Carbonation and decarbonation reactions: Implications for planetary habitability ⚓

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Abstract

The geologic carbon cycle plays a fundamental role in controlling Earth's climate and habitability. For billions of years, stabilizing feedbacks inherent in the cycle maintained a surface environment that could sustain life. Carbonation/decarbonation reactions are the primary mechanisms for transferring carbon between the solid Earth and the ocean–atmosphere system. These processes can be broadly represented by the reaction: $CaSiO_3$ (wollastonite) $+ CO_2$ (gas) $\leftrightarrow CaCO_3$ (calcite) $+ SiO_2$ (quartz). This class of reactions is therefore critical to Earth's past and future habitability. Here, we summarize their significance as part of the Deep Carbon Obsevatory's "Earth in Five Reactions" project. In the forward direction, carbonation reactions like the one above describe silicate weathering and carbonate formation on Earth's surface. Recent work aims to resolve the balance between silicate weathering in terrestrial and marine settings both in the modern Earth system and through Earth's history. Rocks may also undergo carbonation reactions at high temperatures in the ultramafic mantle wedge of a subduction zone or during retrograde regional metamorphism. In the reverse direction, the reaction above represents various prograde metamorphic decarbonation processes that can occur in continental collisions, rift zones, subduction zones, and in aureoles around magmatic systems. We summarize the fluxes and uncertainties of major carbonation/decarbonation reactions and review the key feedback mechanisms that are likely to have stabilized atmospheric CO_2 levels. Future work on planetary habitability and Earth's past and future climate will rely on an enhanced understanding of the long-term carbon cycle.

Keywords: Decarbonation, carbonation, Urey reaction, carbon flux; Earth in Five Reactions: A Deep Carbon Perspective

Introduction

Life has existed on planet Earth for more than three billion years. In that time there have been profound changes in the brightness of the Sun, the temperature of the deep Earth, and even the length of a day, yet throughout all of these changes, the environment has remained stable enough to support life. The global carbon cycle is generally agreed to have played a critical role in maintaining this habitable climate on Earth. Carbon dioxide (CO_2) acts as a greenhouse gas, in effect trapping solar energy and raising the temperature of the planet. Over geologic timescales (about one million years or longer), carbon is exchanged between the solid Earth and the atmosphere. The rate of atmospheric CO_2 removal increases with temperature, thus the exchange acts as a global thermostat, stabilizing atmospheric CO_2 concentrations and therefore moderating Earth's surface temperature. Carbon dioxide is exchanged between the solid Earth and the atmosphere via carbonation reactions such as the archetypal:

$$CaSiO_3 \text{ (wollastonite)} + CO_2 \text{ (gas)} \leftrightarrow CaCO_3 \text{ (calcite)} + SiO_2 \text{ (quartz)} \quad (1)$$
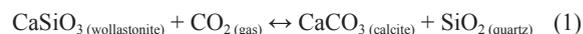
and its reverse, decarbonation:

$$CaCO_3 \text{ (calcite)} + SiO_2 \text{ (quartz)} \leftrightarrow CaSiO_3 \text{ (wollastonite)} + CO_2 \text{ (fluid)} \quad (2)$$

Consequently, these reactions are critical controls on the long-term atmospheric composition, climate, and habitability of Earth, and they form an essential piece of the Deep Carbon Observatory's "Earth in Five Reactions" initiative (introduced by Li et al. 2019). Note that these two simple reactions are used to represent many decarbonation/carbonation reactions involving other cations (especially Mg^{2+}) and other silicate minerals (see below).

Carbonation reactions such as reaction 1 occur when carbon in a gas or fluid reacts with silicate minerals to form a solid, commonly a carbonate mineral. Studies of these reactions have a long history in petrology and geochemistry. As early as 1894, the Swedish chemist Arvid G. Högbom suggested that geologic processes could remove CO_2 from the atmosphere (Högbom 1894; see review by Berner 1995). In particular, the weathering of silicate rocks provides the necessary chemistry to form carbonate minerals, ultimately transforming gaseous CO_2 into solid rock. This fundamental carbonation reaction was discussed in detail

by Nobel Prize-winning chemist Harold Urey more than 50 years later. In his 1952 book, *The Planets*, Urey rearticulated the relationship between carbonate and silicate rocks, writing reaction 1, known today as one of the "Urey reactions." Furthermore, he suggested that such reactions have controlled atmospheric CO_2 concentrations throughout Earth history.

Decarbonation (e.g., reaction 2) generally occurs when a rock containing carbonate minerals, such as a siliceous limestone, is metamorphosed at elevated temperatures and pressures. Victor Moritz Goldschmidt (1912) was the first to recognize the significance of metamorphic decarbonation. Goldschmidt noted that the minerals quartz (SiO_2) and calcite ($CaCO_3$) react to form wollastonite ($CaSiO_3$) and CO_2 gas when a rock is heated to a high enough temperature; his work was among the earliest to use thermodynamic principles to calculate a mineral equilibrium and to quantitatively constrain the conditions of metamorphism.

Norman L. Bowen (1940) demonstrated that, depending on bulk composition, 13 different decarbonation reactions might occur as a siliceous limestone or dolomite is progressively heated. In 1956, Harker and Tuttle produced wollastonite in the laboratory via reaction 2. Their experiments more tightly constrained the *P-T* (pressure-temperature) conditions of reaction, yet, remarkably, Goldschmidt's thermodynamic estimate from more than 40 years earlier was close to their result.

Today, researchers continue to study carbonation/decarbonation reactions in essentially all of Earth's geotectonic settings (Fig. 1) through numerical simulations, measurements of modern CO_2 fluxes, and examination of the history preserved in the rock record. A detailed accounting of the rates, timing, location, and magnitude of these reactions is essential to understanding CO_2 fluxes and our planet's past, present, and future habitability.

CARBONATION

The Urey reactions

The two Urey reactions, one of which is mentioned above, are the quintessential exemplars of carbonation reactions on Earth. The other reaction is quite similar to reaction 1 and may run in parallel. The only difference is that it involves the Mg^{2+} cation instead of Ca^{2+}:

$$MgSiO_{3\ (enstatite)} + CO_{2\ (gas)} \leftrightarrow MgCO_{3\ (magnesite)} + SiO_{2\ (quartz)}. \quad (3)$$

From here forward we will focus our discussion on reaction 1, but note that reaction 3 functions essentially identically (Urey 1952).

In fact, reactions 1 and 3 as written do not often occur on the surface of the Earth. For one, the mineral wollastonite actually makes up very little of the Earth's crust. About 50% of the crust is composed of feldspars (e.g., Ronov et al. 1990). These are also silicate minerals, but with more complicated chemistry and extensive solid solution. Plagioclase feldspars, for example, are a solid solution between $CaAl_2Si_2O_8$ (anorthite) and $NaAlSi_3O_8$ (albite). In nature, weathering of these more complex Ca-bearing silicates may produce phases in addition to calcite and quartz, such as aluminous clays. Similarly, reaction 3 references the carbonate mineral magnesite, which is also relatively rare on Earth's surface in its pure form. Thus reactions 1 and 3 are used as exemplars of carbonation reactions in general but do not reflect the typical mineralogy involved.

Additionally, on Earth's surface, carbonation reactions involve a series of reaction steps as follows (after Siever 1968).

First, CO_2 gas in the atmosphere is dissolved in water (H_2O) to form carbonic acid (H_2CO_3):

$$CO_{2\ (gas)} + H_2O_{(liquid)} \leftrightarrow H_2CO_{3\ (aqueous)}. \quad (1A)$$
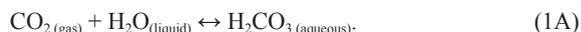
This carbonic acid can dissociate to form a negatively charged bicarbonate anion (HCO_3^-) and positively charged H^+ cation:

$$H_2CO_{3\ (aqueous)} \leftrightarrow HCO_{3\ (aqueous)}^- + H_{(aqueous)}^+. \quad (1B)$$
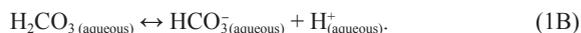
The acidity (H^+ cations) in the water allows a calcium-bearing silicate mineral, here wollastonite ($CaSiO_3$), to dissolve and form silicic acid (H_4SiO_4):

$$CaSiO_{3\ (wollastonite)} + 2H_{(aqueous)}^+ + H_2O_{(liquid)} \leftrightarrow Ca_{(aqueous)}^{2+} + H_4SiO_{4\ (aqueous)}. \quad (1C)$$
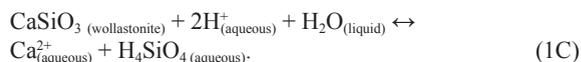
The Ca^{2+} cation is now free to react with the HCO_3^- anions to form the mineral calcite ($CaCO_3$), more CO_2, and water:
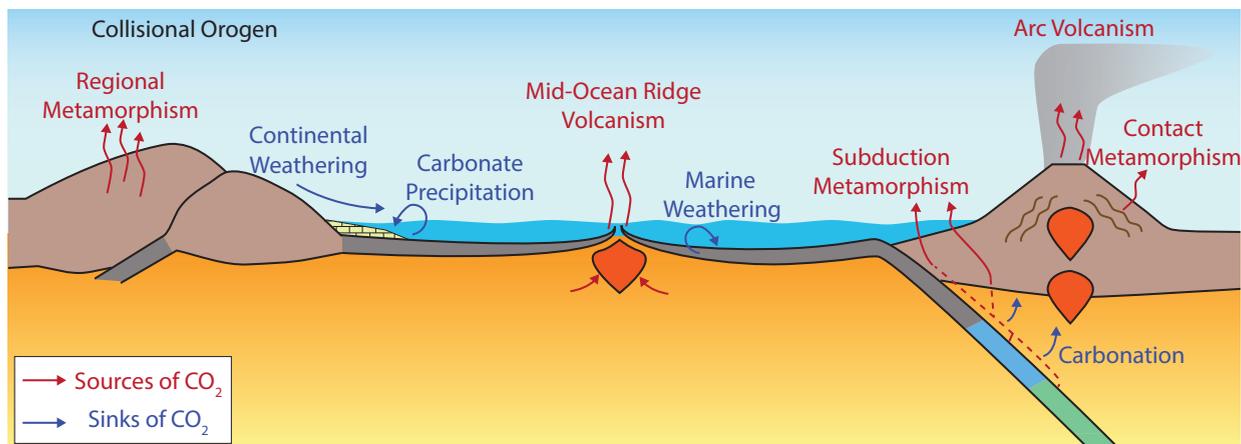
FIGURE 1. Schematic cross section showing the tectonic context of major carbonation/decarbonation processes. Sources of atmospheric CO_2 are indicated in red, whereas sinks are in blue.

$$Ca^{2+}_{(aqueous)} + 2HCO^-_{3\,(aqueous)} \leftrightarrow$$
$$CaCO_{3\,(calcite)} + CO_{2\,(gas)} + H_2O_{(liquid)}. \qquad (1D)$$
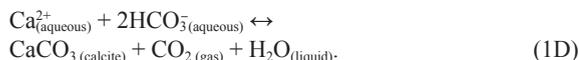
Finally, the mineral quartz (SiO_2) may grow from the silicic acid in solution with more water as a by-product:

$$H_4SiO_{4\,(aqueous)} \leftrightarrow SiO_{2\,(quartz)} + 2H_2O_{(liquid)}. \qquad (1E)$$
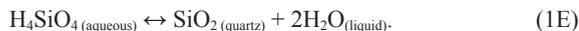
We can sum up these five sub-reactions (doubling reactions 1A and 1B for balance) to make one total reaction:

$$2CO_{2\,(g)} + 3H_2O_{(l)} + 2H_2CO_{3\,(aq)} + CaSiO_{3\,(wol)} + 2H^+_{(aq)} +$$
$$Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} + H_4SiO_{4\,(aq)} \leftrightarrow$$
$$2H_2CO_{3\,(aq)} + 2HCO^-_{3\,(aq)} + 2H^+_{(aq)} + Ca^{2+}_{(aq)} +$$
$$H_4SiO_{4\,(aq)} + CaCO_{3\,(cc)} + CO_{2\,(g)} + 3H_2O_{(l)} + SiO_{2(q)} \qquad (1F)$$
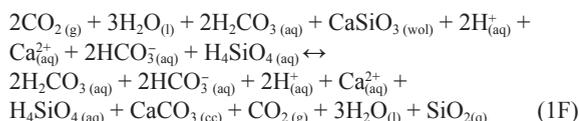
and by cancelling species present on both sides of the reaction return to the simplified reaction 1.

This reaction sequence has several important aspects to note. First, there are some nuances of the full reaction 1F that one cannot observe in the simplified reaction 1. For example, the full reaction 1F is only 50% efficient at storing CO_2; for every two molecules of CO_2 that are dissolved in water, only one molecule is transformed into calcite while the other molecule is re-released as CO_2 gas. Second, note also that each of the steps may occur at a different point in space and time. A silicate mineral may weather and dissolve in a river in the middle of a continent (reaction 1C), but the Ca^{2+} ion may travel thousands of kilometers before forming calcite in the ocean (reaction 1D). Since the evolution of marine calcifiers, carbonate mineral precipitation has often been facilitated by biological processes (e.g., the formation of a foraminifera skeleton), although abiotic precipitation also occurs. In either case, the formation of carbonate minerals from solution functions as a key piece of this Urey reaction sequence.

The most important take-away from the Urey reactions is this: surface carbonation reactions are a major sink for atmospheric CO_2. In fact, more than 99% of all carbon in the crust, biosphere, and ocean-atmosphere system is stored in sedimentary and metasedimentary rocks (e.g., Archer 2010). Throughout Earth history, carbonation has been the primary way that CO_2 is removed from the atmosphere (Urey 1952), and without this process life on Earth could not exist (e.g., Berner and Caldeira 1997). For comparison, consider our neighboring planet, Venus, where the Urey reactions rarely occur. Much less carbon is stored in the solid rock of Venus, thus the Venusian atmosphere contains massive amounts of CO_2, contributing to average surface temperatures of more than 400 °C (Sagan 1962).

Silicate weathering

On geologic timescales, silicate weathering is the rate-limiting step of the Urey reaction. Because CO_2 dissolution, carbonic acid dissociation, and the other intermediate reactions occur relatively quickly, the availability of silicate-bound Ca^{2+} (or Mg^{2+}) (reaction 1C) is of critical importance. This can be thought of in terms of the seawater's alkalinity, that is, its ability to neutralize acid. Silicate weathering increases the alkalinity of the seawater that drives carbonate precipitation. Note that any contribution to total alkalinity drives carbonation, thus weathering of Mg-silicate minerals could ultimately drive the formation of Ca-carbonates.

Traditionally, geologists have considered continental rocks to be the primary contribution to global silicate weathering (e.g., Walker et al. 1981; Berner et al. 1983). Continental weathering depends on a sequence of discrete processes. First, continental rocks must be exposed at Earth's surface. Surface rocks are then physically (or mechanically) weathered, that is, broken apart into smaller pieces. Chemical weathering can then occur on the exposed surfaces (as seen in Fig. 2a), partially dissolving the rock and releasing aqueous ions (i.e., reaction 1C). There is a positive association between physical and chemical weathering–mineral dissolution can contribute to denudation while physical weathering can expose more reactive surface area and facilitate chemical weathering. The ions resulting from weathering are transported by rivers and ultimately delivered to the ocean where they continue along the Urey reaction sequence.

Many key factors can affect the rate of continental weathering. For example, tectonic collisions that form high mountain belts help to expose more rock at Earth's surface, which may increase
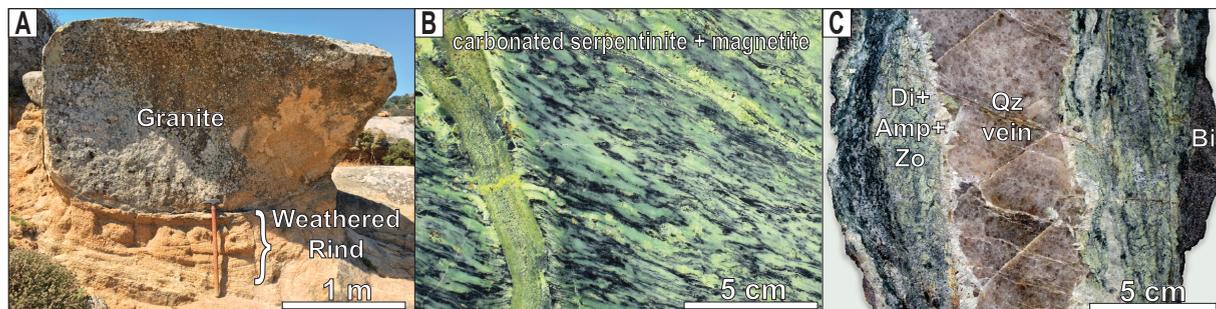
FIGURE 2. Photographs of carbonation/decarbonation processes. (**a**) Silicate weathering: granite exposed at Earth's surface undergoes spheroidal weathering resulting in discrete boulders with thick physical and chemical weathering rinds. Volax, Tinos Island, Greece. (**b**) High-temperature carbonation: yellow Ni-bearing calcite has precipitated in an ultramafic rock of the Maltby Lakes Metavolcanics, Connecticut. (**c**) Infiltration-driven decarbonation: quartz vein (center; Qz) with diopside (Di) + amphibole (Amp) + zoisite (Zo) selvages cutting biotite-bearing metacarbonate rock (dark margins; Bi) of the Wepawaug Schist, Connecticut. Prograde reactions, such as Phlogopite + 3 Calcite + 6 Quartz = 3 Diopside + K-feldspar + 3 CO_2 + H_2O, generated significant CO_2 (Ague 2003; Stewart and Ague 2018).

the potential for weathering (e.g., Raymo and Ruddiman 1992; Edmond et al. 1995; Dessert et al. 2003). Increased precipitation can lead to more physical erosion, and the additional water can also drive more chemical weathering (H_2O is a necessary reactant in reaction 1C) (Jenny 1941; Loughnan 1969; Amiotte et al. 1995; White and Blum 1995; Maher and Chamberlain 2014). At higher temperatures any chemical reaction will have a faster reaction rate (Arrhenius 1915); thus, increasing surface temperatures may result in faster continental weathering (Walker et al. 1981; Berner et al. 1983; Manabe and Stouffer 1993).

Marine weathering

More recently, some researchers have proposed that marine weathering processes have an important role to play in global carbon cycling (e.g., Staudigel et al. 1989; Brady and Gíslason 1997; Wallmann et al. 2008; Coogan and Gillis 2013; Coogan and Dosso 2015). The concept is the same; silicate minerals undergo chemical reaction that supplies alkalinity to the oceans and helps form carbonate minerals. Marine weathering can occur within the marine sediment pile (e.g., Wallmann et al. 2008; Solomon et al. 2014) or in basalts in "off axis" hydrothermal systems (Coogan and Dosso 2015). Evidence for chemical weathering of silicate minerals within the sediment pile comes from deep anoxic (oxygen-free) sediments (Wallmann et al. 2008; Solomon et al. 2014).

In "off-axis" hydrothermal systems, large amounts of seawater flow through the oceanic crust (off-axis simply refers to the fact that these systems are not located directly adjacent to mid-ocean ridge volcanoes). Along its flow path the water is heated to moderate temperatures (tens of degrees Celsius) and dissolves silicate minerals as in reaction 1C. Once again, this dissolution delivers the alkalinity that allows carbonate minerals to form (e.g., Staudigel et al. 1989; Brady and Gíslason 1997; Gillis and Coogan 2011). Hydrothermal circulation may also affect ultramafic rocks, creating carbonated serpentinites in both mid-ocean ridge and off-axis systems (Kelemen et al. 2011). The impact these marine processes have on global carbon cycling may be just as significant as the effect of continental weathering (e.g., Wallmann et al. 2008; Coogan and Dosso 2015).

Reverse weathering

Reverse weathering refers to the formation of silicate clay minerals from solution. It is "reverse" weathering in the sense that it consumes the alkalinity and silica that the forward silicate weathering reaction 1C provides (Sillén 1961; Garrels 1965; Mackenzie and Garrels 1966). Reverse weathering is regarded as a net positive source of atmospheric CO_2. In other words, reverse weathering allows for efficient recycling of carbon within the ocean-atmosphere system, elevating atmospheric CO_2 concentrations. Recent work suggests that changes in the amount of reverse weathering may have had profound climatic impacts over the course of Earth history (Isson and Planavsky 2018).

High-temperature carbonation in subduction zones and orogens

Carbonation reactions also take place deeper in Earth and at higher pressure-temperature conditions. High-temperature carbonation occurs via many different reactions that are ex-

emplified by reaction 1. When CO_2-bearing fluid infiltrates a silicate rock (especially a mafic or ultramafic rock with a high concentration of Mg^{2+}) this fluid may react with the silicate minerals, removing CO_2 from the fluid phase and forming new carbonate minerals (see Fig. 2b). The particular silicate minerals involved in the reaction will depend upon the rock composition and the P-T conditions.

One locus of such carbonation is the mantle wedge above a subducting slab (Falk and Kelemen 2015; Piccoli et al. 2016, 2018; Scambelluri et al. 2016). As oceanic crust is subducted into the mantle, it releases fluid into the overriding plate. This fluid may be dominantly H_2O, but subduction zone decarbonation reactions may supply CO_2 as well (see section on decarbonation). The ultramafic rocks of the mantle are highly reactive with CO_2 fluids, so when the slab-derived fluid rises into the mantle, carbonation reactions are fast (Sieber et al. 2018). Because the degree of carbonation increases with lower temperatures (Sieber et al. 2018), mantle wedge carbonation probably dominates in the cooler (but still hot at $< \sim700$ °C) fore-arc region and is less pronounced in the hotter mantle directly below the volcanic arc.

The fate of this carbonated mantle is not well known. It may serve as a location of long-term deep carbon storage (Kelemen and Manning 2015). Alternatively, melting of carbonated mantle material may ultimately contribute CO_2 to the atmosphere when the melt erupts from overlying arc volcanoes (Kerrick and Connolly 2001; Gorman et al. 2006; Kelemen and Manning 2015; Mason et al. 2017).

Similar high-temperature carbonation of ultramafic rocks can also occur in orogenic belts during prograde regional (Evans and Trommsdorff 1974; Ferry et al. 2005) and contact (Ferry 1995) metamorphism. In addition, fluid infiltration during retrograde metamorphism (i.e., metamorphism as rocks cool down from peak T) may drive carbonation reactions. For example, the mineral wollastonite is stable at high temperatures (see below). As the temperature falls, the wollastonite will react with any available CO_2 to create calcite and quartz (Ferry 2000). Critically, this retrograde carbonation reaction cannot occur in the absence of a CO_2-bearing fluid (Tian and Ague 2014).

DECARBONATION

Decarbonation reactions, such as reaction 2, are a major source of atmospheric CO_2 in geologic history. In the example reaction, a carbonate mineral (calcite) reacts with a silicate mineral (quartz) to form the Ca-silicate mineral wollastonite and CO_2. Reaction 2 represents myriad decarbonation reactions that all share these features: (1) a carbonate mineral reacts with a silicate mineral, (2) a new silicate mineral is formed using divalent cations from the carbonate (e.g., Ca^{2+}, Mg^{2+}, ...), and (3) CO_2 is released. (Rarely, decarbonation reactions may occur in the absence of silicate minerals when a carbonate mineral breaks down into a mineral oxide and CO_2.)

Increasing temperature drives decarbonation. Certain carbonate–silicate mineral assemblages (such as calcite and quartz) are only stable together up to a certain temperature at a given pressure and fluid composition. When the temperature rises beyond that point, they react and release CO_2 (Goldschmidt 1912; Bowen 1940; Harker and Tuttle 1956). Figure 4 is a P-T phase diagram showing that mineral assemblage is stable at a
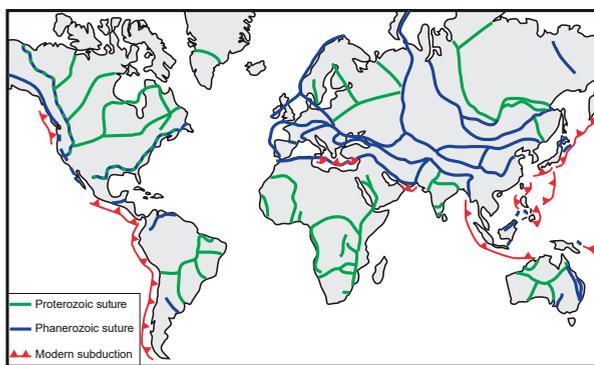
FIGURE 3. Global map indicating the locations of modern subduction (red lines with carets), and ancient sutures formed in the Phanerozoic (blue) and Proterozoic (green). Sutures that were active during both eons are dashed blue and green. Modified after Orme (2015) and Burke et al. (1977).

given *P-T* condition and fluid composition.

Therefore, these reactions generally occur when a mixed carbonate-silicate rock undergoes significant increases in temperature and pressure (Goldschmidt 1912; Bowen 1940; Harker and Tuttle 1956). On Earth, this can take place via prograde metamorphism, that is, metamorphism of a rock driven in part by increasing temperature. Geologists recognize different categories of metamorphism relating to different tectonic environments (Fig. 1).

Contact metamorphism

Contact metamorphism occurs when a magma intrudes into solid rocks, and so can be located anywhere volcanism and/or magmatism are active (Delesse 1858). In contact metamorphism, rocks are not necessarily tectonically buried; they are simply heated by the adjacent magma. Therefore, pure contact metamorphism is associated with higher geothermal gradients (e.g., high temperatures at relatively low pressures) compared to regional metamorphism. Additionally, it is more restricted in area, occurring in haloes (aureoles) around magmatic intrusions. It has been suggested that degassing in contact aureoles around large igneous provinces drove catastrophic global warming associated with some of Earth's largest mass extinctions (e.g., Ganino and Arndt 2009; Burgess et al. 2017), but the relative importance of this metamorphism remains debated (e.g., Nabelek et al. 2014).

Regional metamorphism

Regional-scale metamorphism takes place where two tectonic plates converge and ultimately collide (subduction zones and continental collisions) or pull apart (e.g., continental rifts) (Kennedy 1948; Miyashiro 1972). Figure 3 shows a map of both modern and ancient collisional belts on Earth. As can be seen, such convergent plate boundaries are common features. During regional-scale metamorphism, rocks are subjected to both high pressures (~0.2 to more than 2.0 GPa) and high temperatures (~250 up to ~1000 °C). Note that wollastonite is a relatively uncommon mineral in regionally metamorphosed rocks, and other silicate minerals, such as biotite and plagioclase, are more commonly produced (Ferry 1988).

Decarbonation in subduction zones

Subduction zones are a particularly important setting of CO_2 exchange. As oceanic crust sinks into the mantle, it brings carbon-bearing minerals into the deeper Earth (Plank and Langmuir 1998). However, metamorphic decarbonation reactions in both the subducting slab and the overriding plate may consume carbonate minerals and release CO_2 back toward the surface. Thus, subduction may transfer carbon from the crust into the ocean-atmosphere system or into the deep mantle.

Another mechanism of CO_2 production has recently been documented in subduction zones. In the presence of a fluid, carbonate minerals may undergo congruent carbonate dissolution such as:

$$CaCO_{3 \, (calcite)} + 2H^+_{(aq)} \leftrightarrow H_2O_{(fluid)} + Ca^{2+}_{(aq)} + CO_{2 \, (aq)} \qquad (4)$$

(Frezzotti et al. 2011; Ague and Nicolescu 2014). The $CO_{2(aq)}$ in reaction 4 represents aqueous carbon species in general; carbonate and bicarbonate ions (Pan and Galli 2016), as well as organic carbon species (Sverjensky et al. 2014), may be more important at depth. This reaction is different from reaction 2 in two important ways: First, it does not require the presence of a silicate mineral to proceed, and it could, therefore, occur in a pure carbonate rock. Second, it has the potential to be highly efficient at releasing carbon. For example, in subducted rocks on the Greek islands of Syros and Tinos, carbonate dissolution released 60–90% of the solid carbon from some rocks, while decarbonation reactions might be expected to release considerably less (Ague and Nicolescu 2014). Thus, a small proportion of carbonate dissolution could have a relatively large effect.

Whatever the decarbonation mechanism, CO_2 released by subducting rocks may follow several paths. It could flow through the many kilometers of overriding lithosphere (or perhaps along the subduction interface) to escape to the atmosphere as part of a diffuse (i.e., spatially widespread) metamorphic flux (e.g., Sakai et al. 1990; Sano and Williams 1996; Campbell et al. 2002), or it could become trapped in the overlying mantle wedge by a carbonation reaction (e.g., Piccoli et al. 2016, 2018; Scambelluri et al. 2016; Sieber et al. 2018). Once in the mantle wedge, that carbon could be stored for millions of years. If carbonated mantle melts, however, this carbon could form part of a magma and ultimately be released to the atmosphere as part of the arc volcanic CO_2 flux (Varekamp et al. 1992; Kelemen and Manning 2015; Poli 2015). Thus, decarbonation in a subducted slab could contribute CO_2 to both a diffuse metamorphic flux and the associated volcanic flux.

Decarbonation reactions also occur in the overriding plate in subduction zones, driven by elevated temperatures from magma ascent and magmatic dewatering that would result in aqueous fluid infiltration. This decarbonation flux should be more significant in continental arcs with thick carbonate layers and less prominent when subduction occurs beneath oceanic crust (i.e., island arcs). Lee et al. (2013) recognized a relationship between total continental arc length and global temperature in the past. They suggested that contact metamorphism-driven decarbonation in these continental arcs may be an important source of atmospheric CO_2.
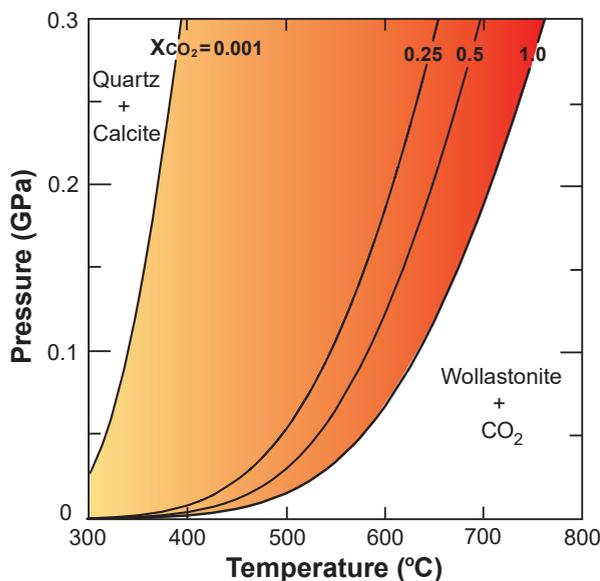
FIGURE 4. Pressure-Temperature diagram showing the stability of the assemblage calcite + quartz relative to wollastonite + CO_2. Conditions of this reaction are calculated for equilibrium between minerals and fluid of differing CO_2 content (X_{CO_2} is the mole fraction of CO_2 in fluid). Calculations made using the program Theriak-Domino (de Capitani and Petrakakis 2010) with the Holland and Powell (1998) database.

Infiltration-driven decarbonation

The presence of a water-bearing fluid (either liquid or gas) has a profound effect on the stability of carbonate minerals. Metamorphism in a closed system will not evolve much CO_2 until relatively high temperatures are reached (Greenwood 1975). On the other hand, infiltration of a water-rich fluid into a reactive rock can depress the required temperature of a given decarbonation reaction (e.g., Ferry 1976, 2016; Kerrick 1977; Tracy et al. 1983; Ague 2002; Penniston-Dorland and Ferry 2006). This can be observed in zones of enhanced decarbonation around fluid conduits, as shown in Figure 2c. Classic studies in the metamorphic belts of the Appalachian Mountains were among the first to demonstrate that fluid infiltration was essential for driving reactions and releasing CO_2 (e.g., Ferry 1978, 1980; Rumble et al. 1982; Tracy et al. 1983).

As a demonstration, we calculate the *P-T* conditions of reaction 2. Figure 4 is a *P-T* phase diagram showing the mineral assemblage that is stable at a given *P-T* condition and fluid composition. When the X_{CO_2} (the mole fraction of CO_2) in an H_2O–CO_2 fluid is low, the reaction can occur at a much lower temperature. For example, at 0.2 GPa the reaction occurs at ~350 °C when $X_{CO_2} = 0.001$ and ~700 °C when $X_{CO_2} = 1.0$ (Fig. 4).

This effect has two important implications. First, a rock that is metamorphosed in the presence of a water-bearing fluid can release over 500% more CO_2 than the metamorphism of the same rock in a closed system at the same pressure and temperature (Stewart and Ague 2018). This enhanced decarbonation could ultimately result in a greater concentration of CO_2 in the atmosphere and a correspondingly higher global surface temperature. Second, CO_2 generated by infiltration is automatically released into a regional fluid flow system that provides the mechanism for transporting evolved CO_2 from the deep crust to the atmosphere and hydrosphere.

DISCUSSION: CARBON FLUXES AND PLANETARY HABITABILITY

Carbonation/decarbonation reactions play a vital role in carbon transfer on Earth. To understand how these reactions relate to planetary habitability, we must consider how different processes interact and balance through the long-term (geologic) carbon cycle. A great deal of the work done by geochemists focuses on constraining the magnitudes of major geologic carbon fluxes. These fluxes are broadly divided into sources (inputs into the ocean-atmosphere system) and sinks (outputs from the ocean-atmosphere system). Thus, decarbonation reactions are sources of atmospheric CO_2, and carbonation reactions are sinks (Fig. 5).

Carbonation reaction fluxes

It is generally agreed that the primary long-term sink of CO_2 from the ocean-atmosphere system is the precipitation of carbonate rocks using alkalinity derived from silicate weathering (the Urey reactions). The continental silicate weathering flux can be estimated from measurements of river discharge, although on a very heterogeneous planet there are many complexities to consider. Nevertheless, continental silicate weathering is estimated, with reasonable uncertainty, to consume ~11.5 to 23 Tmol CO_2 yr^{-1} (e.g., Gaillardet et al. 1999 and references therein).

The marine silicate weathering flux is less studied. One estimate of CO_2 drawdown resulting from chemical weathering of deep-sea sediments is ~5 to ~20 Tmol CO_2 yr^{-1}, comparable in magnitude to the continental flux (Wallmann et al. 2008). Off-axis carbonation of basaltic oceanic crust may provide an additional sink of ~0.2 to ~3.7 Tmol CO_2 yr^{-1} (e.g., Coogan and Gillis 2018 and references therein). However, reverse weathering recycles some CO_2 back into the surface environment, effectively acting as a source of ~0.5 to ~1.25 Tmol CO_2 yr^{-1} (Isson and Planavsky 2018).

Decarbonation reaction fluxes

Earth's major decarbonation reaction fluxes are the result of metamorphic outgassing reactions in continental collisions, subduction zones, and contact metamorphic aureoles. Metamorphism in continental rifts is less well-studied, but it may also make a significant contribution.

Metamorphic outgassing in continental collisions has primarily been studied at the regional scale. As shown by Stewart and Ague (2018), multiple estimates from ancient and modern mountain belts converge on an area-normalized flux of ~0.5 × 10^6 to ~7 × 10^6 moles CO_2 km^{-2} yr^{-1} (Kerrick and Caldeira 1998; Chiodini et al. 2000; Becker et al. 2008; Skelton 2011). These estimates are derived from independent, quite disparate methods, ranging from thermodynamic modeling of metacarbonate rocks in the Appalachians (Stewart and Ague 2018) to modern direct measurements of CO_2 escaping from springs in the Himalayas and Italian Apennines (Chiodini et al. 2000; Becker et al. 2008). The agreement between estimates from deeply exhumed rocks and measurements at Earth's surface suggests that most devolatilized CO_2 is ultimately released to the ocean-atmosphere system. We can multiply this areal flux estimate by the area of active continental collision for a rough global collisional metamorphic flux. The present area, dominated by the Himalayas with the area ~7.5 × 10^5 km^2 (Becker et al. 2008), is estimated on the order

Modern Flux to Ocean - Atmosphere System
(Tmol yr^{-1})
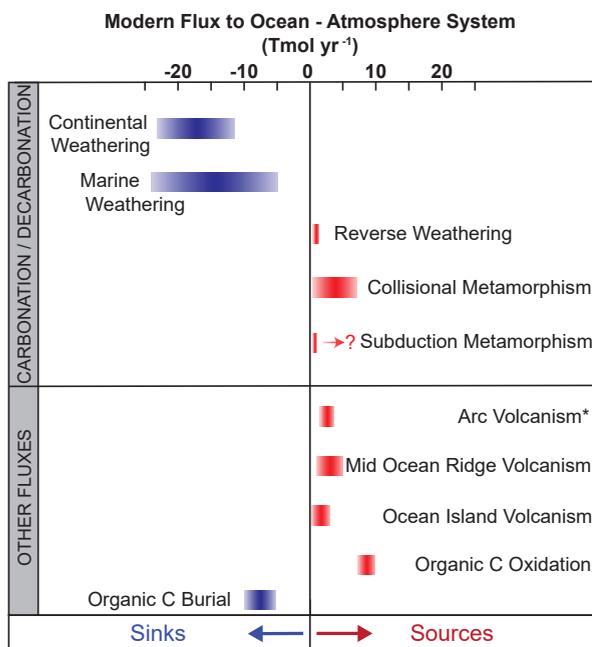
FIGURE 5. Estimates of modern CO_2 fluxes to the ocean-atmosphere system. Error bars indicate a range of possible values, not necessarily a normal distribution. * Note that the flux from Arc Volcanism includes some contribution from decarbonation of subducting slabs; in fact, slab decarbonation could account for the vast majority of the arc volcanic flux. Arc magmas may also incorporate partially melted carbonate lithologies and drive contact metamorphism in adjacent rocks.

of ~10^6 km^2. The resultant estimated global flux is ~0.5 to ~7 Tmol CO_2 yr^{-1}, but note that this value is not constant through geologic time (Fig. 3).

Estimates of metamorphic degassing fluxes at subduction zones also cover a considerable range. In their compilation, Kelemen and Manning (2015) estimate ~0.3 to ~4.9 Tmol CO_2 yr^{-1} are released from the slab via metamorphic reaction and dissolution. This estimate in itself carries significant uncertainties, largely due to uncertainties in the degree and nature of fluid infiltration during metamorphism. Closed-system calculations predict that the majority of subducted carbon is not released (e.g., the negligible flux estimate from Kerrick and Connolly 2001). Models that allow for fluid infiltration predict more decarbonation (e.g., 0.35 to 3.12 Tmol CO_2 yr^{-1}, Gorman et al. 2006), with intermediate fluxes also suggested (Cook-Kollars et al. 2014). Carbonate dissolution, only recently identified in subduction zones (e.g., Ague and Nicolescu 2014), could significantly increase these estimates.

In addition, it is highly uncertain what proportion of the devolatilized CO_2 makes it to the atmosphere (either escaping through arc volcanoes or through its own diffuse outgassing) and how much is stored in the overlying lithosphere. Kelemen and Manning (2015) report a diffuse outgassing flux of ~0.3 to 1.0 Tmol CO_2 yr^{-1}, but emphasize that they suspect it might actually be much larger.

Contact metamorphism, though spatially limited, has the potential to contribute large quantities of CO_2. High temperature–low pressure conditions can drive decarbonation reactions such as reaction 2 particularly efficiently. Contact metamorphism, in particular, may occur over short timescales (e.g., Lyubetskaya and Ague 2010). The total contact metamorphic flux is difficult to estimate, but some researchers suggest it has played an important role in changing climate conditions through Earth history (e.g., Lee et al. 2013).

Although our discussion of CO_2 sources is focused on decarbonation reaction fluxes, we can compare their magnitudes to other important CO_2-generating fluxes. Typical estimates for the three major volcanic fluxes in the modern era are as follows: ~1.5 to ~3.1 Tmol CO_2 yr^{-1} for arc volcanism (Marty and Tolstikhin 1998; Hilton et al. 2002; Dasgupta and Hirschmann 2010), ~0.5 to ~5.0 Tmol CO_2 yr^{-1} for mid-ocean ridge volcanism (Marty and Tolstikhin 1998; Dasgupta and Hirschmann 2006, 2010; Le Voyer et al. 2019) and ~0.12 to ~3 Tmol CO_2 yr^{-1} from ocean island volcanoes (Marty and Tolstikhin 1998; Dasgupta and Hirschmann 2010). Volcanogenic CO_2 may also reach the atmosphere via diffuse outgassing (Allard 1992). Organic carbon weathering is somewhat larger at ~7.5 to ~10 Tmol CO_2 yr^{-1} (Holland 1978; Kump and Arthur 1999), but is largely balanced out by the organic carbon burial flux of ~5.3 to ~10 Tmol CO_2 yr^{-1} (Berner 1982; Kump and Arthur 1999). Thus, metamorphic outgassing fluxes are of the same order of magnitude as other major source fluxes. Metamorphic decarbonation reactions are therefore more important to the net global carbon budget than is often appreciated (Fig. 5).

Earth's habitability and the need for balance

It has been commonly argued that surface temperatures on Earth have been remarkably stable for billions of years. Sedimentary rocks record the presence of liquid water since at least ~3.8 billion years ago (Lowe 1980), which requires global surface temperatures to remain between 0 and 100 °C for a vast amount of time. Some researchers suggest there is evidence for liquid water even earlier (e.g., 4.3 billion years ago by Mojzsis et al. 2001; 4.4 billion years ago by Wilde et al. 2001).

In an apparent contradiction, the Sun has been increasing in luminosity and, therefore, supplying more heat to Earth over time. It is estimated that the sun's luminosity in early Earth history was only ~70% of the modern intensity (Sagan and Mullen 1972); thus, one might expect Earth's temperature to have changed markedly in response to these changes in incoming solar energy. As Sagan and Mullen pointed out in 1972, an Earth with today's atmospheric composition would have been completely frozen (below 0 °C) until about 2 billion years ago. This is at odds with geologic evidence for a warm climate early in Earth's history (e.g., Knauth and Epstein 1976). This logical problem has been referred to as the "Faint Young Sun Paradox," and remains the subject of active debate today (see Kasting 2010). However, one simple solution to this paradox lies in Earth's atmosphere. A more carbon-rich atmosphere would result in a more intense greenhouse effect and, perhaps, higher surface temperatures even with a weaker sun (Owen et al. 1979; Walker et al. 1981).

On the other side of the spectrum, Earth has likewise never become too hot since the emergence of the earliest life forms. If CO_2 concentrations became extremely high, the temperature could skyrocket and the oceans could boil. Thus, we find ourselves on a type of Goldilocks planet: CO_2 concentrations never get excessively high or excessively low, but, within relatively

narrow limits, they remain just right.

In their classic analysis, Berner and Caldeira (1997) argue that this cannot be a coincidence. On long timescales, the amount of CO_2 added to the atmosphere must equal the amount of CO_2 removed. Without this balance, atmospheric CO_2 concentrations would run-away, resulting in an extreme hot house or ice house climates. Berner and Caldeira (1997) demonstrate this with a simple calculation of the effect of only small (25%) imbalances between CO_2 inputs and outputs (Fig. 6).

Major CO_2 fluxes have been changing throughout Earth history. To maintain balance, then, some stabilizing mechanism or negative feedback must be in place, ensuring that inputs and outputs eventually reach a steady state. By simply summing modern flux estimates (Fig. 5), we find that the predicted net change of the atmospheric reservoir is between ~ -45 and $\sim +11$ Tmol CO_2 yr^{-1}. This estimate does overlap the necessary value of zero net change, but the large uncertainty is obvious. Nonetheless, we can outline several different end-member Earth states. With high weathering rate estimates (e.g., with large marine weathering fluxes; Wallmann et al. 2008; Coogan and Gillis 2018) upper-end-member outgassing rates are required. High amounts of reverse weathering (e.g., Rahman et al. 2017) could also help balance high silicate weathering rates with outgassing estimates. In contrast, in the traditional view—where silicate weathering occurs predominantly in continental settings—only the lowest outgassing fluxes allow the modern Earth to be close to a steady state.

The continental silicate weathering feedback. The silicate weathering feedback is the most prominent suggested mechanism for stabilizing the global carbon cycle. It was first proposed by Walker et al. (1981) and stated that the rate of continental silicate weathering and resultant carbonate precipitation (whether abiotic or biologically mediated) speeds up at higher temperatures and higher CO_2 concentrations. Recall that silicate weathering is the primary pathway for removing CO_2 from the atmosphere, thus this constitutes negative feedback: rising CO_2 concentrations drive increasing global temperatures and increased silicate weathering that, in turn, draws more CO_2 out of the atmosphere, lowering CO_2 concentrations and global temperature.

This does not imply that CO_2 concentrations are essentially fixed throughout time. If CO_2 input fluxes are permanently doubled, the atmospheric CO_2 and temperature will not return to previous values as a result of this feedback. Rather, the concentration of CO_2 and global temperature will increase until the CO_2 output flux—silicate weathering—again matches the inputs. The system will then reach a new steady state such that the concentration of CO_2 and the temperature are higher than before, but they are stable. This also implies that there will be periods of Earth history when inputs and outputs are *temporarily* imbalanced. For example, Dutkiewicz et al. (2018) suggest that Cenozoic carbonation has outpaced solid earth decarbonation, causing a global cooling trend. Recall, also, that the "Faint Young Sun Paradox" of Sagan and Mullen (1972) requires that the atmosphere has systematically lost CO_2 over billions of years. As a consequence, feedback does not guarantee fixed temperatures, but it prevents run-away warming or cooling trends.

The nature of the relationship between temperature and silicate weathering remains the subject of vigorous debate. Some
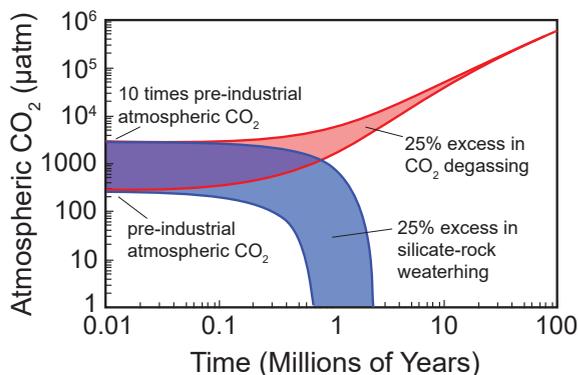
FIGURE 6. Predicted atmospheric CO_2 concentrations in an Earth system where CO_2 sources and sinks do not balance, modified after Berner and Caldeira (1997). Regardless of starting CO_2 concentration, a 25% excess in CO_2 degassing (red curves) or a 25% excess in silicate weathering (blue curves) result in a run-away atmospheric composition within $\sim$1 million years.

have proposed that global surface temperatures exert direct control on silicate weathering through a simple temperature-dependent reaction rate. In laboratory experiments, the rate of chemical weathering of silicate minerals (e.g., reaction 1C) has been demonstrated to increase with increasing temperature (e.g., Lagache 1976; Brady and Carroll 1994), yet in field studies results are mixed. Edmond et al. (1995) report no evidence of increased chemical weathering at higher temperatures, while Meybeck (1979) finds a significant relationship. This work is complicated by the correlations between, for example, river runoff and temperature that exist in nature.

Another possible mechanism relates CO_2 to chemical weathering directly: as atmospheric CO_2 concentrations increase, more CO_2 will be dissolved in water to from carbonic acid. This more acidic surface environment could also contribute to faster chemical weathering of silicate minerals (e.g., Berg and Banwart 2000). This factor is likely more important prior to the rise of land plants and the onset of extensive soil respiration.

Most research today focuses on indirect relationships between temperature and silicate weathering. In particular, higher temperatures drive increased global precipitation rates and increased river runoff (Holland 1978; Manabe and Stouffer 1993). Therefore, many models suggest that it is primarily this invigoration of the water cycle that enhances silicate weathering and CO_2 drawdown (Berner and Berner 1997; Maher and Chamberlain 2014). Teasing out the influence of temperature, precipitation, or other factors can be extremely challenging in such complex systems, but modern statistical techniques (e.g., machine learning) could be an effective means to probe the factors driving the silicate weathering feedback.

Marine weathering feedback. Because weathering of continental material has historically been considered as the primary contribution to global silicate weathering, it has also been assumed to be the source of the associated negative feedback. However, recent studies have demonstrated that seafloor weathering and carbonation may offer an additional, complementary negative feedback. The general idea is the same: rising CO_2 concentrations

and global temperatures increase the rate of marine weathering, thereby drawing down more CO_2 and stabilizing the system. Indeed, off-axis hydrothermal alteration of the basaltic crust is enhanced at higher temperatures (Coogan and Dosso 2015). The rate of silicate mineral dissolution will be significantly faster when the ocean bottom water temperature is elevated. On the other hand, it has been suggested that chemical weathering of marine anoxic sediments is largely independent of temperature (Wallmann et al. 2008). Importantly, CO_2 that is stored in the oceanic crust may, in the future, contribute to a metamorphic decarbonation flux when it is inevitably subducted (Fig. 1).

Reverse weathering feedback. It was recently proposed that reverse weathering can act as important stabilizing feedback for carbon cycling (Isson and Planavsky 2018). In this case, increasing atmospheric CO_2 makes the ocean more acidic, reducing the amount of clay formation, and thus CO_2 release, from reverse weathering. This, in turn, lowers atmospheric CO_2, pushing ocean water pH back toward less acidic values. Today this feedback is less effective—clay formation is limited by the availability of SiO_2 dissolved in the ocean. There is evidence, however, that this process was much more important early in Earth's history. Prior to the Cambrian Period (~542 million years ago) oceanic silica concentrations were much higher. This would allow for more reverse weathering and, perhaps, enhanced efficiency of a reverse weathering negative feedback (Isson and Planavsky 2018).

IMPLICATIONS

Future work

Major gaps remain in our understanding of global carbonation/decarbonation reactions. More work is needed on constraining the magnitude of the various carbon fluxes and how they balance one another throughout time. One area of particular uncertainty is the fate of subducted carbon. As of today, it is unknown whether most of the carbonate minerals in the oceanic crust are ultimately delivered to the deep mantle, or if they devolatilize during subduction. And for the CO_2 that does escape the downgoing slab, is most of it ultimately released to the atmosphere, or is it stored in the subarc lithosphere (Kelemen and Manning 2015)? Observations made in ancient and modern subduction zones in concert with constraints from experiments and numerical modeling must begin to answer these questions if we are to make progress in a global understanding of carbon mobility.

Another significant uncertainty is the strength of the silicate weathering feedback. This feedback is not perfectly efficient—the Earth has swung between the hot house and ice house conditions many times in the past (e.g., Royer et al. 2004). In fact, the strength of the feedback is certainly not fixed. We see evidence for periods of reduced and enhanced feedback efficiency in the geologic record (e.g., Caves et al. 2016). Nevertheless, the ability to constrain the magnitude of the effect of silicate weathering in ancient and modern Earth systems will allow us to make more accurate calculations of past and future climate. Both theoretical (e.g., Winnick and Maher 2018) and observational approaches could provide valuable new insights.

There is limited work on the behavior of carbonate minerals at high pressures. For example, recent work suggests carbon

in subduction zones is hosted in the minerals dolomite and magnesite (Tao et al. 2018), yet experimental constraints on their solubilities at these conditions are lacking. Recent theoretical work is addressing the issue (e.g., Sverjensky et al. 2014; Connolly and Galvez 2018), and should be supplemented by a new generation of experimental data.

Exoplanet habitability

Each of the processes discussed has important implications in the study of distant exoplanets and our search for other habitable worlds. The presence of a silicate weathering feedback, for example, will significantly increase the size of the "habitable zone" around a given star—the range of planetary distances from the star that falls within a habitable temperature range (Kasting et al. 1993). The balance between continental and marine weathering feedbacks is also important. If marine weathering is *not* a significant negative feedback mechanism, then we would not expect planets that are mostly ocean ("water worlds") to have a stable, habitable climate (Abbot et al. 2012). If, on the other hand, marine weathering is strongly temperature dependent, these worlds would be more likely to sustain life. The presence of volcanism and/or plate tectonics could also have profound effects on an exoplanet's carbon cycle and potential habitability (e.g., Sleep and Zahnle 2001). Studying these processes on Earth may lead to better predictions of which distant planets might be hospitable to life.

Carbonation reactions and anthropogenic climate change

Since the industrial revolution, Earth's global carbon cycle has been subject to a fast and massive perturbation, evidently unequaled in geologic history. Through the burning of fossil fuels, deforestation, and other human activity, ~795 Tmol CO_2 are added to the ocean-atmosphere system every year (Friedlingstein et al. 2010). This is more than 100 times greater than the global volcanic CO_2 flux or, as Gerlach (2011) notes, equivalent to about 9500 Kilauea volcanoes. One could, perhaps, take comfort in the knowledge that the natural geologic carbon cycle can eventually stabilize global temperatures, but most will consider a lag time of about 1 million years unacceptable. With this in mind, some researchers are attempting to harness and accelerate the power of silicate weathering to counteract human-driven climate change in our lifetimes (O'Connor et al. 2001; Lackner 2003; Park and Fan 2004; Kelemen and Matter 2008; Lal 2008; Wilson et al. 2009; Lechat et al. 2016; Power et al. 2016; Kelemen et al. 2018).

In many cases, ultramafic rocks are used. These rocks are composed of Mg-rich silicate minerals that are particularly unstable at Earth's surface, which facilitates dissolution (like reaction 1C) and subsequent carbonation. In some cases, these rocks are merely ground up and exposed at Earth's surface to undergo natural reaction with the atmosphere (e.g., Lechat et al. 2016), while other studies consider more active processes, such as pumping a CO_2-rich fluid through the rocks (this is more similar to off-axis hydrothermal alteration; e.g., Park and Fan 2004; Matter et al. 2016). In either case, understanding natural geologic carbonation reactions have the potential to inform future work on carbon sequestration and contribute to the continued habitability of planet Earth.

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