

Magmatic carbon outgassing and uptake of CO₂ by alkaline waters [♠]

MARIE EDMONDS^{1,*†}, BENJAMIN TUTOLO², KAYLA IACOVINO³, AND YVES MOUSSALLAM^{4,5}

¹Earth Sciences Department, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K. Orcid 0000-0003-1243-137X

²Department of Geoscience, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

³NASA Johnson Space Center, 2101 E NASA Parkway, Houston, Texas 77058, U.S.A.

⁴Lamont-Doherty Earth Observatory, 101NCL, P.O. Box 1000, 61 Route 9W, Palisades, New York 10964, U.S.A.

⁵Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France

ABSTRACT

Much of Earth's carbon resides in the “deep” realms of our planet: sediments, crust, mantle, and core. The interaction of these deep reservoirs of carbon with the surface reservoir (atmosphere and oceans) leads to a habitable surface environment, with an equitable atmospheric composition and comfortable range in temperature that together have allowed life to proliferate. The *Earth in Five Reactions* project (part of the Deep Carbon Observatory program) identified the most important carbon-bearing reactions of our planet, defined as those which perhaps make our planet unique among those in our Solar System, to highlight and review how the deep and surface carbon cycles connect. Here we review the important reactions that control the concentration of carbon dioxide in our atmosphere: outgassing from magmas during volcanic eruptions and during magmatic activity; and uptake of CO₂ by alkaline surface waters. We describe the state of our knowledge about these reactions and their controls, the extent to which we understand the mass budgets of carbon that are mediated by these reactions, and finally, the implications of these reactions for understanding present-day climate change that is driven by anthropogenic emission of CO₂.

Keywords: Deep carbon cycle, anthropogenic carbon, alkaline lakes, CO₂ degassing, silicate melts; Earth in Five Reactions: A Deep Carbon Perspective

INTRODUCTION

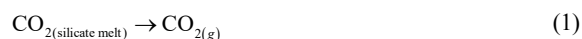
We present this paper as part of the “Earth in Five Reactions” series, which identifies the most important carbon-bearing reactions in Earth from the perspective of the “deep” carbon cycle. The concentration of CO₂ in our atmosphere controls the habitability of our planet via our equitable climate and the existence of photosynthesizing organisms. How does the deep carbon cycle impact the concentration of CO₂ in our atmosphere?

The Earth's “surface reservoir,” i.e., the atmosphere, oceans, and sediments combined, of carbon makes up only a small fraction of the Earth's total carbon budget, with most of the carbon inventory of the planet (estimates vary from 75 to 99%) residing in the Earth's core (Wood 1993; Dasgupta and Hirschmann 2010a; Dasgupta et al. 2013; DePaolo 2015; Li et al. 2019). Over long geological timescales, fluxes of carbon from the mantle to the atmosphere and oceans via magmatism, volcanism, and metamorphic decarbonation, modulate the composition of Earth's atmosphere and climate (Sleep and Zahnle 2001; Dasgupta 2013) (Fig. 1). The delicate carbon balance of the surface reservoir is largely maintained (Berner and Caldeira 1997), despite the immense size of Earth's internal reservoirs and fluxes, which requires equally important fluxes of carbon back into the mantle, through subduction (Dasgupta 2013; Kelemen and Manning 2015; Hirschmann 2018). This return flux replenishes the carbon lost from the mantle via melting and degassing (Dasgupta 2013; Hirschmann 2018).

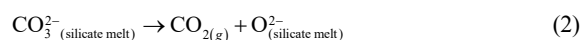
The volcanic, tectonic, and metamorphic flux of CO₂ from

Earth's interior is large. For the volcanic portion, current estimates range from 280 to 360 Tg CO₂ per year (equivalent to 6.4 to 8.2 × 10¹² mol CO₂ per year) (Burton et al. 2013; Gerlach 2011; Werner et al. 2019). Volcanic C is derived from the outgassing of silicate melts at low pressure. The tectonic flux includes direct outgassing of mantle-derived CO₂ fluids (Chiodini et al. 2010; Mörrer and Etiope 2002), as well as metamorphic decarbonation in orogenic belts (Kerrick and Caldeira 1998). Degassing of crustal- and mantle-derived fluids associated with extensional tectonic regimes (e.g., outgassing from continental rifts) constitutes a large fraction of the total outgassing flux; a recent estimate (which is also included in the “volcanic” estimate above), is hundreds of Tg per year of CO₂ (Tamburello et al. 2018).

The majority of the volcanic flux is derived from the degassing of carbon from silicate melts generated in the mantle, linked to mantle plumes or plate boundary processes, which ascend toward the surface of the Earth. It has been shown that the mantle is heterogeneous with respect to carbon (Saal et al. 2002; Hirschmann and Dasgupta 2009; Hauri et al. 2018, 2019), which leads to melts produced in different settings containing different amounts of carbon. Mid-ocean ridge melts are largely carbon-depleted relative to those formed in arcs and hotspot settings (Blundy et al. 2010; Hauri et al. 2019). Carbon solubility in silicate melts falls with decreasing pressure, which causes melts to outgas their carbon almost entirely once they reach the shallow crust. This reaction might be represented by:



and



* E-mail: marie.edmonds@esc.cam.ac.uk

♠ Open access: Article available to all readers online. This article is CC-BY.

† Special collection papers can be found online at <http://www.minsocam.org/MSA/AmMin/special-collections.html>.

for dissolved molecular CO₂ and dissolved carbonate, respectively (where O²⁻ is a non-bridging oxygen) (Guillot and Sator 2011). Both species are present in silicate melts, with molecular CO₂ becoming more important as the silica content of the melt increases (and temperature decreases) (Stolper and Holloway 1988). The controls on silicate melt degassing (reactions 1 and 2) are explored further below. Melts may also assimilate carbon from the mantle lithosphere, or from the crust (Lee et al. 2013; Carter and Dasgupta 2015; Mason et al. 2017), where carbon resides as carbonate and organic carbon, and transfer this carbon to the atmosphere. Because of the low solubility of carbon in silicate melts, intrusive magmatism contributes to the outgassing flux of carbon, leading to diffuse emissions of CO₂ in volcanic regions, often mediated by large-scale faults and fractures (Allard et al. 1991; Chiodini et al. 1995; Farrar et al. 1995; Hunt et al. 2017).

Volcanoes and extensional tectonic regions pump CO₂ into the atmosphere (Fig. 1), triggering a systematic response in the surface reservoir (Berner 1999). An equilibrium exists between the CO₂ in the atmosphere and in the oceans. On short timescales, the atmosphere-ocean system responds to an increase in atmospheric CO₂ by allowing more carbon to dissolve in the ocean:



Aqueous CO₂ dissociates to carbonate and bicarbonate, with the relative proportions dependent on the pH of the ocean water:



Adding more CO₂ to the ocean increases acidity (at the expense of carbonate); increasing the alkalinity of the ocean will tend to draw down CO₂. The residence time of carbon in the atmosphere-ocean-sediment system is relatively short; only ~100 ka (Berner 1994). Carbon is removed from the surface reservoir through weathering and removal of bicarbonate through rivers into the ocean. Then, carbon is precipitated from the ocean water as carbonate above the carbonate compensation depth (CCD), forming limestones on the ocean floor and carbonate in oceanic crust, which may eventually be returned to the mantle via subduction. A fraction of this carbon may be removed from the slab during subduction, via dissolution or metamorphic decarbonation (Kerrick and Connolly 2001; Gorman et al. 2006; Ague and Nicolescu 2014; Faq et al. 2014), migrating back to the surface in the forearc or subarc in the form of CO₂-rich fluids and by dissolution within primary arc melts and transport to the surface through volcanism (Dutkiewicz et al. 2018).

The transfer of CO₂ between gas and water and silicate melts therefore plays an outsized role in connecting its various “spheres.” Metamorphic and magmatic CO₂ inputs from Earth’s interior enter the atmosphere through the forward expression of reactions 1 and 2, dissolve into its hydrosphere through the forward expression of reaction 3, and ultimately interact with cations derived from lithospheric weathering to form carbonate minerals, often through biosphere-mediated processes (Garrels 1983). Indeed, this silicate weathering feedback is the primary reason that the surface of our planet is clement (Stewart et al. 2019). Moreover, much of the carbon available to biological metabolisms such as photosynthesis (see Sheik et al. in revision) ultimately originates through a coupling of reactions 1+2 and 3. Due to their significance in connecting Earth’s spheres, reactions 1 (and 2) and 3 together

were chosen as one of the five most important reactions that make Earth unique in the solar system by delegates of the Deep Carbon Observatory’s Earth in Five Reactions workshop.

In this paper, we review the current state of understanding of both reactions in detail, with application to the case of alkaline melts and fluids generated in continental rifts, which have had considerable importance for supplying CO₂ fluxes to the surface reservoir through supercontinent cycles of the past (Brune et al. 2017) and in the modern day (Lee et al. 2016; Hunt et al. 2017; Werner et al. 2019). We discuss the dependence of these reactions on other parameters in the geological system, and we consider their importance for the Earth’s deep carbon cycle, tracking carbon reactions from the mantle to the surface. Finally, we draw attention to the relevance of both of these naturally occurring reactions, which have played such an important role in shaping Earth’s climate and surface environment over its long history, to our present-day societal challenges related to anthropogenic CO₂ release and ocean drawdown of CO₂.

CARBON DEGASSING FROM SILICATE MELTS

Carbon exists in many forms in the Earth’s mantle: as fluids, dissolved as oxidized carbonate species (Pan and Galli 2016) or as reduced hydrocarbons (Sverjensky and Huang 2015) or as solid carbonate (Boulard et al. 2015; Cerantola et al. 2019); as elemental carbon (graphite and diamond; Shirey et al. 2013) in the deep mantle; and as Fe-metal carbide in the mantle (McCammon et al. 2020, this issue) core (Li and Fei 2003; Wood et al. 2013). Carbonated silicate melts may be ubiquitous in the mantle and may be the precursor to mid-ocean ridge basalts, kimberlites, and melts derived from subducting slabs (Dasgupta and Hirschmann 2010a; Moussallam et al. 2015). As silicate melts generated in the mantle ascend into the crust, they transport their dissolved carbon load toward the surface of the Earth. As they decompress, carbon dioxide exsolves and forms a separated supercritical fluid, transforming to a gas phase close to the surface. In this way, carbon may be transferred from the interior of the Earth to the surface; this is

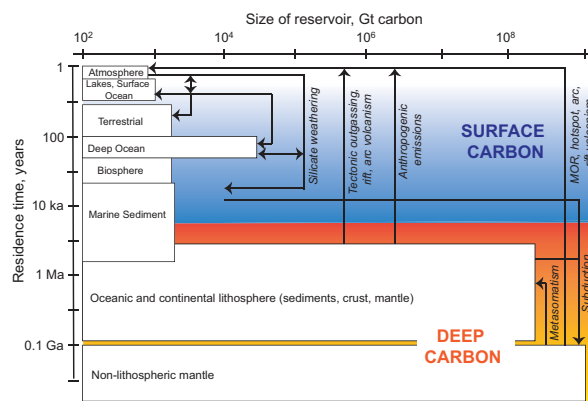


FIGURE 1. Simplified box model to show the carbon reservoirs and fluxes of Earth (excluding the core). The size of each reservoir is approximately indicated by the horizontal dimension of the box; the approximate residence time for carbon in each reservoir by the vertical dimension (Sundquist 1993; Dasgupta and Hirschmann 2010b; Friedlingstein et al. 2010; Burton et al. 2013; DePaolo 2015; Lee et al. 2019; Werner et al. 2019). The types of fluxes between each reservoir are shown against the arrows; the size of these fluxes is not indicated.

a critical flux of the deep carbon cycle (Fig. 1).

Because of the relatively high pressures in the crust and upper mantle (at depths of perhaps up to 40–50 km) under which silicate melt degassing occurs, generated CO₂-rich fluid may migrate semi-independently of the magma through the crust, leading to large areas of so-called “diffuse” degassing at the surface (Chiodini et al. 2004), with the fluid making use of fractures in the crust to reach the atmosphere. Diffuse degassing takes place in a range of tectonic settings, e.g., at mid-ocean ridges, volcanic arcs over subduction zones, and submarine arc vents, in continental rifts (Hunt et al. 2017), and in large silicic calderas (Werner and Brantley 2003). In this way, the carbon content of unerupted magmas may yet reach the atmosphere, despite the source magma stalling in the crust. In the case of volcanic eruptions, CO₂ is carried directly to the surface in ascending magmas (in both dissolved and exsolved forms), and is outgassed to the atmosphere either prior to or during eruption. In this section, we review our state of understanding of carbon degassing from silicate melts.

CONTROLS ON CO₂ SOLUBILITY IN SILICATE MELTS

CO₂ exists as both dissolved carbonate and as molecular CO₂ in silicate glasses (Mysen et al. 1975; Fine and Stolper 1985; Fine and Stolper 1986). In basalts, basanites, and other silica-undersaturated magmas, carbon exists solely as carbonate (Blank and Brooker 1994; Moussallam et al. 2016), whereas in rhyolitic glasses, only molecular CO₂ is found (Fogel and Rutherford 1990). Intermediate magmas and evolved, silica-undersaturated glasses such as phonolites, have both species present (Behrens et al. 2004). Carbon speciation in silicate melts is a strong function not only of melt silica content but also of melt structure and availability of cations such as Na⁺, Ca²⁺, and Mg²⁺ (Fine and Stolper 1985). The speciation of carbon dioxide in glasses (i.e., at surface *P-T* conditions) however is not necessarily that of the melt (i.e., at depth). Evidence from annealing experiments (Morizet et al. 2001; Nowak et al. 2003), molecular dynamics simulation studies (Guillot and Sator 2011; Morizet et al. 2015; Moussallam et al. 2016) and in situ spectroscopy studies (Konschak and Keppler 2014) show that the CO₂ + O²⁻ = CO₃²⁻ equilibrium in the melt shifts toward CO₂ with increasing temperature and that in the melt, molecular CO₂ is present even in basaltic and carbonated melt compositions.

CO₂ solubility in silicate melts is controlled by the melt composition via the attractive-repulsive behavior of each component with CO₂ (Papale et al. 2006). Of these, Si and Al are by far the dominant factors, with CO₂ solubility decreasing drastically with increasing Si and Al and increasing with increasing Ca, K, and Na content (plus more minor effect with increasing Mg and Fe; Fig. 2a) (Blank and Brooker 1994; Dixon et al. 1997; Shishkina et al. 2014; Moussallam et al. 2015). This is illustrated by the empirical relationship between CO₂ solubility and the compositional “ π parameter” (π , Dixon et al. 1997), which incorporates negative Si and Al terms and positive Ca, K, Na, Mg, and Fe terms.

The relatively dry and shallow melting regime beneath rift margins relative to other plate boundaries results in the generation very low-degree (<3%) partial mantle melts. Such melts are characteristically low in Si and rich in Ca, K, Na, and Mg resulting in a stronger propensity to dissolve available carbon (as carbonate). At mantle pressures, primary melts may dissolve several weight percent of carbon (up to 6 wt% at mantle pressures; Fig. 2a).

The solubility of CO₂ increases with pressure for all silicate melt compositions (Fig. 2b). At 300 MPa in the crust, for example, basalts may hold 3000–4000 ppm in solution, depending on the amount of other volatile species present, decreasing to only a couple of 100 ppm at 50 MPa. Much of the CO₂ load of a basaltic melt, which may reach 0.5 or even 1 wt% in the crust, therefore resides in the exsolved magmatic volatile phase in the mid- and upper-crust.

The presence of other volatiles affects the solubility of CO₂ in silicate melts. Henry’s Law applies to volatile solubility at pressures pertaining to the mid- and upper-crust. For a vapor-saturated melt, where more than one volatile species is present, the concentration, or activity, of a particular species is diluted, thereby reducing its solubility in the melt (Moore 2008). The magnitude of this effect on melt CO₂ solubility is illustrated in Figure 2b, whereas the co-existing vapor phase becomes more H₂O-rich, the concentration (solubility) of CO₂ in the melt is reduced (Dixon and Stolper 1995; Dixon et al. 1995; Moore et al. 1998; Newman and Lowenstern 2002; Moore 2008). This occurs in nature during a process known as second boiling, where magmas crystallize at a fixed pressure in the crust (Candela 1997). During crystallization, the melt volume reduces, and volatiles are forced out of solution and outgassed.

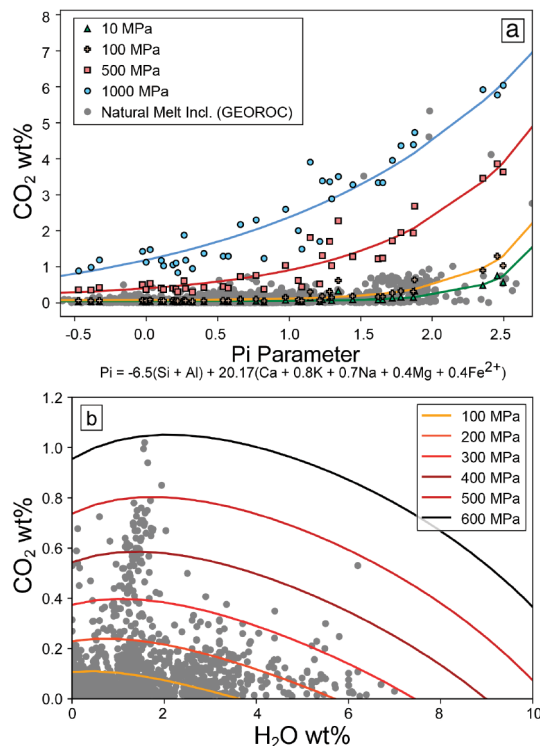


FIGURE 2. Summary diagram to illustrate the major controls (melt composition and pressure) on CO₂ solubility in silicate melts. (a) Compositionally dependent π (π) parameter and melt CO₂ content at saturation for 50 synthetic basalt to alkali basalt melt compositions (colored symbols). CO₂ concentrations calculated at 4 saturation pressures using MagmaSat (Ghiorso and Gualda 2015) in the ENKI framework (<http://enki-portal.org/>). Colored curves are best-fit to the data at each pressure and illustrate the π parameter as a good predictor of CO₂ solubility. (b) Natural basalt melt CO₂ and H₂O contents (gray dots, data from GEOROC) plotted with isobars (colored curves; calculated for an alkali basalt using MagmaSat in the ENKI framework), which represent the saturation surface at given pressures.

Over time, the vapor phase thus produced gets progressively more water-rich, thereby reducing the solubility of CO₂ in the remaining melt, as observed in quartz melt inclusions erupted in the Bishop Tuff, for example (Wallace et al. 1999). Conversely, underplating mafic magmas producing exsolved CO₂ may “flush” overlying stored magmas (Cashman 2004; Blundy et al. 2010; Caricchi et al. 2018). In this case, the addition of CO₂ raises the concentration of CO₂ in the coexisting vapor phase, thereby enhancing CO₂ solubility in the silicate melt. This process of CO₂ flushing has been invoked to explain anomalously high CO₂ concentrations in olivine-hosted melt inclusions from Etna, for example (Métrich and Wallace 2008).

The volcanic and tectonic flux of CO₂ to the surface environment encompasses contributions from mid-ocean ridges (which is released dominantly into the oceans), from continental rifts, volcanic arcs, hotspots, extensional regions where the Earth’s mantle supplies CO₂-rich fluids direct to the surface, and orogenic belts where limestones are heated and devolatilized (Sleep and Zahnle 2001). The fraction of this CO₂ that is released directly into the atmosphere, and that which is absorbed into water bodies such as oceans, lakes, and groundwater aquifers, is unknown. It has been well documented that a large fraction of the CO₂ released in extensional regions are trapped by aquifer systems, which, in turn, allow quantification of the CO₂ produced over large areas, e.g., in the eastern Himalayas (Evans et al. 2008) and in the Apennines region of Italy (Chiodini et al. 2000).

UPTAKE OF MAGMATIC CO₂ BY SURFACE WATER BODIES

Alkalinity and carbon storage in surface water bodies

Earth’s surface water bodies can play a vital role in controlling the ultimate fate of carbon degassed from silicate melts. The amount of inorganic carbon in a solution in equilibrium with gaseous CO₂ is a function of the solution’s alkalinity and its pH (Fig. 3). In essence, alkalinity is a charge-balance equation defined in relation to the speciation of dissolved inorganic carbon. Formally, carbonate alkalinity is defined (Stumm and Morgan 1996) as:

$$[\text{Alkalinity}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (5)$$

where the brackets indicate concentrations of the bracketed species in mole-based units (e.g., molal).

Inorganic carbon enters solution through reaction 3, and, depending on the partial pressure of CO₂ and the alkalinity and pH of the solution, is speciated into carbonic acid (CO_{2(aq)}), bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻). Examination of Equation 5 shows that dissolving/exsolving CO_{2(g)}, an electrically neutral molecule, into/out of solution cannot directly impact alkalinity, although it may have the side effect of making minerals more or less soluble, which will, in turn, impact the solution alkalinity. Equation 5 shows that the total inorganic carbon in solution can be directly related to pH and alkalinity (Fig. 3). Nonetheless, meaningful use of Equation 4 in the study of dynamic aqueous environments begs the question—what are the concentrations of cations other than HCO₃⁻, CO₃²⁻, H⁺, and OH⁻, and how might they contribute to the overall behavior (i.e., pH, carbon storage capacity) of the solution and/or reflect its history? Basalt has an excess of cations over CO₂. Atmospheric CO₂ binds with the cations once the rock weathers, making the weathering of basalt a carbon sink. For this purpose, an “alternative definition” of alkalinity reflecting the

non-carbonate carbon portion of the charge balance (Stumm and Morgan 1996) is:

$$[\text{Alkalinity}] = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - 2[\text{NO}_3^-]. \quad (6)$$

In Equation 6, the impact of water chemistry on alkalinity and hence carbon storage and pH (Fig. 3) can be more readily discerned. Notably, this is a functional version of the equation that includes the “major” cationic and anionic species representative of most natural waters; it would need to be expanded for waters where other ions may be important. Equation 6 shows that the alkalinity is reduced by concentrations of anions such as Cl⁻ and SO₄²⁻, two of the dominant anions in seawater.

Aqueous carbon storage at rifted margins

At the same time as our understanding of carbon fluxes from continental rifts has increased through the efforts of DCO members and others (Lee et al. 2016; Brune et al. 2017; Hunt et al. 2017), attention has also been refocused on the fluxes of CO₂ from mid-ocean ridges (e.g., Lund et al. 2016) and their variability in relation to long-term geologic variations. In the case of mid-ocean ridge systems, much of the CO₂ degassing from the system is rapidly absorbed by the overlying seawater due to its high solubility at seafloor depths. For example, although CO₂ concentrations of continuously venting hydrothermal fluids are commonly in the tens to hundreds of millimolal (e.g., Lilley et al. 2003), it is rare, although not unheard of to observe free-phase CO₂ in the vicinity of submarine hydrothermal systems (Lupton et al. 2008).

It is now clear that continental rifts are important sites of magmatic CO₂ release (Hunt et al. 2017): the eastern branch of the East African Rift, for example, may be emitting more CO₂ (~3.9–32.7 Mt/year) than all of the world’s mid-ocean ridges combined (Lee et al. 2016; Hunt et al. 2017; Hauri et al. 2019), although there are large uncertainties attached to these estimates. Sites of continental breakup tap directly the vast volatile storage region in the sub-continental lithosphere, where small fraction, volatile-rich melts freeze as they cross their solidus as they ascend from the convecting mantle (Foley and Fischer 2017). Over geological time, supercontinent breakup may have released enormous fluxes of CO₂ held both in the sub-continental lithosphere but also in the form of sediments on the continents, which may have played an important role in shaping Earth’s climate (Lee et al. 2013; Brune et al. 2017). Today, the CO₂ emitted from the East African Rift may vary along-rift (Hunt et al. 2017). The CO₂ migrates to the surface along faults at the rift margins (Hutchison et al. 2015), where it may be intercepted by surface water in the form of rift lakes.

The geology of the watersheds feeding rift lakes exerts an important control on the aqueous geochemistry of the lake waters (Cerling 1979, 1994; Wright 2012). Analyses presented by Cerling (1994) demonstrates that weathering of the volcanic rocks feeding East African Rift-hosted lakes provides mainly Na⁺, Ca²⁺, HCO₃⁻, and relatively little Cl⁻ and SO₄²⁻ to the lake waters. When examined in the alkalinity framework represented by Equation 5, one can see the alkalinity of these lakes tends to be quite high (Fig. 3). If the lakes are in a closed basin, evaporation-dominated setting, then the alkalinity, and hence pH, tends to increase during evaporation (Garrels and MacKenzie 1967; Tutolo and Tosca 2018). As both pH and alkalinity increase, the amount of inorganic carbon stored

in the lake also increases (Fig. 3), such that evaporation-dominated rift basin lake waters can contain concentrations of inorganic carbon significantly greater than seawater. This inorganic carbon can be deposited as carbonate minerals or converted to biomass and stored in lake sediments, often through interactions with cyanobacterial or algal communities (Wright 2012). Hence, a significant amount of carbon emitted from silicate melts in continental rifts may not go much further than the sediments deposited in the overlying lakes. Because the rift environment is dynamic, with lakes changing in size and alkalinity over time, intimately linked to the tectonics of rifting, the system does not necessarily reach a steady-state equilibrium; and the total carbon sequestered by lakes in rift environments remains unquantified. In this way, rifted margins are locations where the lithosphere, in the form of magmatic degassing, the hydrosphere, in the form of rift-basin lakes or seawater, and the biosphere, in the form of cyanobacteria, algae, and higher-order organisms, all interact with one another.

IMPLICATIONS FOR PRESENT-DAY ANTHROPOGENIC CO₂ RELEASE AND OCEAN RESPONSE

We have shown that the flux of carbon from Earth's interior, and the potential for uptake of CO₂ by alkaline surface waters, are first-order controls on the concentration of CO₂ in our atmosphere. Up to now, we have confined our discussion to the natural cycles of magmatism and tectonics that have characterized our planet for the past two billion years. However, the processes that we discuss here are also relevant to a pressing predicament facing humankind in the 21st century. Namely, is anthropogenic CO₂ generation a stronger driver of climate than CO₂ injected into the atmosphere by natural processes? And how is the atmosphere-ocean system responding?

The answer to the first is unequivocally yes. Numerous estimates of CO₂ delivered into the atmosphere by volcanism lead to an inescapable conclusion: anthropogenic sources of CO₂ far exceed the volcanic and tectonic flux of CO₂ into the atmosphere.

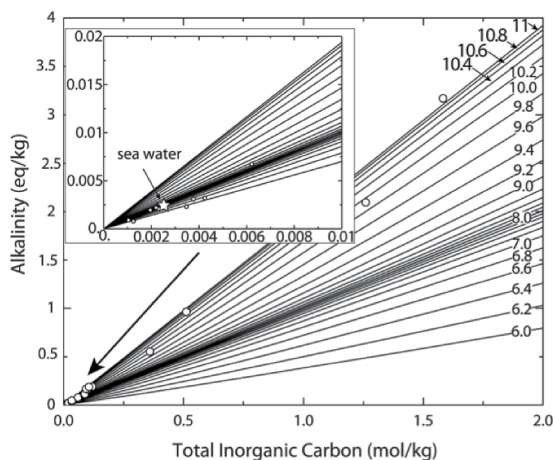


FIGURE 3. Diagram showing the relationship between pH, alkalinity, and total carbonate carbon concentration (after Deffeyes 1965); calculated by speciating solutions along axes using the Geochemist's Workbench (Bethke et al. 2018). Labels on lines indicate the pH of the solution, and circles are analyses of East African Rift lakes collected by (Cerling 1979). Inset is plotted to emphasize the magnitude of the difference in carbon and alkalinity concentrations between seawater and alkaline rift lakes.

The burning of fossil fuels and the manufacture of cement released $31\,000 \pm 1845$ Tg CO₂ into the atmosphere in 2009 (Friedlingstein et al. 2010). Volcanic regions annually supply 280–360 Tg CO₂ per year to the atmosphere and ocean system (Gerlach 2011; Burton et al. 2013; Werner et al. 2019), that is 83 to 137 times less than anthropogenic sources. The massive fluxes of carbon into the surface reservoir caused by anthropogenic activities, principally the burning of fossil fuels, has exceeded the Earth system's ability to compensate, upsetting the delicate balance in the geologic carbon cycle (Berner and Caldeira 1997).

The ocean has absorbed around a third of the CO₂ produced anthropogenically since the mid-20th century (Sabine et al. 2004) through Equation 3. Uptake of CO₂ in ocean water decreases the pH by:



thereby increasing CO₂ and bicarbonate at the expense of carbonate. Since the mid-20th century, it is estimated that ocean pH has dropped by 0.1 log units, which represents an almost 30% increase in H⁺ ions (Caldeira and Wickett 2003). The increase in acidity lowers the saturation state of calcite and aragonite in the oceans and is slowing or shutting down calcification in many marine organisms, including those that inhabit coral reefs (Orr et al. 2005; Zeebe et al. 2008; Doney et al. 2009).

Recent work has attempted to compare the recent rates of anthropogenic CO₂ release to periods of dramatic carbon release from deep reservoirs to the atmosphere-ocean system in Earth's history, which are recorded as light carbon isotope excursions in sedimentary records (Zeebe et al. 2016). A large carbon isotopic excursion and associated mass extinction at the end of the Permian has been linked to the outpouring of 7–15 million km³ basalt (Saunders 2005; Reichow et al. 2009; Black et al. 2012; Black and Gibson 2019) as well as the metamorphic devolatilization (Svensen et al. 2009) and combustion (Ogden and Sleep 2012) of buried coal by sills. This event may have released 20 000 to 30 000 Pg C over as long as 10⁵ years, but probably in discrete pulses over much shorter timescales (Black et al. 2018). The fastest large carbon release of the Cenozoic (past 66 Myr) occurred at the onset of the Palaeocene–Eocene Thermal Maximum (~56 Myr ago) (Zachos et al. 2005), when 2500 to 4500 Pg carbon was emitted to the ocean-atmosphere system over up to 4000 yr (Bowen et al. 2015; Zeebe et al. 2016). These estimates yield annual carbon emissions during the PETM perhaps as little as 1 Pg carbon per year (Stocker et al. 2013; Zeebe et al. 2016) or as much as ~9.5 Pg carbon per year, which is similar to present-day anthropogenic fluxes (Bowen et al. 2015). The PETM was associated with massive extinction of benthic foraminifera, synchronous with a large decline in oceanic productivity and oxygenation (Winguth et al. 2012). CO₂ released from combustion of fossil fuels in our atmosphere equilibrates, as discussed above, among the carbon reservoirs of the ocean, atmosphere, and biosphere over timescales of centuries. Geological sequestration of the CO₂ from the surface reservoir; however, takes much longer: weathering processes and deposition of carbonate in oceanic crust occurs on timescales of 10⁵–10⁶ years (Lenton and Britton 2006; Archer et al. 2009).

ACKNOWLEDGMENTS AND FUNDING

We acknowledge the support of the Alfred P. Sloan Foundation through the Deep Carbon Observatory. The basis of this paper was provided by discussion with

Deep Carbon Observatory colleagues at the Earth in Five Reactions workshop in Washington, D.C., in March 2018.

REFERENCES CITED

- Ague, J.J., and Nicolescu, S. (2014) Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nature Geoscience*, 7(5), 355–360.
- Allard, P., Carbone, J., Dajčević, D., Le Bronec, J., Morel, P., Robe, M., Maurenas, J., Faivre-Pierret, R., Martin, D., and Sabroux, J. (1991) Eruptive and diffuse emissions of CO₂ from Mount Etna. *Nature*, 351, 387–391.
- Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K., Matsumoto, K., Munhoven, G., and Montenegro, A. (2009) Atmospheric lifetime of fossil fuel carbon dioxide. *Annual Review of Earth and Planetary Sciences*, 37, 117–134.
- Behrens, H., Tamic, N., and Holtz, F. (2004) Determination of the molar absorption coefficient for the infrared absorption band of CO₂ in rhyolitic glasses. *American Mineralogist*, 89, 301–306.
- Berner, R.A. (1994) GEOCARB II: A revised model of atmospheric CO₂ over Phanerozoic time. *American Journal of Science*, 294(1).
- (1999) A new look at the long-term carbon cycle. *GSA Today*, 9(11), 1–6.
- Berner, R.A., and Caldeira, K. (1997) The need for mass balance and feedback in the geochemical carbon cycle. *Geology*, 25(10), 955–956.
- Bethke, C.M., Farrell, B., and Yeakel, S. (2018) The Geochemist's Workbench Release 12.0—Reaction Modeling Guide. Aqueous Solutions, Champaign, Illinois.
- Black, B.A., and Gibson, S.A. (2019) Deep carbon and the life cycle of large igneous provinces. *Elements*, DOI: 10.2138/gselements.15.5.319.
- Black, B.A., Elkins-Tanton, L.T., Rowe, M.C., and Peate, I.U. (2012) Magnitude and consequences of volatile release from the Siberian Traps. *Earth and Planetary Science Letters*, 317, 363–373.
- Black, B.A., Neely, R.R., Lamarque, J.-F., Elkins-Tanton, L.T., Kiehl, J.T., Shields, C.A., Mills, M.J., and Bardeen, C. (2018) Systemic swings in end-Permian climate from Siberian Traps carbon and sulfur outgassing. *Nature Geoscience*, 11(12), 949.
- Blank, J.G., and Brooker, R.A. (1994) Experimental studies of carbon dioxide in silicate melts; solubility, speciation, and stable carbon isotope behavior. *Reviews in Mineralogy and Geochemistry*, 30, 157–186.
- Blundy, J., Cashman, K.V., Rust, A., and Witham, F. (2010) A case for CO₂-rich arc magmas. *Earth and Planetary Science Letters*, 290(3), 289–301.
- Boulard, E., Pan, D., Galli, G., Liu, Z., and Mao, W.L. (2015) Tetrahedrally coordinated carbonates in Earth's lower mantle. *Nature Communications*, 6, 6311.
- Bowen, G.J., Maibauer, B.J., Kraus, M.J., Röhl, U., Westerhold, T., Steimke, A., Gingerich, P.D., Wing, S.L., and Clyde, W.C. (2015) Two massive, rapid releases of carbon during the onset of the Palaeocene–Eocene thermal maximum. *Nature Geoscience*, 8(1), 44.
- Brune, S., Williams, S.E., and Müller, R.D. (2017) Potential links between continental rifting, CO₂ degassing and climate change through time. *Nature Geoscience*, 10(12), 941.
- Burton, M.R., Sawyer, G.M., and Granieri, D. (2013) Deep carbon emissions from volcanoes. *Reviews in Mineralogy and Geochemistry*, 75(1), 323–354.
- Caldeira, K., and Wickett, M.E. (2003) Oceanography: anthropogenic carbon and ocean pH. *Nature*, 425, 365.
- Candela, P.A. (1997) A review of shallow, ore-related granites: textures, volatiles, and ore metals. *Journal of Petrology*, 38(12), 1619–1633.
- Caricchi, L., Sheldrake, T.E., and Blundy, J. (2018) Modulation of magmatic processes by CO₂ flushing. *Earth and Planetary Science Letters*, 491, 160–171.
- Carter, L.B., and Dasgupta, R. (2015) Hydrous basalt–limestone interaction at crustal conditions: Implications for generation of ultracalcic melts and outflux of CO₂ at volcanic arcs. *Earth and Planetary Science Letters*, 427, 202–214.
- Cashman, K.V. (2004) Volatile controls on magma ascent and eruption. *The State of the Planet: Frontiers and Challenges in Geophysics*, 109–124.
- Cerling, T.E. (1979) Paleochemistry of plio-pleistocene lake Turkana, Kenya. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 27, 247–285.
- Cerling, T. (1994) Chemistry of closed basin lake waters: a comparison between African Rift Valley and some central North American rivers and lakes. *The Global Geological Record of Lake Basins*, 1, 29–30.
- Cerantola, V., Wilke, M., Kantor, I., Ismailova, L., Kuppenko, I., McCammon, C., Pascarelli, S., and Dubrovinsky, L.S. (2019) Experimental investigation of FeCO₃ (siderite) stability in Earth's lower mantle using XANES spectroscopy. *American Mineralogist*, 104, 1083–1091.
- Chiodini, G., Frondini, F., and Ponziani, F. (1995) Deep structures and carbon dioxide degassing in central Italy. *Geothermics*, 24(1), 81–94.
- Chiodini, G., Frondini, F., Cardellini, C., Parello, F., and Peruzzi, L. (2000) Rate of diffuse carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: the case of central Apennine, Italy. *Journal of Geophysical Research: Solid Earth*, 105(B4), 8423–8434.
- Chiodini, G., Cardellini, C., Amato, A., Boschi, E., Caliro, S., Frondini, F., and Ventura, G. (2004) Carbon dioxide Earth degassing and seismogenesis in central and southern Italy. *Geophysical Research Letters*, 31(7).
- Chiodini, G., Granieri, D., Avino, R., Caliro, S., Costa, A., Minopoli, C., and Vilardo, G. (2010) Non-volcanic CO₂ Earth degassing: Case of Mefite d'Ansanto (southern Apennines), Italy. *Geophysical Research Letters*, 37(11).
- Dasgupta, R. (2013) In-gassing, storage, and outgassing of terrestrial carbon through geologic time. *Reviews in Mineralogy and Geochemistry*, 75, 183–229.
- Dasgupta, R., and Hirschmann, M.M. (2010a) The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters*, 298(1–2), 1–13.
- (2010b) The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters*, 298(1), 1–13.
- Dasgupta, R., Chi, H., Shimizu, N., Buono, A.S., and Walker, D. (2013) Carbon solution and partitioning between metallic and silicate melts in a shallow magma ocean: Implications for the origin and distribution of terrestrial carbon. *Geochimica et Cosmochimica Acta*, 102, 191–212.
- Deffeyes, K.S. (1965) Carbonate equilibrium: A graphic and algebraic approach I. *Limnology and Oceanography*, 10(3), 412–426.
- DePaolo, D.J. (2015) Sustainable carbon emissions: The geologic perspective. *MRS Energy & Sustainability*, 2.
- Dixon, J.E., and Stolper, E.M. (1995) An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part II: applications to degassing. *Journal of Petrology*, 36(6), 1633–1646.
- Dixon, J.E., Stolper, E.M., and Holloway, J.R. (1995) An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part I: calibration and solubility models. *Journal of Petrology*, 36(6), 1607–1631.
- Dixon, J.E., Clague, D.A., Wallace, P., and Poreda, R. (1997) Volatiles in alkalic basalts from the North Arch Volcanic Field, Hawaii: extensive degassing of deep submarine-erupted alkalic series lavas. *Journal of Petrology*, 38(7), 911–939.
- Doney, S.C., Fabry, V.J., Feely, R.A., and Kleypas, J.A. (2009) Ocean acidification: the other CO₂ problem.
- Dutkiewicz, A., Müller, R.D., Cannon, J., Vaughan, S., and Zahirovic, S. (2018) Sequestration and subduction of deep-sea carbonate in the global ocean since the Early Cretaceous. *Geology*, 47(1), 91–94.
- Evans, M.J., Derry, L.A., and France-Lanord, C. (2008) Degassing of metamorphic carbon dioxide from the Nepal Himalaya. *Geochemistry, Geophysics, Geosystems*, 9(4).
- Facq, S., Daniel, I., Montagnac, G., Cardon, H., and Sverjensky, D.A. (2014) In situ Raman study and thermodynamic model of aqueous carbonate speciation in equilibrium with aragonite under subduction zone conditions. *Geochimica et Cosmochimica Acta*, 132, 375–390.
- Farrar, C., Sorey, M., Evans, W., Howle, J., Kerr, B., Kennedy, B.M., King, C.-Y., and Southon, J. (1995) Forest-killing diffuse CO₂ emission at Mammoth Mountain as a sign of magmatic unrest. *Nature*, 376, 675–678.
- Fine, G., and Stolper, E. (1985) The speciation of carbon dioxide in sodium aluminosilicate glasses. *Contributions to Mineralogy and Petrology*, 91(2), 105–121.
- (1986) Dissolved carbon dioxide in basaltic glasses: concentrations and speciation. *Earth and Planetary Science Letters*, 76(3), 263–278.
- Fogel, R.A., and Rutherford, M.J. (1990) The solubility of carbon dioxide in rhyolitic melts; a quantitative FTIR study. *American Mineralogist*, 75, 1311–1326.
- Foley, S.F., and Fischer, T.P. (2017) An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nature Geoscience*, 10(12), 897.
- Friedlingstein, P., Houghton, R., Marland, G., Hackler, J., Boden, T., Conway, T., Canadell, J., Raupach, M., Ciais, P., and Le Quéré, C. (2010) Update on CO₂ emissions. *Nature Geoscience*, 3, 811–812.
- Garrels, R.M. (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *American Journal of Science*, 283, 641–683.
- Garrels, R., and MacKenzie, F. (1967) Origin of the chemical compositions of some springs and lakes: equilibrium concepts in natural waters systems. *American Chemical Society Advances in Chemistry*, 222–242.
- Gerlach, T. (2011) Volcanic versus anthropogenic carbon dioxide. *Eos, Transactions, American Geophysical Union*, 92(24), 201–202.
- Ghiorso, M.S., and Gualda, G.A. (2015) An H₂O–CO₂ mixed fluid saturation model compatible with rhyolite-MELTS. *Contributions to Mineralogy and Petrology*, 169(6), 1–30.
- Gorman, P.J., Kerrick, D., and Connolly, J. (2006) Modeling open system metamorphic decarbonation of subducting slabs. *Geochemistry, Geophysics, Geosystems*, 7(4).
- Guillot, B., and Sator, N. (2011) Carbon dioxide in silicate melts: A molecular dynamics simulation study. *Geochimica et Cosmochimica Acta*, 75(7), 1829–1857.
- Hauri, E.H., MacLennan, J., McKenzie, D., Gronvold, K., Oskarsson, N., and Shimizu, N. (2018) CO₂ content beneath northern Iceland and the variability of mantle carbon. *Geology*, 46(1), 55–58.
- Hauri, E.H., Cottrell, E., Kelley, K.A., Tucker, J.M., Shimizu, K., Le Voyer, M., Marske, J., and Saal, A.E. (2019) Carbon in the Convecting Mantle. *Earth's Deep Carbon: past to present*. Cambridge.
- Hirschmann, M.M. (2018) Comparative deep Earth volatile cycles: The case for C recycling from exosphere/mantle fractionation of major (H₂O, C, N) volatiles and from H₂O/Ce, CO₂/Ba, and CO₂/Nb exosphere ratios. *Earth and Planetary Science Letters*, 502, 262–273.
- Hirschmann, M.M., and Dasgupta, R. (2009) The H/C ratios of Earth's near-surface and deep reservoirs, and consequences for deep Earth volatile cycles. *Chemical Geology*, 262(1–2), 4–16.
- Hunt, J.A., Zafu, A., Mather, T.A., Pyle, D.M., and Barry, P.H. (2017) Spatially variable CO₂ degassing in the Main Ethiopian Rift: Implications for magma storage, volatile transport, and rift-related emissions. *Geochemistry, Geophysics, Geosystems*, 18(10), 3714–3737.

- Hutchison, W., Mather, T.A., Pyle, D.M., Biggs, J., and Yirgu, G. (2015) Structural controls on fluid pathways in an active rift system: A case study of the Aluto volcanic complex. *Geosphere*, 11(3), 542–562.
- Kelemen, P.B., and Manning, C.E. (2015) Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Sciences*, 112(30), E3997–E4006.
- Kerrick, D.M., and Caldeira, K. (1998) Metamorphic CO₂ degassing from orogenic belts. *Chemical Geology*, 145(3–4), 213–232.
- Kerrick, D., and Connolly, J. (2001) Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature*, 411, 293–296.
- Konschak, A., and Keppler, H. (2014) The speciation of carbon dioxide in silicate melts. *Contributions to Mineralogy and Petrology*, 167(5), 998.
- Lee, C.-T.A., Shen, B., Slotnick, B.S., Liao, K., Dickens, G.R., Yokoyama, Y., Lenardic, A., Dasgupta, R., Jellinek, M., and Lackey, J.S. (2013) Continental arc–island arc fluctuations, growth of crustal carbonates, and long-term climate change. *Geosphere*, 9(1), 21–36.
- Lee, H., Muirhead, J.D., Fischer, T.P., Ebinger, C.J., Kattenhorn, S.A., Sharp, Z.D., and Kianji, G. (2016) Massive and prolonged deep carbon emissions associated with continental rifting. *Nature Geoscience*, 9(2), 145.
- Lee, C.T., Jiang, H., Dasgupta, R., and Torres, M. (2019) A Framework for Understanding Whole-Earth Carbon Cycling. In B. Orcutt, I. Daniel, and R. Dasgupta, Eds., *Earth's Deep Carbon: Past to Present*, pp. 313–357. Cambridge.
- Lenton, T.M., and Britton, C. (2006) Enhanced carbonate and silicate weathering accelerates recovery from fossil fuel CO₂ perturbations. *Global Biogeochemical Cycles*, 20(3).
- Li, J., and Fei, Y. (2003) Experimental constraints on core composition. *Treatise on Geochemistry*, 2, 568.
- Li, J., Chen, B., Mookherjee, M., and Morard, G. (2019) Carbon versus other light elements in Earth's core. In B. Orcutt, I. Daniel, and R. Dasgupta, Eds., *Earth's Deep Carbon: Past to Present*, p. 40–65. Cambridge.
- Lilley, M.D., Butterfield, D.A., Lupton, J.E., and Olson, E.J. (2003) Magmatic events can produce rapid changes in hydrothermal vent chemistry. *Nature*, 422, 878.
- Lund, D.C., Asimow, P.D., Farley, K.A., Rooney, T.O., Seeley, E., Jackson, E.W., and Durham, Z.M. (2016) Enhanced East Pacific Rise hydrothermal activity during the last two glacial terminations. *Science*, 351(6272), 478–482.
- Lupton, J., Lilley, M., Butterfield, D., Evans, L., Emsley, R., Massoth, G., Christenson, B., Nakamura, K.I., and Schmidt, M. (2008) Venting of a separate CO₂-rich gas phase from submarine arc volcanoes: Examples from the Mariana and Tonga-Kermadec arcs. *Journal of Geophysical Research: Solid Earth*, 113(B8).
- Mason, E., Edmonds, M., and Turchyn, A.V. (2017) Remobilization of crustal carbon may dominate volcanic arc emissions. *Science*, 357, 290–294.
- McCammon, C., Bureau, H., Cleaves, H.J. II, Cottrell, E., Dorfman, S.M., Kellogg, L.H., Li, J., Mikhail, S., Moussallam, Y., Sanloup, C., and others. (2020) Deep Earth carbon reactions through time and space. *American Mineralogist*, 105, 22–27.
- Métrich, N., and Wallace, P.J. (2008) Volatile abundances in basaltic magmas and their degassing paths tracked by melt inclusions. *Reviews in Mineralogy and Geochemistry*, 69, 363–402.
- Moore, G. (2008) Interpreting H₂O and CO₂ contents in melt inclusions: constraints from solubility experiments and modeling. *Reviews in Mineralogy and Geochemistry*, 69, 333–362.
- Moore, G., Vennemann, T., and Carmichael, I.S.E. (1998) An empirical model for the solubility of H₂O in magmas to 3 kilobars. *American Mineralogist*, 83, 36–42.
- Morizet, Y., Kohn, S., and Brooker, R. (2001) Annealing experiments on CO₂-bearing jadeite glass: an insight into the true temperature dependence of CO₂ speciation in silicate melts. *Mineralogical Magazine*, 65(6), 701–707.
- Morizet, Y., Vuilleumier, R., and Paris, M. (2015) A NMR and molecular dynamics study of CO₂-bearing basaltic melts and glasses. *Chemical Geology*, 418, 89–103.
- Mörner, N.-A., and Etiope, G. (2002) Carbon degassing from the lithosphere. *Global and Planetary Change*, 33(1), 185–203.
- Moussallam, Y., Morizet, Y., Massuyeau, M., Laumonier, M., and Gaillard, F. (2015) CO₂ solubility in kimberlite melts. *Chemical Geology*, 418, 198–205.
- Moussallam, Y., Florian, P., Corradini, D., Morizet, Y., Sator, N., Vuilleumier, R., Guillot, B., Iacono-Marziano, G., Schmidt, B.C., and Gaillard, F. (2016) The molecular structure of melts along the carbonate–kimberlite–basalt compositional joint: CO₂ and polymerisation. *Earth and Planetary Science Letters*, 434, 129–140.
- Mysen, B.O., Arculus, R., and Eggler, D.H. (1975) Solubility of carbon dioxide in melts of andesite, tholeiite, and olivine nephelinite composition to 30 kbar pressure. *Contributions to Mineralogy and Petrology*, 53(4), 227–239.
- Newman, S., and Lowenstein, J.B. (2002) VolatileCalc: a silicate melt–H₂O–CO₂ solution model written in Visual Basic for excel. *Computers & Geosciences*, 28(5), 597–604.
- Nowak, M., Porbatzki, D., Spickenbom, K., and Diedrich, O. (2003) Carbon dioxide speciation in silicate melts: a restart. *Earth and Planetary Science Letters*, 207, 131–139.
- Ogden, D.E., and Sleep, N.H. (2012) Explosive eruption of coal and basalt and the end-Permian mass extinction. *Proceedings of the National Academy of Sciences*, 109(1), 59–62.
- Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., and Joos, F. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature*, 437, 681.
- Pan, D., and Galli, G. (2016) The fate of carbon dioxide in water-rich fluids under extreme conditions. *Science Advances*, 2(10), e1601278.
- Papale, P., Moretti, R., and Barbato, D. (2006) The compositional dependence of the saturation surface of H₂O+CO₂ fluids in silicate melts. *Chemical Geology*, 229(1–3), 78–95.
- Reichow, M.K., Pringle, M., Al-Mukhamedov, A., Allen, M., Andreichev, V., Buslov, M., Davies, C., Fedoseev, G., Fitton, J., and Inger, S. (2009) The timing and extent of the eruption of the Siberian Traps large igneous province: Implications for the end-Permian environmental crisis. *Earth and Planetary Science Letters*, 277(1), 9–20.
- Saal, A.E., Hauri, E.H., Langmuir, C.H., and Perfit, M.R. (2002) Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature*, 419, 451–455.
- Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C., Wallace, D.W., and Tilbrook, B. (2004) The oceanic sink for anthropogenic CO₂. *Science*, 305, 367–371.
- Saunders, A.D. (2005) Large igneous provinces: origin and environmental consequences. *Elements*, 1(5), 259–263.
- Shirey, S.B., Cartigny, P., Frost, D.J., Keshav, S., Nestola, F., Nimis, P., Pearson, D.G., Sobolev, N.V., and Walter, M.J. (2013) Diamonds and the geology of mantle carbon. *Reviews in Mineralogy and Geochemistry*, 75, 355–421.
- Shishkina, T.A., Botcharnikov, R.E., Holtz, F., Almeev, R.R., Jazwa, A.M., and Jakubiak, A.A. (2014) Compositional and pressure effects on the solubility of H₂O and CO₂ in mafic melts. *Chemical Geology*, 388, 112–129.
- Sleep, N.H., and Zahnle, K. (2001) Carbon dioxide cycling and implications for climate on ancient Earth. *Journal of Geophysical Research: Planets*, 106(E1), 1373–1399.
- Stewart, E.M., Ague, J.J., Ferry, J.M., Schriffies, C.M., Tao, R.-B., Isson, T.T., and Planavsky, N.J. (2019) Carbonation and decarbonation reactions: Implications for planetary habitability. *American Mineralogist*, 104, 1369–1380.
- Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P.M. (2013) Climate change 2013: The physical science basis. Intergovernmental Panel on Climate Change, Working Group I Contribution to the IPCC Fifth Assessment Report (AR5), 25. Cambridge.
- Stolper, E., and Holloway, J.R. (1988) Experimental determination of the solubility of carbon dioxide in molten basalt at low pressure. *Earth and Planetary Science Letters*, 87(4), 397–408.
- Stumm, W., and Morgan, J.J. (1996) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley.
- Sundquist, E.T. (1993) The global carbon dioxide budget. *Science*, 934–941.
- Svensen, H., Planke, S., Polozov, A.G., Schmidbauer, N., Corfu, F., Podladchikov, Y.Y., and Jamveit, B. (2009) Siberian gas venting and the end-Permian environmental crisis. *Earth and Planetary Science Letters*, 277(3), 490–500.
- Sverjensky, D.A., and Huang, F. (2015) Diamond formation due to a pH drop during fluid–rock interactions. *Nature Communications*, 6, 8702.
- Tamburello, G., Pondrelli, S., Chiodini, G., and Rouwet, D. (2018) Global-scale control of extensional tectonics on CO₂ Earth degassing. *Nature Communications*, 9(1), 4608.
- Tutolo, B.M., and Tosca, N.J. (2018) Experimental examination of the Mg-silicate-carbonate system at ambient temperature: Implications for alkaline silicate sedimentation and lacustrine carbonate formation. *Geochimica et Cosmochimica Acta*, 225, 80–101.
- Wallace, P.J., Anderson, A.T., and Davis, A.M. (1999) Gradients in H₂O, CO₂, and exsolved gas in a large-volume silicic magma system: Interpreting the record preserved in melt inclusions from the Bishop Tuff. *Journal of Geophysical Research: Solid Earth*, 104(B9), 20097–20122.
- Werner, C., and Brantley, S. (2003) CO₂ emissions from the Yellowstone volcanic system. *Geochemistry, Geophysics, Geosystems*, 4, 1061, doi:10.1029/2002GC000473.
- Werner, C., Fischer, T.P., Aiuppa, A., Edmonds, M., Cardellini, C., Carn, S., Chiodini, G., Cottrell, E., Burton, M., Shinohara, H., and Allard, P. (2019) Carbon dioxide emissions from subaerial volcanic regions: Two decades in review. In B. Orcutt, I. Daniel, and R. Dasgupta, Eds., *Earth's Deep Carbon: Past to Present*, pp. 188–236. Cambridge University Press.
- Winguth, A.M., Thomas, E., and Winguth, C. (2012) Global decline in ocean ventilation, oxygenation, and productivity during the Paleocene-Eocene Thermal Maximum: Implications for the benthic extinction. *Geology*, 40(3), 263–266.
- Wood, B.J. (1993) Carbon in the core. *Earth and Planetary Science Letters*, 117(3–4), 593–607.
- Wood, B.J., Li, J., and Shahar, A. (2013) Carbon in the core: its influence on the properties of core and mantle. *Reviews in Mineralogy and Geochemistry*, 75, 231–250.
- Wright, V.P. (2012) Lacustrine carbonates in rift settings: the interaction of volcanic and microbial processes on carbonate deposition. *Geological Society, London, Special Publications*, 370, SP370, 2.
- Zachos, J.C., Röhl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E., Nicolo, M., Raffi, I., and Lourens, L.J. (2005) Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science*, 308, 1611–1615.
- Zeebe, R.E., Zachos, J.C., Caldeira, K., and Tyrrell, T. (2008) Carbon emissions and acidification. *Science*, 321, 51–52.
- Zeebe, R.E., Ridgwell, A., and Zachos, J.C. (2016) Anthropogenic carbon release rate unprecedented during the past 66 million years. *Nature Geoscience*, 9(4), 325.

MANUSCRIPT RECEIVED FEBRUARY 1, 2019

MANUSCRIPT ACCEPTED AUGUST 20, 2019

MANUSCRIPT HANDLED BY JIE LI