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Deep Carbon Emissions from Volcanoes

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INTRODUCTION: VOLCANIC CO_2 EMISSIONS IN THE GEOLOGICAL CARBON CYCLE

Over long periods of time (~Ma), we may consider the oceans, atmosphere and biosphere as a single exospheric reservoir for CO_2. The geological carbon cycle describes the inputs to this exosphere from mantle degassing, metamorphism of subducted carbonates and outputs from weathering of aluminosilicate rocks (Walker et al. 1981). A feedback mechanism relates the weathering rate with the amount of CO_2 in the atmosphere via the greenhouse effect (e.g., Wang et al. 1976). An increase in atmospheric CO_2 concentrations induces higher temperatures, leading to higher rates of weathering, which draw down atmospheric CO_2 concentrations (Berner 1991). Atmospheric CO_2 concentrations are therefore stabilized over long timescales by this feedback mechanism (Zeebe and Caldeira 2008). This process may have played a role (Feulner et al. 2012) in stabilizing temperatures on Earth while solar radiation steadily increased due to stellar evolution (Bahcall et al. 2001). In this context the role of CO_2 degassing from the Earth is clearly fundamental to the stability of the climate, and therefore to life on Earth. Notwithstanding this importance, the flux of CO_2 from the Earth is poorly constrained. The uncertainty in our knowledge of this critical input into the geological carbon cycle led Berner and Lagasa (1989) to state that it is the most vexing problem facing us in understanding that cycle.

Notwithstanding the uncertainties in our understanding of CO_2 degassing from Earth, it is clear that these natural emissions were recently dwarfed by anthropogenic emissions, which have rapidly increased since industrialization began on a large scale in the 18th century, leading to a rapid increase in atmospheric CO_2 concentrations. While atmospheric CO_2 concentrations have varied between 190-280 ppm for the last 400,000 years (Zeebe and Caldeira 2008), human activity has produced a remarkable increase in CO_2 abundance, particularly in the last 100 years, with concentrations reaching ~390 ppmv at the time of writing. This situation highlights

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the importance of understanding the natural carbon cycle, so that we may better determine the evolution of the anthropogenic perturbation.

The principle elements of the multifaceted and complex geological carbon cycle are summarized in Figure 1. The main sources of carbon are active and inactive volcanism from arcs and rift zones and metamorphism of crustal carbonates. The main sinks for geological carbon are silicate weathering and carbonation of oceanic crust. Knowledge of both the total magnitude of carbon ingassing during subduction and carbon released from volcanism and metamorphism would allow quantification of the evolution and relative distribution of volatiles in the crust and mantle (Dasgupta and Hirschmann 2010).

The main focus of this work is the role of volcanism in producing CO_2 in the atmosphere and oceans. Volcanic CO_2 sources can be divided into several categories, direct and diffuse degassing from active arc and rift volcanoes, diffuse degassing from inactive volcanoes and regional diffuse degassing from intrusive plutonic structures with associated crustal metamorphism. We focus here on non-eruptive degassing because, as shown below, continuous emission of CO_2 from multiple sources appears to dominate short-lived eruptive emissions from point sources.

CO_2 released directly from active volcanoes has three main sources, CO_2 dissolved in the mantle, recycled CO_2 from subducted crustal material (e.g., Marty and Tolstikhin 1998) and decarbonation of shallow crustal material (e.g., Troll et al. 2012). Separating the relative proportions of mantle and crustal carbon is possible through investigation of the isotopic composition of emitted carbon (e.g., Chiodini et al. 2011) and is increasingly important given that during eruptions magmatic intrusions may interact with crustal material, strongly enhancing the CO_2 output of the volcanic system (Troll et al. 2012), at least temporarily. The magnitude of diffuse mantle CO_2 can also be identified isotopically in mixed metamorphic and magmatic gases using Carbon (Chiodini et al. 2011) or Helium isotopes as a proxy for deep mantle sources in both major fault systems (Pili et al. 2011) and crustal tectonic structures (Crossey et al. 2009).

Our current estimates of volcanic carbon emissions are poorly constrained due to a lack of direct measurements. Measuring CO_2 in subaerial volcanic plumes is a challenge, because while CO_2 typically makes up ~10 mol% of volcanic gas emissions (the majority of which is normally water vapor), mixing with the atmosphere rapidly dilutes the volcanic CO_2 signature. Nevertheless, technological advances and an increase in the number of volcanoes studied have

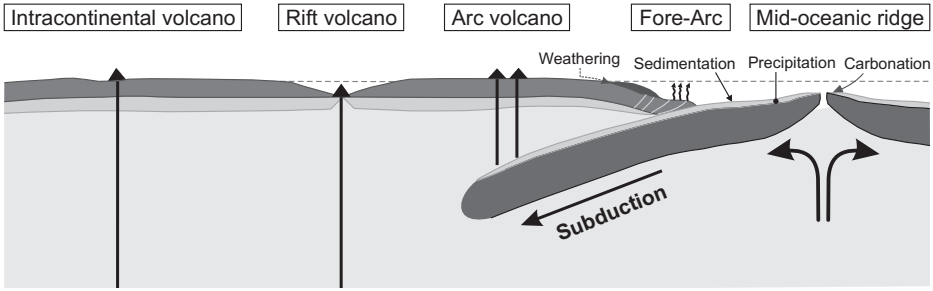

Figure 1. Schematic diagram showing the main sources and sinks for volcanic CO_2 on Earth within the geological carbon cycle. CO_2 is released at MORs during crustal genesis, but it is also absorbed into the newly formed crust in high temperature hydrothermal reactions. Carbonates precipitate directly into oceanic crust and collect in sediments before the subducting slab is carried under the mantle wedge. Volcanism then produces CO_2 emissions from the fore-arc (through cold seeps), arc volcanism, rift volcanism, intracontinental volcanoes and hotspots. The CO_2 emitted into the atmosphere reacts in weathering reactions with silicate rocks, carrying C back into the ocean where the geological carbon cycle is eventually closed through carbon sequestration into the subducting slab material.

greatly increased our knowledge of volcanic CO_2 fluxes over the last 10 years. One of the main goals of this work is to update global geological CO_2 flux estimates (e.g., Kerrick 2001; Mörner and Etiope 2002; Fischer 2008) using the recently acquired volcanic CO_2 flux data.

Diffuse CO_2 degassing from both volcanic and tectonic structures is a large contributor to the global geological CO_2 emission, but is difficult to measure due to the large areal extent that may be in play, and the large number of degassing sites throughout the globe. Measuring the CO_2 degassing rates into volcanic lakes and from submarine volcanism have significant technical challenges. In the following we review the state of the art of volcanic CO_2 measurements and present a catalogue of reported, quantified emissions from geological sources. These measurements are then extrapolated to produce estimates of the global volcanic CO_2 flux. These estimates are compared with previously published estimates of total CO_2 emissions, silicate weathering rates and the rate of carbon consumption during subduction. We then examine the dynamic role of CO_2 within magmatic systems and the magnitude of CO_2 released during eruptions.

Carbon species in Earth degassing

CO_2 is not the only carbon-containing molecule emitted from the Earth. In order of decreasing emissions, CO_2, CH_4, CO and OCS all contribute to the total carbon budget. Mörner and Etiope (2002) estimated that the global emission of CO_2 from Earth degassing was ~600 million tonnes of CO_2 per year (Mt/yr, 1 Mt = 10^{12} g), with ~300 Mt/yr produced from subaerial volcanism, and another 300 Mt/yr produced from non-volcanic inorganic degassing, mostly from tectonically active areas (Chiodini et al. 2005). For comparison, Cadle (1980) estimated that volcanic activity produces 0.34 Mt/yr of CH_4. Mud volcanoes in Azerbijan were estimated to produce ~1 Mt/yr of CH_4, however the global flux from mud volcanism is not known. Hydrocarbon seepage of CH_4 globally is estimated to produce between 8 and 68 Mt/yr (Hornafius et al. 1999). Etiope et al. (2008) estimated that global CH_4 emissions from geological sources to be 53 Mt/yr, a significant proportion of the geological C output.

CO is emitted directly from volcanoes, with a CO_2/CO ratio that varies between ~10 and ~1000 depending on the oxygen fugacity and temperature of the fluid co-existing with melt prior to outgassing. OCS is also directly emitted within volcanic plumes, but in even smaller relative amounts than CO, typically 1000-10,000:1 for CO_2:OCS (Mori and Notsu 1997; Burton et al. 2007a; Oppenheimer and Kyle 2008; Sawyer et al. 2008a). OCS is the most abundant S bearing gas species in the atmosphere, contributes to stratospheric sulfuric acid aerosol generation (Crutzen 1976) and is an efficient greenhouse gas (Brühl et al. 2012). Its budget is dominated by emissions from oceans and anthropogenic processes. From a total global output of ~1.3 Mt/yr of OCS only 0.03 Mt is estimated to arise from volcanism (Watts 2000). CS_2 is the final trace carbon gas emission from volcanoes, with a similar flux and chemistry to OCS.

While recent estimates of geological emissions of CH_4 (Etiope et al. 2008) clearly indicate that these emissions are significant compared with geological CO_2 on the global scale, in this work we focus on CO_2 emissions, and use the most recent volcanic CO_2 flux data to update the measured global volcanic CO_2 flux.

METHODS FOR MEASURING GEOLOGICAL CO_2 EFFLUX

Ground-based measurements of volcanic plumes

Directly quantifying volcanic CO_2 fluxes in the atmosphere is challenging due to the relatively abundant concentration of background CO_2, currently ~390 ppm. To put this in context, a strong volcanic CO_2 source such as Mt. Etna, Italy, produces a gas plume where 1 km downwind the average concentration of volcanic CO_2 is only ~4 ppm (based on calculations with VOLCALPUFF plume dispersal model, Barsotti et al. 2008). Thus, an *in situ* measure-

ment 1 km downwind needs to resolve a mere 1% excess CO_2 compared with the background concentration. Most volcanoes emit less CO_2 than Mt. Etna, so this is an optimistic scenario. This difficulty has led most researchers to focus on measurements of the volcanic emissions close to the source, using *in situ* and proximal remote sensing techniques. In such measurements, volcanic CO_2 fluxes are normally determined by measuring the ratio of volcanic CO_2 to another volcanic gas, typically SO_2 due to the ease with which its flux can be measured (Oppenheimer et al. 2011), and then calculating the CO_2 flux as the product of the CO_2/SO_2 ratio and the SO_2 flux. The objective of the majority of the following techniques in the context of quantifying CO_2 fluxes is therefore the determination of the CO_2/SO_2 ratio in the volcanic gas.

An exception to this combined CO_2/SO_2 and SO_2 flux approach was adopted by Marty and Le Cloarec (1992) who utilized global volcanic flux estimates of ^{210}Po and $^{210}Po/CO_2$ ratios measured in direct sampling (see below) to derive estimates of global CO_2 fluxes.

Direct sampling of a volcanic gas can be achieved with the use of Giggenbach bottles (Giggenbach and Goguel 1989), where high temperature fumarolic gases are collected in an alkaline solution for later laboratory analysis. This approach allows both bulk and trace gas species to be quantified, but the fact that the most abundant gas component, H_2O, can condense in the tube leading to the alkali solution bottle means that H_2O is challenging to quantify, and therefore absolute concentrations of the other species can be difficult to define. Air contamination is difficult to avoid, and can further increase the difficulty in determining the original volcanic gas concentrations. Such measurements require working in extremely close proximity to the degassing vent, and are ideally performed on the hottest and most highly pressurized emissions (to avoid air contamination), making their collection challenging and potentially hazardous. In addition, some of the most voluminous volcanic gas sources release very little volatiles from fumaroles, instead the bulk of the emission is open-vent degassing from craters. These plume emissions are impossible to sample without air contamination with such an approach.

The MultiGas approach (Shinohara 2005) has greatly simplified the measurement of volcanic CO_2/SO_2 ratios, allowing automatic, unattended analysis of volcanic plumes for extended periods of time (Aiuppa et al. 2007). This instrument combines a near-infrared spectroscopic measurement of CO_2 and H_2O concentrations with a solid-state chemical sensor for quantification of SO_2 and H_2S. The relatively low cost, low power requirement and ease of use of the instrument make it probably the most convenient and cost-effective way of determining *in situ* CO_2/SO_2 ratios available today. Some potential errors can arise, however, due to the different response time of the CO_2 and SO_2 sensors. Typical response times for the near-infrared optical technique used to measure CO_2 is ~1 s, while response times for SO_2 chemical sensors is typically longer, e.g., ~13-31 s for an Alphasense chemical sensor (Roberts et al. 2012). This means that fast changes in chemical composition or concentration are challenging to capture, however through the use of longer integration times problems arising from diverse sensor response times can be avoided. Quickly changing gas concentrations could instead be captured in theory with an optically based SO_2 measurement.

Remote sensing measurements of CO_2 amounts can be performed with infrared spectroscopy if the volcanic gas concentration is sufficiently high above the background atmospheric CO_2 amount. The first such pioneering infrared measurements of volcanic CO_2 amounts were conducted remarkably early, in 1969 by Naughton et al. (1969), during a lava fountain on Kīlauea, Hawai'i. Since then, open-path Fourier transform infrared (OP-FTIR) spectroscopy (Mori and Notsu 1997) has become a well-utilized tool to measure *in situ* volcanic gas compositions. Modern FTIR spectrometers are light (~8 kg), relatively low power (~30 W) and require no cryogenic cooling (e.g., La Spina et al. 2010), yet allow the simultaneous measurement of many volcanic gases, including H_2O, CO_2, SO_2, HCl, HF, CO OCS and SiF_4. Measurements of volcanic CO_2 require an infrared light source, either an infrared lamp (Burton et al. 2000) or hot volcanic rocks (Allard et al. 2005; Burton et al. 2007a; Sawyer et al. 2008a). Infrared radiation

is absorbed by volcanic gases before being measured with the infrared spectrometer and the resulting spectra can be analyzed (Burton et al. 2000, 2007a) to produce relative abundances of volcanic H_2O, CO_2, SO_2 and several other gases. Smith et al (2011) concluded that such analytical approaches could deliver accuracies of ~5% in CO_2 amounts. The greatest challenge in performing OP-FTIR measurements is obtaining a suitable source of IR radiation, with sufficient volcanic gas between the source and the spectrometer. Recent innovations in applying the remote-controlled mode at the summit of Stromboli (La Spina et al. 2013) show that it can be used for high temporal resolution monitoring of multiple gas sources.

CO_2 emissions from fumarole fields can be determined through the introduction of a known flux of a tracer gas, such as SF_6, and then measuring the volcanic CO_2/SF_6 ratio in the downwind gas emission. Mori et al. (2001) successfully used this approach to measure CO_2 flux emissions from fumarolic vents on Izu-Oshima (Japan), Kirishima (Japan) and Teide (Canary Islands, Spain).

A recent innovation has been the use of portable mass spectrometers to determine *in situ* volcanic gas compositions (Diaz et al. 2010). This approach was used successfully before and after the 5th January 2010 eruption of Turrialba (Costa Rica), revealing significant changes in CO_2, SO_2 and He concentrations.

Volcanic SO_2 flux measurements

As described above the determination of CO_2 flux requires a further step after measurement of CO_2/SO_2 ratios, multiplication with an SO_2 flux. Several assessments of arc volcanic CO_2 emissions have been produced (e.g., Hilton et al. 2002; Fischer and Marty 2005) by interpreting volcanic SO_2 inventories (e.g., Andres and Kasgnoc 1998; Halmer et al. 2002) Since errors on the SO_2 flux propagate into the CO_2 flux we briefly examine here the methods used to measure SO_2 flux, together with their associated errors. The SO_2 flux is much easier to measure directly than the CO_2 flux for two reasons: firstly, SO_2 is not present in the unpolluted troposphere and secondly, SO_2 has a convenient, relatively strong absorption band in the ultraviolet, easily accessible using scattered sunlight as a source. This has allowed the creation of automatic networks of UV scanners, that permit volcanic SO_2 fluxes to be monitored (Edmonds et al. 2003; Burton et al. 2009; Galle et al. 2010; Oppenheimer et al. 2011). Typically in the literature the greatest quoted source of error in SO_2 flux measurements derives from wind speed estimates, and this error is normally indicated to be ~20-30%. A recent innovation in ground-based measurements of SO_2 fluxes is the SO_2 imaging camera, which uses an imaging sensor sensitive to the UV and optical filters to produce specific sensitivity to SO_2 (e.g., Mori and Burton 2006). This approach has the potential to correct implicitly for wind velocity but it suffers potentially from cross-talk between SO_2 and volcanic ash or aerosol.

Recent work on subtle radiative transfer issues relating to ground-based UV SO_2 flux measurements highlight that there could be large, previously ignored, errors associated with light dilution (Kern et al. 2012). This is a process where light scattering from below the volcanic plume enters the instrument, diluting the light which passed through the volcanic plume from above, resulting in a net underestimation in the SO_2 flux, of up to 90%. The true significance and importance of this effect, and the number of published SO_2 fluxes that require re-analysis, has yet to be evaluated. It should be noted therefore that estimates of global CO_2 flux based on published SO_2 flux data may be subject to revision, depending on the impact of light dilution on SO_2 flux measurements.

In addition to ground-based measurements of SO_2 flux, satellite-based measurements are often used, working in both the ultraviolet (e.g., OMI, SCIAMACHY) and infrared (e.g., MODIS, ASTER, IASI) wavelengths. These instruments can produce maps of SO_2 abundance with a repeat time of ~days. With such a repeat rate the same plume is normally not observed in two different images, and it is therefore not possible to perform a simple cross-correlation

to determine plume velocity and therefore flux from images of SO_2 abundance. The conversion from SO_2 abundance image to a quantitative degassing rate is therefore not trivial, because both the age and velocity of the plume at each point in the image must be derived using an independent method (e.g., Merucci et al. 2011). An additional challenge with satellite-based measurements of SO_2 flux is that the sensitivity to SO_2 decreases in the lower atmosphere, such that low-lying volcanoes are difficult to measure unless they are in eruption, and even higher altitude volcanoes require a relatively large SO_2 degassing rate to be reliably quantified (Carn et al. in press).

Measurements of CO_2 flux using the combination of CO_2/SO_2 ratios and SO_2 fluxes therefore reflect uncertainties in both measurements, typically estimated to be 10-20% and 25-30% respectively. As mentioned above, recent work in radiative transfer analysis highlights the potentially important, but largely overlooked, role that light dilution may play in producing potentially significant underestimates of SO_2 fluxes from UV measurements (Kern et al. 2012). Notwithstanding these drawbacks, at the current time these data are the main constraints available for subaerial deep CO_2 output from volcanoes.

Recent technological advances have allowed such integrated CO_2/SO_2, SO_2 flux measurements to be fully automated for the first time, allowing real-time monitoring of CO_2 fluxes. This is particularly important because the low solubility of CO_2 in magmas means that deep, pre-eruptive, magmatic intrusions may be heralded at the surface by increases in CO_2 flux. Aiuppa et al. (2011) reported the first time series of CO_2 flux collected using combined MultiGas and SO_2 flux networks (Burton et al. 2009) on Stromboli volcano. These revealed distinct oscillations in CO_2 emissions, with periods of relatively high CO_2 degassing followed by periods of low CO_2 degassing, producing a steady average CO_2 degassing rate of ~550 t/d. Such a pattern suggests a steady state supply of CO_2 which is modulated by gas accumulation / permeability / magma supply processes within the magma feeding system. Interestingly, more intense explosive activity was observed after a period of intense CO_2 degassing, opening the possibility of using such observations to forecast explosive volcanic activity at this volcano.

Airborne measurements of volcanic plumes

Two main approaches have been used to measure volcanic CO_2 fluxes from the air. A direct method consists of flying an *in situ* CO_2 analyzer (typically a closed-path near-infrared spectrometer) in a raster or ladder traverse across the cross-section of a volcanic plume (Gerlach et al. 1997; Werner et al. 2008). The resulting data can be interpolated to produce a CO_2 concentration map, which can be integrated over the cross-sectional area of the plume and multiplied with wind speed to produce a CO_2 flux. This approach has the advantage of being a direct measurement of the CO_2 emissions, however each measurement requires ~1 hour and therefore very stable wind conditions are required in order to avoid errors in the flux calculation.

The second airborne approach combines plume traverse measurements with an ultraviolet spectrometer to derive SO_2 flux with *in situ* measurement of the CO_2/SO_2 ratio provided with a closed-path FTIR spectrometer, sampling ambient air as the plane flies through the plume (Gerlach et al. 1998). This is probably the most robust methodology currently available for measuring CO_2 fluxes, as the SO_2 flux analysis can be performed close enough to the plume that light dilution is insignificant. Flying has its own challenges, however, due to the technical constraints involved in performing measurements on a vibrating platform, as well as the costs associated with flight time and difficulties presented from flying within the volcanic plume.

Airborne measurements of volcanic CO_2 may also be achieved by viewing infrared radiance from the ground through a volcanic plume with a hyperspectral radiometer, and this has been successfully demonstrated on Kīlauea, Hawai'i using the AVIRIS hyperspectral imager (Spinetti et al. 2008). Results obtained with AVIRIS agreed well with ground-based measurements of CO_2 emissions, validating the method.

More recently, similar measurements to those performed by Gerlach et al. (1998) have been conducted from an unmanned aerial vehicle platform (UAV) (McGonigle et al. 2008). Such an approach is appealing due to the significantly reduced cost and risk, as well as increased accessibility. However, the legal framework for conducting such measurements is complex and varies greatly between countries, making general take-up of such methodologies so far quite limited. Future longer distance stand-off measurements may be possible using larger UAVs offering an intermediate option to space-based satellite retrievals of air column soundings.

Space-based measurements of volcanic plumes

Global measurements of volcanic CO_2 emissions would be the ideal approach to quantifying the global volcanic deep CO_2 budget. The most promising observing platform for volcanic CO_2 is the aptly named Orbiting Carbon Observatory (OCO) (Crisp et al. 2004). The rocket carrying the OCO failed to reach orbit when launched in 2009, and a new launch with a replacement satellite is currently planned for 2014. The OCO utilizes a single telescope to feed light to spectrometers which measure the columnar abundance of both O_2 and CO_2, using absorption bands at wavelengths of 0.67 micron for O_2, and 1.61 and 2.06 micron for CO_2. The purpose of the O_2 column amount measurement is to normalize the CO_2 column measurement to an average CO_2 mole fraction in ppmv. The final error on the average CO_2 concentration in the column is 0.3 wt%. The footprint of the OCO will be 1 km by 1.5 km at nadir, and will have a repeat observation period of 16 days.

A simple calculation of the CO_2 emission from a strong emitter such as Mt. Etna allows a direct estimation of the feasibility of such measurements with OCO. Etna degasses CO_2 at an average rate of 16,000 t/d or ~190 kg s^{-1} (Allard et al. 1991; Aiuppa et al. 2006, 2008; La Spina et al. 2010). Assuming an optimal geometry in which the gas source was at one edge of a single OCO footprint and the entire plume contained within the 1.5 km length of the pixel, with a windspeed of 5 m s^{-1} the maximum age of CO_2 in the footprint would be ~300 seconds, and the total volcanic CO_2 mass would be ~57,000 tonnes. Converting this CO_2 mass to molecules and averaging over the OCO nadir footprint area produces a vertical column amount of ~5 × 10^{19} molecules cm^{-2}. The atmospheric vertical column amount of CO_2 at the average altitude of Etna is ~6 × 10^{21} molecules cm^{-2} and therefore the volcanic signal would be ~0.8 % of the atmospheric column, which is above the 0.3% error limit of OCO. A slower wind would produce a higher volcanic CO_2 amount, while a less optimal geometry would decrease the relative contribution from the volcano. OCO therefore has the potential for measuring passive CO_2 emissions from Mt. Etna, in optimal conditions. During eruptions the CO_2 emission rate would increase, allowing for easier detection. The majority of degassing volcanoes are less productive than Mt. Etna, however, and would present a challenge for detection from OCO, unless they were undergoing an eruption.

Ground-based measurements of diffuse deep CO_2

Significant amounts of diffuse CO_2 are released from active volcanic areas, not only during eruptions but also during quiescent periods. This volcanic CO_2 discharge occurs over the flanks of the volcanic edifice as diffuse soil emanations (Allard et al. 1991; Baubron et al. 1990), and adds to the voluminous and more obvious degassing from fumaroles and summit craters. Many CO_2 soil flux measurement techniques have been applied to quantify these gases and include both direct and indirect methods (e.g., Reiners 1968; Kucera and Kirkham 1971; Kanemasu et al. 1974; Parkinson 1981).

The indirect methods are based on the determination of the CO_2 concentration gradient in the soil (Camarda et al. 2006). These methods can be applied only if the transport of the gas is dominated by the diffusion and some properties of the medium are known. Direct methods require dynamic or static procedures, whether or not a flux of air is used to extract gas from the soil. The dynamic procedures require some corrections depending on the physical properties of

the soil in the measurement point and on the design of the instrumental apparatus. Furthermore, all dynamic procedures are affected by overpressurization or depressurization depending upon the magnitude of the air flux chosen by the operator and according to Kanemasu et al. (1974) results are strongly affected by the physical modifications induced by pumping under different flux regimes. Camarda et al. (2006) present a demonstration of the indirect method applied to measuring CO_2 fluxes from Vulcano (Italy), and show that with low pumping rates the sensitivity of the method to soil permeability is reduced.

The accumulation chamber method (or closed-chamber method) is a direct, static method originally used in agricultural sciences to determine soil respiration (Parkinson 1981) and then successfully adapted to measure CO_2 soil flux of volcanological interest by Tonani and Miele (1991). This method is based on the measurement of the CO_2 concentration increase inside an open-bottomed chamber of known volume, inverted on the soil surface. The initial rate of change of the concentration is proportional to the CO_2 flux (Tonani and Miele 1991; Chiodini et al. 1996). The method does not require either assumptions about soil characteristics or the regime of the flux (advective/diffusive). The method has been tested by several authors under controlled laboratory conditions and provides reproducibility of 10% (Chiodini et al. 1998). In a field reproducibility test of the method, carried out at two points with high and low CO_2 flux, Carapezza and Granieri (2004) found an uncertainty of 12% for high fluxes and 24% for low fluxes. Multiple measurements performed by ground-based methodologies allow a mapping of CO_2 flux and an estimation of the total CO_2 release by use of interpolation algorithms (Cardellini et al. 2003; Chiodini et al. 2005).

Eddy covariance or alternately Eddy correlation (EC) is a micrometeorological technique (e.g., Baldocchi 2003) recently proposed as a method to monitor volcanic CO_2 emissions (Werner et al. 2000, 2003; Anderson and Farrar 2001; Lewicki et al. 2008). The basis of the EC is the calculation of the flux at the surface through the covariance between the fluctuations of the vertical component of the wind and the fluctuations of the gas concentration in atmosphere. The EC provides advantage of being an automated, time-averaged and area-integrated technique with a spatial scale significantly larger (square meter to square kilometer) than that of the ground-based methods (e.g., accumulation chamber). However the volcanic environment is often too heterogeneous for EC application, as suggested by the theory underlying EC, in terms of spatial and temporal variability of surface fluxes and morphology of the measuring field.

Diffusive degassing of deep CO_2 in tectonically active areas

Since the early work of Irwin and Barnes (1980), it has become clear that a close relationship exists between active tectonic areas and anomalous crustal emissions of CO_2. Due to their high crustal permeability, faults act as preferential pathways for the upward migration and eventual release of deep gases to the aquifers or directly to the atmosphere. Regional aquifers located in areas of high CO_2 flux can dissolve most or part of the deeply generated gas because the relatively high solubility of CO_2 in water. A carbon mass balance in the involved aquifer can be used to obtain an estimation of the amount of CO_2 dissolved by groundwater. However, the large range of $^{13}\delta C_{CO_2}$ observed in such aquifers suggests that carbon can derive from multiple sources: atmospheric C, biogenic C, carbonate minerals derived C and deeply derived C. Therefore, an approach by coupling groundwater chemistry with hydrologic and isotopic data has to be applied in order to differentiate shallow versus deep sources. Chiodini et al. (2004) showed that in the tectonically active area of the Italian Apennines, approximately 40% of the inorganic carbon in the groundwater derives from magmatic sources. This observation suggests that there may be significant amounts of magmatic CO_2 released in tectonic areas, perhaps a similar order of magnitude as subaerial volcanic degassing (Chiodini et al. 2004). Indeed, in volcanic areas, the dissolved CO_2 in groundwater can be a significant component of the total CO_2 flux at the volcano (e.g., Rose and Davisson 1996; Sorey et al. 1998; Inguaggiato et al. 2012).

Submarine measurements

Volatile emissions from the axis of mid-ocean ridges (MORs) in the form of black smokers are dramatic examples of submarine deep carbon emissions, however they tend to be short-lived and unpredictable, making collection of gas samples challenging. Nevertheless measurements of the composition and flux of such emissions have been conducted at dozens of sites (Kelley et al. 2004), using a wide range of gas collection techniques from piloted and remotely controlled submersible craft, allowing later analysis of gas samples in the laboratory. Direct measurements have been performed on only a fraction of the world's MOR, and therefore previous work on the fluxes of CO_2 from MOR has focused on quantifying emissions relative to a better-constrained global production parameter. These have included crustal production rates and the C content of the mantle (Gerlach 1989, 1991; Javoy and Pineau 1991; Holloway 1998; Cartigny et al. 2001; Saal et al. 2002), global mantle ^{3}He flux (Corliss et al. 1979; Des Marais and Moore 1984; Marty and Jambon 1987; Sarda and Graham 1990; Graham and Sarda 1991; Marty and Zimmerman 1999), hydrothermal fluid flux (Elderfield and Schultz 1996) and the $CO_2/^3$He ratio in hydrothermal plumes. The latter two require estimates of global ^{3}He fluxes, which are produced primarily at MORs (Allard et al. 1992).

An important aspect of MOR volcanism is that during the process of formation CO_2 reacts with hot rock, sequestering CO_2. In addition, dissolved carbonate in seawater reacts progressively within the shallowest ~60 m oceanic crust, producing steadily higher carbonate concentrations with increasing crustal age. Measurements of drill cores of the upper oceanic crust allowed Alt and Teagle (1999) to quantify the magnitude of the CO_2 sink produced by crust reactions as of the magnitude of 150 Mt/yr CO_2. This is of similar magnitude to the MOR CO_2 flux of 97 ± 40 Mt/yr CO_2, indeed it is probable that reactions in the oceanic crust absorb more CO_2 than is emitted from MORs.

As well as emissions from the main axis of the MOR, degassing takes place on the flanks of the ridge, driving circulation of seawater through the crust. Sansone et al. (1998) sampled gas emissions from the eastern flank of the Juan de Fuca ridge with the Alvin deep sea vessel, both directly and through inverted funnels to concentrate the gas flow into titanium gas-tight samplers (Massoth et al. 1989). Further samples were collected using titanium syringe samples (Von Damm et al. 1985). Gas samples were acidified and then vacuum-extracted at sea with a glass/stainless-steel vacuum line. The total gas volume was determined with high precision capacitance manometers, and the extracted gas from each sample was sealed in break-seal glass ampoules for analysis ashore with gas chromatography and mass spectrometry.

Gas emissions also occur from active submarine arc volcanoes. Lupton et al. (2008) measured gas output from eleven volcanoes along the Mariana and Tonga-Kermadec arcs with remote controlled vehicles during three expeditions. Four of these volcanoes were found to produce distinct gas and liquid CO_2 gas emissions, together with hydrothermal emissions from the main vents. Vent emissions were sampled using seawater-filled titanium alloy gas-tight bottles connected via tubing to a Ti sampling snout inserted directly into the vent. A valve was then opened and hydraulic pressure filled the bottle with a sample of vent gas. On the ship, samples were acidified and transferred under vacuum ampoules made of Pyrex and low-He permeability alumino-silicate glass for later laboratory analysis. Collection of liquid CO_2 droplets was challenging due to the ~1000 fold expansion of liquid CO_2 when converted to CO_2 gas at 1 atm pressure, necessitating the use of a small volume Ti gas-tight bottle. Gas bubbles were collected with a plastic cylinder with relief valve that was placed over the emission until filled.

Understanding of the carbon balance in a subduction zone requires knowledge of the amount of carbon entering the zone within the subducting slab, CO_2 loss from main arc volcanism and back arc, and the submarine fore-arc (see Fig. 1). This latter was measured

from seeps in the Central America subduction zone by Füri et al. (2010). Seep fluids were collected over a 12 month period at the submarine segment of the Costa Rica fore-arc margin using 1/8 inch diameter copper tubing attached to a submarine flux meter operating in continuous pumping mode to measure CO_2 and CH_4 fluxes. Temporal variations during the sampling period were revealed by cutting the copper tubing in 0.4 m sections under vacuum and extracting the stored volatile samples in the laboratory for isotope ratios and compositions.

Volcanic lakes are significant, but previously unrecognized (Pérez et al. 2011) contributors to global deep CO_2 budgets. CO_2 gas emissions from volcanic lakes are in the form of both diffuse degassing from the lake surface and bubbling (Mazot and Taran 2009). Lake CO_2 emissions were therefore measured with a floating gas accumulation chamber with an in-built NIR sensor to measure CO_2 concentrations. Conversion of CO_2 concentrations to fluxes was made using simultaneous measurements of pressure and temperature.

REPORTED MEASUREMENTS OF DEEP CARBON FLUXES

Subaerial volcanism

During the Holocene, ~1500 volcanoes on land erupted and in recorded history there have been 550 known eruptions. Typically 50-70 volcanoes erupt explosively each year and ~500 produce a gas emission either through hydrothermal systems or open-vent degassing (Siebert and Simkin 2002). Of these, only a small fraction have had their CO_2 flux measured directly, however the number of measured volcanoes has greatly increased in recent years. In this section we first present published data on measured volcanic CO_2 emission rates from active volcanoes, diffuse degassing of volcanic areas and tectonically active areas, followed by volcanic lakes and submarine emissions. We conclude by producing a global sum of CO_2 emission rates.

We report in Table 1 all known volcanic plume CO_2 flux measurements from persistently degassing volcanoes. We have chosen data in which CO_2 fluxes were measured either by near simultaneous measurement of CO_2/SO_2 ratios and SO_2 / gas flux, or direct measurement of the CO_2 flux. This was done because the number of volcanoes for which CO_2 flux has been measured accurately has greatly increased in the last years, with 40 new measurements reported since 2000. We performed a simple average of the reported CO_2 flux measurements for each volcano to produce Table 2, a summary which allows the total CO_2 flux from 33 measured volcanic gas plumes to be calculated as 59.7 Mt/yr. We note that this measured flux by itself is higher than the maximum estimated for global passive degassing from Williams et al. (1992), highlighting the fundamental importance of direct measurements of volcanic CO_2 fluxes in quantifying the volcanic CO_2 inventory.

In Table 3, we report diffuse CO_2 fluxes from historically active volcanoes, which have been verified through isotopic analysis to be of magmatic origin. This list is not an exhaustive collation of all diffuse CO_2 degassing measurements, but relfects the most updated or complete diffuse CO_2 flux measured at each volcano. The total CO_2 flux from the 30 measured volcanoes is 6.4 Mt/yr, including emissions from diffuse soil degassing and those measured in groundwater.

CO_2 fluxes from tectonic structures, hydrothermal systems or inactive volcanic areas are reported in Table 4, distinguishing between measured (or estimated) fluxes from soils from those dissolved in groundwaters. The two major measured contributors to the total tectonic, hydrothermal and inactive volcano CO_2 flux of 66 Mt/yr are tectonic degassing in Italy (10 Mt/yr, Chiodini et al. 2004) and hydrothermal emissions from Yellowstone (8.6 Mt/yr, Werner and Brantley 2003). We also include in this list an estimate of the total CO_2 flux produced by hydrothermal activity in Indonesia-Philippines (1.8 Mt/yr, Seward and Kerrick 1996) and

Table 1. Volcanic plume CO_2 fluxes from persistently degassing volcanoes (alphabetically ordered by country)

Volcano	Location	CO_2 Flux (t/d)	CO_2 Flux (Mt/yr)	Method	Date	Reference
Erebus	Antarctica	1,930	0.70	Airborne Li-COR	Dec 1997, Dec 1999, Jan 2001	Wardell et al. (2004)
Erebus	Antarctica	1,330	0.49	Ground-based OP-FTIR and scanning UV spectrometer	Dec 2004	Oppenheimer & Kyle (2008)
Villarrica	Chile	477	0.17	Ground-based OP-FTIR and airborne UV spectrometer traverses	Mar 2009	Sawyer et al. (2011)
Galeras	Colombia	1,020	0.37	High temp. summit fumarole sampling and COSPEC	1989-1995	Zapata et al. (1997)
Nyiragongo	DR Congo	95,500	34.86	Direct sampling with video footage of plume dimensions and rise rate	1959, 1972	Le Guern (1987)
Nyiragongo	DR Congo	9,320	3.40	Ground-based OP-FTIR and UV spectrometer vehicle traverses	May/Jun 2005, Jan 2006	Sawyer et al. (2008a)
Sierra Negra	Ecuador (Galápagos)	394	0.14	Ground-based multi-gas sensor and UV spectrometer walking traverses	Jun-Jul 2006	Padron et al. (2012)
Erta Ale	Ethiopia	54	0.02	Based on heat budget calculations	1971, 1973, 1974	Le Guern et al. (1979)
Erta Ale	Ethiopia	60	0.02	Ground-based OP-FTIR and UV spectrometer walking traverses	15 Oct 2005	Sawyer et al. (2008b)
Grímsvötn	Iceland	532	0.19	Sampling of subglacial crater lake	1954-1991	Agustdottir & Brantley (1994)
Merapi	Indonesia	240	0.09	High temp. dome fumarole sampling and routine SO_2 flux measurements		Toutain et al. (2009)
Etna	Italy	35,000	12.8	Plume sampling or airborne IR analysers and ground-based and airborne COSPEC;	1977-1984	Allard et al. (1991)

Table 1 (continued). Volcanic plume CO_2 fluxes

Volcano	Location	CO_2 Flux (t/d)	CO_2 Flux (Mt/yr)	Method	Date	Reference
Etna	Italy	9,000	3.29	Ground-based multi-gas (Voragine and NE) and UV spectrometer vehicle traverses	Sept 2004-Sept 2005	Aiuppa et al. (2006)
Etna	Italy	5,090	1.86	Ground-based multi-gas (Voragine) and UV spectrometer vehicle traverses	May 2005-Nov 2006	Aiuppa et al. (2008)
Stromboli	Italy	4,350	1.59	Fumarole and quiescent plume sampling and airborne COSPEC	1980-1993	Allard et al. (1994)
Stromboli	Italy	1,073	0.39	Ground-based OP-FTIR automated UV spectrometer network	9 Apr 2002 (IR) 2006 (UV)	Burton et al. (2007a,b)
Stromboli	Italy	550	0.20	Ground-based multi-gas sensor and automated UV spectrometer network	Sept 2008-Jul 2010	Aiuppa et al. (2011)
Vulcano	Italy	420	0.15	Ground-based multi-gas measurement and UV spectrometer vehicle traverses	Dec 2004	Aiuppa et al. (2005)
Vulcano	Italy	170	0.06	UAV mounted electrochemical sensors and UV spectrometer	Apr 2007	McGonigle et al. (2008)
Vulcano	Italy	362	0.13	High temp. fumarole sampling and UV spectrometer vehicle traverses	Sept 2007	Inguaggiato et al. (2012)
Miyakejima	Japan	14,500	5.29	Airborne Li-COR, SO_2 electrochemical sensor or pulsed fluorescence SO_2 analyzer and COSPEC	2000-2001	Shinohara et al. (2003)
Satsuma-Iwojima	Japan	100	0.04	High temp. fumarole sampling and COSPEC;	Oct 1999	Shimoike et al. (2002)
Popocatépetl	Mexico	9,000	3.29	Airborne Li-COR ladder surveys	Jun 1995	Gerlach et al. (1997)
Popocatépetl	Mexico	40,000	14.6	Airborne Li-COR ladder surveys	1996-1998	Delgado et al. (1998)
Popocatépetl	Mexico	38,000	13.87	Passive OP-FTIR and COSPEC	Feb 1998	Goff et al. (2001)

Soufrière Hills	Montserrat	1,468	0.54	Ground-based multi-gas sensor and automated UV spectrometer network	Jul 2008	Edmonds et al. (2010)
White Island	New Zealand	950	0.35	High temp. fumarole sampling and airborne COSPEC	1982-1984	Rose et al. (1986)
White Island	New Zealand	2,610	0.95	Airborne Li-COR ladder survey	Jan 1998	Wardell et al. (2001)
Masaya	Nicaragua	2,940	1.07	Ground-based OP-FTIR and COSPEC vehicle traverses	1998-1999	Burton et al. (2000)
Masaya	Nicaragua	930	0.34	Ground-based OP-FTIR and UV spectrometer vehicle traverses	Mar 2009	Martin et al. (2010)
Kudryavy	Russia	50	0.02	Fumarole sampling and ground-based COSPEC	Aug 1995	Fischer et al. (1998)
Bezymianny	Russia	990	0.37	Dome fumarole sampling and FLYSPEC ground-based scanning and airborne traverses	Aug 2007, Jul 2009	Lopez et al. (in press)
Gorely	Russia	660	0.24	Ground-based multi-gas measurement and UV camera	6 Sept 2011	Aiuppa et al. (2012)
Oldoinyo Lengai	Tanzania	6,630	2.42	Airborne Li-COR measurements	Jun 1994	Brantley & Koepenick (1995)
Augustine	USA	1,760	0.64	Restored gas samples and COSPEC	1986-1987	Symonds et al. (1992)
Douglas	USA	trace	trace	Airborne Li-COR measurements	2000-2006	Doukas & McGee (2007)
Griggs	USA	not detected	not detected	Airborne Li-COR measurement	1 Jul 2002	Doukas & McGee (2007)
Iliamna	USA	131	0.05	Airborne Li-COR measurements	1996-2005	Doukas & McGee (2007)
Kīlauea, Pu′u ′Ō′ō	USA	3,950	1.45	Airborne closed-path FTIR	15 Feb 1984, 4 Mar 1984	Greenland et al. (1985)
Kīlauea, Pu′u ′Ō′ō	USA	300	0.11	Airborne Li-COR, closed-path FTIR and COSPEC	19 Sept 1995	Gerlach et al. (1998)
Kīlauea, Pu′u ′Ō′ō	USA	396	0.14	Airborne Visible/Infrared Imaging Spectrometer (AVIRIS)	26 Apr 2000	Spinetti et al. (2008)

Table 1 (continued). Volcanic plume CO_2 fluxes

Volcano	Location	CO_2 Flux (t/d)	CO_2 Flux (Mt/yr)	Method	Date	Reference
Kīlauea summit	USA	1,600	0.58	Airborne closed-path FTIR	13 Feb 1984	Greenland et al. (1985)
Kīlauea summit	USA	8,500	3.10	Ground-based Li-COR, closed-path FTIR and COSPEC	20 Sept 1995, 20 Oct 1998, 6 May 1999	Gerlach et al. (2002)
Kīlauea summit	USA	4,900	1.79	Ground-based Li-COR, Interscan electrochemical SO_2 analyzer and COSPEC;	Jun-Jul 2003	Hager et al. (2008)
Mageik	USA	341	0.12	Airborne Li-COR measurements	2000-2006	Doukas & McGee (2007)
Martin	USA	56	0.02	Airborne Li-COR measurements	1998-2006	Doukas & McGee (2007)
Mt. Baker	USA	187	0.07	Airborne Li-COR measurement	13 Sept 2000	McGee et al. (2001)
Mt. Baker	USA	150	0.05	Airborne Li-COR measurement	2007	Werner et al. (2009)
Peulik	USA	not detected	not detected	Airborne Li-COR measurement	24 May 1998	Doukas & McGee (2007)
Reboubt	USA	18	0.01	Airborne Li-COR measurements	1997-2005	Doukas & McGee (2007)
Spurr	USA	633	0.23	Airborne Li-COR measurements	2004-2006	Doukas & McGee (2007)
Spurr Crater Peak	USA	334	0.12	Airborne Li-COR measurements	1996-2006	Doukas & McGee (2007)
Ukinrek Maars	USA	187	0.07	Airborne Li-COR measurement	24 May 1998	Doukas & McGee (2007)
Veniaminof	USA	not detected	not detected	Airborne Li-COR measurement	2 Aug 2003	Doukas & McGee (2007)
Ambrym	Vanuatu	20,000	7.30	Multi-gas sensor & airborne UV spectrometer traverses	2007	Allard et al. (2009)
Yasur	Vanuatu	840	0.31	Ground-based multi-gas sensor and UV spectrometer vehicle traverses	21 Oct 2007	Métrich et al. (2011)

Table 2. Mean volcanic plume CO_2 fluxes from persistently degassing volcanoes (ordered by CO_2 flux)

Volcano	Country	CO_2 Flux (t/d)	CO_2 Flux (Mt/yr)
Nyiragongo	DR Congo	52,410	19.13
Popocatépetl	Mexico	29,000	10.59
Ambrym	Vanuatu	20,000	7.30
Etna	Italy	16,363	5.97
Miyakejima	Japan	14,500	5.29
Oldoinyo Lengai	Tanzania	6,630	2.42
Kīlauea	USA	6,549	2.39
Stromboli	Italy	1,991	0.73
Masaya	Nicaragua	1,935	0.71
White Island	New Zealand	1,780	0.65
Augustine	USA	1,760	0.64
Erebus	Antarctica	1,630	0.59
Soufrière Hills	Montserrat	1,468	0.54
Galeras	Colombia	1,020	0.37
Bezymianny	Russia	990	0.36
Spurr	USA	967	0.35
Yasur	Vanuatu	840	0.31
Gorely	Russia	660	0.24
Grímsvötn	Iceland	532	0.19
Villarrica	Chile	477	0.17
Sierra Negra	Ecuador (Galápagos)	394	0.14
Mageik	USA	341	0.12
Vulcano	Italy	317	0.12
Merapi	Indonesia	240	0.09
Ukinrek Maars	USA	187	0.07
Mt. Baker	USA	169	0.06
Iliamna	USA	131	0.05
Satsuma-Iwojima	Japan	100	0.04
Erta Ale	Ethiopia	57	0.02
Martin	USA	56	0.02
Kudryavy	Russia	50	0.02
Redoubt	USA	18	0.01
Douglas	USA	trace	trace
	Total	**163,562**	**59.70**

Table 3. Diffuse CO_2 emissions from historically active volcanoes (alphabetically ordered by country)

Volcano	Country	CO_2 soil gas flux (t/yr)	Dissolved CO_2 flux (t/yr)	Reference
Erebus	Antarctica	14,600		Wardell et al. (2003)
Sierra Negra	Ecuador (Galápagos)	220,825		Padron et al. (2012)
Santa Ana	El Salvador	59,130		Salazar et al. (2004)
Nea Kameni	Greece	5,621		Chiodini et al. (1998)
Nisyros	Greece	24,784		Caliro et al. (2005)
Hengill volcanic system	Iceland	165,345		Hernández et al. (2012)
Krafla geothermal system	Iceland	84,000		Ármannsson et al. (2007)
Reykjanes volcanic sys.	Iceland	12,660		Óskarsson & Fridriksson (2011)
Merapi	Indonesia	78,475		Toutain et al. (2009)
Etna	Italy	1,000,000	250,000	D'Alessandro et al. (1997)
Ischia	Italy	468,940	9,461	Pecoraiano et al. (2005)
Pantelleria	Italy	361,000	34,000	Favara et al. (2001)
Solfatara, Campi Flegrei	Italy	556,260		Chiodini et al. (2001)
Stromboli	Italy	82,125		Carapezza & Federico (2000)
Vesuvio	Italy	55,115		Frondini et al. (2004)
Vulcano	Italy	41,975	2,190	Inguaggiato et al. (2012)
Miyakejima (Oyama)	Japan	43,618		Hernández et al.(2001a)
Satsuma-Iwojima	Japan	7,300		Shimoike et al. (2002)
Showa-Shinzan	Japan	3,760		Hernández et al. (2006)
Usu	Japan	60,712		Hernández et al.(2001b)
Popocatépetl	Mexico	not detected		Varley & Armienta (2001)
Cerro Negro	Nicaragua	1,022,000		Salazar et al. (2001)
Masaya caldera	Nicaragua	630,720		Pérez et al (2000)
Masaya, Comalito	Nicaragua	6,935		Chiodini et al. (2005)
Rabaul	Papua New Guineau	876,000		Pérez et al. (1998)
Furnas	Portugal		9,358	Cruz et al. (1999)
Oldoinyo Lengai	Tanzania	36,432		Koepenick et al. (1996)
Teide	Tenerife	38,836	64,605	Hernández et al. (2000); Marrero et al. (2008)
Lassen	USA	35,000	7,600	Rose & Davisson (1996)
Mt. Shasta	USA		8,500	Rose & Davisson (1996)
Ukinrek Maars	USA	11,863	1,095	Evans et al. (2009)
	Total (t/yr)	**6,004,031**	**386,809**	
	Total (Mt/yr)	**6.00**	**0.39**	

Table 4. CO_2 emissions from tectonic, hydrothermal or inactive volcanic areas (alphabetically ordered by country)

Area or vent	Country	CO_2 soil gas flux (t/yr)	Dissolved CO_2 flux (t/yr)	Reference
Tengchong Cenozoic volcanic field	China		3,580	Cheng et al. (2012)
Albani Hills	Italy	26,840	157,960	Chiodini & Frondini (2001)
Bossoleto, Siena	Italy	3,500		Mörner & Etiope (2002)
Caldara di Manziana	Italy	73,000		Chiodini et al. (1999)
Campanian degassing structure	Italy		3,080,000	Chiodini et al. (2004)
Castiglioni, Siena	Italy	4,400		Mörner & Etiope (2002)
Latera	Italy	127,750		Chiodini et al. (2007)
Mefite d'Ansanto	Italy	730,000		Chiodini et al. (2010)
Naftìa Lake area	Italy	72,217		Giammanco et al. (2007)
Pienza	Italy	4,015		Rogie et al. (2000)
Poggio dell'Ulivo	Italy	73,000		Chiodini et al. (1999)
Rapalano Cecilia	Italy	17,520		Rogie et al. (2000)
Rapalano Mofete Diambra	Italy	35,040		Rogie et al. (2000)
San Sisto	Italy	21,600		Italiano et al. (2000)
Selvena	Italy	6,205		Rogie et al. (2000)
Telese	Italy	20,000		Italiano et al. (2000)
Tuscan Roman degassing structure	Italy		6,160,000	Chiodini et al. (2004)
Umbertide	Italy	5,840		Rogie et al. (2000)
Ustica	Italy	260,000		Etiope et al. (1999)
Hakkoda	Japan	27,010		Hernández et al. (2003)
Taupo	New Zealand		440,000	Seward & Kerrick (1996)
Yangbajain	Tibet	50,370		Chiodini et al. (1998)
Mammoth Mountain	USA	189,800	14,600	Sorey et al. (1998)
Mt Washington and Belknap Crater	USA		2,400	James at al. (1999)
Mt Jefferson	USA		8,000	James at al. (1999)
Mt Bachelor	USA		1,800	James at al. (1999)
Salton Trough	USA		44,000	Kerrick et al. (1995)
Three Sisters	USA		4,400	James at al. (1999)
Yellowstone	USA	8,580,000		Werner & Brantley (2003)
Indonesia-Philippines		1,800,000		Seward & Kerrick (1996)
Subaerial Pacific rim		44,000,000		Seward & Kerrick (1996)
	Total (t/yr)	**56,128,107**	**9,916,740**	
	Total (Mt/yr)	**56.13**	**9.92**	

the subaerial Pacific rim (44 Mt/yr, Seward and Kerrick 1996). These estimates are based on extrapolations from the CO_2 emissions observed from the 150 km long Taupo Volcanic Zone (New Zealand) to the 18,000 km long Pacific Rim.

The global emissions of CO_2 from volcanic lakes were recently assessed by Pérez et al. (2011), who pointed out that volcanic lakes had not been included in previous estimates of global geological carbon efflux (e.g., Kerrick et al. 2001; Mörner and Etiope 2002). They found that CO_2 emissions increased with increasing acidity in volcanic lakes, reflecting the acidity of the volcanic gas discharge. Measurements were conducted on 32 volcanic lakes which were divided into three types of water based on pH, alkali, neutral and acid. Average flux per unit area for each type was then used to calculate a global volcanic lake estimate, extrapolating to an estimated number of volcanic lakes in the world (769). This number of lakes is greater than the number of lakes reported in the literature (138) by a factor which reflects the regional under-sampling between actual lakes and lakes reported in the scientific literature. This methodology assumes that the average acidity-emission rate relationship in the 32 measured lakes is a faithful average representation of the global lake population. A further estimate was produced by defining 4 populations in the measured data set based on frequency, emission rate and lake size and extrapolating to all 769 volcanic lakes. The combination of these two approaches yielded a global volcanic lake CO_2 emission of 117 ± 19 Mt/yr, of which 94 Mt/yr is attributed to magmatic degassing.

Submarine volcanism

There are three main submarine sources of CO_2, MOR, arc volcanoes and fore-arc degassing (which appears to be dominated by CH_4 emissions (Füri et al. 2010)). Global emissions from MOR have been determined by various authors, as reported in Table 5. The large spread of MOR fluxes, from 4.4 to 792, reflects uncertainties in the dissolved contents of C and global ^{3}He fluxes. Marty and Tolstikhin (1998) performed a careful examination of the $CO_2/^3$He ratios used and determined a median value of 2.2×10^9 with standard deviation of 0.7×10^9. Using a ^{3}He flux of 1000 ± 250 mol/yr (Farley et al. 1995) they derived a MOR CO_2 flux of 97 ± 40 Mt/yr CO_2. The more recent determination of MOR CO_2 flux from Resing et al. (2004) who measured $CO_2/^3$He in MOR hydrothermal plumes of 55 ± 33 Mt/yr is in reasonable agreement with that estimate.

While measurements of CO_2 release from the cooler flanks of MORs and submarine arc volcanoes increase in number each year, global estimates of submarine CO_2 emissions are extremely difficult to make. The large areal extent and our relatively poor knowledge of the submarine surface suggests that there is ample opportunity for unknown or unrecognized active volcanism (e.g., cold liquid CO_2 emissions, Lupton et al. 2008), but at the current time it is not possible to make quantitative estimates of the global CO_2 emissions from such sources.

INVENTORIES OF GLOBAL VOLCANIC DEEP CARBON FLUX: IMPLICATIONS FOR THE GEOLOGICAL CARBON CYCLE

Estimates of global deep carbon emission rates

In Table 6, we summarize the measured fluxes from the subaerial sources and MOR, and attempt to extrapolate from these measurements to global estimates of the CO_2 flux for each source. In the case of volcanic plume passive degassing the GVN catalogue (Siebert and Simkin 2002) indicates that there are ~150 such actively degassing volcanoes on Earth. While our catalogue of 33 CO_2 flux plume measurements (Table 2: total flux 59.7 Mt/yr) is significantly larger than previously collated, it reflects only 22% of the total number of active volcanoes. While our current compilation includes some large emitters, suggesting that the major sources have been already identified, we highlight how this total flux has increased due

Table 5. MOR global CO_2 flux (Mt/yr)

Method	Min	Max	Reference
Crustal production rates and C content of mantle	10	35	Gerlach (1989)
	22	39.6	Gerlach (1991)
	572	748	Javoy & Pineau (1991)
	128	255	Holloway (1998)
	176	792	Cartigny et al. (2001)
	28.6	41	Saal et al. (2002)
$CO_2/^3He$ in MORB glass, global mantle ^3He flux	75	119	Marty & Jambon (1987)
	18	44	Sarda & Graham (1990)
	106	264	Graham & Sarda (1991)
	66	119	Marty & Zimmerman (1999)
$CO_2/^3He$ in MOR fluids, global mantle ^3He flux	44	70	Corliss et al. (1979)
	20	57	Des Marais & Moore (1984)
Hydrothermal fluid flux and composition	4.4	53	Elderfield & Schultz (1996)
$CO_2/^3He$ in plumes	22	88	Resing et al. (2004)
Summary	**4.4**	**792**	

Table 6. Summary of measured volcanic CO_2 fluxes and estimated global emissions (Mt/yr)

Source	Measured CO_2 flux	Nº measured	Nº global	% global	Estimated Global CO_2 flux	Ref.
Volcanic plume passive degassing	59.7	33	~150	22	271	[1]
Diffuse emissions from historically active volcanoes	6.4	30	~550	5.5	117	[1]
Emissions from tectonic, hydrothermal or inactive volcanic areas	66	—	—	—	>66	[1]
Volcanic lakes	6.7	32	769	4.2	94	[2]
MOR	97	—	—		97	[3]
			Total		637	
			Total (no MOR)		540	

References: [1] This work; [2] Perez et al. (2011); [3] Marty and Tolstikhin (1998)

to previously unrecognized large emissions from e.g., Ambrym (Vanuatu). Further large, but as yet unquantified, sources of CO_2 emissions may be present in Papua New Guinea, the Banda Sunda arc and the Vanuatu island chain. We therefore conclude that the clearest and probably most accurate way to extrapolate from the current catalogue of plume emissions to a global estimate is through a linear extrapolation. Extrapolating from the measured 33 to an estimated 150 plume-creating, passively degassing volcanoes we estimate that the global plume CO_2 flux is ~271 Mt/yr (see Table 6).

The total number of historically active volcanoes reported by GVN is ~550, and 30 (5.5%) of these have had diffuse CO_2 soil degassing fluxes quantified, as reported in Table 3, for a total of 6.4 Mt/yr. Extrapolating to a global flux, assuming a similar distribution of fluxes in the unmeasured fluxes as seen in those measured, produces a total of 117 Mt/yr from diffuse degassing from the flanks of historically active volcanoes (Table 6).

The total diffuse CO_2 flux from inactive volcanoes, hydrothermal and tectonic structures reported in Table 4 is more challenging to extrapolate to a global scale. Our current constraints on the tectonic CO_2 flux comes almost entirely from the work of Chiodini et al. (2004) who examined actively degassing tectonic structures in Italy. The abundance of such structures on Earth is unknown, and this therefore represents a source of great uncertainty in estimates of total deep carbon flux. This uncertainty makes it challenging to sensibly extrapolate to a global estimate of tectonic CO_2 fluxes, and therefore we use only reported fluxes, and highlight the possibility that the true total may be significantly larger. Emissions from hydrothermal systems estimated by Seward and Kerrick (1996) are already extrapolated to cover a significant proportion of the volcanically active surface of the Earth. We therefore use the total presented in Table 4 for the CO_2 emissions from tectonic, hydrothermal and inactive volcanoes as a lower limit for the global emission of CO_2 from these sources.

Summing the extrapolated passive plume, diffuse degassing, lake degassing global estimates and emissions from inactive, hydrothermal and tectonic structures produces a total subaerial volcanic flux of 540 Mt/yr, and a global emission (including MOR emissions) of 637 Mt/yr (Table 6). Thus global volcanic CO_2 fluxes are only ~1.8% of the anthropogenic CO_2 emission of 35,000 Mt per year (Friedlingstein et al. 2010).

Comparison with previous estimates of subaerial volcanic CO_2 flux

There have been several papers which estimate the global CO_2 flux, as shown in Table 7. Our update of the global volcanic CO_2 flux, 637 Mt/yr, is larger than the maximum suggested by Marty and Tolstikhin (1998) of 440 Mt/yr. This is in part because CO_2 emissions from volcanic lakes were not addressed in that work. The total subaerial flux we calculate of 540 Mt/year is also higher than that proposed by Mörner and Etiope (2002), due primarily to the improvement in measurements of persistently degassing volcanoes. We note that Mörner and Etiope (2002) included the fluxes from single eruptive events from Pinatubo (1991) and Mt. St. Helens (1980) in their inventory of volcanoes contributing to the annual global CO_2 flux. Other papers cited in Table 7 appear to have significantly underestimated the global subaerial CO_2 flux, primarily due to a lack of field measurements.

Table 7. Global volcanic subaerial CO_2 flux (Mt/yr)

CO_2 flux	Reference
79	Gerlach (1991)
145	Varekamp et al. (1992)
66	Allard (1992)
88	Marty and Le Cloarec (1992)
65	Williams et al. (1992)
136	Sano and Williams (1996)
242	Marty and Tolstikhin (1998)
99	Kerrick (2001)
300	Mörner and Etiope (2002)
540	This work

Balancing CO_2 emission rates with weathering and subduction rates

In the absence of a continual supply of CO_2 from volcanic and tectonic degassing the CO_2 content of the atmospheres and oceans would be gradually depleted through CO_2 removal by weathering (Gerlach 1991). The fact that, instead, pre-industrial CO_2 concentrations are relatively stable suggest a balance between CO_2 removal by weathering and CO_2 supply by Earth degassing on timescales of ~0.5 Ma (Walker et al. 1987; Berner 1991). Over such timescales weathering of carbonates has no impact on removal of atmospheric CO_2, because

HCO_3^- supplied to the ocean by carbonate weathering releases the CO_2 it captured from the atmosphere during calcite precipitation (Berner 1991). Therefore in the long timescale of the geological carbon cycle CO_2 emissions from geological sources should balance consumption from silicate weathering and oceanic crust alteration. Gaillardet et al. (1999) found that CO_2 consumption from continental silicate weathering was 515 Mt/yr, which matches well with our estimates of subaerial volcanic CO_2 degassing (540 Mt/yr). However, inclusion of 300 Mt/yr CO_2 released by metamorphism (Morner and Etiope 2002) produces a total lithospheric subaerial CO_2 emission of 840 Mt/yr. This is larger than the current estimates of silicate weathering, suggesting that, assuming steady-state, weathering rates might be slightly higher to absorb all the emitted CO_2.

Dasgupta and Hirschmann (2010) calculated the total ingassing of CO_2 into subduction zones from the combination of three lithologies in the subducting slab, altered oceanic crust, sediments and mantle, producing an estimated CO_2 consumption rate of 403 Mt/yr. We note that this is lower than the CO_2 consumption rate due to silicate weathering (515 Mt/yr, Gaillerdet et al. 1999), which is slightly inconsistent (but within uncertainties of such estimates), as the eventual destiny of CO_2 consumed by silicate weathering will be deposition on the seafloor or precipitation within the oceanic crust. In order to maintain steady-state quantities of CO_2 in the exosphere this consumption should be balanced by the total emission from MORs, subaerial degassing and metamorphism (calculated here to be 937 Mt/yr). Given the likely underestimate in our total lithospheric CO_2 emissions arising from lack of knowledge of tectonic degassing, it appears reasonable to conclude that the ingassing rate may be an underestimate. However, it is clear that there are large uncertainties in both sums.

THE ROLE OF DEEP CARBON IN VOLCANIC ACTIVITY

Original CO_2 contents of magma

The volatile content of magmas, together with their evolving viscosity and degassing behavior during ascent, helps to determine whether a volcano will be quietly degassing or violently erupting for a given magma input rate. Models of magma dynamics require knowledge of original volatile content in order to reproduce physically accurate processes occurring during an eruption and in quiescent phases. Furthermore, knowledge of the original volatile contents of magmas allows calculation of the magma mass required to produce an observed gas flux, permitting quantitative comparison of fluxes with geophysical and volcanological observations. Measurements of original volatile contents are therefore of great interest.

Melt inclusions (MIs) provide records of original volatile contents, through analysis of pockets of melt trapped inside growing crystals during magma ascent or storage, and such studies have been carried out on many eruption products. However, the presence of a separate fluid phase at the moment of inclusion entrapment will produce an underestimate in the concentrations of dissolved volatiles. Wallace (2005) concluded that no melt inclusions sample arc magmas undegassed with respect to CO_2. Blundy et al. (2010) used MI measurements from Mt. St. Helens to show that the dissolved volatile contents of shallow magmas were strongly affected by CO_2-rich fluids rising from magmas at greater depth, concluding that the original CO_2 contents of arc magmas was likely to be significantly higher than that recorded in MIs. Using inferred CO_2 contents in arc andesites and dacites of 1.5 wt% they calculate that the CO_2 contents of parental, mantle-derived basalts would contain 0.3 wt%. This relatively high CO_2 content is in agreement with previous estimates of volatile contents of arc magmas (Wallace 2005).

Original CO_2 contents of magmas can also be estimated by assuming a steady-state condition for a persistently degassing volcano, and comparing the observed CO_2 flux together with the flux of a more soluble gas species whose original volatile content has been well-characterized, such as SO_2. Gerlach et al. (2002) performed such a calculation for Kīlauea

volcano, Hawai'i, concluding that the bulk CO_2 concentration required to match magma input rates and CO_2 output rates was 0.70 wt%. Dixon and Clague (2001) measured a dissolved CO_2 content of at a depth of 1500-2000 m at the Loihi seamount in the Hawai'i chain. While the CO_2 concentrations were very low, the samples contained fluid-filled vesicles with high CO_2 contents, which allowed a bulk CO_2 concentration of up to 0.63 wt% to be determined, in fair agreement with the estimate from Gerlach et al. (2002). A recent study (Barsanti et al. 2009) introduced a more complex note to the examination of original CO_2 contents at Hawai'i, with a statistical analysis of MI CO_2 and H_2O concentrations which revealed distinct magma batches some of which could contain 2-6 wt% CO_2. High CO_2 contents of magmas feeding Etna and Stromboli have also been proposed based on degassing mass balance calculations, with amounts ranging between 1.6 and 2.2 wt% (Spilliaert et al. 2006; Burton et al. 2007a). These few available estimates of original CO_2 contents from mass balance determinations open the possibility that CO_2 contents of magmas feeding active volcanoes are in general higher than is expected based on CO_2 contents of melt inclusions.

Importance of a deep exsolved volatile phase on magma dynamics and eruptive style

The presence of a CO_2-rich volatile phase at great pressure can strongly affect the dynamics of magma ascent and eruption, because the style and intensity of eruptive activity is controlled in part by the distribution of gas phase in a magma during eruption (Eichelberger et al. 1986; Jaupart and Vergniolle 1988). Persistently degassing volcanoes can release vast amounts of gas at the surface non-explosively, implying storage within the crust of large volumes of degassed magma (Crisp 1984, Francis et al. 1993) via magma convection (Kazahaya et al. 1994).

Exsolved volatiles can ascend from depth, accumulating in foams that can produce Strombolian activity (e.g., Menand and Phillips 2007; Jaupart and Vergniolle 1988). Gas can stream through magma from depth to the surface (Wallace et al. 2005), as surmised to occur at Soufrière Hills volcano, Montserrat (Edmonds et al. 2010) and Stromboli volcano (Aiuppa et al. 2010). Perhaps most importantly of all however, exsolved gas accumulation can produce powerful explosive eruptions. The eruption of Pinatubo in 1991 (Pallister et al. 1992) was one of the most violent in recorded history. It produced a much greater mass of S than was to be expected from dissolved S contents and the volume of erupted material, suggesting the presence of a voluminous pre-eruptive gas phase (Wallace and Gerlach 1994), likely produced from basaltic underplating crystallizing as anhydrite (Matthews et al. 1992) which triggered the eruption (Pallister et al. 1992).

MAGNITUDE OF ERUPTIVE DEEP CARBON EMISSIONS

It is useful to compare the CO_2 emission rates for subaerial volcanism of 540 Mt/yr reported in Table 7 with a single large eruption such as the ~5 km^3 eruption of Mt. Pinatubo in 1991, producing ~50 Mt of CO_2 (Gerlach et al. 2011), equivalent to merely ~5 weeks of global subaerial volcanic emissions. The Pinatubo 1991 syn-eruptive emission is therefore dwarfed by the time-averaged continuous CO_2 emissions from global volcanism. Indeed, the present day CO_2 emission rate from the lake filling the crater formed during the eruption of Pinatubo is 884 t/d (Perez et al. 2011), suggesting that in the 31 years since that eruption ~10 Mt of CO_2 has been produced, ~20% of that emitted during the eruption.

Using the volumes of erupted material produced by the three largest eruptions of the last 200 years (Self et al. 2006) we may estimate their CO_2 emissions, assuming a similar erupted volume to CO_2 emission amount to that estimated for Pinatubo (10 Mt CO_2 per km^3 erupted, equivalent to ~1 wt% CO_2 content). The eruption of Tambora (Indonesia) in 1815 is estimated to have produced 30 km^3 of products (Self et al. 2006), with an inferred output of 300 Mt of CO_2. Krakatua in 1883 (Indonesia) and Katmai-Novarupta in 1912 (Alaska) each produced 12

km^3, and ~120 Mt of CO_2. The total CO_2 output of the four largest eruptions in the last 200 years is therefore ~600 Mt of CO_2, slightly less than we estimate for subaerial volcanic degassing in a single year, and therefore only 0.6% of the amount of gas released through continuous volcanic activity in the same time period. It therefore appears that the continuous degassing of active and inactive volcanoes dominates the short-lived paroxysmal emissions produced in large eruptions.

Crisp (1984) calculated that the average eruption rate from volcanoes over the last 300 years was 0.1 km^3 magma per year, which with ~1 wt% CO_2 content suggests an annual output of ~1 Mt CO_2, only 0.2% of the estimated annual subaerial CO_2 emissions. This demonstrates that degassing of unerupted magma dominates degassing of erupted lava on the planet, and emphasizes the fundamental role that unerupted magmatic intrusions must have in contributing to the global volcanic CO_2 flux. Such intrusions may produce unexpectedly high CO_2 emissions if they interact with crustal carbonates (Troll et al. 2012). This important process could be assessed quantitatively if a method could be developed for measuring volcanic $^{12}C/^{13}C$ ratios in the field.

SUMMARY

In recent years, measurements of CO_2 flux from volcanoes and volcanic areas have greatly increased, particularly on persistently degassing volcanoes, of which ~22% have had their CO_2 flux quantified. Notwithstanding this progress, it is clear that the CO_2 emissions from the majority of volcanic sources are still unknown. Using the available data from plume measurements from 33 degassing volcanoes we determine a total CO_2 flux of 59.7 Mt/yr. Extrapolating this to ~150 active volcanoes produces a total of 271 Mt/yr CO_2. Extrapolation of the measured 6.4 Mt/yr of CO_2 emitted from the flanks of 30 historically active volcanoes to all 550 historically active volcanoes produces a global emission rate of 117 Mt/yr. Perez et al. (2011) calculated the global emission from volcanic lakes to be 94 Mt/yr CO_2. The sum of these fluxes produces an updated estimate of the global subaerial volcanic CO_2 flux of 474 Mt/yr. Emissions from tectonic, hydrothermal and inactive volcanic areas contribute a further 66 Mt/yr to this total (Table 6), producing a total subaerial volcanic emission of 540 Mt/yr. An extrapolation to a global estimate is not straightforward for tectonic-related degassing, as the number of areas which produce such emissions is not known. Given the fact that ~10 Mt/yr is produced by Italy alone it is possible that the global total is significant, and this merits further investigation. We highlight also that the magnitude of CO_2 emissions from both cold and hot non-MOR submarine volcanic sources are currently effectively unknown.

Our subaerial volcanic CO_2 flux matches well with estimates of CO_2 removal rates of 515 Mt/yr due to silicate weathering, which, over timescales of 0.5 Ma, should balance lithospheric CO_2 emissions. However, inclusion of the metamorphic CO_2 flux of 300 Mt/yr calculated by Morner and Etiope (2002) produces a total subaerial lithospheric flux of 840 Mt/yr, suggesting that, assuming steady-state, weathering rates might be slightly higher in order to absorb all the CO_2 emitted from the lithosphere.

The global subaerial CO_2 flux we report is higher than previous estimates, but remains insignificant relative to anthropogenic emissions, which are two orders of magnitude greater at 35,000 Mt/yr (Friedlingstein et al. 2010). Nevertheless, it is clear that uncertainties in volcanic CO_2 emission rates remain high and significant upward revisions of the lithospheric CO_2 flux cannot be ruled out. This uncertainty also limits our understanding of global volcanic carbon budgets and the evolution of the distribution of CO_2 between the crust and the mantle. Furthermore, with the notable exception of continuous CO_2 flux monitoring at a handful of volcanoes we have very little data with which to assess CO_2 flux variations across different timescales. It is clear that there is much further work to be done surveying CO_2 emissions from both active and inactive volcanoes.

Continuous global CO_2 emissions from passively degassing volcanoes over timescales longer than a few months dominate CO_2 emissions produced by relatively short-lived eruptions. Nevertheless, we highlight that dramatic CO_2 emissions may occur during magmatic intrusion events, and that the sporadic and short-term nature of field measurements to date may lead to such events being missed. To this end, robust field-portable instruments capable of measuring $^{12}C/^{13}C$ ratios in volcanic CO_2 emissions would be of great utility in order to distinguish CO_2 produced during metamorphism of crustal carbonates from magmatic CO_2.

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