Magmatic carbon outgassing and uptake of CO₂ by alkaline waters

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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; Mörner 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:

\[ \text{CO}_2(\text{silicate melt}) \rightarrow \text{CO}_2(g) \]  \hspace{1cm} (1)

and

\[ \text{CO}_3^{2-}(\text{silicate melt}) \rightarrow \text{CO}_2(g) + \text{O}_2(\text{silicate melt}) \]  \hspace{1cm} (2)
Carbon exists in many forms in the Earth’s mantle: as fluids, dissolved as oxidized carbonate species (Pan and Galí 2016) or as reduced hydrocarbons (Sverjensky and Huang 2015) or as solid carbonate (Bouard 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 (McCammom 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.](Image)
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 (Chiiodini 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 “Pi parameter” (z, 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 characterizedly 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.
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:

\[
\text{[Alkalinity]} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \tag{5}
\]

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 carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), and carbonate (CO₂⁻). Examination of Equation 5 shows that dissolving/exsolving CO₂(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 CO₃²⁻, CO₂⁻, 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:

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

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 SO₄⁻, 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 (Carling 1979; 1994; Wright 2012). Analyses presented by Carling (1994) demonstrate that weathering of the volcanic rocks feeding East African Rift-hosted lakes provides mainly Na⁺, Ca²⁺, HCO₃⁻, and relatively little Cl⁻ and SO₄⁻ 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. The burning of fossil fuels and the manufacture of cement released 31 000 ± 1 845 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:

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_3^{2-} + 2\text{H}^+ \quad (6)
\]

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 10⁷ 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 Paleocene–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 10⁶–10⁹ years (Lenton and Britton 2006; Archer et al. 2009).

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