 12 Tg C/year for diffuse degassing of CO_2 through arcs based on work in the Taupo volcanic zone, while James et al. (2000) use ground water flow to estimate a global ARC CO_2 flux of 4 Tg C/year. These fluxes are likely underestimates, and Burton et al. (2013) argue that a flux of 6.4 Mt CO_2/year (or 1.7 Tg C/year) has been measured at 30 volcanoes globally. They further state that 550 volcanoes globally are historically active and that a linear extrapolation to these 550

volcanoes would result in 117 Mt CO_2/year (or 32 Tg C/year) from diffuse volcanic degassing (Figure 1). The number 550 is from the Global Volcanism Program, which states that 570 volcanoes have had historical eruptions (Siebert et al., 2010) and assumes that the average amount of diffuse C degassing from historically active volcanoes is about 0.06 Tg C/year per volcano. This is significantly smaller than the 1.8 Tg C/year per volcano estimated for plume degassing and assuming that there are 150 currently active volcanoes with (detectable) plumes. This estimate therefore implies that about 400 volcanoes, which have no currently detectable plume, still degas CO_2 from their flanks. The emission estimate by Burton et al. also contains the flux of CO_2 from volcanic lakes (estimated at 6.7 Tg CO_2/year, or 1.8 Tg C/year) (Pérez et al., 2011), as well as diffuse emissions from tectonic, hydrothermal, and inactive volcanic areas (66 Tg CO_2/year, or 18 Tg C/year) (Burton et al., 2013).

3. Current Understanding

3.1. Discrepancies in Flux Estimates

Flux estimates are compiled in Table 1, and illustrated in Figure 1, for both ARC fluxes and global subaerial fluxes that include Ocean Islands. In general, crater degassing fluxes vary by an order of magnitude, from ~13 to ~270 Tg CO_2/year. Some of the likely reasons for these apparent discrepancies have been discussed above with the analyses of recent examples of flux compilations being based on different flux "proxies" such as SO_2 and ^{3}He in combination with C/S ratios, C/^{3}He, and magma emplacement rates. The situation is worse when considering total global subaerial fluxes (crater + diffusive) in Table 1, where estimates vary to as high as ~540 Tg CO_2/year. Here, however, it is important to realize that different authors included different sources of emissions in their global extrapolations. For example, the emission estimate by Burton et al. also contains the flux of CO_2 from volcanic lakes (Pérez et al., 2011), as well as diffuse emissions from historically active volcanoes (117 Tg CO_2/year, or 32 Tg C/year) and tectonic, hydrothermal, and inactive volcanic areas (66 Tg CO_2/year, or 18 Tg C/year) (Burton et al., 2013). The Burton et al. estimate is therefore a comprehensive attempt to include all measured volcanic and tectonic sources of CO_2 flux to the atmosphere using diverse available data on a global scale for a total subaerial CO_2 flux of 540 Tg CO_2/year, or 147 Tg C/year. This is the only attempt at such a comprehensive inclusion of all types of CO_2 emissions, hence resulting in the highest emission estimate to date (Figure 1). The approach of Shinohara (2013) is similar, but he focuses on the well-studied Japan arc, where a tremendous amount of diverse data is available. He includes volatile emissions from persistently degassing volcanoes (2,300 t CO_2/day), hot springs (150 t CO_2/day), cold springs (1,200 t CO_2/day), and soil degassing (1,010 t CO_2 day) to obtain a global ARC flux estimate of 53 Tg CO_2/year, an order of magnitude smaller than the Burton et al. flux yet including all the diverse degassing modes.

3.2. Recent Gas Flux Cataloging Efforts: Crater Degassing

A major breakthrough in the field has recently arisen from the DECADE (https://deepcarboncycle.org/about-decade) research initiative of the Deep Carbon Observatory (https://deepcarbon.net/project/decade#Overview). This 8-year research program (2011–2019) has represented the first coordinated effort to link international research on volcanic CO_2 (Fischer, 2013). The DECADE initiative has funded installation of a gas (Multi-GAS; Aiuppa et al., 2005; Shinohara, 2005) monitoring network that covers some (>10) of the world's 90 top degassing volcanoes, allowing for volcanic CO_2 observations of much improved continuity and temporal resolution, with obvious benefits for volcano monitoring (Aiuppa et al., 2019; Aiuppa, Bitetto, et al., 2017; de Moor, Aiuppa, Avard, et al., 2016; de Moor, Aiuppa, Pacheco, et al., 2016; de Moor et al., 2019). DECADE, in combination with other international research initiatives (e.g., http://www.trailbyfire.org), has also funded campaign-style surveys and/or temporary Multi-GAS deployments at many strongly degassing volcanoes whose CO_2 flux was previously unknown (e.g., Aiuppa et al., 2014; Tamburello et al., 2014, 2015; Bani, Rose-Koga, et al., 2017, Bani, Alfianti, et al., 2017; Battaglia et al., 2018; de Moor et al., 2017; Moussallam et al., 2017).

Following these initiatives, the number of volcanoes measured for their CO_2 flux has more than tripled, from 33 in 2013 (Burton et al., 2013) to 102 in 2019. The most updated catalog, reviewed in Werner et al. (2019), includes both direct (airborne) CO_2 flux measurements (e.g., Werner et al., 2009) and indirect CO_2 flux estimates from ground-based SO_2 fluxes and plume/fumarole CO_2/SO_2 ratios. The Werner et al. (2019) catalog

implies a total (cumulative) measured CO_2 flux (for the 102 volcanoes) of 44 Tg CO_2/year, roughly two thirds of the measured CO_2 output quoted in Burton et al. (2013) (59.7 Tg CO_2/year; see section 2.1). This lower measured flux, in spite of the larger number of volcanoes measured, reflects the diminished estimates for some of top volcanic CO_2 emitters (e.g., Nyiragongo, Popocatepetl, and Miyakejima), whose passive emissions are now better characterized thanks to more continuous observations (past data sets were biased toward strong emissions during eruptive periods or degassing unrests).

Robustness of the above airborne-/ground-based catalog is tested in Werner et al. (2019) by comparison with the CO_2 fluxes obtained by Aiuppa et al. (2019). The latter authors derive their CO_2 fluxes by pairing the 2005–2015 satellite Ozone Monitoring Instrument (OMI)-based time-averaged SO_2 fluxes of Carn et al. (2017) with the characteristic (mean) CO_2/SO_2 ratios in the corresponding high-temperature magmatic gases (Aiuppa, Fischer, et al., 2017). The data set of Aiuppa et al. (2019) is thus representative of the subset of 57 volcanoes that have positive OMI detection (for their SO_2 flux) and that have been characterized (although episodically) for volcanic gas compositions. This corresponds to roughly 62% of the 91 strongest volcanic SO_2 sources globally of Carn et al. (2017) and to ~56% of the (102) volcanoes measured from ground or with airborne profiling (Werner et al., 2019). The measured 57 volcanic sources of Aiuppa et al. (2019) contribute a cumulative "measured" flux of 27.4 ± 3.6 Tg CO_2/year. Overall, Werner et al. (2019) estimated a total global flux of 88 ± 21 Tg CO_2/year for passive degassing from volcanic craters, and Fischer et al. (2019) estimated 51.3 ± 5.7 Tg CO_2/year for global passive degassing from volcanic craters (Table 1).

Werner et al. (2019) compares the satellite-based CO_2 fluxes (Aiuppa et al., 2019) and the ground/airborne CO_2 fluxes (Werner et al., 2019) for those volcanic targets for which both are available, finding a positive correlation ($R^2 = 0.91$) with a slope of the best fit regression approaching unity (~1.2), ultimately raising confidence on the two independent methodologies. However, at the scale of each individual volcano, the two data sets show discrepancies sometimes exceeding 1 order of magnitude (~40% average). Further work is warranted to better examine causes for such mismatch and potentialities/limitations of each of the two approaches. We foresee the following areas in which work should be prioritized. (i) A rigorous, systematic intercomparison study between satellite- and ground-based SO_2 flux data sets should be carried out. (ii) A transition from campaign-based toward network-based gas observations should occur. Instrumental networks are central to capturing the temporal variability in volcanic gas records and thus to more fully constraining the time-averaged CO_2/SO_2 ratios and CO_2 fluxes. Ideally, a global network covering the 10–20 top emitter volcanoes would be required aim. (iii) The source of uncertainties for both ground and satellite measurements needs to be reduced by improved measurement and processing techniques.

3.3. Recent Gas Flux Cataloging Efforts: Diffuse Degassing

New impulse to this field has recently arisen from the MaGa Web database (www.magadb.net114), the first online catalog of diffuse volcanic gas emissions. This database gathers together published information on diffuse degassing structures (degassing soils, volcano-hosted aquifers, and crater lakes) from several active volcanoes worldwide and, although manifestly incomplete (information is missing from the majority of degassing systems in South America and Southeast Asia), can serve as a basis for some global consideration and extrapolation (see section 4). Analysis of the database (Werner et al., 2019) shows that 136 diffuse degassing manifestations are currently known. Roughly 30% of these diffuse manifestations emit 100–500 t CO_2/day, and mostly include quiescent volcanoes in hydrothermal stage of activity. An additional 20% exhibit even large emissions (between 500 and 5,000 CO_2/day) and correspond to large caldera-hosting magmatic systems (e.g., Mammoth Mountain and Yellowstone in the United States and Campi Flegrei in Italy). CO_2 emissions from these long-lived calderas, especially those undergoing degassing unrests (Chiodini et al., 2016), can thus rival emissions from large (and better studied) crater plumes. A special case is that of regional volcanic degassing structures (the Tuscanian-Roman and Campanian degassing structures in Italy and the East African Rift system in Africa). While not volcanic per se (diffuse degassing predominantly occurs along extensional faults; Tamburello et al., 2019), these regional degassing structures may represent a significant flux of mantle-derived CO_2 to the atmosphere. Recent estimates of diffuse CO_2 flux from the East African Rift, for example, range from 3.9–33 Tg CO_2/year (Hunt et al., 2017) to 38–104 Tg CO_2/year (Lee et al., 2016). More work is needed to quantify the

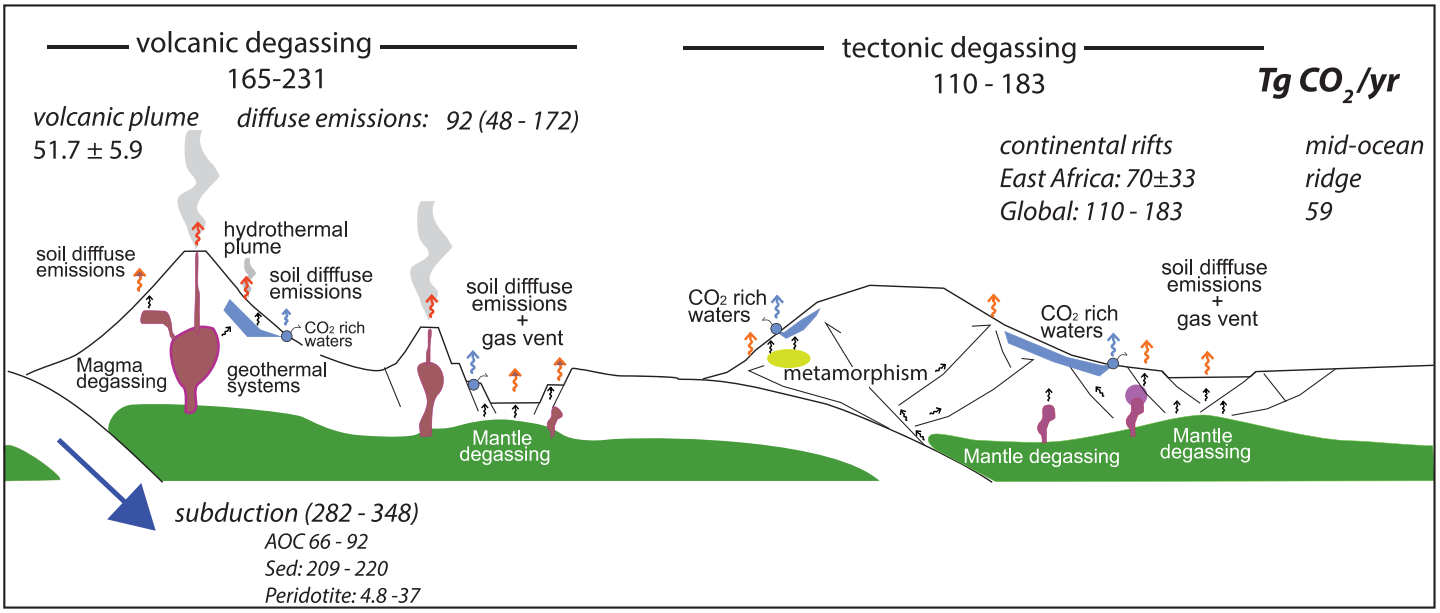

Figure 2. Summary of global volcanic and tectonic CO_2 degassing in teragrams of CO_2 per year as discussed in the text. The subduction input flux is from Plank and Manning (2019), and the mid-ocean ridge degassing flux is from *Le* Voyer et al. (2019).

flux CO_2 from continental rifts, but it may be quite significant and around 30–40 Tg CO_2/year (or 8–11 Tg C/year) and potentially on the same order as global arc fluxes.

Werner et al. (2019) quantified the cumulative annual CO_2 emissions from the known (e.g., measured) diffuse degassing structures at 83 Tg CO_2/year, or ~60% more of the annual measured CO_2 emissions from volcanic craters (52 Tg CO_2/year).

4. Challenges and Open Questions for Future Research

4.1. Extrapolating the "Measured" CO_2 Flux

In spite of the recent efforts summarized above, the volcanoes for which volcanic CO_2 flux measurements are available remain a small fraction of the total population of actively degassing volcanoes worldwide. This means that any attempt to quantify the global volcanic CO_2 flux inventory still involves the challenge of extrapolating the available gas catalog to account for the CO_2 contribution from "unmeasured" volcanoes. Since use of both the power law (Brantley & Koepenick, 1995) and linear (Burton et al., 2013) extrapolation has been questioned by recent research (de Moor et al., 2017; Mori et al., 2013), new directions and methodologies have recently been explored. A common approach that has been persued is that of categorizing active volcanoes into subgroups of distinct degassing behavior, as discussed below.

4.1.1. Extrapolating the "Measured" CO_2 Flux From Strong Volcanic Gas Emitters (S_{vge})

One first category of volcanoes that has clearly been identified is that of the strong volcanic gas emitters (S_{vge}), which includes those strongly degassing volcanoes whose emissions can systematically be detected by satellites (Carn et al., 2017) (Figure 2). One novel extrapolation methodology that has been set out recently (Aiuppa et al., 2019) for this category is to use regional/global trends in volcanic gas compositions, and their relationship with the trace element signature of arc volcanic rocks. In brief, Aiuppa, Fischer, et al., (2017, 2019) studied the along-arc, inter-arc, and arc-to-arc variability of CO_2/S ratios in high-temperature, magmatic arc gases (those characteristic of S_{vge}). They found that arc magmatic gas CO_2/S ratios are primary controlled by the composition (C content) of the sediments being subducted at the corresponding trenches and by the extent of fluid (melt and/or aqueous fluid) delivery from the subducting slab into the mantle wedge—the same key slab processes that control arc magma compositions (Pearce & Peate, 1995; Plank & Langmuir, 1993). It was found that the ARC gas CO_2/S ratios correlate (both globally and at the scale of individual arc segments) with the whole-rock trace element slab fluid tracers (e.g., the Ba/La ratio) (Aiuppa, Fischer, et al., (2017, 2019). Aiuppa et al. (2019) used the regional/global relationships between CO_2/S

ratios of volcanic gases and whole-rock trace element compositions (e.g., Ba/La) to predict the CO_2/S_T gas ratio of 34 top degassing remote volcanoes with no available gas measurements. By scaling to the volcanic SO_2 fluxes from Carn et al. (2017), the cumulative CO_2 output from these "unmeasured" 34 volcanoes was estimated at 11.4 ± 1.1 Tg CO_2/year. Ultimately, by combination with the cumulative "measured" flux of 27.4 ± 3.6 Tg CO_2/year (see section 3.2), this was used to extrapolate a cumulative CO_2 flux from Earth's 91 most actively degassing subaerial volcanoes of 38.7 ± 2.9 Tg CO_2/year (Figures 1 and 2).

The Aiuppa et al. (2019) approach has been elaborated further by Fischer et al. (2019). These authors refined estimates for the 2005–2015 averaged global volcanic SO_2 flux (24.9 ± 2.3 Tg SO_2/year; it was 23 ± 2 Tg SO_2/year in Carn et al., 2017), by including new OMI data and ground-based SO_2 flux data from the Network for Volcanic and Atmospheric Change (NOVAC) (Galle et al., 2010) for 35 additional volcanoes. They then extended the procedure of Aiuppa et al. (2019) to the new catalog of 125 individual degassing volcanoes (91 in Carn et al., 2017) to obtain a cumulative CO_2 flux from Earth's 125 most actively degassing subaerial volcanoes of 36.0 ± 2.4 Tg CO_2/year. This is very close to the initial Aiuppa et al. (2019) estimate of 38.7 ± 2.9 Tg CO_2/year. The slightly lower number, despite including more volcanoes in the estimate, highlights the need for representative flux measurements carried out over comparable time intervals. The fact that these two estimates are the same within error shows that the currently most active volcanoes make up the bulk of the current volcanic emissions.

The approach described above is promising but presents several potential caveats. One major challenge for future research will be to more fully understand the processes that determine the observed regional/global gas versus whole-rock trace element associations. These relationships implicate that the time-averaged CO_2/S_T ratios of volcanic gases is a proxy for the volatile ratios in the parental (undegassed) melt, a fact that is problematic to reconcile with the well-established solubility contrast between the two gases in silicate melts and that will need testing from the perspective of physical models of magmatic degassing. Also, the gas versus whole-rock trace element associations are currently based on a relatively limited data set from a few "better studied" volcanoes and urgently need refinement and validation from additional gas observations in remote, poorly explored (or even unexplored) regions such as Papua New Guinea (Arellano et al., 2019), Sandwich Islands, Solomon Islands, Sumatra, east Sunda-Banda, and north Vanuatu.

4.1.2. Weak Volcanic Gas Emitters (W_{vge})

While thus current CO_2 flux estimates for the strong volcanic gas emitters—those that have strong enough plumes and emit sufficient SO_2 to have been detected from space—seem to have finally converged to relatively consistent numbers (S_{vge}; Figures 1 and 2), much remains to be done on extrapolating the global CO_2 flux from weak volcanic gas emitters (W_{vge}). This category includes those volcanoes that are weak emitters of SO_2 (undetectable from space; here referred to as $W_{vge}1$) and those hydrothermal-stage volcanoes that emit no SO_2 at all but may still be contributing CO_2 via low-temperature fumaroles, steaming ground, and bubbling pools (here referred to as $W_{vge}2$). The challenge here is that (1) the number of weakly degassing volcanoes measured for their CO_2 flux is very low (38 volcanoes Fischer et al., 2019), which means that (2) the "characteristic" CO_2 flux for such category of volcanoes is poorly known, and (3) the total number of weakly degassing volcanoes worldwide is similarly poorly constrained.

The most complete and recent attempt to quantify the global CO_2 output from W_{vge} is that of Fischer et al. (2019). These authors applied a graphical statistical approach (GSA) method to the CO_2 flux population of 38 W_{vge}, from which they assigned the "characteristic" CO_2 fluxes of 431 and 36 t/day to $W_{vge}1$ and $W_{vge}2$, respectively. They then utilized global volcano catalogs (Syracuse & Abers, 2006; Global Volcanism Program, 2013) and local volcano observatory reports and photographs to estimate the number of $W_{vge}1$ (74) and $W_{vge}2$ (278) volcanoes globally (they also found that ~400 out of the ~900 volcanoes in Syracuse and Abers (2006), currently show no sign of active degassing at all). Finally, using these data, they extrapolated a global CO_2 flux from W_{vge} of 15.3 Tg CO_2/year (with respective contributions from $W_{vge}1$ and $W_{vge}2$ volcanoes of 11.6 and 3.7 Tg CO_2/year, respectively) (Figures 1 and 2).

The Fischer et al. (2019) estimate above is clearly preliminary and subject to a number of uncertainties. One key open question that will have to be addressed by future research is how many volcanoes degas CO_2 without detectable SO_2 (by satellite or ground). This question has been tackled by recent research, but answers have been disparate. As noted above (see section 2.1), Burton et al. (2013) stated that there exists only 150

with "plumes" globally. This, considering the S_{vge} number of 125 quoted above, would imply there are only 25 W_{vge} volcanoes worldwide with plumes, which per se seems excessively low and also does not address the question of how many W_{vge} volcanoes that emit CO_2 quiescently without visible plumes exist (e.g., $W_{vge}2$ volcanoes). The Fischer et al. (2019) approach involved visual examinations of reports and images in global (Global Volcanism Program, 2013) and local volcano catalogs to evaluate whether an unmeasured volcano is likely to exhibit "magmatic" ($W_{vge}1$) or "hydrothermal" ($W_{vge}2$) characteristics. The authors assigned a magmatic CO_2 flux signature where visible fumarolic plume and/or recent (2005–2017) eruptive activity was reported, while a hydrothermal category was assigned to volcanoes that have warm, potentially steaming ground, degassing through mud pools or water (but no coherent plume and no large fumaroles). Nondegassing volcanoes (404 out of the 900 in Syracuse and Abers, 2006) were identified as those lacking all of the above characteristics. This approach is certainly a refinement of earlier attempt, but still remains somewhat subjective, and is based upon sources (catalogs and online repositories) that are not homogenous and of disparate level of detail. Clearly, coordinated data basing efforts of volcano degassing characteristics are urgently needed.

One related aspect that requires improvement and further research is that related to measuring the CO_2 output from W_{vge}. Refining estimates of global CO_2 flux contribution from W_{vge} volcanoes will remain impossible until a more complete set of measurement (comprising a statistically significant number of gas targets) becomes available. Unfortunately, CO_2 flux measurement from SO_2-free hydrothermal emissions remains technically challenging, in spite of recent advances in tunable laser spectroscopy (Pedone et al., 2014) and lidar (Aiuppa et al., 2015). New in situ mapping techniques are being developed (Aiuppa et al., 2013; Tamburello et al., 2019) under the pressing need of quantifying the fumarolic gas output from caldera systems in unrest (e.g., Campi Flegrei), but these methods remain site condition dependent and will unlikely be a solution for systems of large areal extent. In such conditions, direct remote sensing methods based on infrared spectroscopy (Queißer et al., 2016), indirect estimates based on thermal surveys (which use the relationship between thermal and gas output at hydrothermal systems; Chiodini et al., 2004), and drone-based in-plume gas mapping (Liu et al., 2019) are emerging fields research should be focusing on in the near future.

4.1.3. Diffuse Degassing (W_{vge})

The question of how many volcanoes have flank degassing is currently even more challenging to answer, complicating any extrapolation effort of the (yet very limited) data set available (see section 3.2). Globally, only 221 unique volcanoes have detectable deformation, which are indicators of magmatic and hydrothermal processes at depth (Biggs & Pritchard, 2017). If we assume that 90 (Carn et al., 2017) or 150 (Burton et al., 2013) volcanoes degas from craters, then that would leave between 70 and 130 volcanoes that currently have CO_2 flank degassing without detectable plumes. However, many volcanoes with no recent deformation activity may still be accompanied by CO_2 degassing along their flanks. Werner et al. (2019) used recent catalogs of geothermal systems capable of power production as a proxy for the numbers of hydrothermal volcanoes worldwide that are likely to exhibit diffuse flank degassing. On this basis, they suggested that there may exist 670 hydrothermal regions worldwide with no recent eruptive active but still degassing CO_2 from their flanks at a "characteristic" rate of 340 $\pm$ 628 t/day. These calculations allowed extrapolating a global diffuse flux of 83 Tg CO_2/year, or approximately 30% more than the measured diffuse degassing output (64 Tg CO_2/year; see section 3.2) (Figures 1 and 2). Fischer et al. (2019) refined these calculations by using a subset of MaGa diffuse degassing results in which the "volcanic" CO_2 contribution is explicitly separated from the biogenic one. Applying a Monte Carlo simulation to this subset, they estimated a characteristic CO_2 diffuse degassing rate of 490 t/day (95% confidence interval, 247–916 t/day). This, multiplied by an estimated total number of 487 degassing volcanoes hosting diffuse degassing structures, would lead to an estimated global diffuse degassing output of 93 Tg/year (47–174 Tg/year, 95% confidence interval) (Figures 1 and 2).

These calculations above clearly highlight the current challenges in estimating the diffuse contribution to the total CO_2 output. One general conclusion is that characterizing the carbon isotope signature of soil CO_2 (Chiodini et al., 2008) should be prioritized in future soil degassing surveys, as it would be key to better resolving the volcanic versus biogenic contributions. One additional challenge will be to identify techniques to resolve, in large volcanic provinces such as the East African Rift, the fraction of deep

CO_2 that is magma sourced from that derived by tectonic degassing (e.g., mantle and metamorphic degassing): the two contributions may spatially overlap at sites (Tamburello et al., 2018) and may be difficult to resolve isotopically. Ultimately, any future attempt to refine estimates of the global diffuse CO_2 output will have to rely on a more robust and comprehensive data set than available today and on more accurate global quantification of the number of volcanoes that are actively degassing CO_2 in diffuse form. To accomplish this latter goal, it is perhaps only with the future improvement of satellite-based CO_2 observations that the required global coverage will be achieved. At the level of present knowledge, it is clear, however, that the global diffusive CO_2 contribution is in the order of several tens of teragrams per year (possibly in the 83–93 range) and thus comparable to, or even larger than, the cumulative CO_2 output from crater degassing. The current best guess value for the total (S_{vge} + W_{vge}) global CO_2 crater emission is about 53.1 Tg CO_2/year (Figures 1 and 2 and Table 1; Fischer et al., 2019). This value also includes 1.8 Tg/year of eruptive degassing (Fischer et al., 2019).

4.2. Contribution From Carbonate in Arc Crust to Volcanic Degassing

The question of whether release of carbon in the form of carbonate or organic C materials in the overriding arc crust significantly contributes to the global ARC CO_2 emissions remains largely unresolved. It has long been recognized that subducted carbonate and organic carbon contributes to the CO_2 degassing from volcanoes (Allard, 1983; Marty & Jambon, 1987; Sano & Marty, 1995; Sano & Williams, 1996), that sufficient carbon is subducted under a specific volcano to supply its measured CO_2 flux (Fischer et al., 1998), and that along entire arcs more carbon is subducted than what is emitted through the volcanoes (Hilton et al., 2002). The most recent evaluation of subducted carbon inputs and volcanic CO_2 output supports earlier ideas that more subducted organic- and carbonate-derived C is supplied to the zone of arc magma generation than what is released back to the atmosphere through volcanism (Plank & Manning, 2019). The idea that limestone-sourced crustal carbon contributes to the high CO_2 flux measured at a volcano was probably first quantitatively introduced by Goff et al. (2001), who showed that during heightened activity at Popocatepetl in 1997, C/S ratios increased intermittently from the usual background levels of <8 to up to 140 measured by Fourier Transform Infrared (FTIR) in the plume. These high ratios were accompanied by extremely high SO_2 fluxes resulting in CO_2 fluxes of up to 190,000 t CO_2/day. Detailed investigations of erupted ash showed the occurrences of key minerals that indicate metamorphism of calcareous sedimentary rocks and contact metamorphism of carbonate-bearing rocks. Assimilation of carbonate-bearing rocks that underlie the volcanic edifice was proposed to result in the high C/S and CO_2 fluxes during times of increased activity. Later work at Merapi (Troll et al., 2012) proposed a similar process based on variations in C and helium isotopes of fumaroles. A global compilation of C isotopes from volcanic systems suggested that the contribution of carbonate-derived crustal carbon to volcanic emissions is pervasive and significant and may dominate ARC CO_2 fluxes (Mason et al., 2017). However, this interpretation has been questioned using a similar fumarole C and He data set (Oppenheimer et al., 2014; Werner et al., 2019) and based on the global distribution of C/S ratios (Aiuppa, Fischer, et al., 2017). The global significance of crustal carbon release and its potential impact on atmospheric CO_2 concentrations through geologic time has been proposed by Lee et al. (2013).

Resolving this issue remains a challenge because we do not have an unequivocal tracer of crustal carbonate that is able to distinguish it from subducted carbonate, and we therefore rely correlations with other parameters (Aiuppa, Fischer, et al., 2017). The current best estimate of crater plus diffuse degassing from arcs is 164 Tg CO_2/year (Table 1). If we want to assess whether emplaced magma alone can supply the degassed CO_2, we need to know current and past magma addition rates. Ratschbacher et al. (2019) recently compiled arc magma addition rates through time using geological constraints and showed that these addition rates, even for the present day, depend highly on what arc widths are used. Using this approach with current average global continental arc magma addition rates (Figure 3a), and assuming a ratio of magma flare-up to lull of 50:50 and a 1.5 wt% initial CO_2 in the magma (Ratschbacher et al., 2019), results in a volcanic CO_2 flux of 25 Tg CO_2/year from continental arcs. Assuming that 30% of the currently estimated global arc CO_2 flux (164 Tg CO_2/year) is from continental arcs (Lee et al., 2013) results in an estimated CO_2 flux from continental arcs of 54 Tg CO_2/year, only a factor of about 2 higher than what could potentially be produced by present-day continental arc magma degassing (Figure 3b). Clearly, these estimates are still burdened with large uncertainties, and future work needs to focus on individual volcanoes and arc segments to evaluate the potential contribution of crustal carbonate to volcanic CO_2 flux in combination with estimates of magma fluxes.

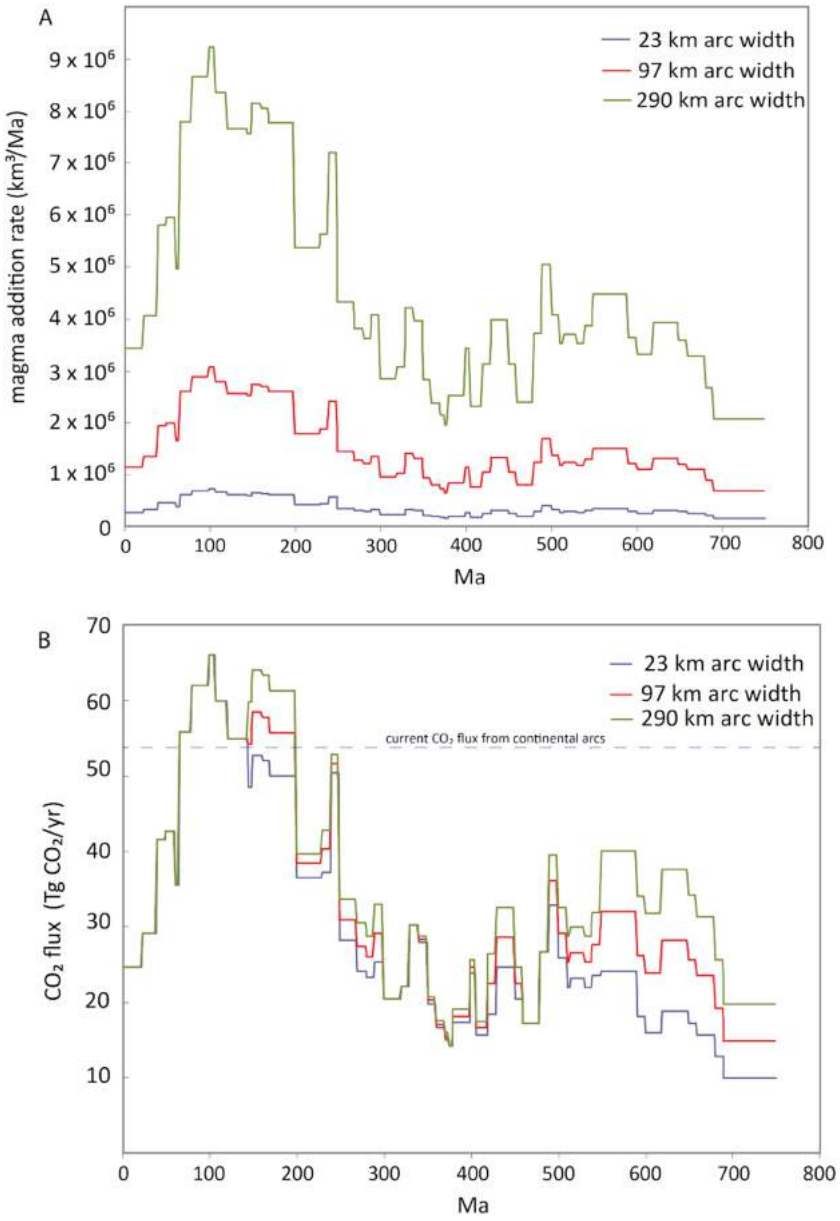

Figure 3. Arc magma addition rates and associated estimated CO_2 flux through geologic time from Ratschbacher et al. (2019). (a) The flare-up magma addition rates estimated for different arc widths. (b) The associated CO_2 flux for a ratio of flare-up to lull of 50:50 and assuming complete degassing of magma with 1.5 wt% initial CO_2. Current CO_2 flux is shown for comparison.

4.3. Extrapolating the CO_2 Output Over Geological Timescales

The current best estimates thus assess the total (crater + diffusive) CO_2 output from subaerial volcanism at 164 to 232 Tg CO_2/year (Table 1 and Figure 2). Extrapolations of these (current) volcanic and tectonic CO_2 fluxes over geologic timescales remain an important yet still inadequately addressed issue. The Berner-Lasaga-Garrels models (Berner et al., 1983; Lasaga et al., 1985) provided some insights in terms of relating the rate of subduction or essentially MOR spreading rate to the rate of volcanic degassing. However, present-day arc CO_2 degassing does not appear to vary systematically and in relationship to subduction rate (Fischer, 2008; Hilton et al., 2002), and Kerrick (2001) has shown that the correlation of subduction rate and volcanic CO_2 degassing is a questionable model assumption. In summary, there are no correlations between subduction rates and the number of active volcanoes; the assumption that

subduction rate correlates with degassing rates assumes that all plates subduct the same material, which we know is not true (Alt & Teagle, 1999; Plank & Langmuir, 1998); likewise, the amount of CO_2 released from subducted plates varies depending on pressure, temperature, and composition (Kerrick & Connolly, 2001); and lastly, the majority of present-day degassing comes from only a few volcanoes (Aiuppa et al., 2019) without any relationship to subduction speed. Kerrick (2001) provided valuable guidelines for better assessing the volcanic and magmatic CO_2 emissions through geologic time. He showed that the total volume of flood basalts peaked in the Cretaceous, releasing over 3×10^{18} mol CO_2/Myr (132 Tg CO_2/year); that the volumes of erupted andesites and rhyolites also peaked in the Cretaceous, with a second peak in the Ordovician for andesites; and that the volume of intrusive rocks was significantly higher in the Cenozoic to the early Cretaceous than in the mid-Cretaceous to the Jurassic. Whether increased volcanism drives long-term global cooling or warming continues to be debated, not surprising because increased arc magmatism will cause outpour of CO_2 but then weathering of arc rocks sequesters atmospheric CO_2 (Lee & Dee, 2019). Recently, Soreghan et al. (2019) proposed that the late Paleozoic Ice Age (360–260 Ma) correlates with an episode of increased explosive volcanism that injected sulfate aerosol into the stratosphere at rates at least 8 times higher than today and also caused additional CO_2 drawdown due to fertilization of the oceans resulting in increased biological productivity. While volcanic sulfate aerosol forcing is an important impact of explosive volcanism, an aspect usually ignored in the connections between volcanism and climate is the fact that volcanoes degas CO_2 without eruptions and that in fact only about 1–2% of CO_2 is released during eruptions globally compared to the amount released during passive degassing (Fischer et al., 2019; Werner et al., 2019). The importance of CO_2 released during passive degassing is amplified by CO_2 released from "cryptic" or plutonic degassing during arc formation. Ratschbacher et al. (2019) showed that over the past 800 Ma, CO_2 fluxes from continental arcs peaked in the Cretaceous (~3 times the present-day volcanic flux). These estimates are directly linked to arc magma addition rates as shown in Figure 3 (Ratschbacher et al., 2019). A recent review paper by Wong et al. (2019) uses the GPlates reference tectonic model (Müller et al., 2018) to estimate the lengths of continental rifts, MORs, and arcs through time and couples these with present-day fluxes from these tectonic settings to reconstruct the CO_2 fluxes over the past 200 Ma, including contributions from intersection of carbonate-rich arc crust (Lee et al., 2013). Compared to the reconstruction of arc CO_2 fluxes by Ratschbacher et al. (2019) that does not take into account addition of CO_2 from the intersection of magmas with carbonate-rich continental arc crust, the Wong et al. (2019) estimate is significantly higher but also has large uncertainties. In addition, the Wong et al. (2019) estimate uses a global plate tectonic reconstruction approach that extrapolates to arcs that are no longer visible geologically, resulting in more extensive arcs spatially.

Release of additional CO_2 from decarbonation reactions in continental arc crust (Lee et al., 2013) would further increase atmospheric CO_2 in addition to the relatively small amounts released during eruptions. In contrast, passive degassing of sulfur does not reach the stratosphere and therefore does not have a climate impact.

A fruitful avenue forward to quantify volcanic and tectonic CO_2 degassing in the geologic past is to accept the notion that magmas contain much higher CO_2 contents than what is preserved in melt inclusions (Fischer & Marty, 2005; Wallace, 2005), consistent with the idea that arc magmas start degassing CO_2 at great depths of ~80 km, approaching the depths of the zone of arc magma generation (Giggenbach, 1996). Future work to improve our understanding of past volcanic CO_2 emissions should establish the links between volcanic CO_2 fluxes, melt inclusion CO_2 contents (reconstructed to their predegassing values), magma production rates, and subduction forcing functions. While isolated progress has been made for a few well-studied subduction zones, a global, broadly applicable model linking subduction parameters to magma and gas fluxes is still lacking. This requires adequate melt volume estimates, chronology, better global constraints on arc growth rates, and an understanding of the relative proportions of degassing in the arc, backarc, forearc and diffuse degassing.

A related aspect is that continental rift degassing remains poorly constrained between 18 ± 14 Tg CO_2/year (Hunt et al., 2017) and 70 ± 33 Tg CO_2/year (Lee et al., 2017) and depends on which sector of the East African Rift is measured and used to extrapolate to the entire rift length. The causes for this variability remain a still open question and may be related to the efficiency of lithospheric age and efficiency

of C storage and release (Foley & Fischer, 2017), the efficiency of melting during rift extension and assumed C content in the upper mantle (Hunt et al., 2017), or localization of C release along faults and degree of extensional processes (Muirhead et al., 2016). Recent work shows that continental rifts potentially contribute between 40% and 60% of the total C outgassing to the atmosphere, significantly more than ARCs and MORs, and that this high contribution persisted through the past 200 Ma (Wong et al., 2019). However, this estimate remains burdened with above large uncertainties, rendering the actual contribution of continental rifts to the global deep C emissions challenging to evaluate. Future work needs to build on the limited but growing attempts to measure fluxes from the East African Rift and elsewhere. Fluxes in these regions are heterogeneous, and more densely spaced flux measurements are needed to understand the link between degassing at the surface, rifting, and melt generation at depth (Foley & Fischer, 2017). Contrary to arcs, melt inclusion studies of volcanic rocks in continental rifts have been lagging behind and initial CO_2 contents of rift magmas remain poorly constrained. However, as for arc magmas, these are needed to provide meaningful constraints for extrapolation of fluxes into the geologic past and their potentially significant effect on climate (Brune et al., 2017; Wong et al., 2019).

5. Societal Implications

Earth's global surface expressed CO_2 budget is shown in Figure 4. Anthropogenic fluxes are from le Quere et al. (2016). We see that the emissions from burning of fossil fuels are the largest slice of these anthropogenic emissions and short-circuit what would otherwise be a slow natural release of C from geologic reservoirs. Volcanic (crater and diffuse CO_2 emission of 165 to 231 Tg CO_2/year; Figure 2) CO_2 emissions are 0.05 $\pm$ 0.01 Gt C/year and <1% of current total anthropogenic emissions. Inclusion of the tectonic (110–183 Tg CO_2/year; Figure 2) CO_2 emissions then sums to a maximum of 0.11 Gt C/year or <2% of the current global anthropogenic CO_2 produced by burning of fossil fuel energy sources and the smallest values in the global CO_2 budget related to the surface reservoir (Figure 4).

In the geologic past, the volcanic CO_2 emissions from volcanic and tectonic sources have likely been somewhat higher during some of Earth's history (see discussion above); therefore, such higher past emissions provide a proxy for the effect on global climate, albeit more long-term. Atmospheric CO_2 contents are well constrained over the past 65 Ma and had levels of 500 to 1,100 ppm from 35 to 55 Ma. Deep sea temperatures generally track atmospheric CO_2 contents and were up to 12 °C higher about 50 Ma (Beerling & Royer, 2011). Such high CO_2 contents in the Eocene resulted in complete melting of the Antarctic ice sheets and associated sea level rises. While the causes for these high CO_2 levels may be several, higher volcanic CO_2 emissions due to more extensive distributions of continental arcs (Lee et al., 2013), 3–4 times longer global continental rift lengths (Brune et al., 2017) and ~2 times higher arc magma addition rates (Ratschbacher et al., 2019) all likely played an important role in raising the CO_2 levels during this time to ~2 times current levels. Current global subaerial volcanic (crater and diffuse) CO_2 fluxes are estimated at only 165 to 231 Tg CO_2/year, or 0.04 to 0.06 Gt C/year (Figure 2), and our current anthropogenic CO_2 emissions of 9.9 $\pm$ 0.5 Gt C/year would then represent times in Earth's history where volcanic and tectonic CO_2 fluxes were about 245 times higher than today. Given what we know about the distribution of continental rifts, continental arcs, and arc magma productions rates over the past 800 Ma of Earth's history, there is no support for the notion that volcanic CO_2 emissions were higher by more than 10 times of what they are today [Brune et al., 2017; Kerrick, 2001; *C-T A* Lee et al., 2013; Ratschbacher et al., 2019] including the highest estimate by Wong et al. (2019) of 0.2 Gt C/year about 120 Ma. Even massive, recent eruptions such as the Holhuraun eruption of Iceland that occurred in 2014, emitted a daily CO_2 flux of 20,000–40,000 t CO_2/day (Pfeffer et al., 2018) or only about 0.004 Gt C/year. Therefore, about 2,400 Holuhraun eruptions would be needed per year, or one such eruption every 3.5 hr, to emit the equivalent of our current annual anthropogenic CO_2 emissions in addition to the global volcanic background. A recent, more well-known, large eruption is the eruption of Pinatubo volcano in 1991. This eruption emitted approximately 20 Tg SO_2 (Carn et al., 2015); the C/S ratio of eruptions are poorly constrained but given the C/S ratio of volcanoes in the region of 1.2 (Aiuppa et al., 2019) would imply a CO_2 emission of about 0.006 Gt C. Therefore, in order to match the current anthropogenic CO_2 emissions would require about 1,650 Pinatubo-sized eruptions in any

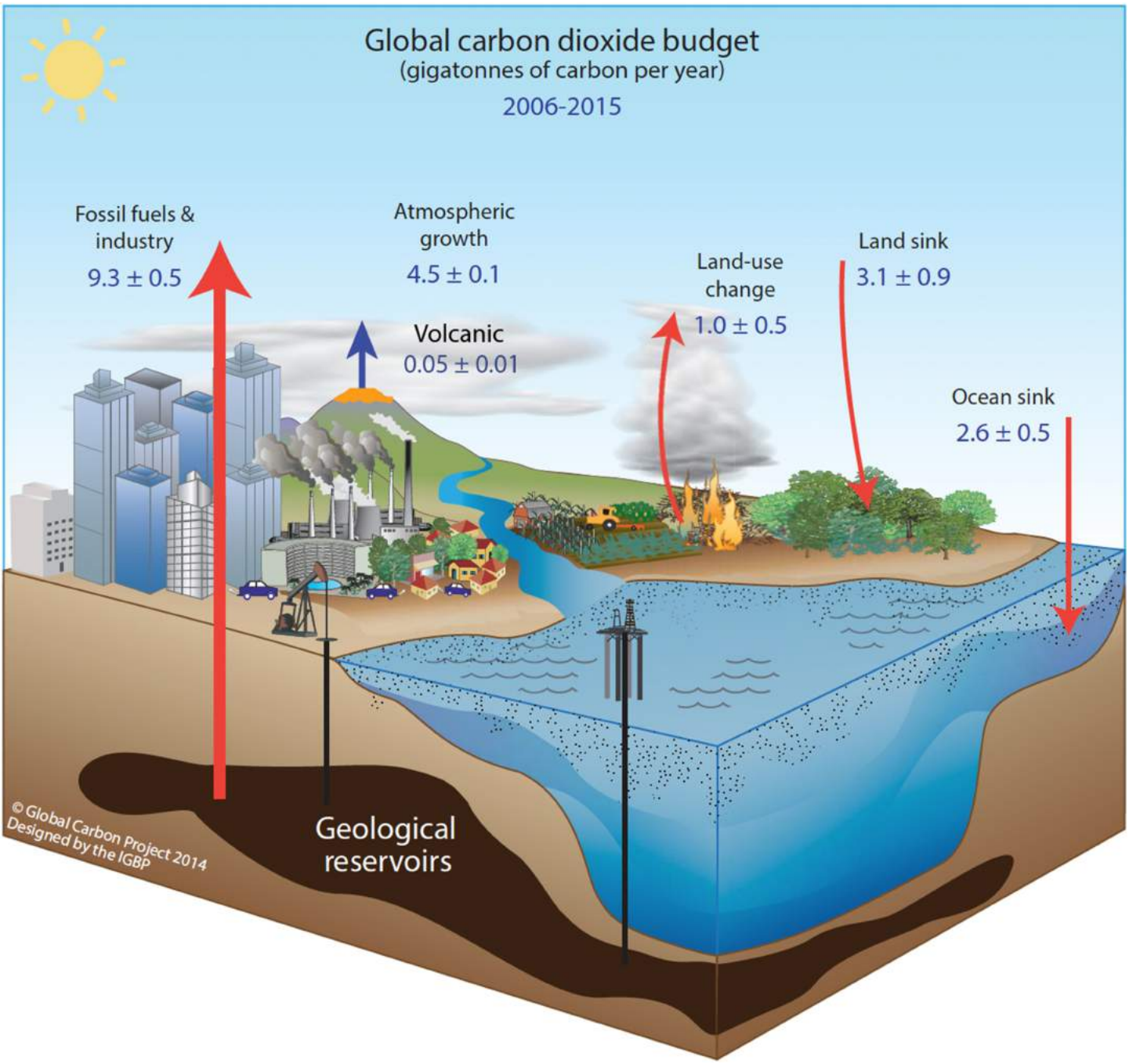

Figure 4. The global CO_2 budget from le Quere et al. (2016). All data are in gigatons of C per year for comparison. The volcanic CO_2 flux in this diagram is data presented in this contribution.

year. The fact that there are only about 80 eruptions in any given year (Global Volcanism Program, 2016; Simkin & Siebert, 1994) demonstrates how huge current anthropogenic CO_2 emissions are within the Earth system and within geologic time as a whole. Comparisons of various natural CO_2 emission scenarios are shown in Figure 5.

While volcanic CO_2 emissions are negligible in comparison to anthropogenic emissions, CO_2 is an extremely powerful tracer of volcanic activity due to its low solubility in magmas (Holloway & Blank, 1994). Over the

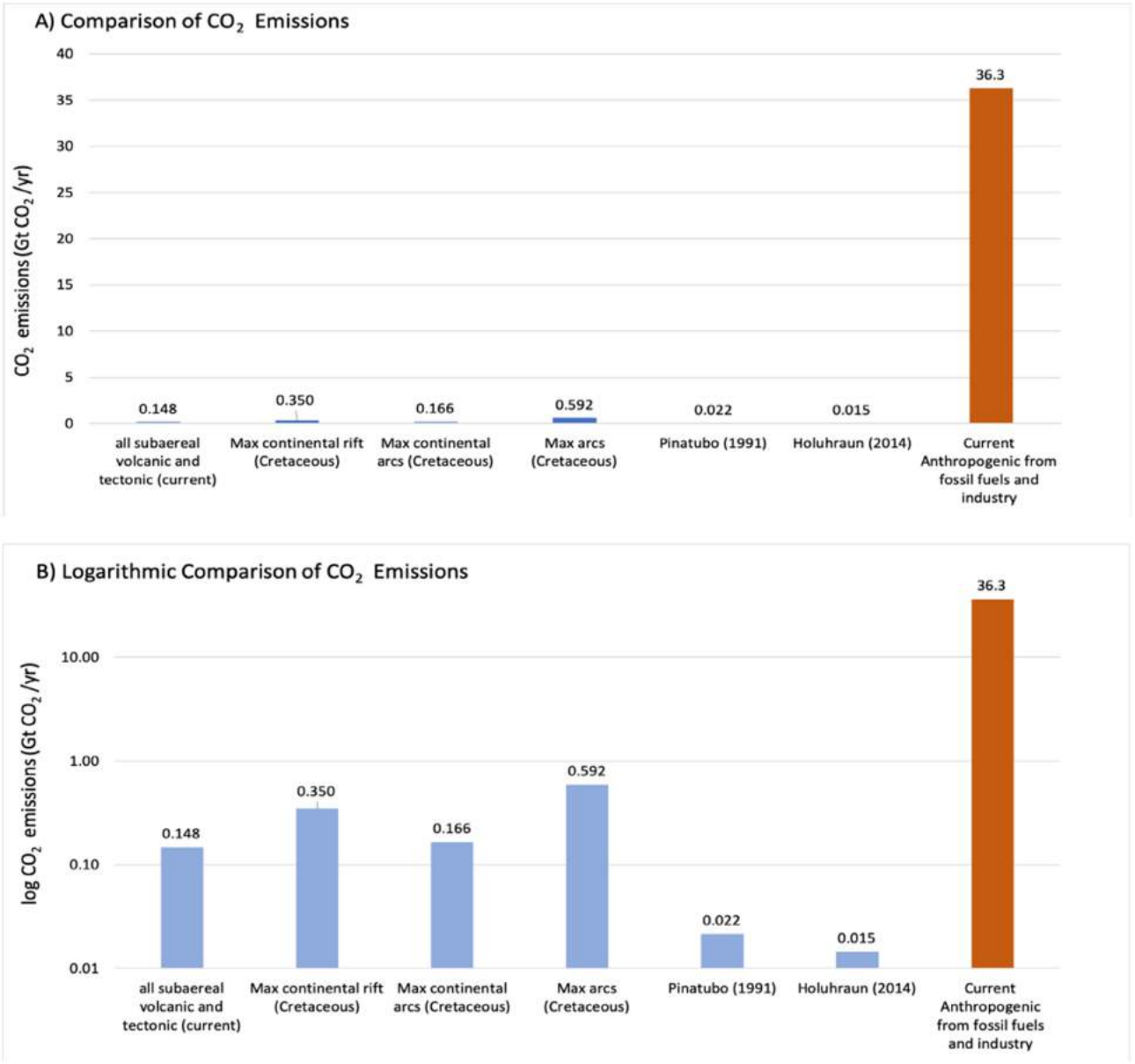

Figure 5. Comparison of various volcanic CO_2 emissions including the current global volcanic and tectonic emissions, the maximum continental rift and arc emissions, and emissions associated with the 1991 Pinatubo and 2014 Holuhraun eruptions. (a) Emission comparisons and (b) emission comparisons on a logarithmic scale.

past decade, the technological advances shown in Figure 1 have resulted in our improved ability to continuously measure CO_2 and other gases in volcanic plumes. In combination with improvements in satellite- and ground-based remote sensing methods, volcanic eruption forecasting using volcanic gases has gained in potential. Several recent examples have used nearly continuous C/S ratio monitoring to develop conceptual and quantitative models of explosive and phreatic volcanic eruptions (Aiuppa et al., 2009; Aiuppa, Bitetto, et al., 2017; Aiuppa et al., 2018; de Moor Aiuppa, Avard, et al., 2016; de Moor, Aiuppa, Pacheco, et al., 2016; de Moor et al., 2019). A continuing challenge is to maintain these systems at active volcanoes globally, telemeter the data in real time to observatories, and adequately interpret the data in order to forecast eruptions with high accuracy. In combination with other volcano-monitoring techniques, such as seismic and deformation, much progress can be made to build more accurate and universally applicable physical-chemical models of volcanoes that enable volcanic eruption forecasting to save lives and property.

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