PRESENT AND PAST NONANTHROPOGENIC CO_2 DEGASSING FROM THE SOLID EARTH

Derrill M. Kerrick
Department of Geosciences,
Pennsylvania State University,
University Park, Pennsylvania, USA

Abstract. Global carbon cycle models suggest that CO_2 degassing from the solid Earth has been a primary control of paleoatmospheric CO_2 contents and through the greenhouse effect, of global paleotemperatures. Because such models utilize simplified and indirect assumptions about CO_2 degassing, improved quantification is warranted. Present-day CO_2 degassing provides a baseline for modeling the global carbon cycle and provides insight into the geologic regimes of paleodegassing. Mid-ocean ridges (MORs) discharge $1–3 \times 10^{12}$ mol/yr of CO_2 and consume $\sim 3.5 \times 10^{12}$ mol/yr of CO_2 by carbonate formation in MOR hydrothermal systems. Excluding MORs as a net source of CO_2 to the atmosphere, the total CO_2 discharge from subaerial volcanism is estimated at $\sim 2.0–2.5 \times 10^{12}$ mol/yr. Because this flux is lower than estimates of the global consumption of atmospheric CO_2 by subaerial silicate weathering, other CO_2 sources are required to balance the global carbon cycle. Nonvolcanic CO_2 degassing (i.e., emission not from the craters or flanks of volcanos), which is prevalent in high heat flow regimes that are primarily located at plate boundaries, could contribute the additional CO_2 that is apparently necessary to balance the global carbon cycle. Oxidation of methane emitted from serpentinization of ultramafics and from thermocatalysis of organic matter provides an additional, albeit unquantified, source of CO_2 to the atmosphere. Magmatic CO_2 degassing was probably a major contributor to global warming during the Cretaceous. Metamorphic CO_2 degassing from regimes of shallow, pluton-related low-pressure regional metamorphism may have significantly contributed to global warming during the Cretaceous and Paleocene/Eocene. CO_2 degassing associated with continental rifting of Pangaea may have contributed to the global warming that was initiated in the Jurassic. During the Cretaceous, global warming initiated by CO_2 degassing of flood basalts, and consequent rapid release of large quantities of CH_4 by decomposition of gas hydrates (clathrates), could have caused widespread extinctions of organisms.

1. INTRODUCTION

Through the greenhouse effect, natural *nonanthropogenic CO_2 degassing* from the Earth is considered to have been a major factor in controlling global paleotemperature [*Kump et al*., 1999]. (Terms in italic are defined in the glossary, which follows the main text.) Accurate modeling of the paleoatmospheric CO_2 content through time requires quantification of the temporal variation of CO_2 emission rates (fluxes) from a variety of geologic sources and environments.

This review considers CO_2 emission from sources that are not on or near the Earth's surface. Accordingly, CO_2 of biologic and soil origins is excluded. Much of the carbon dioxide considered herein originated from igneous or metamorphic sources.

2. THE GLOBAL CARBON CYCLE

Berner and Lasaga [1989, p. 59] state that "The most vexing problem we have encountered in modeling the global carbon cycle is to calculate the rate of degassing of carbon dioxide due to igneous and metamorphic activity." The Berner-Lasaga-Garrels (BLAG) [*Berner et al*., 1983; *Lasaga et al*., 1985] and derivative [*Berner*, 1991, 1994] models of the global carbon cycle have been some of the major geochemical models for tracking paleoatmospheric CO_2 content through time and, via the greenhouse effect, retain global paleotemperatures. These models predict that on a long (>1 Myr) timescale the paleoatmospheric CO_2 content is controlled by the competing effects of the consumption (drawdown) of atmospheric CO_2 by continental silicate chemical weathering and associated precipitation of marine carbonates versus the addition of CO_2 to the atmosphere by Earth degassing. The models require quantifying the contemporary nonanthropogenic CO_2 degassing rate as a baseline for forward model convergence to the present. The present-day natural CO_2 degassing rate is obtained by the steady state assumption that the CO_2 degassing flux is equivalent to the atmospheric CO_2 drawdown by silicate weathering. In general, this assumption is justified by the correlation (feedback) between degassing and silicate weathering that is necessitated by the preclusion

Reviews of Geophysics, 39, 4 / *November 2001*
pages 565–585
8755-1209/01/2001RG000105*$15.00*
Paper number 2001RG000105

of unrealistically warm or cold global paleotemperatures [*Sundquist*, 1991; *Berner and Caldeira*, 1997; *Broecker and Sanyal*, 1998; *Kerrick and Caldeira*, 1999; *Kump et al*., 1999]. In the BLAG and derivative models, CO_2 paleodegassing fluxes are derived by assuming that they were controlled primarily by CO_2 discharged into the atmosphere by volcanism and metamorphism at convergent plate boundaries. These models assume that CO_2 paleofluxes correlated with the rates of subduction and thus with the spreading rates at mid-ocean ridges. As epitomized by the above quotation, there is a clear need to supplant such indirect estimates of CO_2 degassing rates with more direct estimates.

Although not universally accepted [*Veizer et al*., 2000], the link between elevated atmospheric CO_2 content and global warmth remains a reasonable working hypothesis [*Kump*, 2000; *Kürschner*, 2001]. Consequently, periods of enhanced CO_2 degassing from the Earth should correlate with periods of global warmth. The validity of this hypothesis is assessed in this review.

3. CONTEMPORARY CO_2 DEGASSING

3.1. Introduction

Through the *Principle of uniformitarianism*, analysis of the sources, transport, and expulsion of CO_2 in a variety of contemporary tectonic and geologic settings provides important insight into the geologic regimes of CO_2 paleodegassing. However, although the processes affecting CO_2 degassing are assumed to be the same as in the past, this does not imply that the present-day CO_2 fluxes from various sources are assumed to be the same.

3.2. CO_2 Emission From Subaerial Volcanos

3.2.1. Active subaerial volcanos. Active volcanos are clearly a primary source for expulsion of magmatic CO_2 to the atmosphere. Subaerial volcanos are particularly efficient because they directly discharge gas into the atmosphere. CO_2 discharged from submarine volcanos dissolves in seawater and enhances atmospheric CO_2 content by seawater-atmosphere exchange.

Gas discharge into the atmosphere from the craters of active volcanos forms a "plume" in which gas transport occurs in the direction of the prevailing wind. Airborne measurements of *volcano plume* CO_2 fluxes are obtained by coupling measurements of the CO_2 concentration within cross sections of plumes (using an infrared detector on an aircraft) with the cross-sectional areas and wind speeds of the plumes [*Harris et al*., 1981; *Gerlach et al*., 1997]. Because SO_2 is a definitive magmatic gas component that is readily measured by direct and remote methods [*Rose and Bluth*, 1998], volcano CO_2 emission rates have been derived by coupling measurements of CO_2/SO_2 ratios of volcanic gases with the SO_2 flux (by correlation spectrometry) [*Love et al*., 2000; *Burton et al*., 2000]. However, because of the high ambient CO_2 concentration, remote measurements of CO_2 emission rates are challenging [*Francis et al*., 2000]. In addition to plumes, CO_2 discharged from craters flows down volcano flanks [*Ryan*, 2001].

TABLE 1. CO_2 Fluxes From Nonerupting (Passive) Subaerial Volcanos

Volcano	*Flux, 10^{10} mol/yr*
Mount Etna[a]	58
Popocatépetl[b]	34
Kilauea[c]	7.2–7.3
Oldoinyo Lengai[d]	6.0
Augustine[a]	5.0
Mount St. Helens[a]	4.0
Stromboli[e]	2.5–5
Masaya[f]	2.3–2.6
White Island[g]	2.1
Galeras[h]	1.7
Erebus[g]	1.5
Merapi[i]	1.4
Redoubt[a]	1.5
Solfatara[j]	1.5
Grimsvotn[k]	0.3
Mammoth Mountain[l]	0.2
Vulcano[a]	0.2

[a]*Gerlach* [1991b].
[b]*Delgado et al*. [1998].
[c]Gerlach et al. (submitted manuscript, 2001).
[d]*Koepenick et al*. [1996].
[e]*Allard et al*. [1994].
[f]*Burton et al*. [2000].
[g]*Wardell and Kyle* [1998].
[h]*Goff et al*. [1994].
[i]*Voight et al*. [2000].
[j]*Chiodini et al*. [2001].
[k]*Brantley et al*. [1993].
[l]*Gerlach et al*. [1999].

Degassing occurs during noneruptive and eruptive stages of volcanism. Most measurements of degassing from active volcanos have been made during noneruptive periods (i.e., "passive" degassing).

As is summarized in Table 1, there are significant differences in the plume CO_2 fluxes from passive degassing of various active volcanos. The fluxes from Mount Etna and Popocatépetl are much larger than those of other volcanos. Because CO_2 solubility in alkaline magmas is considered to be higher than calc-alkaline magmas [*Bailey and Hampton*, 1990], the unusually high CO_2 flux of Mount Etna had been attributed to the alkaline composition of the Mount Etna volcanics [*Gerlach*, 1991a]. This conclusion was bolstered by the large CO_2 flux of Oldoinyo Lengai, which is the only active *carbonatite* volcano [*Brantley and Koepenick*, 1995]. However, because the Popocatépetl volcanics are andesitic and because the CO_2 flux of Mount Erebus is relatively small in spite of the alkaline nature of the extrusives [*Wardell and Kyle*, 1998], the relative CO_2 fluxes of volcanos cannot be directly correlated with magma composition.

In addition to the CO_2 content of magma chambers, the flux of CO_2 emitted from volcanos should correlate

with the size of the magma chamber and thus with the size of the volcanic edifice. Indeed, the large CO_2 fluxes from Mount Etna and Popocatépetl are commensurate with the fact that they are two of the largest active volcanos in the world.

Different origins of CO_2 must be considered in assessing and comparing CO_2 fluxes of various volcanos. Helium and carbon isotopic data suggest that the CO_2 emitted from Mount Etna is largely of mantle origin [*Allard et al*., 1997; *D'Alessandro et al*., 1997]. The large CO_2 discharge from Mount Etna may be attributed to a relatively shallow (up-arched) *asthenosphere* in this region [*D'Alessandro et al*., 1997; *Nicolich et al*., 2000]. *Gerlach et al*. [1997] concluded that the CO_2/SO_2 ratios of gases from Popocatépetl are not consistent with assimilation or breakdown of the subjacent carbonate sediments. However, the helium and carbon isotopic compositions of the Popocatépetl fumaroles imply a significant contribution from marine carbonates [*Goff et al*., 1998]. Furthermore, the Popocatépetl extrusives contain *xenoliths* of carbonate rocks derived from the carbonate basement [*Goff et al*., 2001]. Thus assimilation and/or metamorphic decarbonation of the intruded carbonate rocks may be responsible for the elevated CO_2 fluxes from Popocatépetl. Indeed, melting and assimilation of limestone may accompany *skarn* formation of metacarbonate rocks due to interaction with magma-derived aqueous fluids [*Lentz*, 1999].

Both airborne and ground-based methods have been used to measure CO_2 emission rates of the flanks of subaerial volcanos. The first airborne measurements of flank emission were carried out by *Allard et al*. [1991] on Mount Etna. Subsequent studies [*Gerlach et al*., 1999] suggest that airborne measurements of volcano flank degassing could be complicated by wind dispersal. Ground-based methods include direct measurements of the CO_2 flux at the surface [*Chiodini et al*., 1996, 1998], soil CO_2 gas concentrations coupled with computations of diffusive exchange between the soil and atmosphere [*Giammanco et al*., 1995, 1998; *Williams-Jones et al*., 2000], and measurements of the influx of magmatic CO_2 into groundwater [*D'Alessandro et al*., 1997]. In assessing the accuracy of fluxes measured at the Earth's surface, it is important to carry out careful calibrations. The study by *Evans et al*. [2001] summarizing comparative fluxmeter measurements under controlled laboratory conditions is a notable example.

Large transient CO_2 fluxes are expected to accompany large explosive eruptions of volcanos. *Gerlach et al*. [1996] estimated that $\sim 9.6 \times 10^{11}$ mol of CO_2 were discharged during the climactic June 15, 1991, eruption of Mount Pinatubo. For comparison, this flux is ~1.5 times the annual CO_2 discharge of Mount Etna (Table 1). Clearly, the integrated CO_2 flux of explosive volcanism over a long time period could significantly add to the atmospheric CO_2 content.

We lack data on the CO_2 fluxes from the flanks of most active volcanos. To complicate matters, there are significant differences in the various estimates of the flank degassing rates at Mount Etna [*Allard*, 1998]. Compilation of available data suggests that the flank degassing of Mount Etna [*Giammanco*, 1998] and Stromboli [*Allard et al*., 1994] may not exceed 10% of the crater CO_2 flux. CO_2 flank degassing at Oldoinyo Lengai is estimated at <2% of the crater degassing [*Brantley and Koepenick*, 1995]. *Varley and Armienta* [2001] concluded that virtually no diffuse magmatic CO_2 emission is occurring on the flanks of Popocatépetl. Channelized gas emission through fractures and faults [*Williams-Jones et al*., 2000] complicates assessment of the flux of CO_2 through the flanks of active volcanos.

3.2.2. Dormant subaerial volcanos. Dormant volcanos are traditionally considered as having no historical eruptive activity. However, as noted by *Francis* [1993, p. 17], this definition is not entirely satisfactory because some volcanos are located in remote areas. For this review I arbitrarily consider volcanos as dormant if no activity has occurred during the past ~500 years.

In spite of the lack of recent eruptive activity, elevated CO_2 emission is common in dormant volcanos. One of the best studied examples is Mammoth Mountain, California. Seismic activity in 1989 triggered strong emission of CO_2 that resulted in the death of trees in large areas around the flanks of the mountain [*Farrar et al*., 1995]. Geochemical [*Sorey et al*., 1998] and seismic [*Julian et al*., 1998] evidence suggests that the CO_2 was emitted from a reservoir of gas that was derived from magma degassing. Continuous monitoring of soil CO_2 contents [*McGee and Gerlach*, 1998; *McGee et al*., 2000; *Gerlach et al*., 2001], measurements of the CO_2 discharge rates at the surface [*Sorey et al*., 1999; *Rogie et al*., 2001], and radiocarbon studies of plant leaves and tree rings [*Cook et al*., 2001] provide insight into the temporal variation of the CO_2 flux from Mammoth Mountain. *Gerlach et al*. [1999] utilized airborne methods to measure a flux of ~250 t/d. This estimate is compatible with the flux obtained by ground-based measurements [*Sorey et al*., 1999; *Rogie et al*., 2001; *Anderson and Ferrar*, 2001]. Detailed measurements of CO_2 discharge with a continuous fluxmeter system, coupled with repeated measurements with a portable fluxmeter, suggest that since 1997 the total CO_2 emission from the Horseshoe Lake tree kill area, the largest tree kill area of Mammoth Mountain, has been relatively constant on annual timescales [*Rogie et al*., 2001]. However, *Rogie et al*. [2001] documented large variations in the day-to-day emission rate. The study by *Rogie et al*. [2001] epitomizes the effort and care needed to accurately quantify the temporal variation of diffuse CO_2 degassing flux.

As exemplified by the catastrophic release of CO_2 from Lake Nyos and Lake Monoun, Cameroon, discharge of CO_2 into lakes occupying volcanic craters provides evidence of diffuse degassing of dormant volcanos. In some cases (e.g., the Laacher See, a *maar* lake in Germany), CO_2 continuously escapes to the surface as a free gas phase [*Giggenbach et al*., 1991]. However, in

TABLE 2. Contemporary Annual Subaerial Volcano CO_2 Fluxes[a]

Reference	*Arc Volcano Flux*	*Non Arc Volcano Flux*	*Total Flux*	*Method*
Le Guern [1982]	···	···	1.1	flux measurements
Marty et al. [1989]	0.3	···	···	C/S and S flux
Williams et al. [1992]	···	···	0.4–2.5	C/S and S flux
Gerlach [1991b]	···	···	1.8	flux measurements
Allard [1992]	0.7	0.82	1.5	flux measurements
Marty and Le Cloarec [1992]	···	···	1.5–2.5	C/^{210}Po and Po flux
Varekamp et al. [1992]	1.5	···	3.3	C/^{3}He and volcanic mass flux
Brantley and Koepenick [1995]	···	···	2–3	flux measurements
Sano and Williams [1996]	3.1	0.03	3.1	C/^{3}He and ^{3}He flux
Marty and Tolstikhin [1998]	~2.5	0.1–3	···	see text

[a]From *Marty and Tolstikhin* [1998, Table 2]. All fluxes are in units of teramoles (10^{12} mol) per year.

other cases the CO_2 dissolves into deep lake water, leading to dangerously high CO_2 contents [*Aguilera et al.*, 2000]. In the 1980s the sudden overturn of deep CO_2-charged lake waters from Lake Nyos and Lake Monoun, Cameroon, released large quantities of CO_2 that resulted in many deaths [*Giggenbach et al.*, 1991]. The influx of CO_2 has been estimated as $1.1 \pm 0.3 \times 10^8$ mol/yr for the Laacher See [*Aeschbach-Hertig et al.*, 1996] and 2.6×10^8 mol/yr for Lake Nyos [*Evans et al.*, 1993]. Considering that at least 1300 volcanos have erupted during the Holocene [*Simkin and Siebert*, 2000], the worldwide integrated CO_2 flux from the craters of dormant volcanos could be globally significant.

Yellowstone is one of the world's largest centers of late-Cenozoic explosive volcanism. The Yellowstone *caldera* formed from three eruptions (0.6, 1.2, and 2.1 Ma), and the last eruptive activity occurred ~70 kyr ago [*Smith and Braile*, 1994]. The Yellowstone magmatism is produced by a *mantle plume* [*Smith and Braile*, 1994]. Helium isotopic signatures of the gases discharged from Yellowstone support a mantle origin. *Werner et al.* [2000a] determined a total CO_2 flux of $2.4–4 \times 10^9$ mol/yr from measurements of vents and diffuse emission in a small (~4 km^2) area within the Yellowstone caldera. Eddy correlation measurements [*Werner et al.*, 2000b] provide supplementary CO_2 flux data for Yellowstone. In light of the anomalously large heat flow throughout the caldera, the total CO_2 discharge from the Yellowstone caldera could approach that of Mount Etna (C. Werner, personal communication, 2001).

On a larger scale, diffuse CO_2 emission from a belt of dormant volcanos has been quantified for the central Oregon Cascades [*James et al.*, 1999]. Isotopic analyses of springwaters in this region suggest that CO_2 was incorporated in the groundwater by diffuse magmatic degassing. Discharge of CO_2 to the atmosphere occurs upon degassing of the groundwater at springs [see also *Chiodini et al.*, 1999, 2000]. Coupling carbon isotopic compositions of springwater with spring discharge, *James et al.* [1999] derived a diffuse magmatic CO_2 flux (into the groundwater) of $\sim 3 \times 10^8$ mol/yr over the 75-km-long belt. Extrapolating over the entire length of volcanic arcs worldwide, they derived an approximate CO_2 flux of $\sim 3 \times 10^{11}$ mol/yr. Accordingly, the total CO_2 flux from diffuse degassing of dormant volcanos may be globally significant.

3.2.3. Global subaerial volcanic CO_2 flux. Because CO_2 fluxes have been measured for only a fraction (~10%) of the >100 active subaerial volcanos, estimating the total CO_2 discharge from volcanos worldwide requires considerable extrapolation. *Brantley and Koepenick*'s [1995] estimate of subaerial passive volcanic CO_2 discharge ($2–3 \times 10^{12}$ mol/yr) was derived by coupling measured CO_2 flux (primarily on volcano plumes) with the assumption that the CO_2 fluxes from various volcanos follow a lognormal distribution.

Many estimates of global volcanic CO_2 degassing have been derived by scaling with the fluxes of tracers that are particularly indicative of volcanic gases, for example, ^{3}He, ^{210}Po, and SO_2 [*Le Cloarec and Marty*, 1991]. *Williams et al.* [1992] computed a global subaerial volcanic CO_2 flux of $0.4–2.5 \times 10^{12}$ mol/yr by coupling measurements of the volcanic gas CO_2/SO_2 ratios with SO_2 flux. Because they considered the CO_2 flux from Mount Etna to be uniquely anomalous, their total subaerial volcanic CO_2 flux was derived by adding the flux from Mount Etna to fluxes obtained by extrapolation of measured data to the total number of eruptive (17) and noneruptive (101) active volcanos. *Allard*'s [1992] estimate of global subaerial volcanic CO_2 degassing ($\sim 1.5 \times 10^{12}$ mol/yr) was derived by combining volcanic SO_2 fluxes and CO_2/SO_2 ratios. Assuming that atmospheric ^{210}Po is largely of volcanic origin, *Marty and Le Cloarec* [1992] coupled C/^{210}Po measurements of a subset of active volcanos with an estimate of the global volcanic ^{210}Po budget of the atmosphere. *Sano and Williams* [1996] computed arc volcanic CO_2 fluxes by combining estimates of total arc ^{3}He fluxes with data on $CO_2/^3$He of arc volcanic fumaroles, and CO_2 fluxes from hot spot (mantle plume) volcanism were derived from an estimate of the total mantle plume ^{3}He flux coupled with data on the $CO_2/^3$He contents of mid-ocean ridge basalt

(MORB). *Marty and Tolstikhin* [1998] (Table 2) extended this computational strategy to include estimates of the mean partial melting rate and rate of lava production for arc and *hot spot magmatism*. On the basis of Marty and Tolstikhin's estimate (Table 2) the CO_2 flux from arc magmatism may be considerably larger than that of hot spot magmatism. If so, arc magmatism would be the dominant volcanic source of atmospheric CO_2. This conclusion is consistent with estimates of the global flux of nitrogen from arc and hot spot volcanos [*Sano et al*., 2001].

Because of the large extrapolation it is difficult to definitively assess the relative accuracy of the various methodologies for determining contemporary annual subaerial volcano CO_2 fluxes. Marked uncertainty in CO_2 fluxes derived from scaling to the ^3He flux [*Sano and Williams*, 1996] arises from large differences in estimates of the ^3He flux from subaerial volcanos [*Allard*, 1992]. *Marty and Tolstikhin* [1998] attempted to circumvent this dilemma by deriving the ^3He flux by coupling an estimate of the CO_2 content and percent of melting in the mantle source with the volumetric rates of intrusive and extrusive arc magmatism. However, their estimate of arc ^3He flux is clouded by potentially significant uncertainties in the percent of melting and in the volumetric rates of magmatism. Derivation of CO_2 fluxes from crater degassing is a well-established and well-tested methodology that provides consistent results for volcanic plumes [*Williams et al*., 1992; *Symonds et al*., 1994; *Gerlach et al*., 1994, 1997; *Harris and Rose*, 1996; *Burton et al*., 2000]. This methodology constrains contemporary subaerial volcanic CO_2 flux to $0.3–2.5 \times 10^{12}$ mol/yr (Table 2). By extrapolating crater CO_2 flux measurements to the total number of active volcanos, the estimates of *Gerlach* [1991b] and *Allard* [1992] yield consistent results (Table 2). *Brantley and Koepenick*'s [1995] estimate of the maximum flux (Table 2) is compatible with the flux estimates of *Gerlach* [1991b] and *Allard* [1992]. If the recent measurement of the CO_2 flux from Popocatépetl [*Delgado et al*., 1998] is added to *Gerlach*'s [1991a] and *Allard*'s [1992] estimates, I conclude that the best approximation of the total contemporary CO_2 flux from subaerial passive volcanic degassing is $\sim 2.0–2.5 \times 10^{12}$ mol/yr. This is in agreement with T. M. Gerlach's unpublished value (2.5×10^{12} mol/yr (T. M. Gerlach, personal communication, 2001)). Clearly, this estimate will be revised as additional CO_2 fluxes are measured. If no additional volcanos are found with anomalously high CO_2 flux (such as Popocatépetl and Mount Etna), this flux estimate will probably not be significantly changed by further measurements of CO_2 fluxes from active subaerial volcanos.

There are several important caveats in using contemporary subaerial volcanic CO_2 flux for quantification of the global carbon cycle. Contemporary volcanism represents a "snapshot" in geologic time and thus is inadequate for modeling with long time steps. Most measurements of volcano plume fluxes have been made over the past 2 decades; however, the baseline "recent" CO_2 flux for modeling paleoatmospheric CO_2 contents requires measurement over a much longer time span. Modeling the global carbon cycle with a time step of 1 Myr [*Berner*, 1991] requires a baseline recent CO_2 flux that is averaged over much of the Quaternary. Measurements show that the CO_2 flux of individual arc volcanos can vary considerably over time [*Harris and Rose*, 1996; *Delgado et al*., 1998; *Allard*, 1998]. To quantify the long-term CO_2 fluxes from active volcanos, we need integrated fluxes covering eruptive and noneruptive phases. As evidenced by Mount Pinatubo [*Gerlach et al*., 1996], multiple infrequent large eruptions of major volcanos can add considerable CO_2 to the atmosphere over a long timescale. Furthermore, most of the present-day global subaerial volcanic CO_2 emission is from two volcanos (Mount Etna and Popocatépetl). Major variations in gas discharge from these volcanos throughout their eruptive history (>0.1 Myr in the case of Mount Etna [*Allard*, 1998]) would have produced correspondingly large variations in the flux of CO_2 to the atmosphere. For Mount Etna, there was an evolution from early *tholeiitic* to late *alkaline* magmatism [*Tanguy et al*., 1997]. Although the correlation between CO_2 discharge and magma chemistry is not clear (as discussed in section 3.2.1), the evolution of the chemistry of the Mount Etna extrusives through time could nevertheless imply that there were corresponding changes in CO_2 output. The considerable variation in the eruptive versus quiescent history of Popocatépetl [*De la Cruz-Reyna and Siebe*, 1997] suggests that there could have been correspondingly large variations in the CO_2 discharge through time.

Coupling the above caveats with the facts that the plume CO_2 fluxes have been measured for a relatively small proportion of active volcanos and that the flank CO_2 emission fluxes are unknown for many volcanos, cynics could deride attempts to utilize estimates of the present-day volcanic CO_2 flux as a baseline for modeling the global carbon cycle. Considering that 500–600 volcanos have eruptive activity within recorded history [*Simkin*, 1993], we must continue to develop indirect methods for estimating the total CO_2 fluxes of these volcanos.

3.2.4. Submarine volcanism: Mid-ocean ridges. Because ~75% of contemporary extrusive magmatism occurs at mid-ocean ridges (MORs) [*Crisp*, 1984], these ridges are clearly a significant global source for discharge of magmatic volatiles. Because most submarine volcanism occurs along MOR systems, MORs represent the primary discharge of magmatically derived CO_2 into the oceans.

The CO_2 degassing flux from MOR volcanism has been computed by two methods. One method involves measurements of the CO_2 contents of MORB (analytical methods summarized by *Ihinger et al*. [1994]). Coupling estimates of the preeruptive CO_2 content of MOR magmas (by measurement of the CO_2 contents of MORB glasses) with the global rate of MOR volcanism, *Gerlach*

[1991b] estimated MOR CO_2 emission as $0.5–0.9 \times 10^{12}$ mol/yr. More recent measurements of the CO_2 contents of MORB glasses [*Kingsley and Schilling*, 1995] support *Gerlach*'s [1989] estimate (0.12 wt %) of the primary (predegassing) CO_2 content of MORB. Nevertheless, there is uncertainty in the primary CO_2 contents of MORB magmas [*Jambon*, 1994; *Dixon et al*., 1997; *Marty and Tolstikhin*, 1998]. An alternative method for computing MOR CO_2 emission involves ^3He, which provides a unique volatile tracer for mantle-derived magmas [*Lupton*, 1983; *Des Marais*, 1985; *Torgersen*, 1989; *Jambon*, 1994]. Helium 3 is primarily discharged into the oceans from MOR igneous activity [*Allard*, 1992]. Coupling estimates of the global ^3He emission from MORs [*Torgersen*, 1989] with data on the $C/^3He$ content of MORB glasses, the MOR CO_2 flux has been estimated as $\sim 2 \pm 1 \times 10^{12}$ mol/yr [*Sano and Williams*, 1996; *Marty and Tolstikhin*, 1998]. Uncertainties in the quantification of MOR CO_2 degassing are addressed by *Jambon* [1994].

In quantifying the role of MOR systems in the global carbon cycle, it is vital to consider that these systems are not only a CO_2 source (by magma degassing) but also a sink for CO_2. Hydrothermal activity at mid-ocean ridges causes CO_2 to be sequestered in carbonates [*Staudigel et al*., 1989; *Caldeira*, 1995; *Alt and Teagle*, 1999; *Kerrick and Connolly*, 2001b]. On the basis of the quantity of carbonate the CO_2 sequestration of the oceanic crust is estimated at $\sim 3.5 \times 10^{12}$ mol/yr [*Alt and Teagle*, 1999]. Because this consumption exceeds the estimated MOR magmatic CO_2 degassing flux ($\sim 2 \pm 1 \times 10^{12}$ mol/yr), MOR magmatism would not provide an uncompensated source for CO_2. In fact, MOR systems may instead be a net sink for CO_2 [*Staudigel et al*., 1989; *Varekamp et al*., 1992; *Alt and Teagle*, 1999; *Sleep and Zahnle*, 2001].

3.3. Volcanic CO_2 Fluxes and the Global Carbon Cycle

If MOR systems do not provide a net source for atmospheric CO_2 and if we provisionally adopt a contemporary subaerial volcano CO_2 flux of $\sim 2.0–2.5 \times 10^{12}$ mol/yr, there is a marked deficiency in the amount of CO_2 degassed from subaerial volcanism compared with the estimated drawdown fluxes of atmospheric CO_2 by silicate chemical weathering and consequent precipitation of marine carbonates [*Berner*, 1990; *Varekamp and Thomas*, 1998]. Even if uncertainties in the input and output fluxes are taken into account [*Varekamp and Thomas*, 1998], there remains a significant imbalance (several *teramoles* per year) between the amount of atmospheric CO_2 consumed by silicate weathering and the amount expelled from volcanos. Because of this deficiency and the assumption that the Earth degassing flux is approximately equal to the consumption of atmospheric CO_2 by silicate chemical weathering (as discussed in section 2), other major sources of CO_2 have been suggested to balance the global carbon cycle [*Kerrick et al*., 1995; *Varekamp and Thomas*, 1998]. Alternative CO_2 sources include metamorphism and degassing of intrusives that are not associated with volcanic edifices [*Varekamp et al*., 1992; *Kerrick et al*., 1995; *Varekamp and Thomas*, 1998]. Accordingly, such "nonvolcanic" sources are addressed in section 3.4.

3.4. Subaerial Nonvolcanic CO_2 Degassing

3.4.1. Introduction. Following *Kerrick et al*. [1995], I use the term nonvolcanic to specify gas that is not discharged from the craters and flanks of volcanos. As evidenced by fumaroles and well discharge in geothermal systems, regions with high heat flow are primary targets for evaluating emission of nonvolcanic CO_2 to the atmosphere. Some geothermal systems (e.g., Iceland and the Miravalles in Costa Rica) are hosted within volcanic edifices; however, many of the world's major geothermal systems are nonvolcanic. Although recent volcanism is typically associated with non-volcanic geothermal systems, we make the important distinction that CO_2 does not originate in subvolcanic magma chambers and thus is not discharged through volcanic edifices.

Subaerial regions of anomalously high nonvolcanic CO_2 emission were documented in seminal papers by I. Barnes and colleagues [*Irwin and Barnes*, 1975, 1980; *Barnes et al*., 1978]. They showed that this type of emission is prevalent in the circum-Pacific orogenic belt and in the Mediterranean portion of the Tethyan belt. Spatial association with major zones of seismicity implied that escape of the CO_2 from depth is aided by enhanced permeability in seismic zones [*Irwin and Barnes*, 1980]. Most of the areas of elevated nonvolcanic CO_2 emission are characterized by high heat flow that is attributed to subsurface magmas and include many of the world's major geothermal systems (e.g., Geysers, Salton Sea, and Taupo Volcanic Zone).

3.4.2. Regional examples. This section is a summary of well-studied regions of nonvolcanic CO_2 emission.

3.4.2.1. Taupo Volcanic Zone: Coupling data on convective heat flow with the temperatures and CO_2 concentrations of geothermal fluids, *Kerrick et al*. [1995] and *Seward and Kerrick* [1996] computed a CO_2 flux of $\sim 10^{10}$ mol/yr for the Taupo Volcanic Zone (TVZ). Isotopic evidence suggests that CO_2 discharged from the TVZ was derived from intrusive magmas [*Seward and Kerrick*, 1996]. The TVZ geothermal systems occur in a *back-arc basin* associated with a subduction zone. Because the TVZ tectonic setting is similar to that of other geothermal systems in the western Pacific (i.e., Indonesia, Philippines, Japan, and Kamchatka), *Seward and Kerrick* [1996] used the CO_2 flux from the 150-km-long TVZ as a baseline to derive a provisional total CO_2 flux estimate of $\sim 10^{12}$ mol/yr from back arcs of the entire $\sim 1.8 \times 10^4$ km length of western Pacific subduction zones.

3.4.2.2. Salton Trough: Using a strategy analogous to that used to determine the CO_2 flux from the TVZ, *Kerrick et al*. [1995] computed a CO_2 flux of $\sim 10^9$

mol/yr from all geothermal systems in the Salton Trough. The Salton Trough represents a relatively unique example of CO_2 production by thermal metamorphism of carbonate-bearing fluvial sediments in an unusual tectonic setting [*Kerrick et al*., 1995]. As such, it is not useful as a benchmark for extrapolating to other geothermal systems.

3.4.2.3. Europe: Central Italy provides a remarkable example of contemporary nonvolcanic CO_2 degassing. In this area, CO_2 is discharged from dry gas vents, areas of strong diffuse degassing, and from thermal and cold springs. On the basis of measurements of CO_2 fluxes from selected areas of focused degassing (dry gas vents and strong diffuse emission), *Rogie et al*. [2000] suggest that the cumulative discharge from focused CO_2 emission in central Italy could be $\sim 10^{10}$ mol/yr (similar to *Seward and Kerrick*'s [1996] estimate of the CO_2 flux from the entire Taupo Volcanic Zone). Vents and localized areas of strong CO_2 emission may in part result from degassing of groundwater in structural highs of the basement rocks [*Chiodini and Frondini*, 2001].

Influx of deeply derived CO_2 has produced elevated CO_2 contents of groundwaters in central Italy. Combining regional hydrology with data on the geochemistry and carbon isotopic composition of cold groundwater discharging at springs, *Chiodini et al*. [1999, 2000] computed a deeply derived CO_2 flux of 1–3 $\times$ 10^{11} mol/yr. Carbon and helium isotopic data suggest a significant crustal signature for the CO_2 discharged from central Italy. As evidenced by young alkaline volcanics and carbonatites in central Italy and by the isotopic compositions of volcanic fumarole gases, it is possible that the CO_2 was derived by degassing of subjacent magmas [*Chiodini et al*., 2000; *Italiano et al*., 2000]. Thermal springs [*Minissale*, 1991] and associated *travertine* deposits [*Pentecost*, 1995a, 1995b; *Ford and Pedley*, 1996] are abundant along the western (Tyrrhenian) coastal region of central Italy. Discharge of CO_2 would accompany the precipitation of travertine-forming calcite via the reaction $(Ca^{2+})_{aq} + 2(HCO_3)_{aq} = CaCO_3 + H_2O + CO_2$. The quantity of CO_2 released by thermal spring discharge is not known, but in coupling rough estimates of the total thermal spring discharge with the $(HCO_3^-)_{aq}$ content of thermal springwaters (A. Minissale, personal communication, 2001), it appears that the total CO_2 emission from Italian thermal springs could be similar to the total CO_2 discharged from cold springs in central Italy.

The basin of the Tyrrhenian Sea was apparently formed by extensional tectonism [*Faccena et al*., 1997]. On a larger scale, there appears to be an up-arched mantle underlying the Tyrrhenian Sea [*Cella et al*., 1998] and much of central Europe to the north [*Hoernle et al*., 1995]. As in the Tyrrhenian belt, CO_2-rich vents are common in France [*Barnes et al*., 1978, 1984; *Matthews et al*., 1987; *Arthaud et al*., 1994] and Germany [*Barnes et al*., 1978, 1984; *May et al*., 1992; *Griesshaber et al*., 1992]. Isotopic evidence [*Griesshaber et al*., 1992; *Marty et al*., 1992; *Lollar et al*., 1997] suggests that CO_2 emitted from vents in Germany originated from the mantle. Quaternary volcanics in the regions of CO_2 emission in central Europe [*Griesshaber et al*., 1992] support the contention that CO_2 originated from mantle-derived intrusives. Seismic imaging suggests that the Quaternary Eifel volcanic field in Germany is fed by a mantle plume [*Ritter et al*., 2001]. *Ritter et al*. [2001] noted that relatively little extrusive volcanism accompanies the apparently large mantle plume in the Eifel region of Germany. Accordingly, significant quantities of CO_2 could be discharged at the surface from degassing of large intrusive mantle plumes. On the basis of an estimated influx of deeply derived CO_2 into groundwaters of extensional basins in Hungary and Austria, *Lollar et al*. [1997, p. 2295] concluded that "the addition of mantle-derived carbon to the crust in areas of continental extension is significant and may have been previously underestimated."

3.4.2.4. Northern California Coast Ranges: Discharge of nonvolcanic CO_2 is widespread in the north-central Coast Ranges of California [*Barnes et al*., 1975; *Irwin and Barnes*, 1982; *Kerrick et al*., 1995]. The Geysers geothermal system, the largest commercial field in the world, is located in this region. Isotopic data suggest that the CO_2 is derived from the decomposition of calcite and organic material in the basement (Franciscan Complex) [*Bergfeld et al*., 2001a]. This region is at the northern edge of a northward propagating *slabless window* [*Liu and Furlong*, 1992; *Benz et al*., 1992]. The northward decrease in the age of Cenozoic volcanism in the California Coast Ranges is compatible with the northward migration of the upwelling asthenosphere [*Liu and Furlong*, 1992; *Liu*, 1993]. The isotopic data suggesting a mixed mantle-crustal source for the CO_2 are compatible with recent volcanism (0.01 Ma [*Donnelly-Nolan et al*., 1993]), teleseismic data [*Benz et al*., 1992], and xenoliths of high-grade metamorphic rocks in the volcanics [*Stimac et al*., 1992]. Widespread seismic reflections in the lower crust and Moho in this region are interpreted as mafic melts derived from the asthenosphere [*Levander et al*., 1998]. Accordingly, this region may be undergoing metamorphism and anatexis produced by intrusion of asthenospheric melts into the lower crust.

3.4.3. Continental rifts. Continental rifts represent potentially significant sources of nonvolcanic CO_2 emission. A notable example of possible high CO_2 emission is provided by the East African Rift system. CO_2 emission from fumaroles, dry boreholes, and seeps is widespread in the Kenya Rift Valley [*Darling et al*., 1995]. Isotopic data and the presence of carbonatite magmatism suggest that the CO_2 emitted from the Kenya Rift Valley is of mantle origin [*Darling et al*., 1995].

Active continental rifting is occurring in the Basin and Range province [*Kearey and Vine*, 1990; *Snow and Wernicke*, 2000]. This region is characterized by thin crust, high heat flow, and the presence of numerous, small, fault-localized geothermal fields. Geophysical evidence suggests that the lower crust contains abundant

mantle-derived mafic intrusives [*Larkin et al*., 1997]. The limited volcanism attending the rapid extension of the Basin and Range province is attributed to ponding of magmas at middle-to-lower crustal levels [*Gans and Bohrson*, 1998]. However, in contrast to the East African Rift system, fluids expelled in the Basin and Range geothermal systems appear to have a crustal origin [*Bergfeld et al*., 2001b; F. Goff, personal communication, 2001].

3.4.4. CO_2 expulsion from major fault zones. Major fault zones may provide conduits for significant expulsion of deeply derived CO_2 to the atmosphere. Quartz-carbonate vein systems along major shear zones attest to the transport of large quantities of CO_2 along such zones [*Kerrich and Feng*, 1992]. Seismically induced CO_2 degassing along faults has been proposed [*King*, 1986; *Sibson*, 1992]. In the north-central California Coast Ranges, CO_2 vents are aligned along faults [*Goff and Janik*, 1993; *Sims and Rymer*, 1976]. A notable example of fault-controlled CO_2 emission is the alignment of CO_2-rich springs along the 40-km-long Bartlett Springs fault [*Goff and Janik*, 1993]. Because this fault zone has earthquake *hypocenters* that are up to 12 km deep [*Dehlinger and Bolt*, 1984], the CO_2 discharged at the surface could be of deep origin. Faults as conduits for CO_2 expulsion have also been demonstrated in areas other than the California Coast Ranges [*Barberi and Carapezza*, 1994; *Zheng et al*., 2001]. Major transform faults such as the San Andreas could be particularly effective conduits for expulsion of deep CO_2 [*Kharaka et al*., 1999]. However, although CO_2 flux anomalies have been measured in traverses across the San Andreas fault, carbon isotopic data for CO_2 emitted along the Parkfield segment of the San Andreas fault [*Lewicki and Brantley*, 2000] suggest that the CO_2 is largely derived from shallow biogenic processes.

3.4.5. CO_2 derived from abiogenic CH_4. Within a relatively short time period (~10 years [*Wahlen*, 1993]), methane expelled into the atmosphere is oxidized to CO_2. Thus, on a geologic timescale, CH_4 degassing provides a source for atmospheric CO_2. Two geologic regimes are likely for generating significant fluxes of abiogenic methane.

3.4.5.1. MOR hydrothermal vents: Numerous papers have documented emission of CH_4-rich fluids from MOR hydrothermal vents [e.g., *Welhan and Craig*, 1979; *Bougault et al*., 1993]. *Serpentinite* outcrops on the ocean floor are common in the regions of transform-ridge intersections on slow spreading ridges in the Atlantic Ocean [*Cannat*, 1993]. Geochemical signatures of the vent fluids [*Kelley*, 1996] and experimental studies on serpentinization of ultramafics [*Berndt et al*., 1996] strongly suggest that the methane is generated during serpentinization by the Fisher-Tropsch reaction, $CO_2 + 4H_2 = CH_4 + 2H_2O$ [*Berndt et al*., 1996]. In MOR hydrothermal systems the CO_2 is supplied by the seawater, and H_2 is generated by the oxidation of Fe accompanying transformation of olivine to magnetite [*Berndt et al*., 1996]. CH_4 emanation from subaerial exposures of serpentinite [*Abrajano et al*., 1988] confirms this reaction. Not all of the CH_4 emanating from MOR hydrothermal vents necessarily arises from serpentinization since reduction of CO_2 to CH_4 can accompany hydrothermal alteration of MOR basalts [*Welhan*, 1988]. Coupling CH_4/He ratios of fluids discharged from submarine hydrothermal vents with the ^{3}He flux into the oceans from MOR systems, *Welhan and Craig* [1979] estimated a CH_4 flux of 1.3×10^9 m^3/yr (equal to 6.5×10^9 mol/yr). Although this flux suggests that CH_4 emission from MOR systems would not have been a significant factor in the late Cenozoic global carbon cycle, this does not rule out the potential importance of this process earlier in Earth's history.

3.4.5.2. Thermocatalysis of organic matter: Thermal decomposition (thermocatalysis, or "cracking") of organic matter is considered to be the major source of CH_4 in hydrothermal systems [*Welhan*, 1988]. Isotopic data [*Poreda et al*., 1986, 1988] suggest that helium in natural gas deposits associated with many active continental margins has a significant magmatic signature. This conclusion is compatible with the marked late Cenozoic magmatic activity in these margins. *Poreda et al*. [1988] concluded that CH_4 was generated by thermocatalysis of organic matter by *contact metamorphism* of sediments.

An *accretionary prism* is a potentially significant source for large quantities of thermogenically derived CH_4 [*Moore and Vrolijk*, 1992]. Indeed, carbon isotopic data of fluids discharged from accretionary prisms suggest a thermogenic origin for CH_4. Submarine and subaerial mud volcanos [*Barber et al*., 1986] provide focused discharge of CH_4 from accretionary prisms. To the author's knowledge, the total flux of CH_4 from accretionary prisms has not been estimated. If the average concentrations of CH_4 in fluids of accretionary prisms were known, the total CH_4 emission could be calculated from the total volume of fluids expelled from accretionary prisms (~1 km^3/yr [*Kastner et al*., 1991]).

4. PAST CO_2 DEGASSING

4.1. Introduction

Analysis of present-day CO_2 degassing provides insight for a geologically based assessment of paleodegassing. Because most CO_2 released by contemporary degassing appears to have a magmatic origin, the paleomagmatic record should be a primary focus in elucidating CO_2 paleodegassing.

4.2. Magmatic CO_2 Paleodegassing

4.2.1. Weaknesses of the Earth paleodegassing model assumptions. In most geochemical models of the global carbon cycle the CO_2 paleoflux is correlated with the MOR spreading rate. It is assumed that the

quantity of CO_2 released from volcanic arcs was proportional to subduction rates and thus correlated with MOR spreading rates. CO_2 released by arc volcanism is considered to have originated by decarbonation of subducted carbonate-bearing lithologies.

There are several reasons why correlating arc CO_2 degassing with spreading/subduction rate is a questionable model assumption. First, for the circum-Pacific arc volcanism, there is no correlation between the number of active volcanos (i.e., the number of volcanos per unit arc length) and the subduction rate [*Cambray and Cadet*, 1994], and the relative volumes of Quaternary volcanics in the Central American and Antilles arcs are not correlative with the relative subduction rates [*Wadge*, 1984]. Second, correlation between spreading/subduction rate and volcanic arc CO_2 degassing implicitly assumes that the CO_2 contents of subducted slabs are identical for all subduction zones. In fact, there are marked differences in the CO_2 contents of marine sediments entering various subduction zones [*Rea and Ruff*, 1996], and there is considerable variation (and uncertainty) in the amount of CO_2 in metabasaltic rocks of the oceanic crust [*Alt and Teagle*, 1999]. Because the CO_2 content of oceanic metabasalts increases with age [*Alt and Teagle*, 1999], subduction zones with older subducted oceanic crust would have a more fertile CO_2 source than subduction zones with younger subducted oceanic crust. In addition, the accumulation rate of pelagic carbonate has increased through the Cenozoic [*Caldeira*, 1992; *Nakamori*, 2001]; consequently, the proportion of subducted pelagic carbonate has increased during this time period. Third, as was shown by *Kerrick and Connolly* [1998, 2001a, 2001b], the extent and depth of subduction zone metamorphic decarbonation are very dependent upon the pressure-temperature conditions (geotherms) along the tops of subducted slabs. The generalized geochemical models for arc degassing implicitly assume that metamorphic decarbonation and the transfer of metamorphic CO_2 to arc magmas are the same for all subduction zones. Fourth, CO_2 emission from hot spot and continental rift magmatism and from metamorphism resulting from continent-continent collision [*Kerrick and Caldeira*, 1998] is neglected. Fifth, most of the contemporary arc volcanic CO_2 is emitted from only two volcanos (Popocatépetl and Mount Etna). Furthermore, Mount Etna magmatism is not generated by a typical subduction zone process [*Gvirtzman and Nur*, 1999; *Nicolich et al*., 2000], and the rock types are not typical of subduction zones [*Marty et al*., 1994].

4.2.2. Introduction. Extrusive magmas provide a particularly efficient mechanism for transfer of magmatic volatiles to the atmosphere. Thus the role of volcanic CO_2 emission in past periods of global warming has been a major focus. Because the magmatic record is best preserved in younger rocks, most research has focused on correlations between magmatism and paleoclimate in the Mesozoic and (especially) the Cenozoic.

Evaluation of the role of magmatic CO_2 degassing on paleoatmospheric CO_2 levels and thus on greenhouse global warming is a twofold task. First, a temporal coincidence between periods of enhanced magmatism and global warmth must be established. Second, the amount of magmatic CO_2 released during these periods must be quantified. This quantification involves coupling the rate of magma production through time with estimates of the amount of CO_2 contained within the magmas. The latter is obtained through estimates of preeruptive CO_2 solubilities in magmas [*Johnson et al*., 1994]. *Sigurdsson* [2000] published a recent summary of the estimated rates of volcanism for the past 150 Myr.

Quantification of the role of magmatic paleodegassing in global paleoclimate requires independent evidence on paleoatmospheric CO_2 levels. Primary methodologies for determining paleoatmospheric CO_2 contents involve isotopic data of paleosols [e.g., *Cerling*, 1992; *Yapp and Poths*, 1996], marine sediments [e.g., *Pagani et al*., 1999; *Pearson and Palmer*, 2000], and fossil plant cuticles [*Retallack*, 2001]. There is general agreement that elevated atmospheric CO_2 contents were likely during the Cretaceous [*Spicer and Corfield*, 1992; *Berner*, 1992; *Andrews et al*., 1995; *Kuypers et al*., 1999; *Poulsen et al*., 1999] and the late Paleocene–early Eocene [*Sloan and Rea*, 1995; *Pearson and Palmer*, 2000]. However, there is controversy regarding the atmospheric CO_2 levels during other time periods. In particular, in contrast to previous studies [e.g., *Douglas and Woodruff*, 1981], *Pagani et al*. [1999] concluded that atmospheric CO_2 levels were not elevated during the Miocene.

4.2.3. MOR magmatism. Compilations of the global magmatic activity in various geologic regimes show that magmatism at mid-ocean ridges is dominant [*Crisp*, 1984; *Kaiho and Saito*, 1994]. However, as was discussed in section 3.2.4, it is imperative to consider that MOR systems may be a net sink for CO_2. Accordingly, in spite of the fact that the dominant source for global magma production through time is attributed to MOR magmatism, correlation of MOR magma production with periods of elevated atmospheric CO_2 levels and global warmth must be viewed with considerable caution. Suggestions that enhanced CO_2 degassing from MOR magmatism significantly contributed to the Cretaceous warmth [*Kaiho and Saito*, 1994; *Tajika*, 1998] or that diminished MOR CO_2 degassing significantly contributed to global cooling during the Cenozoic [*Kaiho and Saito*, 1994; *Goddéris and François*, 1995] may not be justified. Furthermore, there is controversy as to whether there was enhanced MOR crust production (and, by inference, enhanced MOR CO_2 degassing) during the middle Cretaceous [*Heller et al*., 1996]. Considering that MOR systems are a sink for CO_2, *Sleep and Zahnle* [2001] hypothesized that subduction of carbonated oceanic crust maintained low atmospheric CO_2 contents during the early Earth (*Archean* and *Hadean* eons). To address the validity of such suggestions, considerably more research will be necessary to quantify the

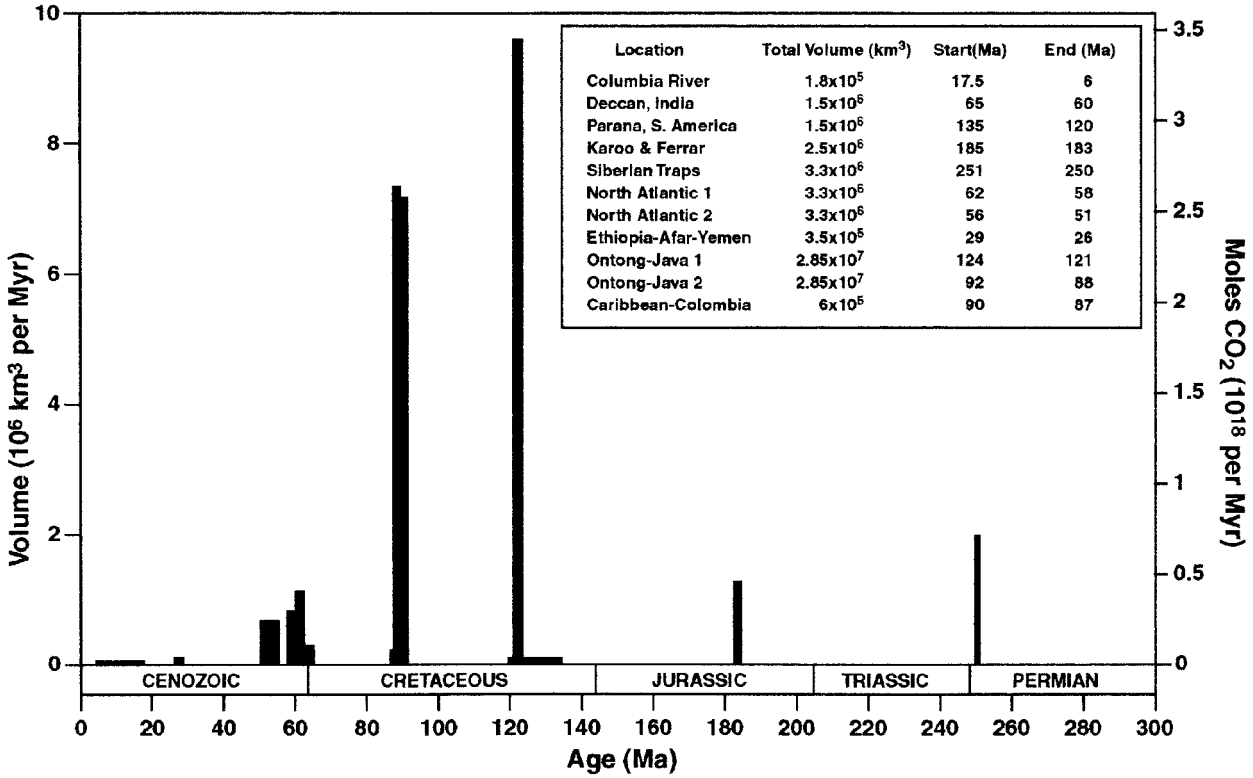

Figure 1. Left ordinate shows estimated total volume of flood basalts (large igneous provinces) since the Permian. Data are compiled using a time step of 1 million years. Data sources for the inset are as follows: Siberian Traps, *Wignall* [2001]; Karoo and Ferrar, *Encarnación et al.* [1996]; all others, *Coffin and Eldholm* [1994], *Mahoney and Coffin* [1997], and *Hooper* [2000]. Right ordinate shows computed CO_2 released from flood basalts (see text for details).

on-axis and off-axis sequestration of CO_2 through time by hydrothermal alteration of the oceanic crust [*Alt and Teagle*, 1999].

4.2.4. Hot spot magmatism: Flood basalts. Large igneous provinces (LIPS) are characterized by aerially extensive flood basalts [*Coffin and Eldholm*, 1994; *Hooper*, 2000]. Flood basalts are the extrusive magmatic products of mantle plumes (hot spot volcanism). Paleomagmatic CO_2 degassing from LIPS has been quantified by coupling estimates of the solubility of CO_2 in magmas with the volumetric rates of extrusion [*Leavitt*, 1982; *Arthur et al.*, 1985; *Eldholm and Thomas*, 1993].

Because there have been numerous relatively short lived periods of voluminous flood basalt extrusion through time [*Coffin and Eldholm*, 1994] and because aerially extensive flood basalt flows would provide particularly efficient transfer of magmatic CO_2 to the atmosphere [*Eldholm and Thomas*, 1993], flood basalts have been a focal point for the correlation between magmatism and paleoatmospheric CO_2 levels. Accordingly, flood basalts have been considered to have affected the atmospheric CO_2 contents at the Permian-Triassic boundary [*Krull and Retallack*, 2000], Triassic-Jurassic boundary [*Hames et al.*, 2000], middle Cretaceous [*Caldeira and Rampino*, 1991; *Tajika*, 1999; *Gibbs et al.*, 1999], Cretaceous-Tertiary (K/T) boundary [*McLean*, 1985; *Caldeira and Rampino*, 1990a, 1990b], late Paleocene–early Eocene [*Rea et al.*, 1990; *Eldholm and Thomas*, 1993; *Bralower et al.*, 1997], and Miocene [*Hodell and Woodruff*, 1994]. Nevertheless, there is controversy regarding the impact of flood basalts on paleoatmospheric CO_2 levels. On the basis of estimates of CO_2 solubilities in basaltic melts and the volumetric rates of extrusion, *Arthur* [2000] concluded that the Deccan flood basalts, which had previously been considered to have a major impact on atmospheric CO_2 at the K/T boundary [*McLean*, 1985], would have produced a very small increase in atmospheric CO_2 concentration. *Caldeira and Rampino* [1990a, 1990b] concluded that CO_2 released to the atmosphere by the Deccan volcanism (Figure 1) resulted in a small (<1°C) degree of global warming.

CO_2 release by LIPS magmatism (Figure 1) was computed from data on the volumes and timing of LIPS magmatism (see inset in Figure 1) coupled with a provisional estimate of 0.5 wt % CO_2 in the preeruptive basaltic magmas [*Johnson et al.*, 1994]. The long-term effect of the computed CO_2 degassing (Figure 1) on global warming must consider the competing drawdown of atmospheric CO_2 by silicate chemical weathering

[*Berner and Caldeira*, 1997; *Kerrick and Caldeira*, 1999; *Berner*, 1999]. Using a geochemical model for the global carbon cycle, *Kerrick and Caldeira* [1993] concluded that over a 1-million-year period, excess CO_2 degassing of $>0.5 \times 10^{18}$ mol would be required to produce notable global warming (i.e., minimal temperature increases of 1°–2°C). The computed CO_2 released by LIPS magmatism during the Cretaceous (Figure 1) would have significantly contributed to global warming during that period. However, it is questionable whether enough CO_2 was released by LIPS magmatism before and after the Cretaceous (Figure 1) to have caused global warming.

There is a significant correlation between periods of LIPS magmatism and widespread extinctions of organisms [*Stothers*, 1993; *Courtillot et al*., 1996; *Pálfy and Smith*, 2000; *Wignall*, 2001]. Primary examples include the Permian-Triassic at ~250 Ma (Siberian flood basalts), the Early Jurassic at ~183 Ma (Karoo and Ferrar basalts) [*Pálfy and Smith*, 2000], and the Cretaceous-Tertiary at ~65 Ma (Deccan flood basalts). However, *Rampino and Self* [2000] concluded that the relatively small increase (<200 ppm) in paleoatmospheric CO_2 produced by flood basalts is unlikely to have been a significant factor in causing mass extinctions. Furthermore, they concluded that emission of acidic volatiles from flood basalts (H_2SO_4, HCl, and HF) was unlikely to have had a major environmental impact. Nevertheless, controversy continues about the role of enhanced CO_2 emission [*Knoll et al*., 1996] and acidic volatiles [*Ray and Pande*, 1999] in extinctions. In a recent review, *Wignall* [2001] demonstrated the strong correlation between LIPS magmatism, global warming, and marine anoxia. It has been hypothesized that global warming produced by CO_2 emission from flood basalts triggered rapid release to the atmosphere of large quantities of CH_4 derived from destabilization and oxidation of seafloor methane hydrates (clathrates) and subsequent rapid oxidation of CH_4 to CO_2 [*Thomas et al*., 2000; *Wignall*, 2001]. The abrupt global warming accompanying the rapid CH_4 emission resulted in marine anoxia [*Wignall*, 2001]. As a corollary, the apparent numerous and relatively abrupt transient increases in paleoatmospheric CO_2 contents over the past 300 Myr are compatible with massive CH_4 release by dissociation of gas hydrates [*Retallack*, 2001]. However, although CO_2 released by flood basalt volcanism could have accounted for extinctions during the Cretaceous (Figure 1), it is questionable whether the small (<2°C) temperature increase produced by CO_2 released by major flood basalt volcanism during other time periods (Figure 1) was sufficient to cause massive dissociation of gas hydrates.

Because of insufficient information on the volume and timing of magmatism [*Nicolaysen et al*., 2000] the Kerguelen LIPS is excluded from Figure 1. Thus assessment of the role of flood basalt degassing on past global warming warrants additional research.

4.2.5. Hot spot magmatism: Ocean island basalts. Ocean island basalt (OIB) is the product of mantle plume (hot spot) volcanism within oceanic plates. As exemplified by the Hawaii-Emperor chain, there are linear chains of seamounts and ocean islands that form from plate movement over stationary hot spots [*Winter*, 2001]. OIB magmatism is characterized by dominant tholeiitic and subordinate alkaline magma types. The primary (undegassed) magma supplying the tholeiitic Kilauea volcano is estimated to have 0.83 wt % CO_2 (T. M. Gerlach et al., Summit CO_2 degassing rate of Kilauea volcano: Implications for primary magma and its supply to the summit reservoir, submitted to *Journal of Geophysical Research*, 2001, hereinafter referred to as Gerlach et al., submitted manuscript, 2001). However, parental (undegassed) CO_2 contents of 1.3 wt % are estimated for alkaline basalts associated with the Hawaiian OIB system [*Dixon et al*., 1997]. These studies are commensurate with the comparatively high CO_2 solubilities in alkaline magmas [*Bailey and Hampton*, 1990; *Holloway and Blank*, 1994]. Thus, although the total volume of OIB magmatism represents only a few percent of all oceanic volcanism, the relatively high CO_2 solubilities imply that the CO_2 flux from OIB alkaline magmatism could be significant. Because the relative volumes of tholeiitic versus alkaline rocks of OIB volcanism are unknown [*Winter*, 2001], we cannot at present estimate CO_2 paleofluxes by coupling estimated CO_2 solubilities in parental magmas with the volumes of OIB magmatism.

4.2.6. Arc magmatism. In comparison with flood basalts, quantifying arc magmatic CO_2 paleodegassing from mass loss computations is complicated by uncertainty regarding the relative volumes of extrusive versus intrusive arc magmatism. *Crisp* [1984] concluded that the ratios of the volumes of intrusive to extrusive magmatism are ~10:1 for continental magmatism. However, more recent analyses of volcanic systems suggest that this ratio may be considerably larger [*Francis et al*., 1993; *Allard et al*., 1994; *D'Alessandro et al*., 1997; *Allard*, 1997]. Thus intrusives may account for the bulk of magmatic CO_2 degassing. It is likely that volcanic conduits overlie intrusive magma bodies in the upper few kilometers of the crust. Consequently, much of the volatiles released from such magmas could have escaped to the atmosphere through the overlying volcanic conduits. Indeed, studies of Stromboli [*Allard et al*., 1994], Mount Etna [*Allard et al*., 1991, 1997; *D'Alessandro et al*., 1997], Popocatépetl [*Gerlach et al*., 1997], and Kilauea (Gerlach et al., submitted manuscript, 2001) suggest that CO_2 is directly degassed from shallow magma chambers (i.e., open system degassing) beneath these volcanos. However, this does not necessarily imply that noneruptive degassing occurs from a stationary magma chamber. The temporal variations of the CO_2 and SO_2 fluxes from Mount St. Helens [*Harris and Rose*, 1996] suggest that the CO_2 is produced by crystallization of a stationary

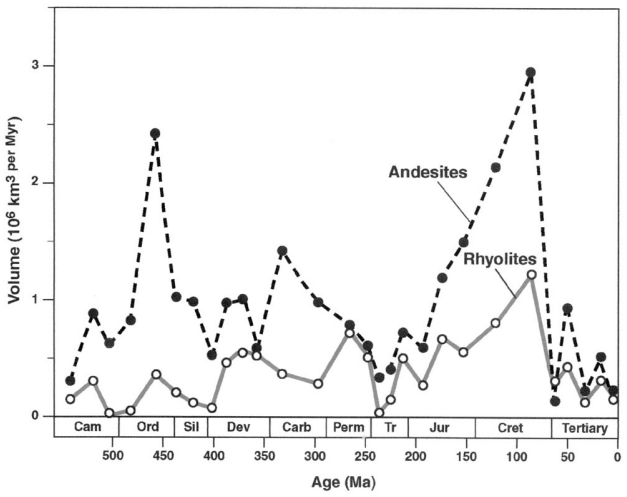

Figure 2. Estimated total volumes of andesites and rhyolites (through the *Phanerozoic* eon) intercalated within sedimentary continental rocks [from *Bogatikov et al*., 2000, Figure 7.6]. Each data point represents the total volume for an epoch; the time for each point corresponds to the midpoint of the epoch (e.g., the Paleogene at ~60 Ma; for details, see *Bogatikov et al*. [2000, Figure 7.6]).

magma chamber coupled with episodic degassing of melts ascending into the magma chamber.

Because of uncertainties regarding the degassing of magma chambers associated with arc volcanism, this review considers only the temporal correlations between the volumes of extrusive and intrusive magmatism and global paleoclimate.

4.2.6.1. Extrusive arc magmatism: Magmatic arcs are dominated by magmas of calc-alkaline composition. Accordingly, the volumes of rhyolites and andesites through time (Figure 2) are an indicator of the temporal evolution of arc volcanism. In the Paleozoic (Figure 2), there was marked andesitic volcanism in the Ordovician. Thus CO_2 expelled from arc volcanos may have contributed to the elevated CO_2 levels during this period [*Gibbs et al*., 2000]. As is shown in Figure 2, there was a marked and steady increase in the amount of andesitic and rhyolitic volcanism from the Early Jurassic to Late Cretaceous followed by a marked decline in the latest Cretaceous. Within the Cenozoic, there were notable spikes in andesite and rhyolite volcanism in the Paleogene (Eocene) and Neogene (Miocene) (Figure 2). The enhanced volcanism in the Eocene (37–42 Myr ago) is supported by Ocean Drilling Program (ODP) drill cores of marine sediments associated with the circum-Pacific and Caribbean arcs [*Cambray and Cadet*, 1994]. In addition to the Eocene, ODP drill cores of these sediments reveal enhanced Cenozoic volcanism in the Miocene (13–17 Ma) and Pliocene-Quaternary (past 5 Myr) [*Cambray and Cadet*, 1994; *Arculus et al*., 1995].

4.2.6.2. Intrusive arc magmatism: Figure 3 is a graphical summary of *Crisp*'s [1984] compilation of the volumes of intrusive (batholithic) magmatism through time. *Crisp* [1984] derived the volumes by coupling the areas and ages of exposed *batholiths* with the generalized assumption that batholiths are 10 km thick. *Crisp*'s [1984] compilation (Figure 3) reveals a marked increase in the volume of intrusive magmatic activity during the Late Cretaceous (Campanian), maximum activity from the Late Cretaceous through the Eocene, and a decline in intrusive activity since the late Eocene. Because of the general correlation between erosional exhumation and age the apparent decline in intrusive activity through the Cenozoic (Figure 3) may not be indicative of the actual rates of intrusive magmatism during this era. However, exposures of Mesozoic intrusives are widespread in orogenic belts; thus estimates of the volumes of intrusive magmatism through the Mesozoic may be more accurate than during the Cenozoic. Because Mesozoic intrusives in the western United States were emplaced at shallow crustal levels [*Barton and Hanson*, 1989], it is possible that a significant fraction of the CO_2 released from these intrusives escaped to the Earth's surface. However, an important caveat to this conclusion is that an unknown fraction of CO_2 released from intrusive magmas would have been sequestered in carbonates formed in hydrothermal aureoles [*Varekamp et al*., 1992].

4.2.7. Carbonatites. Because of the relatively large CO_2 flux from the active carbonatite volcano Oldoinyo Lengai [*Brantley and Koepenick*, 1995] and because of the CO_2-rich magma composition [*Bailey and Hampton*, 1990; *Dawson et al*., 1994; *Dixon et al*., 1997], carbonatite magmatism could have provided a significant paleomagmatic CO_2 flux. *Woolley*'s [1989] compilation of radiometric age data for carbonatites for the past 3000 Myr suggests that there has been an increase in carbonatite magmatism through time. In particular, his data show that post-Jurassic carbonatites are particularly

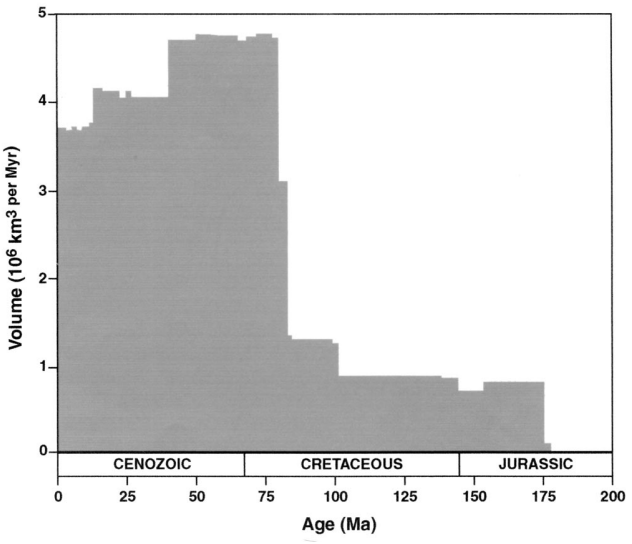

Figure 3. Estimated total volume of intrusive igneous rocks since the Middle Jurassic [from *Crisp*, 1984, Table 3]. Data are compiled using a time step of 1 million years.

abundant in Africa and South America [*Woolley*, 1989]. As is illustrated by *Bailey* [1993, Figure 3], there were four major periods of post-Jurassic carbonatite magmatism in Africa: Early Cretaceous, Late Cretaceous, Eocene-Oligocene, and Miocene-Recent. It is notable that with the exception of the late Cenozoic the time periods of the African carbonatite magmatism correlate with periods of global warmth. However, *Veizer et al*. [1992] considered that the apparent increase in the proportion of carbonatites through time is an artifact of their preservation. Nevertheless, the temporal correlations between carbonatites and periods of global warmth are intriguing and warrant further analysis.

4.2.8. Concluding remarks. Although the role of magmatic CO_2 degassing and global warming may be uncertain for other time periods, there is general agreement that enhanced magmatism was a major contributor to the elevated atmospheric CO_2 levels, and thus to global warmth, during the Cretaceous [*Spicer and Corfield*, 1992; *Kuypers et al*., 1999].

4.3. Paleometamorphic CO_2 Degassing

Most analyses of the global carbon cycle assume that the main role of metamorphism in the global carbon cycle is the release of CO_2 by breakdown of carbonates in subducted marine sediments and/or breakdown of carbonates in subducted hydrothermally altered oceanic crust and transfer of this CO_2 to the atmosphere by arc volcanism [e.g., *Kump et al*., 1999, p. 147].

Areas undergoing widespread, shallow "low-pressure metamorphism" would provide particularly suitable regimes for expulsion of large quantities of metamorphic CO_2 to the atmosphere [*Kerrick and Caldeira*, 1998]. With this scenario, CO_2 is generated by thermal decomposition of carbonates, with heat supplied by regionally extensive intrusives. To emphasize the heat source, *Spear* [1993] referred to this as "regional contact metamorphism" (RCM).

There are two tectonic regimes for RCM. One is in magmatic arcs created by ocean-continent or continent-continent collisions such as the Sierra Nevada (California) and Himalaya mountain ranges, respectively. The other regime is in continental rifts. The Basin and Range is considered a contemporary example of this type of metamorphism [*Spear*, 1993]. Indeed, geophysical data [*Larkin et al*., 1997] and the crustal origin of CO_2 expelled in Basin and Range geothermal systems [*Bergfeld et al*., 2001b] are consistent with derivation of the volatiles from RCM.

Kerrick and Caldeira [1998] quantified metamorphic CO_2 paleofluxes by two methods. One method involves coupling estimates of average fluid fluxes during metamorphism with the CO_2 contents of the fluids. To determine fluid fluxes, *Ferry* [1994] has championed the "reaction progress" method whereby the fluid fluxes through rocks undergoing metamorphism are derived from the extent ("progress") of metamorphic reactions (obtained by modal data of metamorphic rocks). Computation of CO_2 fluxes requires data on fluid compositions and on the duration of the metamorphic event. The other method involves a mass loss approach that requires, for a contiguous belt of metamorphic rocks, estimating the total volume of carbonate rocks, the amount of carbonate consumed by *metamorphic decarbonation*, and the duration of metamorphism. Both of these methods require assumptions regarding the efficacy of expulsion of the deeply generated CO_2 at the Earth's surface. Sequestration of CO_2 by formation of vein carbonate would diminish the amount of metamorphic CO_2 that is expelled at the Earth's surface. From analysis of the quantity of carbonate veins in the Eocene Cordilleran metamorphic belt, *Kerrick and Caldeira* [1998] concluded that ~9–18% of the CO_2 generated by metamorphism was lost to carbonate veins. Accordingly, it is possible that a significant proportion of CO_2 generated by RCM was expelled at the Earth's surface.

For the Cenozoic, *Kerrick and Caldeira* [1993, 1994, 1998, 1999] evaluated the role of metamorphic CO_2 degassing and paleoclimate. Because the late Paleocene to early Eocene is the best documented example of early Cenozoic global warming, we focused on evaluating metamorphic CO_2 degassing from Cenozoic metamorphic belts. Our earlier research [*Kerrick and Caldeira*, 1993, 1994] suggested that regional metamorphism associated with the early Cenozoic India-Asia collision could have significantly enhanced paleoatmospheric CO_2 contents and thus could have contributed to early Cenozoic global warming. However, our subsequent reanalysis [*Kerrick and Caldeira*, 1998, 1999] suggested that regional metamorphism in the Himalayan belt probably had an insignificant effect on the Cenozoic atmospheric CO_2 content. We concluded that the widespread Eocene RCM in the Cordilleran metamorphic belt of North America could have released significant quantities of CO_2 to the atmosphere and thus could have contributed to Eocene global warming [*Nesbitt et al*., 1995; *Kerrick and Caldeira*, 1998]. Quantification of the permeability of the continental crust [*Ingebritsen and Manning*, 1999] supports our contention that in orogens undergoing metamorphism the flux to the surface of CO_2 generated at middle-to-deep crustal levels may be adequate to significantly affect paleoatmospheric CO_2 levels. By combining modeling of mass transfer, chemical reaction, and heat transport with field studies, *Ague* [2000] demonstrated the efficacy of metamorphic decarbonation of carbonate lithologies induced by the influx of H_2O from interbedded *pelitic* lithologies.

Widespread magmatism and regional metamorphism associated with collision and subduction occurred in the circum-Pacific orogen during the Mesozoic. The temporal and spatial correlation between magmatism and RCM has been documented in the western United States [*Barton and Hanson*, 1989]. Consequently, the global warmth during the Mesozoic could be attributed in part to metamorphic CO_2 degassing from RCM asso-

ciated with the widespread emplacement of intrusive batholiths.

As is illustrated by the Basin and Range province, considerable RCM CO_2 degassing could have accompanied periods of widespread continental rifting. Relevant here is the *Wilson cycle*, which is the dispersion and reassembly of supercontinents. The latest Wilson cycle began in the Jurassic (~200 Ma) with the breakup of *Pangaea*. Accordingly, during the Jurassic, there was widespread continental rifting. Within the rifts, extrusive and intrusive magmatism, coupled with RCM, could have released considerable magmatic and metamorphic CO_2 to the atmosphere and thus could have contributed to the global warming that began during the Middle Jurassic [*Condie and Sloan*, 1998]. LIPS magmatism associated with continental breakup [*Dalziel et al*., 2000] could have provided a significant flux of CO_2 to the atmosphere at the beginnings of Wilson cycles.

5. EPILOGUE

Because of the large extrapolation, there are significant uncertainties in the estimates of global CO_2 emission. Quantification of paleodegassing is particularly uncertain at this stage. Assessing global-scale paleodegassing from generalized modeling of volcanic CO_2 emission is clouded by the fact that at present, two volcanos (Popocatépetl and Mount Etna) emit far more CO_2 than do other active volcanos. Nevertheless, this should not be a deterrent to further analysis of the global nonanthropogenic CO_2 emission from the solid Earth. Modeling and quantifying the global carbon cycle is still in its infancy. The author is confident that by protracted diligence, significant advances in the quantification of CO_2 degassing from the Earth will be forthcoming.

GLOSSARY

Accretionary prism: A wedge of sediment associated with trenches of subduction zones.

Alkaline: Igneous rocks with alkalies (Na and K) that are high relative to silica.

Archean: An eon in the Precambrian (~4000–2500 Myr ago).

Asthenosphere: A layer of the Earth that is directly below the lithosphere. It is characterized by relatively slow seismic velocities and is considered to be a zone with partial melt.

Back-arc basin: Region adjacent to a subduction zone magmatic arc on the opposite side of the subducting plate and trench.

Batholith: A large (>100 km^2 aerial exposure) body of intrusive igneous rock.

Caldera: A large eruption-produced depression of a volcano.

Carbonatite: Carbonate-rich igneous rock.

Contact metamorphism: Localized metamorphism caused by the thermal effect of an intrusion.

Hadean: Earliest Precambrian eon (before ~4000 Myr).

Hot spot magmatism: Magmatic activity arising from plumes of melt arising from the deep mantle. The Hawaiian volcanic chain is a classic example.

Hypocenter: Initial point of rupture resulting in an earthquake.

Maar: Low-relief crater formed by explosive volcanism.

Mantle plume: Deeply generated, elongated magma column rising through the Earth's mantle.

Metamorphic decarbonation: Release of carbon dioxide due to metamorphic reactions involving the consumption of carbonate minerals.

Metasomatism: Change in bulk rock composition during metamorphism. Metasomatism results from the influx and/or efflux of chemical elements by diffusion or fluid flow.

Nonanthropogenic CO_2 degassing: Release of gas by processes other than the burning of fossil fuels.

Pangaea: Supercontinent that existed in the late Paleozoic to early Mesozoic (~300–200 Myr ago).

Pelitic: An aluminum-rich sedimentary rock. Most metamorphosed pelites were originally mud rocks.

Phanerozoic eon: All of the geologic time following the Precambrian eon (i.e., the past ~540 Myr).

Principle of uniformitarianism: Posits that processes operating in the present are analogous to those in the past.

Serpentinite: Metamorphic rock containing abundant serpentine group minerals (antigorite, chrysotile, and lizardite). Serpentinites form by the addition of water to ultramafic rocks.

Skarn: Metamorphic rock rich in calcium silicate minerals. Skarns are formed by the *metasomatism* of limestone.

Slabless window: Region undergoing extension, crustal thinning, and upwelling of the asthenosphere.

Teramole: Equivalent to 10^{12} mol.

Tholeiitic: Igneous rocks (basalts) that are characterized by Ca-poor pyroxene and little or no olivine.

Travertine: Carbonate rock formed by precipitation from thermal springs.

Volcano plume: Column of volcanic gas discharged into the atmosphere.

Wilson cycle: Fragmentation and subsequent reassembly of supercontinents. The latest Wilson cycle began with fragmentation of Pangaea ~200 Myr ago.

Xenoliths: Fragments of "foreign" rock within an igneous rock.

ACKNOWLEDGMENTS. I am deeply indebted to Ken Caldeira, my colleague and friend, who was responsible for sparking my interest in the role of CO_2 degassing and global paleoclimate. Ken's coauthorship on several papers relevant to

this topic epitomizes the extent of our subsequent collaborative effort on this topic. I am also grateful to many other colleagues for their active collaboration in my research on CO_2 degassing: G. Chiodini, J. A. D. Connolly, F. Frondini, S. Giammanco, M. A. McKibben, A. Minissale, B. Nesbitt, J. D. Rogie, T. M. Seward, and N. Sturchio. I sadly acknowledge the passing of Bruce Nesbitt, who collaborated with me on a study of metamorphic CO_2 degassing from the Cordilleran belt [*Nesbitt et al*., 1995]. I gratefully acknowledge the thoughtful reviews by Terry Gerlach, Fraser Goff, Lee Kump, John Rogie, Tom Torgersen, and Johan Varekamp. Amy Ehmann provided invaluable assistance in data compilation and preparation of the manuscript. This paper was inspired by my presentation at the Italian Geochemical Society "Scuola di Geochimica dei Fluidi," Arezzo, Italy, August 29 through September 1, 2000. I thank Giulio Ottonello, Orlando Vaselli, and Antonella Buccianti for inviting me and for their excellent organization of this conference. My research on CO_2 degassing was supported by grants from the National Science Foundation (grants EAR 93-04939, EAR 99-09525, and OCE 99-75231) and the National Geographic Society (grant 5354-94).

Thomas Torgersen was the Editor responsible for this paper. He thanks John Varekamp, Terry Gerlach, Fraser Goff, and one anonymous reviewer for technical reviews.

REFERENCES

Abrajano, T. A., N. C. Sturchio, J. K. Bohlke, G. L. Lyon, R. J. Poreda, and C. M. Stevens, Methane-hydrogen gas seeps, Zambales Ophiolite, Phillipines: Deep or shallow origin?, *Chem. Geol*., *71*, 211–222, 1988.

Aeschbach-Hertig, W., R. Kipfer, M. Hofer, D. M. Imboden, R. Wieler, and P. Signer, Quantification of gas fluxes from the subcontinental mantle: The example of Laacher See, a maar lake in Germany, *Geochim. Cosmochim. Acta*, *60*, 31–41, 1996.

Ague, J. J., Release of CO_2 from carbonate rocks during regional metamorphism of lithologically heterogeneous crust, *Geology*, *28*, 1123–1126, 2000.

Aguilera, E., G. Chiodini, R. Cioni, M. Guidi, L. Marini, and B. Raco, Water chemistry of Lake Quilotoa (Ecuador) and assessment of natural hazards, *J. Volcanol. Geotherm. Res*., *97*, 271–285, 2000.

Allard, P., Global emissions of helium-3 by subaerial volcanism, *Geophys. Res. Lett*., *19*, 1479–1481, 1992.

Allard, P., Endogenous magma degassing and storage at Mount Etna, *Geophys. Res. Lett*., *24*, 2219–2222, 1997.

Allard, P., Magma-derived CO_2 budget of Mount Etna (abstract), *Eos Trans. AGU*, *79*(45), Fall Meet. Suppl., F927, 1998.

Allard, P., et al., Eruptive and diffuse emissions of CO_2 from Mount Etna, *Nature*, *351*, 387–391, 1991.

Allard, P., J. Carbonnelle, N. Métrich, H. Loyer, and P. Zettwoog, Sulphur output and magma degassing budget of Stromboli volcano, *Nature*, *368*, 326–330, 1994.

Allard, P., P. Jean-Baptiste, W. D. D'Alessandro, F. Parello, B. Parisi, and C. Flehoc, Mantle-derived helium and carbon in groundwaters and gases of Mount Etna, Italy, *Earth Planet. Sci. Lett*., *148*, 501–516, 1997.

Alt, J. C., and D. A. H. Teagle, The uptake of carbon during alteration of ocean crust, *Geochim. Cosmochim. Acta*, *63*, 1527–1535, 1999.

Anderson, D. E., and C. D. Ferrar, Eddy covariance measurement of CO_2 flux to the atmosphere from an area of high volcanogenic emission, *Chem. Geol*., *177*, 31–42, 2001.

Andrews, J. E., S. K. Tandon, and P. F. Dennis, Concentration of carbon dioxide in the Late Cretaceous atmosphere, *J. Geol. Soc. London*, *152*, 1–3, 1995.

Arculus, R. J., J. B. Gill, H. Cambray, W. Chen, and R. J. Stern, Geochemical evolution of arc systems in the western Pacific: The ash and turbidite record recovered by drilling, in *Active Margins and Marginal Basins of the Western Pacific*, *Geophys. Monogr. Ser*., vol. 88, edited by B. Taylor and J. Natland, pp. 45–65, AGU, Washington, D. C., 1995.

Arthaud, F., J. Dazy, and J.-C. Grillot, Distribution of deep carbon dioxide in relation to the structure and tectonic evolution of south-east France, *Geodin. Acta*, *7*, 86–102, 1994.

Arthur, M. A., Volcanic contributions to the carbon and sulfur geochemical cycles and global change, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 1045–1056, Academic, San Diego, Calif., 2000.

Arthur, M. A., W. E. Dean, and S. O. Schlanger, Variations in the global carbon cycle during the Cretaceous related to climate, volcanism, and changes in atmospheric CO_2, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, *Geophys. Monogr. Ser*., vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 504–529, AGU, Washington, D. C., 1985.

Bailey, D. K., Carbonatite magmas, *J. Geol. Soc. London*, *150*, 637–651, 1993.

Bailey, D. K., and C. M. Hampton, Volatiles in alkaline magmatism, *Lithos*, *26*, 157–165, 1990.

Barber, A. J., S. Tjokrosapoetro, and T. R. Charlton, Mud volcanoes, shale diapirs, wrench faults, and melanges in accretionary complexes, eastern Indonesia, *AAPG Bull*., *70*, 1729–1741, 1986.

Barberi, F., and M. L. Carapezza, Helium and CO_2 soil emission from Santorini (Greece), *Bull. Volcanol*., *56*, 335–342, 1994.

Barnes, I., W. P. Irwin, and H. A. Gibson, Geologic map showing springs rich in carbon dioxide and chloride in California, *U.S. Geol. Surv. Misc. Invest. Map*, 1975.

Barnes, I., W. P. Irwin, and D. E. White, Global distribution of carbon dioxide discharges, and major zones of seismicity, *U.S. Geol. Surv. Open File Rep*., *78-39*, 12 pp., 1978.

Barnes, I., W. P. Irwin, and D. E. White, Global distribution of carbon dioxide discharges and major zones of seismicity, *U.S. Geol. Surv. Misc. Invest. Map*, *I-1528*, 1984.

Barton, M. D., and R. B. Hanson, Magmatism and the development of low-pressure metamorphic belts: Implications from the western United States and thermal modeling, *Geol. Soc. Am. Bull*., *101*, 1051–1065, 1989.

Benz, H. M., G. Zandt, and D. H. Oppenheimer, Lithospheric structure of northern California from teleseismic images of the upper mantle, *J. Geophys. Res*., *97*(B4), 4791–4807, 1992.

Bergfeld, D., F. Goff, and C. J. Janik, Carbon isotope systematics and CO_2 sources in the Geysers–Clear Lake region, northern California, USA, *Geothermics*, *30*, 303–311, 2001a.

Bergfeld, D., F. Goff, and C. J. Janik, Elevated carbon dioxide flux at the Dixie Valley geothermal field, Nevada: Relations between surface phenomena and the geothermal reservoir, *Chem. Geol*., *177*, 43–66, 2001b.

Berndt, M. E., D. E. Allen, and W. E. Seyfried Jr., Reduction of CO_2 during serpentinization of olivine at 300°C and 500 bar, *Geology*, *24*, 351–354, 1996.

Berner, R. A., Global CO_2 degassing and the carbon cycle: Comment on "Cretaceous ocean crust at DSDP sites 417 and 418: Carbon uptake from weathering versus loss by magmatic outgassing," *Geochim. Cosmochim. Acta*, *54*, 2889–2890, 1990.

Berner, R. A., A model for atmospheric CO_2 over Phanerozoic time, *Am. J. Sci*., *291*, 339–376, 1991.

Berner, R. A., Palaeo-CO_2 and climate, *Nature*, *358*, 114, 1992.
Berner, R. A., 3GeocarbII: A revised model of atmospheric CO_2 over Phanerozoic time, *Am. J. Sci*., *294*, 56–91, 1994.
Berner, R. A., A new look at the long-term carbon cycle, *GSA Today*, *9*, 1–6, 1999.
Berner, R. A., and K. Caldeira, The need for mass balance and feedback in the geochemical carbon cycle, *Geology*, *25*, 955–956, 1997.
Berner, R. A., and A. C. Lasaga, Modeling the geochemical carbon cycle, *Sci. Am*., *260*(3), 74–81, March, 1989.
Berner, R. A., A. C. Lasaga, and R. M. Garrels, The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci*., *283*, 641–683, 1983.
Bogatikov, O. A., V. I. Kovalenko, and E. V. Sharkov, General features of magmatic evolution throughout the Earth's history, in *Magmatism and Geodynamics: Terrestrial Magmatism Throughout the Earth's History*, edited by O. A. Bogatikov, pp. 337–367, Gordon and Breach, Newark, N. J., 2000.
Bougault, H., J.-L. Charlou, Y. Fouquet, H. D. Needham, N. Vaslet, P. Appriou, P. J. Baptiste, P. A. Rona, L. Dmitriev, and S. Silantiev, Fast and slow spreading ridges: Structure and hydrothermal activity, ultramafic topographic highs, and CH_4 output, *J. Geophys. Res*., *98*(B6), 9643–9651, 1993.
Bralower, T. J., D. J. Thomas, J. C. Zachos, M. M. Hirschmann, U. Röhl, H. Sigurdsson, E. Thomas, and D. L. Whitney, High-resolution records of the late Paleocene thermal maximum and circum-Caribbean volcanism: Is there a causal link?, *Geology*, *25*, 963–966, 1997.
Brantley, S. L., and K. W. Koepenick, Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes, *Geology*, *23*, 933–936, 1995.
Brantley, S. L., A. M. Agustsdottir, and G. L. Rowe, Crater lakes reveal volcanic heat and volatile fluxes, *GSA Today*, *3*, 176–178, 1993.
Broecker, W. S., and A. Sanyal, Does atmospheric CO_2 police the rate of chemical weathering?, *Global Biogeochem. Cycles*, *12*, 403–408, 1998.
Burton, M. R., C. Oppenheimer, L. A. Horrocks, and P. W. Francis, Remote sensing of CO_2 and H_2O emission rates from Masaya volcano, Nicaragua, *Geology*, *28*, 915–918, 2000.
Caldeira, K., Enhanced Cenozoic chemical weathering and the subduction of pelagic carbonate, *Nature*, *357*, 578–581, 1992.
Caldeira, K., Long-term control of atmospheric carbon dioxide: Low-temperature seafloor alteration or terrestrial silicate-rock weathering?, *Am. J. Sci*., *295*, 1077–1114, 1995.
Caldeira, K., and M. R. Rampino, Deccan volcanism, greenhouse warming, and the Cretaceous/Tertiary boundary, in *Global Catastrophies in Earth History*, edited by V. L. Sharpton and P. L. Ward, *Spec. Pap. Geol. Soc. Am*., *247*, 117–123, 1990a.
Caldeira, K., and M. R. Rampino, Carbon dioxide emissions from Deccan volcanism and a K/T boundary greenhouse effect, *Geophys. Res. Lett*., *17*, 1299–1302, 1990b.
Caldeira, K., and M. R. Rampino, The mid-Cretaceous super plume, carbon dioxide, and global warming, *Geophys. Res. Lett*., *18*, 987–990, 1991.
Cambray, H., and J. P. Cadet, Testing global synchronism in peri-Pacific arc volcanism, *J. Volcanol. Geotherm. Res*., *63*, 145–164, 1994.
Cannat, M., Emplacement of mantle rocks in the seafloor at mid-ocean ridges, *J. Geophys. Res*., *98*(B3), 4163–4172, 1993.
Cella, F., M. Fedi, G. Florio, and A. Rapolla, Gravity modelling of the litho-asthenosphere system in the central Mediterranean, *Tectonophysics*, *287*, 117–138, 1998.
Cerling, T. E., Use of carbon isotopes in paleosols as an indicator of the $P(CO_2)$ of the paleoatmosphere, *Global Biogeochem. Cycles*, *6*, 307–314, 1992.
Chiodini, G., and F. Frondini, Carbon dioxide degassing from the Albani Hills volcanic region, central Italy, *Chem. Geol*., *177*, 67–83, 2001.
Chiodini, G., F. Frondini, and B. Raco, Diffuse emission of CO_2 from the Fossa crater, Vulcano Island (Italy), *Bull. Volcanol*., *58*, 41–50, 1996.
Chiodini, G., R. Cioni, M. Guidi, B. Raco, and L. Marini, Soil CO_2 flux measurements in volcanic and geothermal areas, *Appl. Geochem*., *13*, 543–552, 1998.
Chiodini, G., F. Frondini, D. M. Kerrick, J. D. Rogie, F. Parello, L. Peruzzi, and A. Zanzari, Quantification of deep CO_2 fluxes from central Italy: Examples of carbon balance for regional aquifers and of soil diffuse degassing, *Chem. Geol*., *159*, 205–222, 1999.
Chiodini, G., F. Frondini, C. Cardellini, F. Parello, and L. Peruzzi, Rate of diffuse carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: The case of central Appenine, Italy, *J. Geophys. Res*., *105*(B4), 8423–8434, 2000.
Chiodini, G., F. Frondini, C. Cardellini, D. Granieri, L. Marini, and G. Ventura, CO_2 degassing and energy release at Solfatara volcano, Campi Flegrei, Italy, *J. Geophys. Res*., *106*, 213–216, 221, 2001.
Coffin, M. F., and O. Eldholm, Large igneous provinces: Crustal structure, dimensions, and external consequences, *Rev. Geophys*., *32*, 1–36, 1994.
Condie, K. C., and R. E. Sloan, *Origin and Evolution of Earth: Principles of Historical Geology*, Prentice-Hall, Old Tappan, N. J., 1998.
Cook, A. C., L. J. Hainsworth, M. L. Sorey, W. C. Evans, and J. R. Southon, Radiocarbon studies of plant leaves and tree rings from Mammoth Mountain, California: A long-term record of magmatic release, *Chem. Geol*., *177*, 117–131, 2001.
Courtillot, V., J.-J. Jaeger, Z. Yang, G. Féraud, and C. Hofmann, The influence of continental flood basalts on mass extinctions: Where do we stand?, in *The Cretaceous-Tertiary Event and Other Catastrophies in Earth History*, edited by G. Rider, D. Fastovsky, and S. Gartner, *Spec. Pap. Geol. Soc. Am*., *307*, 513–525, 1996.
Crisp, J. A., Rates of magma emplacement and volcanic output, *J. Volcanol. Geotherm. Res*., *20*, 177–211, 1984.
D'Alessandro, W., S. Giammanco, F. Parello, and M. Valenza, CO_2 output and $\delta^{13}C(CO_2)$ from Mount Etna as indicators of degassing of shallow asthenosphere, *Bull. Volcanol*., *58*, 455–458, 1997.
Dalziel, I. W. D., L. A. Lawver, and J. B. Murphy, Plumes, orogenesis, and supercontinental fragmentation, *Earth Planet. Sci. Lett*., *178*, 1–11, 2000.
Darling, W. G., E. Griesshaber, J. N. Andrews, H. Armannsson, and R. K. O'Nions, The origin of hydrothermal and other gases in the Kenya Rift Valley, *Geochim. Cosmochim. Acta*, *59*, 2501–2512, 1995.
Dawson, J. B., H. Pinkerton, D. M. Pyle, and C. Nyamweru, June 1993 eruption of Oldoinyo Lengai, Tanzania: Exceptionally viscous and large carbonatite lava flows and evidence for coexisting silicate and carbonate magmas, *Geology*, *22*, 799–802, 1994.
Dehlinger, P., and B. A. Bolt, Seismic parameters along the Bartlett Springs fault zone in the Coast Ranges of northern California, *Bull. Seismol. Soc. Am*., *74*, 1785–1798, 1984.
De la Cruz-Reyna, S., and C. Siebe, The giant Popocatépetl stirs, *Nature*, *388*, 227, 1997.
Delgado, H., N. Pieda-Sánchez, L. Galván, P. Julio, J. M.

Alvarez, and L. Cárdenas, CO_2 flux measurements at Popocatépetl volcano, II, Magnitude of emissions and significance (abstract), *Eos Trans. AGU*, *79*(45), Fall Meet. Suppl., F926, 1998.

Des Marais, D. J., Carbon exchange between the mantle and the crust, and its effect upon the atmosphere: Today compared to Archean time, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, *Geophys. Monogr. Ser*., vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 602–611, AGU, Washington, D. C., 1985.

Dixon, J. E., D. A. Clague, P. Wallace, and R. Poreda, Volatiles in alkalic basalts from the North Arch volcanic field, Hawaii: Extensive degassing of deep submarine-erupted alkalic series lavas, *J. Petrol*., *38*, 911–939, 1997.

Donnelly-Nolan, J. M., M. G. Burns, F. E. Goff, E. K. Peters, and J. M. Thompson, The Geysers-Clear Lake area, California: Thermal waters, mineralization, volcanism and geothermal potential, *Econ. Geol*., *88*, 301–316, 1993.

Douglas, R., and F. Woodruff, Deep-sea benthic foraminifera, in *The Sea 7*, edited by C. Emiliani, pp. 1233–1328, Wiley-Interscience, New York, 1981.

Eldholm, O., and E. Thomas, Environmental impact of volcanic margin formation, *Earth Planet. Sci. Lett*., *117*, 319–329, 1993.

Encarnación, J., T. H. Fleming, D. H. Elliot, and H. V. Eales, Synchronous emplacement of Ferrar and Karoo dolerites and the early breakup of Gondwana, *Geology*, *24*, 535–538, 1996.

Evans, W. C., G. W. Kling, M. L. Tuttle, G. Tanyileke, and L. D. White, Gas buildup in Lake Nyos, Cameroon: The recharge process and its consequences, *Appl. Geochem*., *8*, 207–221, 1993.

Evans, W. C., M. L. Sorey, B. M. Kennedy, D. A. Stonestrom, J. D. Rogie, and D. L. Shuster, High CO_2 emissions through porous media: Transport mechanisms and implications for flux measurement and fractionation, *Chem. Geol*., *177*, 15–29, 2001.

Faccenna, C., M. Mattei, R. Funiciello, and L. Jolivet, Styles of back-arc extension in the central Mediterranean, *Terra Nova*, *9*, 126–130, 1997.

Farrar, C. D., M. L. Sorey, W. C. Evans, J. F. Howle, B. D. Kerr, B. M. Kennedy, C.-Y. King, and J. R. Southon, Forest-killing diffuse CO_2 emission at Mammoth Mountain as a sign of magmatic unrest, *Nature*, *376*, 675–678, 1995.

Ferry, J. M., Overview of the petrologic record of fluid flow during regional metamorphism in northern New England, *Am. J. Sci*., *294*, 905–988, 1994.

Ford, T. D., and H. M. Pedley, A review of tufa and travertine deposits of the world, *Earth Sci. Rev*., *41*, 117–175, 1996.

Francis, P., *Volcanoes: A Planetary Perspective*, 443 pp., Oxford Univ. Press, New York, 1993.

Francis, P., C. Oppenheimer, and D. Stevenson, Endogenous growth of persistently active volcanoes, *Nature*, *366*, 554–557, 1993.

Francis, P., L. Horrocks, and C. Oppenheimer, Monitoring gases from andesite volcanoes, *Philos. Trans. R. Soc. London*, *Ser. A*, *358*, 1567–1584, 2000.

Gans, P. B., and W. A. Bohrson, Suppression of volcanism during rapid extension in the Basin and Range Province, United States, *Science*, *279*, 66–68, 1998.

Gerlach, T. M., Degassing of carbon dioxide from basaltic magma at spreading centers, I, Afar transitional basalts, *J. Volcanol. Geotherm. Res*., *39*, 211–219, 1989.

Gerlach, T. M., Etna's greenhouse pump, *Nature*, *351*, 352–353, 1991a.

Gerlach, T. M., Present-day CO_2 emissions from volcanoes, *Eos Trans. AGU*, *72*(23), 249, 254–255, 1991b.

Gerlach, T. M., H. R. Westrich, T. J. Casadevall, and D. L. Finnegan, Vapor saturation and accumulation of magmas of the 1989–1990 eruption of Redoubt volcano, Alaska, *J. Volcanol. Geotherm. Res*., *62*, 317–337, 1994.

Gerlach, T. M., H. R. Westrich, and R. B. Symonds, Preeruption vapor in magma of the climactic Mount Pinatubo eruption: Source of the giant stratospheric sulfur dioxide cloud, in *Fire and Mud: Eruptions and Lahars of Mount Pinatubo*, *Philippines*, edited by C. G. Newhall and R. S. Punongbayan, pp. 415–433, Univ. of Wash. Press, Seattle, 1996.

Gerlach, T. M., H. Delgado, H. McGee, M. P. Doukas, J. J. Venegas, and L. Cárdenas, Application of the LI-COR CO_2 analyzer to volcanic plumes: A case study, volcán Popocatépetl, Mexico, June 7 and 10, 1995, *J. Geophys. Res*., *102*(B4), 8005–8019, 1997.

Gerlach, T. M., M. P. Doukas, K. A. McGee, and R. Kessler, Airborne detection of diffuse carbon dioxide emissions at Mammoth Mountain, California, *Geophys. Res. Lett*., *26*, 3661–3664, 1999.

Gerlach, T. M., M. P. Doukas, K. A. McGee, and R. Kessler, Soil efflux and total emission rates of magmatic CO_2 at the Horseshoe Lake tree kill, Mammoth Mountain, California, 1995–1999, *Chem. Geol*., *177*, 101–116, 2001.

Giammanco, S., Soil CO_2 emissions at Mount Etna (Sicily, Italy): Spatial and temporal variations recorded from 1987 to 1998 (abstract), *Eos Trans. AGU*, *79*(45), Fall Meet. Suppl., F927, 1998.

Giammanco, S., S. Gurrieri, and M. Valenza, Soil CO_2 degassing on Mt. Etna (Sicily) during the period 1989–1993: Discrimination between climatic and volcanic influences, *Bull. Volcanol*., *57*, 52–60, 1995.

Giammanco, S., S. Inguaggiato, and M. Valenza, Soil and fumerole gases of Mount Etna: Geochemistry and relations with volcanic activity, *J. Volcanol. Geotherm. Res*., *81*, 297–310, 1998.

Gibbs, M. T., G. J. S. Bluth, P. J. Fawcett, and L. R. Kump, Global chemical erosion over the last 250 MY: Variations due to changes in paleogeography, paleoclimate, and paleogeology, *Am. J. Sci*., *299*, 611–651, 1999.

Gibbs, M. T., K. L. Bice, E. J. Barron, and L. R. Kump, Glaciation in the early Paleozoic "greenhouse": The roles of paleogeography and atmospheric CO_2, in *Warm Climates in Earth History*, edited by B. T. Huber, K. G. MacLeod, and S. L. Wing, pp. 386–422, Cambridge Univ. Press, New York, 2000.

Giggenbach, W. F., Y. Sano, and H. U. Schmincke, CO_2-rich gases from Lakes Nyos and Monoun, Cameroon; Laacher See, Germany; Dieng, Indonesia; and Mt. Gambier, Australia: Variations on a common theme, *J. Volcanol. Geotherm. Res*., *45*, 311–323, 1991.

Goddéris, Y., and L. M. François, The Cenozoic evolution of the strontium and carbon cycles: Relative importance of continental erosion and mantle exchanges, *Chem. Geol*., *126*, 169–190, 1995.

Goff, F., and C. J. Janik, Gas geochemistry and guide for geothermal features in the Clear Lake region, California, in *Active Geothermal Systems and Gold-Mercury Deposits in the Sonoma-Clear Lake Volcanic Fields*, *California*, *Soc. Econ. Geol. Guideb. Ser*., vol. 16, edited by J. J. Rytuba, pp. 207–216, Soc. of Econ. Geol., Littleton, Colo., 1993.

Goff, F., et al., Gold degassing and deposition at Galeras volcano, Colombia, *GSA Today*, *4*, 241–247, 1994.

Goff, F., et al., Geochemical surveillance of magmatic volatiles at Popocatépetl volcano, Mexico, *Geol. Soc. Am. Bull*., *110*, 695–710, 1998.

Goff, F., S. P. Love, R. G. Warren, D. Counce, J. Obenholzner, C. Siebe, and S. C. Schmidt, Passive infrared remote sensing evidence for large, intermittent CO_2 emissions at Popocatépetl magma, Mexico, *Chem. Geol*., *177*, 133–156, 2001.

Griesshaber, E., R. K. O'Nions, and E. R. Oxburgh, Helium

and carbon isotope systematics in crustal fluids from the Eifel, the Rhine Graben and Black Forest, F.R.G., *Chem. Geol.*, *99*, 213–235, 1992.

Gvirtzman, Z., and A. Nur, The formation of Mount Etna as the consequence of slab rollback, *Nature*, *401*, 782–785, 1999.

Hames, W. E., P. R. Renne, and C. Ruppel, New evidence for geologically instantaneous emplacement of earliest Jurassic central Atlantic magmatic province basalts on the North American margin, *Geology*, *28*, 859–862, 2000.

Harris, D. M., and W. L. Rose, Dynamics of carbon dioxide emissions, crystallization, and magma ascent: Hypotheses, theory, and applications to volcano monitoring at Mount St. Helens, *Bull. Volcanol.*, *58*, 163–174, 1996.

Harris, D. M., M. Sato, T. J. Casadevall, W. I. Rose, and T. J. Bornhorst, Emission rates of CO_2 from plume measurements, in *The 1980 Eruptions of Mount St. Helens*, *Washington*, edited by P. W. Lipman and D. R. Mullineaux, *U.S. Geol. Surv. Prof. Pap.*, *1250*, 201–207, 1981.

Heller, P. L., D. L. Anderson, and C. L. Angevine, Is the middle Cretaceous pulse of rapid seafloor spreading real or necessary?, *Geology*, *24*, 491–494, 1996.

Hodell, D. A., and F. Woodruff, Variations in the strontium isotopic ratio of seawater during the Miocene: Stratigraphic and geochemical implications, *Paleoceanography*, *9*, 405–426, 1994.

Hoernle, K., Y.-S. Zhang, and D. Graham, Seismic and geochemical evidence for large-scale mantle upwelling beneath the eastern Atlantic and western and central Europe, *Nature*, *374*, 34–39, 1995.

Holloway, J. R., and J. G. Blank, Application of experimental results to C-O-H species in natural melts, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 187–230, Mineral. Soc. of Am., Washington, D. C., 1994.

Hooper, P. R., Flood basalt provinces, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 345–359, Academic, San Diego, Calif., 2000.

Ihinger, P. D., R. L. Hervig, and P. F. McMillan, Analytical methods for volatiles in glasses, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 67–121, Mineral. Soc. of Am., Washington, D. C., 1994.

Ingebritsen, S. E., and C. E. Manning, Geological implications of a permeability-depth curve for the continental crust, *Geology*, *27*, 1107–1110, 1999.

Irwin, W. P., and I. Barnes, Effect of geologic structure and metamorphic fluids on seismic behavior of the San Andreas fault system in central and northern California, *Geology*, *3*, 714–716, 1975.

Irwin, W. P., and I. Barnes, Tectonic relations of carbon dioxide discharges and earthquakes, *J. Geophys. Res.*, *85*(B6), 3115–3121, 1980.

Irwin, W. P., and I. Barnes, Map showing relation of carbon dioxide-rich springs and gas wells to the tectonic framework of the conterminous United States, *U.S. Geol. Surv. Misc. Invest. Map*, *1-1301*, 1982.

Italiano, F., M. Martelli, G. Martinelli, and P. M. Nuccio, Geochemical evidence of melt intrusions along lithospheric faults of the Southern Appenines, Italy: Geodynamic and seismogenic implications, *J. Geophys. Res.*, *105*(B6), 13,569–13,578, 2000.

Jambon, A., Earth degassing and large-scale geochemical cycling of volatile elements, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 479–517, Mineral. Soc. of Am., Washington, D. C., 1994.

James, E. R., M. Manga, and T. P. Rose, CO_2 degassing in the Oregon Cascades, *Geology*, *27*, 823–826, 1999.

Johnson, M. C., A. T. Anderson Jr., and M. J. Rutherford, Pre-eruptive volatile contents of magmas, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 281–330, Mineral. Soc. of Am., Washington, D. C., 1994.

Julian, B. R., A. M. Pitt, and G. R. Foulger, Seismic image of a CO_2 reservoir beneath a seismically active volcano, *Geophys. J. Int.*, *133*, F7–F10, 1998.

Kaiho, K., and S. Saito, Oceanic crust production and climate during the last 100 Myr, *Terra Nova*, *6*, 376–384, 1994.

Kastner, M., H. Elderfield, and J. B. Martin, Fluids in convergent margins: What do we know about their composition, origin, role in diagenesis and importance for oceanic chemical fluxes?, *Philos. Trans. R. Soc. London*, *Ser. A*, *335*, 243–259, 1991.

Kearey, P., and F. J. Vine, *Global Tectonics*, 302 pp., Blackwell Sci., Malden, Mass., 1990.

Kelley, D. S., Methane-rich fluids in the oceanic crust, *J. Geophys. Res.*, *101*(B2), 2943–2962, 1996.

Kerrich, R., and R. Feng, Archean geodynamics and the Abitibi-Pontiac collision: Implications for advection of fluids at transpressive collisional boundaries and the origin of giant quartz vein systems, *Earth Sci. Rev.*, *32*, 33–60, 1992.

Kerrick, D. M., and K. Caldeira, Paleoatmospheric consequences of CO_2 released during early Cenozoic regional metamorphism in the Tethyan orogen, *Chem. Geol.*, *108*, 201–230, 1993.

Kerrick, D. M., and K. Caldeira, Metamorphic CO_2 degassing and early Cenozoic paleoclimate, *GSA Today*, *4*, 57–65, 1994.

Kerrick, D. M., and K. Caldeira, Metamorphic CO_2 degassing from orogenic belts, *Chem. Geol.*, *145*, 213–232, 1998.

Kerrick, D. M., and K. Caldeira, Was the Himalayan orogen a climatically significant coupled source and sink for atmospheric CO_2 during the Cenozoic?, *Earth Planet. Sci. Lett.*, *173*, 195–203, 1999.

Kerrick, D. M., and J. A. D. Connolly, Subduction of ophicarbonates and recycling of CO_2 and H_2O, *Geology*, *26*, 375–378, 1998.

Kerrick, D. M., and J. A. D. Connolly, Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle, *Nature*, *411*, 293–296, 2001a.

Kerrick, D. M., and J. A. D. Connolly, Metamorphic devolatilization of subducted oceanic metabasalts: Implications for seismicity, arc magmatism and volatile recycling, *Earth Planet. Sci. Lett.*, *189*, 19–29, 2001b.

Kerrick, D. M., M. A. McKibben, T. M. Seward, and K. Caldeira, Convective hydrothermal CO_2 emission from high heat flow regions, *Chem. Geol.*, *121*, 285–293, 1995.

Kharaka, Y. K., J. J. Thordsen, and W. C. Evans, Crustal fluids: CO_2 of mantle and crustal origins in the San Andreas fault system, California, in *Geochemistry of the Earth's Surface*, edited by H. Armannsson, pp. 515–518, A. A. Balkema, Brookfield, Vt., 1999.

King, C.-Y., Gas geochemistry applied to earthquake prediction: An overview, *J. Geophys. Res.*, *91*(B12), 12,269–12,281, 1986.

Kingsley, R. H., and J.-G. Schilling, Carbon in mid-Atlantic basalt glasses from 28°N to 63°N: Evidence for a carbon-enriched Azores mantle plume, *Earth Planet. Sci. Lett.*, *129*, 31–53, 1995.

Knoll, A. H., R. K. Bambach, D. E. Canfield, and J. P. Grotzinger, Comparative Earth history and Late Permian mass extinctions, *Science*, *273*, 452–457, 1996.

Koepenick, K. W., S. L. Brantley, M. L. Thompson, G. L. Rowe, A. A. Nyblade, and C. Moshy, Volatile emissions from the crater and flank of Oldoinyo Lengai volcano, Tanzania, *J. Geophys. Res.*, *101*(B6), 13,819–13,830, 1996.

Krull, E. S., and G. J. Retallack, $\delta^{13}C$ depth profiles from paleosols across the Permian-Triassic boundary: Evidence for methane release, *Geol. Soc. Am. Bull.*, *112*, 1459–1472, 2000.

Kump, L. R., What drives climate?, *Nature*, *408*, 651–652, 2000.

Kump, L. R., J. F. Kasting, and R. G. Crane, *The Earth System*, 351 pp., Prentice-Hall, Old Tappan, N. J., 1999.

Kürschner, W. M., Leaf sensor for CO_2 in deep time, *Nature*, *411*, 247–248, 2001.

Kuypers, M. M. M., R. D. Pancost, and J. S. Sinninghe Damsté, A large and abrupt fall in atmospheric CO_2 concentration during Cretaceous times, *Nature*, *399*, 342–345, 1999.

Larkin, S. P., A. Levander, T. J. Henstock, and S. Pullammanappallil, Is the Moho flat? Seismic evidence for a rough crust-mantle interface beneath the northern Basin and Range, *Geology*, *25*, 451–454, 1997.

Lasaga, A. C., R. A. Berner, and R. M. Garrels, An improved geochemical model of atmospheric CO_2 fluctuations over the past 100 million years, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, *Geophys. Monogr. Ser.*, vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 397–411, AGU, Washington, D. C., 1985.

Leavitt, S. W., Annual volcanic carbon dioxide emission: An estimate from eruption chronologies, *Environ. Geol.*, *4*, 15–21, 1982.

Le Cloarec, M.-F., and B. Marty, Volatile fluxes from volcanoes, *Terra Nova*, *3*, 17–27, 1991.

Le Guern, F., Les débits de CO_2 et de SO_2 volcaniques dans l'atmosphère, *Bull. Volcanol.*, *45*, 197–202, 1982.

Lentz, D. R., Carbonatite genesis: A reexamination of the role of intrusion-related pneumatolytic skarn processes in limestone melting, *Geology*, *27*, 335–338, 1999.

Levander, A., T. J. Henstock, A. S. Meltzer, B. C. Beaudoin, A. M. Trehu, and S. L. Klemperer, Fluids in the lower crust following Mendocino triple junction migration: Active basaltic intrusion?, *Geology*, *26*, 171–174, 1998.

Lewicki, J. L., and S. L. Brantley, CO_2 degassing along the San Andreas fault, Parkfield, California, *Geophys. Res. Lett.*, *27*, 5–8, 2000.

Liu, M., Thermal-volcanic evolution in the California Coast Ranges, in *Active Geothermal Systems and Gold-Mercury Deposits in the Sonoma-Clear Lake Volcanic Fields*, *California*, *Soc. Econ. Geol. Guideb. Ser.*, vol. 16, edited by J. J. Rytuba, pp. 26–37, Soc. of Econ. Geol., Littleton, Colo., 1993.

Liu, M., and K. P. Furlong, Cenozoic volcanism in the California Coast Ranges: Numerical solutions, *J. Geophys. Res.*, *97*(B4), 4941–4951, 1992.

Lollar, B. S., C. J. Ballentine, and R. K. O'Nions, The fate of mantle-derived carbon in a continental sedimentary basin: Integration of C/He relationships and stable isotope signatures, *Geochim. Cosmochim. Acta*, *61*, 2295–2307, 1997.

Love, S. P., F. Goff, S. C. Schmidt, D. Counce, D. Pettit, B. W. Christenson, and C. Siebe, Passive infrared spectroscopic remote sensing of volcanic gases: Ground-based studies at White Island and Ruapehu, New Zealand, and Popocatépetl, Mexico, in *Remote Sensing of Active Volcanism*, *Geophys. Monogr. Ser.*, vol. 116, edited by P. J. Mouginis-Mark, J. A. Crisp, and J. H. Fink, pp. 117–137, AGU, Washington, D. C., 2000.

Lupton, J. E., Terrestrial inert gases: Isotope tracer studies and clues to primordial components in the mantle, *Annu. Rev. Earth Planet. Sci.*, *11*, 371–414, 1983.

Mahoney, J. J., and M. F. Coffin (Eds.), *Large Igneous Provinces: Continental, Oceanic, and Planetary Flood Volcanism*, *Geophys. Monogr. Ser.*, vol. 100, 438 pp., AGU, Washington, D. C., 1997.

Marty, B., and M. F. Le Cloarec, Helium-3 and CO_2 fluxes from subaerial volcanoes estimated from Polonium-210 emissions, *J. Volcanol. Geotherm. Res.*, *53*, 67–72, 1992.

Marty, B., and I. N. Tolstikhin, CO_2 fluxes from mid-ocean ridges, arcs and plumes, *Chem. Geol.*, *145*, 233–248, 1998.

Marty, B., R. K. O'Nions, E. R. Oxburgh, D. Martel, and S. Lombardi, Helium isotopes in Alpine regions, *Tectonophysics*, *206*, 71–78, 1992.

Marty, B., T. Trull, P. Lussiez, I. Basile, and J.-C. Tanguy, He, Ar, O, Sr and Nd isotope constraints on the origin and evolution of Mount Etna magmatism, *Earth Planet. Sci. Lett.*, *126*, 23–39, 1994.

Marty, G., A. Jambon, and Y. Sano, Helium isotopes and CO_2 in volcanic gases of Japan, *Chem. Geol.*, *76*, 25–40, 1989.

Matthews, A., C. Fouillac, R. Hill, R. K. O'Nions, and E. R. Oxburgh, Mantle-derived volatiles in continental crust: The Massif Central of France, *Earth Planet. Sci. Lett.*, *85*, 117–128, 1987.

May, F., S. Hoernes, and H. J. Neugebauer, Genesis of mineral waters of the Rhenish Massif, central Europe, in *Water-Rock Interaction*, edited by Y. K. Kharaka and A. S. Maest, pp. 1313–1316, A. A. Balkema, Brookfield, Vt., 1992.

McGee, K. A., and T. M. Gerlach, Annual cycle of magmatic CO_2 in a tree-kill soil at Mammoth Mountain, California: Implications for soil acidification, *Geology*, *26*, 463–466, 1998.

McGee, K. A., T. M. Gerlach, R. Kessler, and M. P. Doukas, Geochemical evidence for magmatic CO_2 degassing event at Mammoth Mountain, California, September–December 1997, *J. Geophys. Res.*, *105*(B4), 8447–8456, 2000.

McLean, D. M., Mantle degassing induced dead ocean in the Cretaceous-Tertiary transition, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, *Geophys. Monogr. Ser.*, vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 493–503, AGU, Washington, D. C., 1985.

Minissale, A., Thermal springs in Italy: Their relation to recent tectonics, *Appl. Geochem.*, *6*, 201–212, 1991.

Moore, J. C., and P. Vrolijk, Fluids in accretionary prisms, *Rev. Geophys.*, *30*, 113–135, 1992.

Nakamori, T., Global carbonate accumulation rates from Cretaceous to Present and their implications for the carbon cycle model, *Isl. Arc*, *10*, 1–8, 2001.

Nesbitt, B. E., C. A. Mendoza, and D. M. Kerrick, Surface fluid convection during Cordilleran extension and the generation of metamorphic CO_2 contributions to Cenozoic atmospheres, *Geology*, *23*, 99–101, 1995.

Nicolaysen, K., F. A. Frey, K. V. Hodges, D. Weis, and A. Giret, $^{40}Ar/^{39}Ar$ geochronology of flood basalts from the Kerguelen Archipelago, southern Indian Ocean: Implications for Cenozoic eruption rates of the Kerguelen plume, *Earth Planet. Sci. Lett.*, *174*, 313–328, 2000.

Nicolich, R., M. Laigle, A. Hirn, L. Cernobori, and J. Gallart, Crustal structure of the Ionian margin of Sicily: Etna volcano in the frame of regional evolution, *Tectonophysics*, *329*, 121–139, 2000.

Pagani, M., M. A. Arthur, and K. H. Freeman, Miocene evolution of atmospheric carbon dioxide, *Paleoceanography*, *14*, 273–292, 1999.

Pálfy, J., and P. L. Smith, Synchrony between Early Jurassic extinction, oceanic anoxic events, and the Karoo-Ferrar flood basalt volcanism, *Geology*, *28*, 747–750, 2000.

Pearson, P. N., and M. R. Palmer, Atmospheric carbon dioxide concentrations over the past 60 million years, *Nature*, *406*, 695–699, 2000.

Pentecost, A., The Quaternary travertine deposits of Europe and Asia Minor, *Quat. Sci. Rev.*, *14*, 1005–1028, 1995a.

Pentecost, A., Geochemistry of carbon-dioxide in six travertine-depositing waters of Italy, *J. Hydrol.*, *167*, 263–278, 1995b.

Poreda, R. J., P. D. Jenden, I. R. Kaplan, and H. Craig, Mantle helium in Sacramento basin natural gas wells, *Geochim. Cosmochim. Acta*, *50*, 2847–2853, 1986.

Poreda, R. J., A. W. A. Jeffrey, I. R. Kaplan, and H. Craig, Magmatic helium in subduction-zone natural gases, *Chem. Geol.*, *71*, 199–210, 1988.

Poulsen, C. J., E. J. Barron, C. C. Johnson, and P. Fawcett, Links between major climatic factors and regional oceanic circulation in the mid-Cretaceous, in *Evolution of the Cretaceous Ocean-Climate System*, edited by E. Barrera and C. C. Johnson, *Spec. Pap. Geol. Soc. Am.*, *332*, 73–89, 1999.

Rampino, M. R., and S. Self, Volcanism and biotic extinctions, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 1083–1091, Academic, San Diego, Calif., 2000.

Ray, J. S., and K. Pande, Carbonatite alkaline magmatism associated with continental flood basalts at stratigraphic boundaries: Cause for mass extinctions, *Geophys. Res. Lett.*, *26*, 1917–1920, 1999.

Rea, D. K., and L. J. Ruff, Composition and mass flux of sediment entering the world's subduction zones: Implications for global sediment budgets, great earthquakes, and volcanism, *Earth Planet. Sci. Lett.*, *140*, 1–12, 1996.

Rea, D. K., J. C. Zachos, R. M. Owen, and P. D. Gingerich, Global change at the Paleocene-Eocene boundary: Climatic and evolutionary consequences of tectonic events, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *79*, 117–128, 1990.

Retallack, G. J., A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles, *Nature*, *411*, 287–290, 2001.

Ritter, J. R. R., M. Mordan, U. R. Christensen, and U. Achauer, A mantle plume below the Eifel volcanic fields, Germany, *Earth Planet. Sci. Lett.*, *186*, 7–14, 2001.

Rogie, J. D., D. M. Kerrick, G. Chiodini, and F. Frondini, Flux measurements of nonvolcanic CO_2 emission from some vents in central Italy, *J. Geophys. Res.*, *105*(B4), 8435–8445, 2000.

Rogie, J. D., D. M. Kerrick, M. L. Sorey, G. Chiodini, and D. L. Galloway, Dynamics of carbon dioxide emission at Mammoth Mountain, California, *Earth Planet. Sci. Lett.*, *188*, 535–541, 2001.

Rose, W. I., and G. J. S. Bluth, Remote prospects, *Nature*, *396*, 515–517, 1998.

Ryan, S., Estimating volcanic CO_2 emission rates from atmospheric measurements on the slope of Mauna Loa, *Chem. Geol.*, *177*, 201–211, 2001.

Sano, Y., and S. N. Williams, Fluxes of mantle and subducted carbon along convergent plate boundaries, *Geophys. Res. Lett.*, *23*, 2749–2752, 1996.

Sano, Y., N. Takahata, Y. Nishio, T. P. Fischer, and S. N. Williams, Volcanic flux of nitrogen from the Earth, *Chem. Geol.*, *171*, 263–271, 2001.

Seward, T. M., and D. M. Kerrick, Hydrothermal CO_2 emission from the Taupo Volcanic Zone, New Zealand, *Earth Planet. Sci. Lett.*, *139*, 105–113, 1996

Sibson, R. H., Fault-valve behavior and the hydrostatic-lithostatic fluid pressure interface, *Earth Sci. Rev.*, *32*, 141–144, 1992.

Sigurdsson, H., Volcanic episodes and rates of volcanism, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 271–279, Academic, San Diego, Calif., 2000.

Simkin, T., Terrestrial volcanism in space and time, *Annu. Rev. Earth Planet. Sci.*, *21*, 427–452, 1993.

Simkin, T., and L. Siebert, Earth's volcanoes and eruptions: An overview, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 249–262, Academic, San Diego, Calif., 2000.

Sims, J. D., and M. J. Rymer, Map of gaseous springs and associated faults in Clear Lake, California, scale 1:48,000, *U.S. Geol. Surv. Misc. Field Stud. Map*, *MF-721*, 1976.

Sleep, N. H., and K. Zahnle, Carbon dioxide cycling and implications for climate on ancient Earth, *J. Geophys. Res.*, *106*(E1), 1373–1399, 2001.

Sloan, L. C., and D. K. Rea, Atmospheric carbon dioxide and early Eocene climate: A general circulation modeling sensitivity study, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *119*, 275–292, 1995.

Smith, R. B., and L. W. Braile, The Yellowstone hotspot, *J. Volcanol. Geotherm. Res.*, *61*, 121–187, 1994.

Snow, J. K., and B. Wernicke, Cenozoic tectonism in the central Basin and Range: Magnitude, rate, and distribution of upper crustal strain, *Am. J. Sci.*, *300*, 659–719, 2000.

Sorey, M., B. Evans, B. M. Kennedy, C. D. Farrar, L. J. Hainsworth, and B. Hausback, Carbon dioxide and helium emissions from a reservoir of magmatic gas beneath Mammoth Mountain, California, *J. Geophys. Res.*, *103*(B7), 15,303–15,323, 1998.

Sorey, M. L., W. C. Evans, M. Kennedy, J. Rogie, and A. Cook, Magmatic gas emissions from Mammoth Mountain, *Calif. Geol.*, *52*, 4–16, 1999.

Spear, F. S., *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*, *Mineral. Soc. Am. Monogr.*, vol. 1, 799 pp., Mineral. Soc. of Am., Washington, D. C., 1993.

Spicer, R. A., and R. M. Corfield, A review of terrestrial and marine climates in the Cretaceous with implications for modelling the "Greenhouse Earth," *Geol. Mag.*, *129*, 169–180, 1992.

Staudigel, H., S. Hart, H.-U. Shmincke, and B. M. Smith, Cretaceous ocean crust at DSDP sites 417 and 418: Carbon uptake from weathering versus loss by magmatic outgassing, *Geochim. Cosmochim. Acta*, *53*, 3091–3094, 1989.

Stimac, J. A., F. E. Goff, and W. E. Glassley, Crustal xenoliths in the Clear Lake volcanics, California: Transformation of Franciscan assemblage rocks to continental crust? (abstract), *Eos Trans. AGU*, *73*(43), Fall Meet. Suppl., 505, 1992.

Stothers, R. B., Flood basalts and extinction events, *Geophys. Res. Lett.*, *20*, 1399–1402, 1993.

Sundquist, E. T., Steady- and non-steady-state carbonate-silicate controls on atmospheric CO_2, *Quat. Sci. Rev.*, *10*, 283–296, 1991.

Symonds, R. B., W. I. Rose, G. J. S. Bluth, and T. M. Gerlach, Volcanic gas studies: Methods, results and applications, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 1–66, Mineral. Soc. of Am., Washington, D. C., 1994.

Tajika, E., Climate change during the last 150 million years: Reconstruction from a carbon cycle model, *Earth Planet. Sci. Lett.*, *160*, 695–707, 1998.

Tajika, E., Carbon cycle and climate change during the Cretactous inferred from a biogeochemical carbon cycle model, *Isl. Arc*, *8*, 293–303, 1999.

Tanguy, J.-C., M. Condomines, and G. Kieffer, Evolution of the Mount Etna magma: Constraints on the present feeding system and eruptive mechanism, *J. Volcanol. Geotherm. Res.*, *75*, 221–250, 1997.

Thomas, E., J. C. Zachos, and T. J. Bralower, Deep-sea environments on a warm Earth: Latest Paleocene–early Eocene, in *Warm Climates in Earth History*, edited by B. T. Huber, K. G. MacLeod, and S. L. Wing, pp. 132–160, Cambridge Univ. Press, New York, 2000.

Torgersen, T., Terrestrial helium degassing fluxes and the atmospheric helium budget: Implications with respect to the degassing processes of continental crust, *Chem. Geol.*, *79*, 1–14, 1989.

Varekamp, J. C., and E. Thomas, Volcanic and anthropogenic contributions to global weathering budgets, *J. Geochem. Explor.*, *62*, 149–159, 1998.

Varekamp, J. C., R. Kreulen, R. P. E. Poorter, and M. J. Van

Bergen, Carbon sources in arc volcanism, with implications for the carbon cycle, *Terra Nova*, *4*, 363–373, 1992.
Varley, N. R., and M. A. Armienta, The absence of diffuse degassing at Popocatépetl volcano, Mexico, *Chem. Geol*., *177*, 157–173, 2001.
Veizer, J., K. Bell, and S. L. Jansen, Temporal distribution of carbonatites, *Geology*, *20*, 1147–1149, 1992.
Veizer, J., Y. Godderis, and L. M. François, Evidence for decoupling of atmospheric CO_2 and global climate during the Phanerozoic eon, *Nature*, *408*, 698–701, 2000.
Voight, B., E. K. Constantine, S. Siswowidjoyo, and R. Torley, Historical eruptions of Merapi volcano, central Java, Indonesia, 1768–1998, *J. Volcanol. Geotherm. Res*., *100*, 69–138, 2000.
Wadge, G., Comparison of volcanic production rates and subduction rates in the Lesser Antilles and Central America, *Geology*, *12*, 555–558, 1984.
Wahlen, M., The global methane cycle, *Annu. Rev. Earth Planet. Sci*., *21*, 407–426, 1993.
Wardell, L. J., and P. R. Kyle, Volcanic carbon dioxide emission rates: White Island, New Zealand and Mount Erebus, Antarctica (abstract), *Eos Trans. AGU*, *79*(45), Fall Meet. Suppl., F927, 1998.
Welhan, J. A., Origins of methane in hydrothermal systems, *Chem. Geol*., *71*, 183–198, 1988.
Welhan, J. A., and H. Craig, Methane and hydrogen in East Pacific Rise hydrothermal fluids, *Geophys. Res. Lett*., *6*, 829–831, 1979.
Werner, C., S. L. Brantley, and K. Boomer, CO_2 emissions related to the Yellowstone volcanic system, 2, Statistical sampling, total degassing, and transport mechanisms, *J. Geophys. Res*., *105*(B5), 10,831–10,846, 2000a.
Werner, C., J. C. Wyngaard, and S. L. Brantley, Eddy-correlation measurement of hydrothermal gases, *Geophys. Res. Lett*., *27*, 2925–2928, 2000b.
Wignall, P. B., Large igneous provinces and mass extinctions, *Earth Sci. Rev*., *53*, 1–33, 2001.
Williams, S. N., S. J. Schaefer, M. L. Calvache, and D. Lopez, Global carbon dioxide emission to the atmosphere by volcanoes, *Geochim. Cosmochim. Acta*, *56*, 1765–1770, 1992.
Williams-Jones, G., J. Stix, M. Heiligmann, A. Charland, B. S. Lollar, N. Arner, V. Garzón, J. Barquero, and E. Fernandez, A model of diffuse degassing at three subduction-related volcanoes, *Bull. Volcanol*., *62*, 130–142, 2000.
Winter, J. D., *An Introduction to Igneous and Metamorphic Petrology*, 697 pp., Prentice-Hall, Old Tappan, N. J., 2001.
Woolley, A. R., The spatial and temporal distribution of carbonatites, in *Carbonatites: Genesis and Evolution*, edited by K. Bell, pp. 15–37, Chapman and Hall, New York, 1989.
Yapp, C. J., and H. Poths, Carbon isotopes in continental weathering environments and variations in ancient atmospheric CO_2 pressure, *Earth Planet. Sci. Lett*., *137*, 71–82, 1996.
Zheng, L., S. Wang, Y. Liao, and Z. Feng, CO_2 gas pools in Jiyang sag, China, *Appl. Geochem*., *16*, 1033–1039, 2001.

D. M. Kerrick, Department of Geosciences, 243 Deike Building, Pennsylvania State University, University Park, PA 16802, USA. (kerrick@geosc.psu.edu)