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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 have maintained a surface environment that could sustain life. Carbonation / decarbonation reactions are the primary mechanism 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 a variety of prograde metamorphic decarbonation processes which 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.

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:

$$CaSiO_{3\ (wollastonite)} + CO_{2\ (gas)} \rightarrow CaCO_{3\ (calcite)} + SiO_{2\ (quartz)} \quad (1)$$

and its reverse, decarbonation:

$$CaCO_{3\ (calcite)} + SiO_{2\ (quartz)} \rightarrow CaSiO_{3\ (wollastonite)} + CO_{2\ (fluid)} \quad (2)$$

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 a 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 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 may 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 quite 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):

$$CaSiO_{3\,(wollastonite)} + 2H^+_{(aqueous)} + H_2O_{(liquid)} \Leftrightarrow Ca^{2+}_{(aqueous)} + H_4SiO_{4\,(aqueous)}. \quad (1C)$$

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:

$$Ca^{2+}_{(aqueous)} + 2HCO_3^-{}_{(aqueous)} \Leftrightarrow CaCO_{3\,(calcite)} + CO_{2\,(gas)} + H_2O_{(liquid)}. \quad (1D)$$

Finally, the mineral quartz (SiO_2) may grow from the silicic acid in solution with more water as a byproduct:

$$H_4SiO_{4\,(aqueous)} \Leftrightarrow SiO_{2\,(quartz)} + 2H_2O_{(liquid)}. \quad (1E)$$

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We can sum up these five sub-reactions (doubling reactions (1A) and (1B) for balance) to make one total reaction:

$$2CO_{2\,(g)} + 3H_2O_{(l)} + 2H_2CO_{3\,(aq)} + CaSiO_{3\,(wol)} + 2H^+_{(aq)} + Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} + H_4SiO_{4\,(aq)}$$

$$\Leftrightarrow \qquad (1F)$$

$$2H_2CO_{3\,(aq)} + 2HCO_3^-{}_{(aq)} + 2H^+_{(aq)} + Ca^{2+}_{(aq)} + H_4SiO_{4\,(aq)} + CaCO_{3\,(cc)} + CO_{2\,(g)} + 3H_2O_{\,(l)} + SiO_{2(q)}$$

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 which 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, 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 & 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 which drives carbonate precipitation. Note that any contribution to total alkalinity drives carbonation, thus weathering of Mg-silicate minerals could ultimately drive 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) eroded, 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 erosion and chemical weathering – mineral dissolution can contribute to denudation while erosion 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 which form high mountain belts help to expose more rock at Earth's surface, which may increase the potential for weathering (e.g., Raymo & 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 & Blum 1995; Maher & 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 1981; Berner *et al.* 1983; Manabe & 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 & Gisalson 1997; Wallmann *et al.* 2008; Coogan & Gillis 2013; Coogan & Dosso 2015). The concept is the same – silicate minerals undergo chemical reaction which 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 & 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 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 C) 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 & Gisalson 1997; Gillis & Coogan 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 & Dosso 2015).

Reverse Weathering

Reverse weathering refers 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 & 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 & 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 which are exemplified 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 & 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 < ~700 °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 & Manning 2015). Alternatively, melting of carbonated mantle material may ultimately contribute CO_2 to the atmosphere when melt is erupted from overlying arc volcanoes (Kerrick & Connolly 2001; Gorman *et al.* 2006; Kelemen & Manning 2015; Mason *et al.* 2017).

Similar high-temperature carbonation of ultramafic rocks can also occur in orogenic belts during prograde regional (Evans & Trommsdorf 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 (Fig. 4). 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 & Tuttle 1956). Figure 4 is a *P-T* phase diagram, showing which mineral assemblage is stable at a 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 & 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 & 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 1961). 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 & 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:

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

(Frezzotti *et al.* 2011; Ague & Nicolescu 2014). The $CO_{2(aq)}$ in reaction (4) represents aqueous carbon species in general; carbonate and bicarbonate ions (Pann & 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 island of Syros carbonate dissolution released 60-90% of the solid carbon from the rock, while decarbonation reactions might be expected to release less than ~3% (Ague & 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 & 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 1992; Kelemen & 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.

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

313 of a water-rich fluid into a reactive rock can depress the required temperature of a given
314 decarbonation reaction (e.g., Ferry 1976, 2016; Kerrick 1977; Penniston-Dorland & Ferry 2006;
315 Tracy *et al.*1983; Ague 2002). This can be observed in zones of enhanced decarbonation around
316 fluid conduits as shown in Figure 2C. Classic studies in the metamorphic belts of the
317 Appalachian Mountains were among the first to demonstrate that fluid infiltration was essential
318 for driving reactions and releasing CO_2 (e.g. Ferry 1978, 1980; Rumble *et al.* 1982; Tracy *et*
319 *al.*1983).

320 As a demonstration, we calculate the *P-T* conditions of reaction (2). When the X_{CO_2} (the
321 mole fraction of CO_2) in an H_2O – CO_2 fluid is low, the reaction can occur at a much lower
322 temperature. For example, at 0.2 GPa the reaction occurs at ~350 °C when X_{CO_2} = 0.001 and
323 ~700 °C when X_{CO_2} = 1.0 (Fig. 4).

324 This effect has two important implications. First, a rock that is metamorphosed in the
325 presence of a water-bearing fluid can release more than 500% more CO_2 than the metamorphism
326 of the same rock in a closed system at the same pressure and temperature (Stewart & Ague
327 2018). This enhanced decarbonation could ultimately result in a greater concentration of CO_2 in
328 the atmosphere and a correspondingly higher global surface temperature. Second, CO_2 generated
329 by infiltration is automatically released into a regional fluid flow system that provides the
330 mechanism for transporting evolved CO_2 from the deep crust to the atmosphere and hydrosphere.

331 **DISCUSSION: CARBON FLUXES AND PLANETARY HABITABILITY**

332 Carbonation / decarbonation reactions play a vital role in carbon transfer on Earth. In
333 order to understand how these reactions relate to planetary habitability, we must consider how
334 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 & Gillis 2018 and references therein). However, reverse weathering recycles some CO_2 back into the surface environment, effectively acting as source of ~ 0.5 to ~1.25 Tmol CO_2 yr^{-1} (Isson & 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 & 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 & 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 area ~7.5 × 10^5 km^2 (Becker *et al.* 2008), is estimated on the order 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 & 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 & 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-Collars *et al.* 2014). Carbonate dissolution, only recently identified in subduction zones (e.g., Ague & 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 & 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 & 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 & Tolstikhin 1998; Hilton *et al.* 2002; Dasgupta & Hirschmann 2010), ~0.5 to ~5.0 Tmol CO_2 yr^{-1} for mid-ocean ridge volcanism (Marty & Tolstikhin 1998; Dasgupta & Hirschmann 2006, 2010; Le Voyer *et al.* 2019) and ~0.12 to ~3 Tmol CO_2 yr^{-1} from ocean

island volcanoes (Marty & Tolstikhin 1998; Dasgupta & 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 & 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 & 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 1988) 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 & 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 & 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 *et al.* 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 & 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 extreme hot house or ice house climates. Berner & 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. In order 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 ~ +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; Wallman

444 *et al.* 2008, Coogan & Gillis 2018) upper-end member outgassing rates are required. High
445 amounts of reverse weathering (e.g., Rahman *et al.* 2017) could also help balance high silicate
446 weathering rates with outgassing estimates. In contrast, in the traditional view—where silicate
447 weathering occurs predominantly in continental settings—only the lowest outgassing fluxes
448 allow the modern Earth to be close to a steady state.

449 **The Continental Silicate Weathering Feedback.** The silicate weathering feedback is
450 the most prominent suggested mechanism for stabilizing the global carbon cycle. It was first
451 proposed by Walker *et al.* (1981) and states that the rate of continental silicate weathering and
452 resultant carbonate precipitation (whether abiotic or biologically mediated) speeds up at higher
453 temperatures and higher CO_2 concentrations. Recall that silicate weathering is the primary
454 pathway for removing CO_2 from the atmosphere, thus this constitutes a negative feedback: rising
455 CO_2 concentrations drive increasing global temperatures and increased silicate weathering
456 which, in turn, draws more CO_2 out of the atmosphere, lowering CO_2 concentrations and global
457 temperature.

458 This does not imply that CO_2 concentrations are essentially fixed throughout time. If CO_2
459 input fluxes are permanently doubled, the atmospheric CO_2 and temperature will not return to
460 previous values as a result of this feedback. Rather, the concentration of CO_2 and global
461 temperature will increase until the CO_2 output flux—silicate weathering—again matches the
462 inputs. The system will then reach a new steady state such that the concentration of CO_2 and the
463 temperature are higher than before, but they are stable. This also implies that there will be
464 periods of Earth history when inputs and outputs are *temporarily* imbalanced. For example,
465 Dutkiewicz *et al.* (2018) suggest that Cenozoic carbonation has outpaced solid earth

466 decarbonation, causing a global cooling trend. Recall, also, that the 'faint young sun' paradox of
467 Sagan & Mullen (1972) requires that the atmosphere has systematically lost CO_2 over billions of
468 years. As a consequence, feedback does not guarantee fixed temperatures, but it prevents run-
469 away warming or cooling trends.

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

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

484 Most research today focuses on indirect relationships between temperature and silicate
485 weathering. In particular, higher temperatures drive increased global precipitation rates and
486 increased river runoff (Holland 1978; Manabe & Stouffer 1993). Therefore, many models
487 suggest that it is primarily this invigoration of the water cycle which enhances silicate

488 weathering and CO_2 drawdown (Berner & Berner 1997; Maher & Chamberlain 2014). Teasing
489 out the influence of temperature, precipitation, or other factors can be extremely challenging in
490 such complex systems, but modern statistical techniques (e.g., machine learning) could be an
491 effective means to probe the factors driving the silicate weathering feedback.

492 **Marine Weathering Feedback.** Because weathering of continental material has
493 historically been considered as the primary contribution to global silicate weathering, it has also
494 been assumed to be the source of the associated negative feedback. However, recent studies
495 have demonstrated that seafloor weathering and carbonation may offer an additional,
496 complementary negative feedback. The general idea is the same: rising CO_2 concentrations and
497 global temperatures increase the rate of marine weathering, thereby drawing down more CO_2 and
498 stabilizing the system. Indeed, off-axis hydrothermal alteration of basaltic crust is enhanced at
499 higher temperatures (Coogan & Dosso 2015). The rate of silicate mineral dissolution will be
500 significantly faster when the ocean bottom water temperature is elevated. On the other hand, it
501 has been suggested that chemical weathering of marine anoxic sediments is largely independent
502 of temperature (Wallmann *et al*. 2008). Importantly, CO_2 that is stored in oceanic crust may in
503 the future contribute to a metamorphic decarbonation flux when it is inevitably subducted (Fig.
504 1).

505 **Reverse Weathering Feedback.** It was recently proposed that reverse weathering can act
506 as an important stabilizing feedback for carbon cycling (Isson & Planavsky 2018). In this case,
507 increasing atmospheric CO_2 makes the ocean more acidic, reducing the amount of clay
508 formation, and thus CO_2 release, from reverse weathering. This, in turn, lowers atmospheric
509 CO_2, pushing ocean water pH back towards less acidic values. Today this feedback is less
510 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 & 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 down-going slab, is most of it ultimately released to the atmosphere, or is it stored in the subarc lithosphere (Kelemen & 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 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 & 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 & Galvez 2018), but 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 fall 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.* 2018). 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 & 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

555 Since the industrial revolution, Earth's global carbon cycle has been subject to a fast and
556 massive perturbation, evidently unequaled in geologic history. Through burning of fossil fuels,
557 deforestation, and other human activity, ~795 Tmol CO_2 are added to the ocean-atmosphere
558 system every year (Friedlingstein *et al.* 2010). This is more than one hundred times greater than
559 the global volcanic CO_2 flux or, as Gerlach (2011) notes, equivalent to about 9500 Kilauea
560 volcanoes. One could, perhaps, take comfort in the knowledge that the natural geologic carbon
561 cycle can eventually stabilize global temperatures, but most will consider a lag time of about 1
562 million years unacceptable. With this in mind, some researchers are attempting to harness and
563 accelerate the power of silicate weathering to counteract human-driven climate change in our
564 lifetimes (O'Connor *et al.* 2000; Lackner 2003; Park & Fan 2004; Kelemen & Matter 2008; Lal
565 2008; Wilson *et al.* 2009; Lechat *et al.* 2016; Power *et al.* 2016; Kelemen *et al.* 2018).

566 In many cases ultramafic rocks are used. These rocks are composed of Mg-rich minerals
567 that are particularly unstable at Earth's surface, which facilitates dissolution (like reaction (1C))
568 and subsequent carbonation. In some cases, these rocks are merely ground up and exposed at
569 Earth's surface to undergo natural reaction with the atmosphere (e.g., Lechat *et al.* 2016), while
570 other studies consider more active processes, such as pumping a CO_2 rich fluid through the rocks
571 (this is more similar to off-axis hydrothermal alteration; e.g., Park & Fan 2004; Matter *et al.*
572 2016). In either case, understanding natural geologic carbonation reactions has the potential to
573 inform future work on carbon sequestration and contribute to the continued habitability of planet
574 Earth.

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REFERENCES CITED

Abbot, D. S., Cowan, N. B., & Ciesla, F. J. (2012). Indication of insensitivity of planetary weathering behavior and habitable zone to surface land fraction. The Astrophysical Journal, 756(2), 178.

Ague, J. J. (2002). Gradients in fluid composition across metacarbonate layers of the Wepawaug Schist, Connecticut, USA. Contributions to Mineralogy and Petrology, 143(1), 38-55.

Ague, J. J. (2003). Fluid infiltration and transport of major, minor, and trace elements during regional metamorphism of carbonate rocks, Wepawaug Schist, Connecticut, USA. *American Journal of Science*, *303*(9), 753-816.

Ague, J. J., & Nicolescu, S. (2014). Carbon dioxide released from subduction zones by fluid-mediated reactions. Nature Geoscience, 7(5), 355.

Allard, P. (1992). Diffuse degassing of Carbon Dioxide through volcanic systems: observed facts and implications. Report Geol. Sur. of Japan, 7-11.

Amiotte Suchet, P., and Probst, J. L. (1995). A global model for present-day atmospheric: Soil CO_2 consumption by chemical erosion of continental rocks (GEM-CO_2): Tellus, v. 47B, p. 273–280.

Archer, D. (2010), The Global Carbon Cycle, 205 pp., Princeton Univ. Press, Princeton, N. J.

Arrhenius, S. (1915). Quantitative laws in biological chemistry (Vol. 1915). G. Bell.

Becker, J. A., Bickle, M. J., Galy, A., & Holland, T. J. (2008). Himalayan metamorphic CO_2 fluxes: Quantitative constraints from hydrothermal springs. Earth and Planetary Science Letters, 265(3-4), 616-629.

Berg, A., & Banwart, S. A. (2000). Carbon dioxide mediated dissolution of Ca-feldspar:

615 implications for silicate weathering. Chemical Geology, 163(1-4), 25-42.
616
617 Berner, R. A. (1982). Burial of organic carbon and pyrite sulfur in the modern ocean: its
618 geochemical and environmental significance. American Journal of Science, 282, 451-
619 473.
620
621 Berner, R. A. (1995). AG Högbom and the development of the concept of the geochemical
622 carbon cycle. American journal of science, 295(5), 491-495.
623
624 Berner, R. A., & Berner, E. K. (1997). Silicate weathering and climate. In Tectonic uplift and
625 climate change (pp. 353-365). Springer, Boston, MA.
626
627 Berner, R. A., & Caldeira, K. (1997). The need for mass balance and feedback in the
628 geochemical carbon cycle. Geology, 25(10), 955-956.
629
630 Berner, R. A., Lasaga, A. C., and Garrels, R. M. (1983). The carbonate-silicate geochemical
631 cycle and its effect on atmospheric carbon dioxide over the past 100 million years:
632 American Journal of Science, 283, 641-683.
633
634 Bowen, N. L. (1940). Progressive metamorphism of siliceous limestone and dolomite. The
635 Journal of Geology, 48(3), 225-274.
636
637 Brady, P. V., & Carroll, S. A. (1994). Direct effects of CO_2 and temperature on silicate
638 weathering: Possible implications for climate control. Geochimica et Cosmochimica
639 Acta, 58(7), 1853-1856.
640
641 Brady, P. V., & Gíslason, S. R. (1997). Seafloor weathering controls on atmospheric CO_2 and
642 global climate. Geochimica et Cosmochimica Acta, 61(5), 965-973.
643
644 Burgess, S. D., Muirhead, J. D., & Bowring, S. A. (2017). Initial pulse of Siberian Traps sills as
645 the trigger of the end-Permian mass extinction. Nature communications, 8(1), 164.
646
647 Burke, K., Dewey, J. F., & Kidd, W. S. F. (1977). World distribution of sutures—the sites of
648 former oceans. Tectonophysics, 40(1-2), 69-99.
649
650 Caves, J. K., Jost, A. B., Lau, K. V., & Maher, K. (2016). Cenozoic carbon cycle imbalances and
651 a variable weathering feedback. Earth and Planetary Science Letters, 450, 152-163.
652
653 Campbell, K. A., Farmer, J. D., & Des Marais, D. (2002). Ancient hydrocarbon seeps from the
654 Mesozoic convergent margin of California: carbonate geochemistry, fluids and
655 palaeoenvironments. Geofluids, 2(2), 63-94.
656
657 Chiodini, G., Frondini, F., Cardellini, C., Parello, F., & Peruzzi, L. (2000). Rate of diffuse carbon
658 dioxide Earth degassing estimated from carbon balance of regional aquifers: the case of
659 central Apennine, Italy. Journal of Geophysical Research: Solid Earth, 105(B4), 8423-
660 8434.

Connolly, J. A., & Galvez, M. E. (2018). Electrolytic fluid speciation by Gibbs energy minimization and implications for subduction zone mass transfer. Earth and Planetary Science Letters, 501, 90-102.

Coogan, L. A., & Dosso, S. E. (2015). Alteration of ocean crust provides a strong temperature dependent feedback on the geological carbon cycle and is a primary driver of the Sr-isotopic composition of seawater. Earth and Planetary Science Letters, 415, 38-46.

Coogan, L. A., & Gillis, K. M. (2013). Evidence that low-temperature oceanic hydrothermal systems play an important role in the silicate-carbonate weathering cycle and long-term climate regulation. Geochemistry, Geophysics, Geosystems, 14(6), 1771-1786.

Coogan, L. A., & Gillis, K. M. (2018). Low-Temperature Alteration of the Seafloor: Impacts on Ocean Chemistry. Annual Review of Earth and Planetary Sciences, 46, 21-45.

Cook-Kollars, J., Bebout, G. E., Collins, N. C., Angiboust, S., & Agard, P. (2014). Subduction zone metamorphic pathway for deep carbon cycling: I. Evidence from HP/UHP metasedimentary rocks, Italian Alps. Chemical Geology, 386, 31-48.

Dasgupta, R., & Hirschmann, M. M. (2006). Melting in the Earth's deep upper mantle caused by carbon dioxide. Nature, 440(7084), 659.

Dasgupta, R., & Hirschmann, M. M. (2010). The deep carbon cycle and melting in Earth's interior. Earth and Planetary Science Letters, 298(1-2), 1-13.

de Capitani, C., & Petrakakis, K. (2010). The computation of equilibrium assemblage diagrams with Theriak/Domino software. American Mineralogist, 95(7), 1006-1016.

Delesse, A. (1858). Etudes sur la métamorphisme des roches. Annales de Mines. E. Thunot: Paris.

Dessert, C., Dupré, B., Gaillardet, J., François, L. M., & Allegre, C. J. (2003). Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. Chemical Geology, 202(3-4), 257-273.

Dutkiewicz, A., Müller, R. D., Cannon, J., Vaughan, S., & Zahirovic, S. (2018). Sequestration and subduction of deep-sea carbonate in the global ocean since the Early Cretaceous. Geology, 47(1), 91-94.

Edmond, J. M., Palmer, M. R., Measures, C. I., Grant, B., & Stallard, R. F. (1995). The fluvial geochemistry and denudation rate of the Guayana Shield in Venezuela, Colombia, and Brazil. Geochimica et Cosmochimica Acta, 59(16), 3301-3325.

Evans, B. W., & Trommsdorff, V. (1974). Stability of enstatite + talc and CO_2-metasomatism of

metaperidotite, Val d'Efra, Lepontine Alps. American Journal of Science, 274(3), 274-296.

Falk, E. S., & Kelemen, P. B. (2015). Geochemistry and petrology of listvenite in the Samail ophiolite, Sultanate of Oman: complete carbonation of peridotite during ophiolite emplacement. Geochimica et Cosmochimica Acta, 160, 70-90.

Ferry, J. M. (1976). Metamorphism of calcareous sediments in the Waterville-Vassalboro area, South-central Maine; mineral reactions and graphical analysis. American Journal of Science, 276(7), 841-882.

Ferry, J. M. (1978). Fluid interaction between granite and sediment during metamorphism, south-central Maine. American Journal of Science, 278(8), 1025-1056.

Ferry, J. M. (1980). A case study of the amount and distribution of heat and fluid during metamorphism. Contributions to Mineralogy and Petrology, 71(4), 373-385.

Ferry, J. M. (1988). Infiltration-driven metamorphism in northern New England, USA. Journal of Petrology, 29(6), 1121-1159.

Ferry, J. M. (1995). Fluid flow during contact metamorphism of ophicarbonate rocks in the Bergell aureole, Val Malenco, Italian Alps. Journal of Petrology, 36(4), 1039-1053.

Ferry, J. M. (2000). Patterns of mineral occurrence in metamorphic rocks. American Mineralogist, 85(11-12), 1573-1588.

Ferry, J. M. (2016). Fluids in the crust during regional metamorphism: Forty years in the Waterville limestone. American Mineralogist, 101(3), 500-517.

Ferry, J. M., Rumble, D., Wing, B. A., & Penniston-Dorland, S. C. (2005). A New Interpretation of Centimetre-scale Variations in the Progress of Infiltration-driven Metamorphic Reactions: Case Study of Carbonated Metaperidotite, Val d'Efra, Central Alps, Switzerland. Journal of Petrology, 46(8), 1725-1746.

Friedlingstein, P., Houghton, R. A., Marland, G., Hackler, J., Boden, T. A., Conway, T. J., ... & Le Quere, C. (2010). Update on CO_2 emissions. Nature geoscience, 3(12), 811.

Gaillardet, J., Dupré, B., Louvat, P., & Allegre, C. J. (1999). Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. Chemical geology, 159(1-4), 3-30.

Ganino, C., & Arndt, N. T. (2009). Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. Geology, 37(4), 323-326.

Garrels, R. M. (1965). Silica: role in the buffering of natural waters. Science, 148(3666), 69-69.

Gerlach, T. (2011). Volcanic versus anthropogenic carbon dioxide. Eos, Transactions American Geophysical Union, 92(24), 201-202.

Gillis, K. M., & Coogan, L. A. (2011). Secular variation in carbon uptake into the ocean crust. Earth and Planetary Science Letters, 302(3), 385-392.

Goldschmidt, V. M. (1912). Die Gesetze der Gesteinsmetamorphose mit Beispielen aus der Geologie des Südlichen Norwegens (The laws of rock metamorphism with examples from the geology of southern Norway). Vi denskapsselskapets Skrifter. 1.

Gorman, P. J., Kerrick, D. M., & Connolly, J. A. D. (2006). Modeling open system metamorphic decarbonation of subducting slabs. Geochemistry, Geophysics, Geosystems, 7(4).

Harker, R. I., & Tuttle, O. F. (1956). Experimental data on the P_{CO2}-T curve for the reaction; calcite-quartz ⟷ wollastonite + carbon dioxide. American Journal of Science, 254(4), 239-256.

Hilton, D. R., Fischer, T. P., & Marty, B. (2002). Noble gases and volatile recycling at subduction zones. Reviews in mineralogy and geochemistry, 47(1), 319-370.

Högbom, A. (1894). Om sannolikheten för sekulära förändringar i atmosfärens kolsyrehalt (On the probability of secular variations of atmospheric carbon dioxide). Svensk kemisk tidskrift, 4, 169-177.

Holland, H. D. (1978). The chemistry of the atmosphere and oceans. Wiley: New York, NY.

Holland, T. J. B., & Powell, R. T. J. B. (1998). An internally consistent thermodynamic data set for phases of petrological interest. Journal of metamorphic Geology, 16(3), 309-343.

Isson, T. T., & Planavsky, N. J. (2018). Reverse weathering as a long-term stabilizer of marine pH and planetary climate. Nature, 560(7719), 471.

Jenny, H. (1941). Factors of Soil Formation. McGraw-Hill: New York, NY.

Kasting, J. F. (2010). Early Earth: faint young Sun redux. Nature, 464(7289), 687.

Kasting, J. F., Whitmire, D. P., & Reynolds, R. T. (1993). Habitable zones around main sequence stars. Icarus, 101(1), 108-128.

Kelemen, P. B. & Matter, J. M. (2008) In situ carbonation of peridotite for CO_2 storage. Proceedings of the National Academy of Sciences, USA 105, 17295–17300.

Kelemen, P. B., & Manning, C. E. (2015). Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. Proceedings of the National Academy of Sciences, 201507889.

Kelemen, P. B., Aines, R., Bennett, E., Benson, S. M., Carter, E., Coggon, J. A., ... & Godard, M. (2018). In situ carbon mineralization in ultramafic rocks: Natural processes and possible engineered methods. Energy Procedia, 146, 92-102.

Kennedy, W. Q. (1948). On the significance of thermal structure in the Scottish Highlands. Geological Magazine, 85(4), 229-234.

Kerrick, D. M. (1977). The genesis of zoned skarns in the Sierra Nevada, California. Journal of petrology, 18(1), 144-181.

Kerrick, D. M., & Caldeira, K. (1998). Metamorphic CO_2 degassing from orogenic belts. Chemical Geology, 145(3-4), 213-232.

Kerrick, D. M., & Connolly, J. A. D. (2001). Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. Nature, 411(6835), 293.

Knauth, L. P., & Epstein, S. (1976). Hydrogen and oxygen isotope ratios in nodular and bedded cherts. Geochimica et Cosmochimica Acta, 40(9), 1095-1108.

Kump, L. R., & Arthur, M. A. (1999). Interpreting carbon-isotope excursions: carbonates and organic matter. Chemical Geology, 161(1-3), 181-198.

Lagache, M. (1976). New data on the kinetics of the dissolution of alkali feldspars at 200 °C in CO_2 charged water. Geochimica et Cosmochimica Acta, 40(2), 157-161.

Lal, R. (2008). Carbon sequestration. Philosophical Transactions of the Royal Society of London B: Biological Sciences, 363(1492), 815-830.

Le Voyer, M., Hauri, E. H., Cottrell, E., Kelley, K. A., Salters, V. J., Langmuir, C. H., ... & Füri, E. (2019). Carbon fluxes and primary magma CO_2 contents along the global mid-ocean ridge system. Geochemistry, Geophysics, Geosystems, 20.

Lechat, K., Lemieux, J. M., Molson, J., Beaudoin, G., & Hébert, R. (2016). Field evidence of CO_2 sequestration by mineral carbonation in ultramafic milling wastes, Thetford Mines, Canada. International Journal of Greenhouse Gas Control, 47, 110-121.

Lee, C. T. A., Shen, B., Slotnick, B. S., Liao, K., Dickens, G. R., Yokoyama, Y., ... & Schneider, T. (2013). Continental arc–island arc fluctuations, growth of crustal carbonates, and long-term climate change. Geosphere, 9(1), 21-36.

Li, J., Redfern, S.T.A., & Giovannelli, D. (2019). Introduction: Deep carbon cycle through five reactions. American Mineralogist, 104(4): 465-467.

Loughnan, F. C. (1969). Chemical weathering of the silicate minerals (No. 549.6 L6).

Lyubetskaya, T., & Ague, J. J. (2010). Modeling metamorphism in collisional orogens intruded

by magmas: I. Thermal evolution. American Journal of Science, 310(6), 427-458.

Mackenzie, F. T., & Garrels, R. M. (1966). Chemical mass balance between rivers and oceans. American Journal of Science, 264(7), 507-525.

Maher, K., & Chamberlain, C. P. (2014). Hydrologic regulation of chemical weathering and the geologic carbon cycle. Science, 343(6178), 1502-1504.

Manabe, S., & Stouffer, R. J. (1993). Century-scale effects of increased atmospheric CO_2 on the ocean–atmosphere system. Nature, 364(6434), 215.

Marty, B., & Tolstikhin, I. N. (1998). CO_2 fluxes from mid-ocean ridges, arcs and plumes. Chemical Geology, 145(3), 233-248.

Mason, E., Edmonds, M., & Turchyn, A. V. (2017). Remobilization of crustal carbon may dominate volcanic arc emissions. Science, 357(6348), 290-294.

Matter, J. M., Stute, M., Snæbjörnsdottir, S. Ó., Oelkers, E. H., Gislason, S. R., Aradottir, E. S., ... & Axelsson, G. (2016). Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. Science, 352(6291), 1312-1314.

Meybeck, M. (1979). Concentrations des eaux fluviales en éléments majeurs et apports en solution aux oceans (Concentrations of major elements in fluvial waters and solutions in the oceans), Revue de Géologie Dynamique et de Géographie Physique., 21, 215-246.

Miyashiro, A. (1972). Metamorphism and related magmatism in plate tectonics. American Journal of Science, 272(7), 629-656.

Mojzsis, S. J., Harrison, T. M., & Pidgeon, R. T. (2001). Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago. Nature, 409(6817), 178.

Nabelek, P. I., Bédard, J. H., & Rainbird, R. H. (2014). Numerical constraints on degassing of metamorphic CO_2 during the Neoproterozoic Franklin large igneous event, Arctic Canada. Bulletin, 126(5-6), 759-772.

O'Connor, W. K., Dahlin, D. C., Nilsen, D. N., Rush, G. E., Walters, R. P., & Turner, P. C. (2001). Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status (No. DOE/ARC-2001-029). Albany Research Center (ARC), Albany, OR.

Orme, D. A. (2015). Basin evolution and exhumation of the Xigaze forearc and Indus-Yarlung suture zone, Tibet. PhD Thesis at The University of Arizona.

Owen, T., Cess, R. D., & Ramanathan, V. (1979). Enhanced CO_2 greenhouse to compensate for reduced solar luminosity on early Earth. Nature, 277(5698), 640.

Pan D, Galli G (2016) The fate of carbon dioxide in water-rich fluids under extreme conditions. Science Advances 2(10):e1601278-e1601278

Park, A. H. A., & Fan, L. S. (2004). CO_2 mineral sequestration: physically activated dissolution of serpentine and pH swing process. Chemical Engineering Science, 59(22-23), 5241-5247.

Penniston-Dorland, S. C., & Ferry, J. M. (2006). Development of spatial variations in reaction progress during regional metamorphism of micaceous carbonate rocks, northern New England. American Journal of Science, 306(7), 475-524.

Piccoli, F., Brovarone, A. V., Beyssac, O., Martinez, I., Ague, J. J., & Chaduteau, C. (2016). Carbonation by fluid–rock interactions at high-pressure conditions: implications for carbon cycling in subduction zones. Earth and Planetary Science Letters, 445, 146-159.

Piccoli, F., Brovarone, A. V., & Ague, J. J. (2018). Field and petrological study of metasomatism and high-pressure carbonation from lawsonite eclogite-facies terrains, Alpine Corsica. Lithos, 304, 16-37.

Plank, T., & Langmuir, C. H. (1998). The chemical composition of subducting sediment and its consequences for the crust and mantle. Chemical geology, 145(3), 325-394.

Poli, S. (2015). Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. Nature Geoscience, 8(8), 633.

Power, I. M., Harrison, A. L., & Dipple, G. M. (2016). Accelerating mineral carbonation using carbonic anhydrase. Environmental science & technology, 50(5), 2610-2618.

Rahman, S., Aller, R. C., & Cochran, J. K. (2017). The missing silica sink: Revisiting the marine sedimentary Si cycle using cosmogenic ^{32}Si. Global Biogeochemical Cycles, 31(10), 1559-1578.

Raymo, M. E., & Ruddiman, W. F. (1992). Tectonic forcing of late Cenozoic climate. Nature, 359(6391), 117.

Ronov, A. B., Yaroshevskii, A. A., & Migdisov, A. A. (1990). Chemical Structure of the Earth's Crust and Geochemical Balance of Major Elements.

Royer, D. L., Berner, R. A., Montañez, I. P., Tabor, N. J., & Beerling, D. J. (2004). CO_2 as a primary driver of phanerozoic climate. GSA today, 14(3), 4-10.

Rumble, D., Ferry, J. M., Hoering, T. C., & Boucot, A. J. (1982). Fluid flow during metamorphism at the Beaver Brook fossil locality, New Hampshire. American Journal of Science, 282(6), 886-919.

Sagan, C. (1962). Structure of the lower atmosphere of Venus. Icarus, 1(1-6), 151-169.

Sagan, C., & Mullen, G. (1972). Earth and Mars: Evolution of atmospheres and surface temperatures. Science, 177(4043), 52-56.

Sakai, H., Gamo, T., Kim, E. S., Tsutsumi, M., Tanaka, T., Ishibashi, J., ... & Oomori, T. (1990). Venting of carbon dioxide-rich fluid and hydrate formation in mid-Okinawa trough backarc basin. Science, 248(4959), 1093-1096.

Sano, Y., & Williams, S. N. (1996). Fluxes of mantle and subducted carbon along convergent plate boundaries. Geophysical Research Letters, 23(20), 2749-2752.

Scambelluri, M., Bebout, G. E., Belmonte, D., Gilio, M., Campomenosi, N., Collins, N., & Crispini, L. (2016). Carbonation of subduction-zone serpentinite (high-pressure ophicarbonate; Ligurian Western Alps) and implications for the deep carbon cycling. Earth and Planetary Science Letters, 441, 155-166.

Sieber, M. J., Hermann, J., & Yaxley, G. M. (2018). An experimental investigation of C-O-H fluid-driven carbonation of serpentinites under forearc conditions. Earth and Planetary Science Letters, 496, 178-188.

Siever, R. (1968). Sedimentological consequences of a steady-state ocean-atmosphere. Sedimentology, 11(1-2), 5-29.

Sillén, L. G. (1961). The physical chemistry of sea water. Oceanography 67, 549–581.

Sleep, N. H., & Zahnle, K. (2001). Carbon dioxide cycling and implications for climate on ancient Earth. Journal of Geophysical Research: Planets, 106(E1), 1373-1399.

Solomon, E. A., Spivack, A. J., Kastner, M., Torres, M. E., & Robertson, G. (2014). Gas hydrate distribution and carbon sequestration through coupled microbial methanogenesis and silicate weathering in the Krishna–Godavari basin, offshore India. Marine and Petroleum Geology, 58, 233-253.

Staudigel, H., Hart, S. R., Schmincke, H. U., & Smith, B. M. (1989). Cretaceous ocean crust at DSDP Sites 417 and 418: Carbon uptake from weathering versus loss by magmatic outgassing. Geochimica et Cosmochimica Acta, 53(11), 3091-3094.

Stewart, E. M., & Ague, J. J. (2018). Infiltration-driven metamorphism, New England, USA: Regional CO_2 fluxes and implications for Devonian climate and extinctions. Earth and Planetary Science Letters, 489, 123-134.

Sverjensky, D. A., Stagno, V., & Huang, F. (2014). Important role for organic carbon in subduction-zone fluids in the deep carbon cycle. Nature Geoscience, 7(12), 909.

Tao, R., Zhang, L., Li, S., Zhu, J., & Ke, S. (2018). Significant contrast in the Mg-C-O isotopes

of carbonate between carbonated eclogite and marble from the SW Tianshan UHP subduction zone: Evidence for two sources of recycled carbon. Chemical Geology, 483, 65-77.

Tian, M., & Ague, J. J. (2014). The impact of porosity waves on crustal reaction progress and CO_2 mass transfer. Earth and Planetary Science Letters, 390, 80-92.

Tracy, R. J., Rye, D. M., Hewitt, D. A., & Schiffries, C. M. (1983). Petrologic and stable-isotopic studies of fluid-rock interactions, south-central Connecticut: I. The role of infiltration in producing reaction assemblages in impure marbles. American Journal of Science, 283, 589-616.

Urey, H.C. (1952). The Planets: Their Origin and Development. New Haven, CT: Yale University Press.

Varekamp, J. C., Kreulen, R., Poorter, R. P. E., & Van Bergen, M. J. (1992). Carbon sources in arc volcanism, with implications for the carbon cycle. Terra Nova, 4(3), 363-373.

Walker, J. C., Hays, P. B., & Kasting, J. F. (1981). A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. Journal of Geophysical Research: Oceans, 86(C10), 9776-9782.

Wallmann, K., Aloisi, G., Haeckel, M., Tishchenko, P., Pavlova, G., Greinert, J., ... & Eisenhauer, A. (2008). Silicate weathering in anoxic marine sediments. Geochimica et Cosmochimica Acta, 72(12), 2895-2918.

White, A. F., & Blum, A. E. (1995). Effects of climate on chemical weathering in watersheds. Geochimica et Cosmochimica Acta, 59(9), 1729-1747.

Wilde, S. A., Valley, J. W., Peck, W. H., & Graham, C. M. (2001). Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. Nature, 409(6817), 175.

Wilson, S. A., Dipple, G. M., Power, I. M., Thom, J. M., Anderson, R. G., Raudsepp, M., ... & Southam, G. (2009). Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: Examples from the Clinton Creek and Cassiar chrysotile deposits, Canada. Economic Geology, 104(1), 95-112.

Winnick, M. J., & Maher, K. (2018). Relationships between CO_2, thermodynamic limits on silicate weathering, and the strength of the silicate weathering feedback. Earth and Planetary Science Letters, 485, 111-120.

Figure Captions

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.

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).

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 which were active during both eons are dashed blue and green. Modified after Orme (2015) and Burke *et al.* (1977).

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 a 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 & Petrakakis 2010) with the Holland & Powell (1998) database.

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.

Figure 6. Predicted atmospheric CO_2 concentrations in an Earth system where CO_2 sources and sinks do not balance, modified after Berner & 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 ~1 million years.

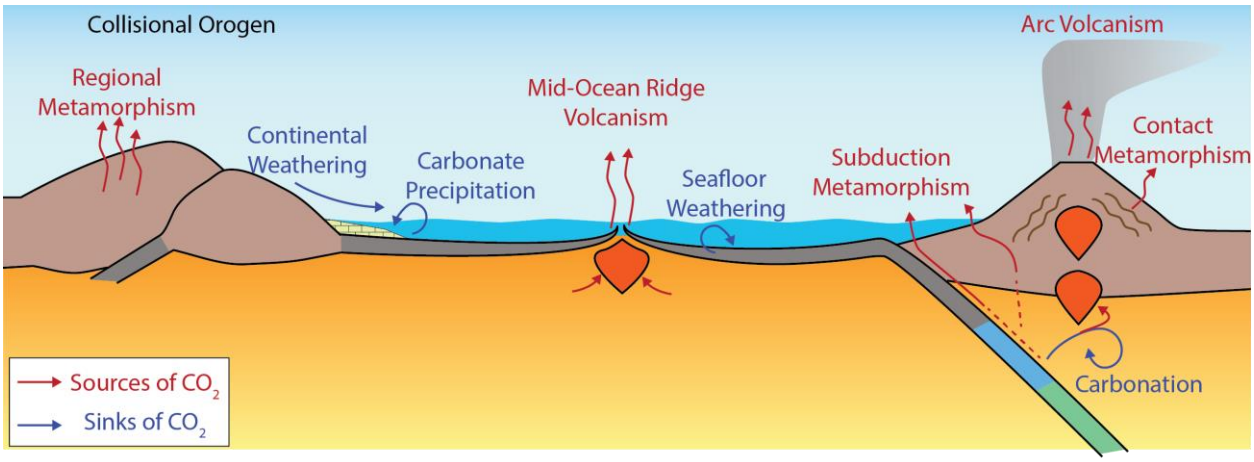

Figure 1

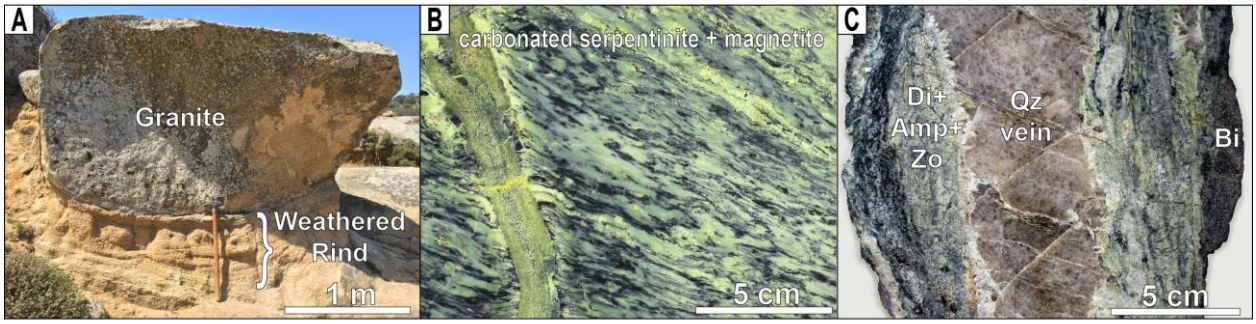

Figure 2

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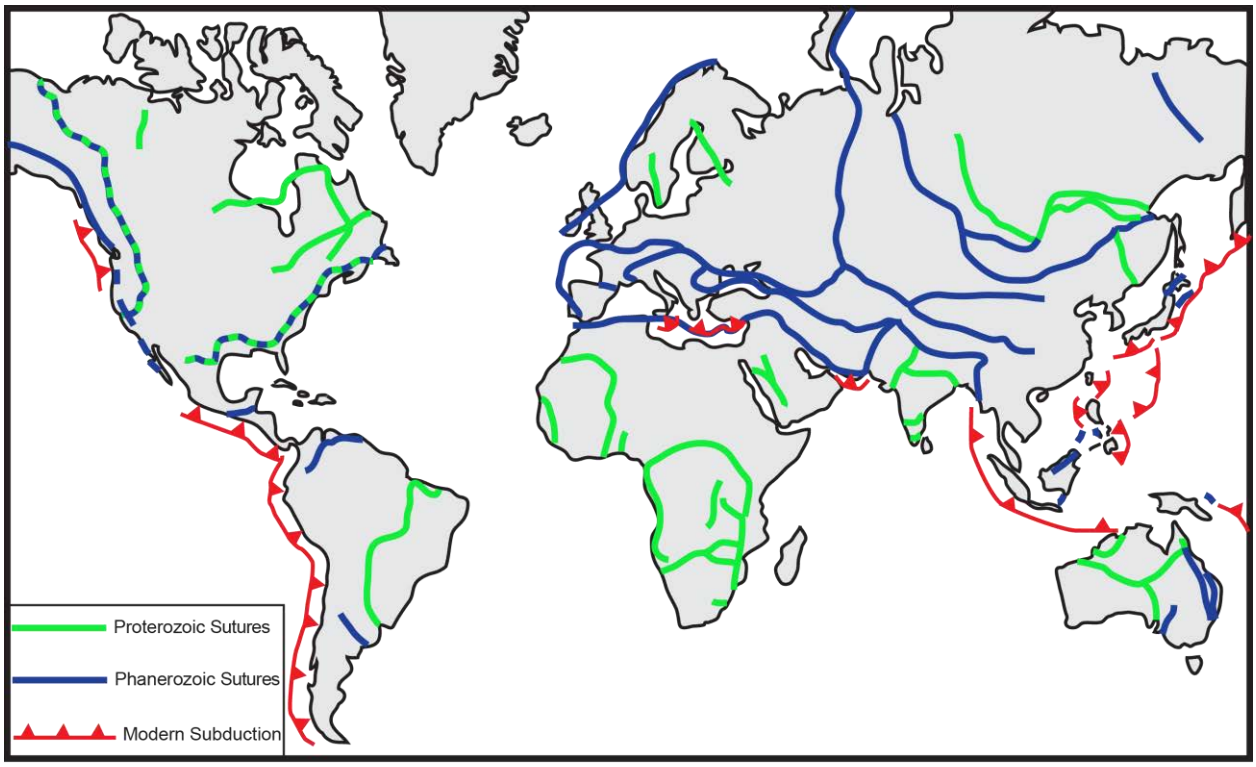

1082 **Figure 3**

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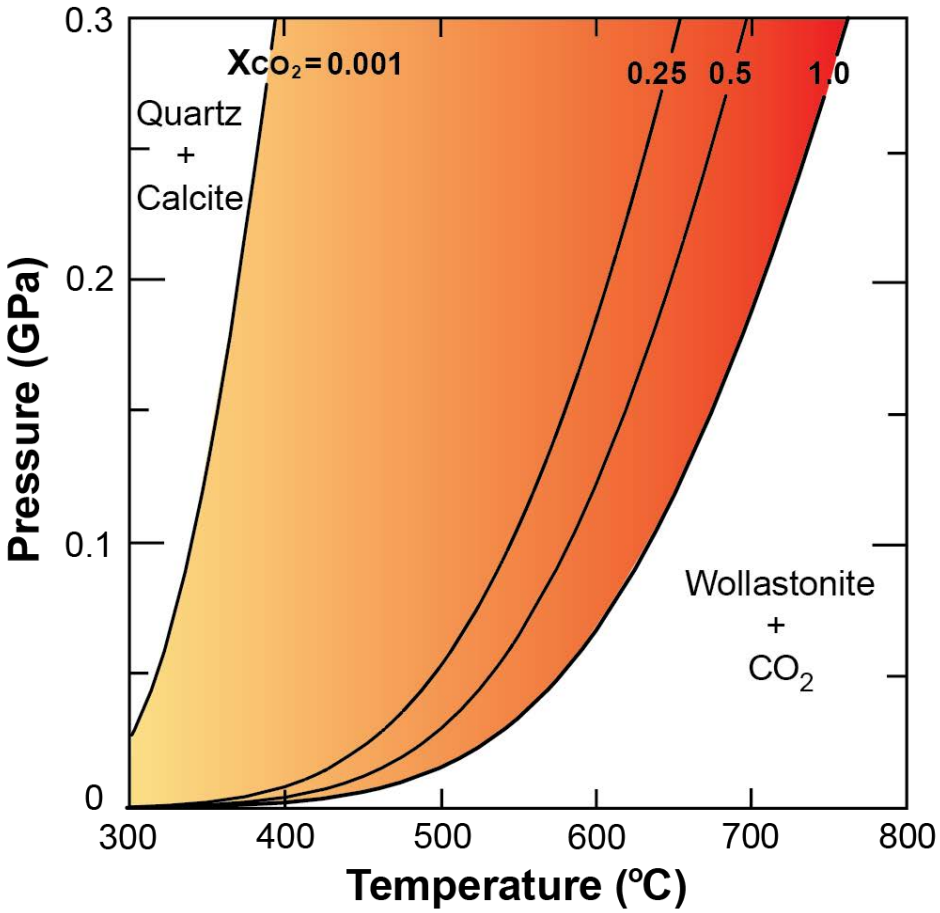

Figure 4

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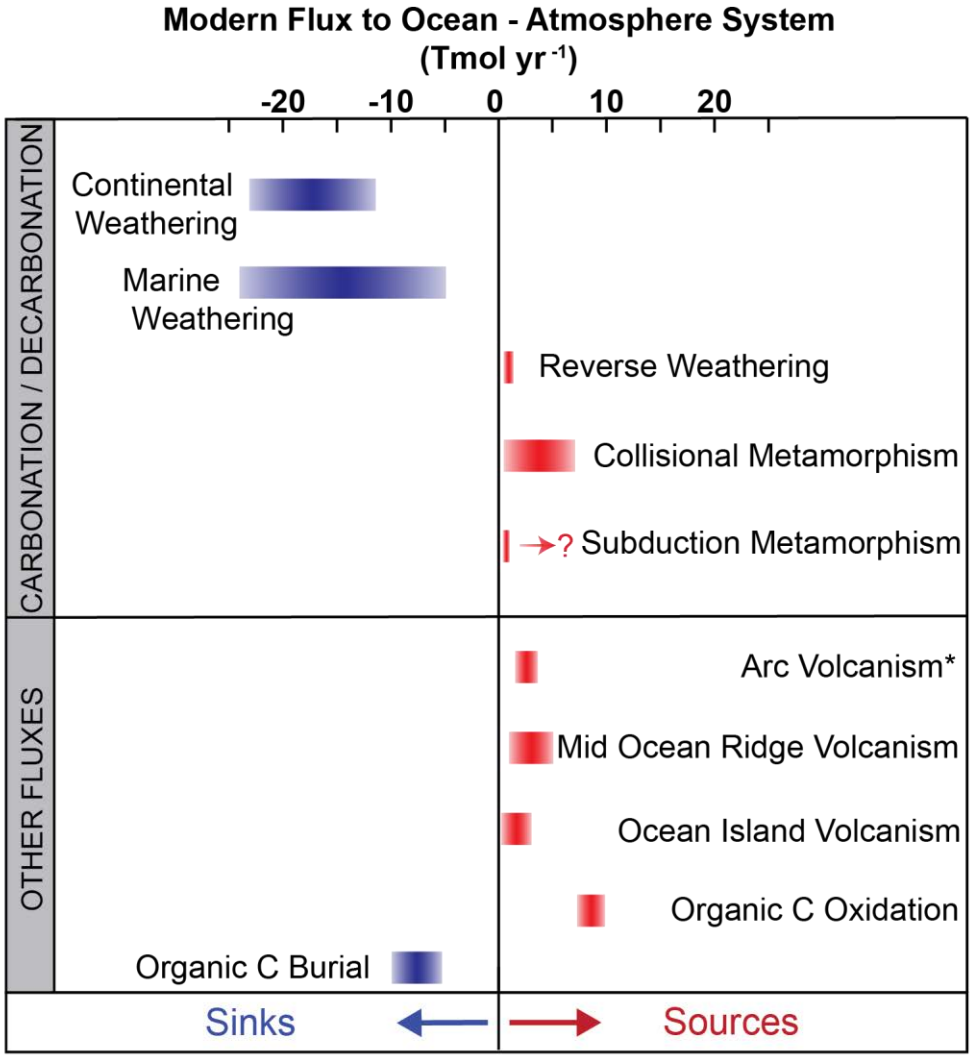

Figure 5

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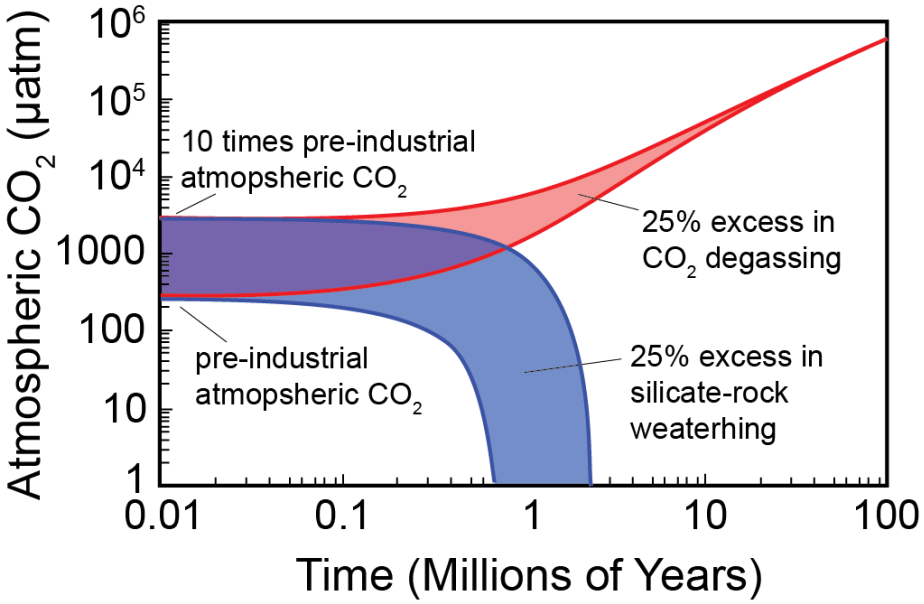

Figure 6

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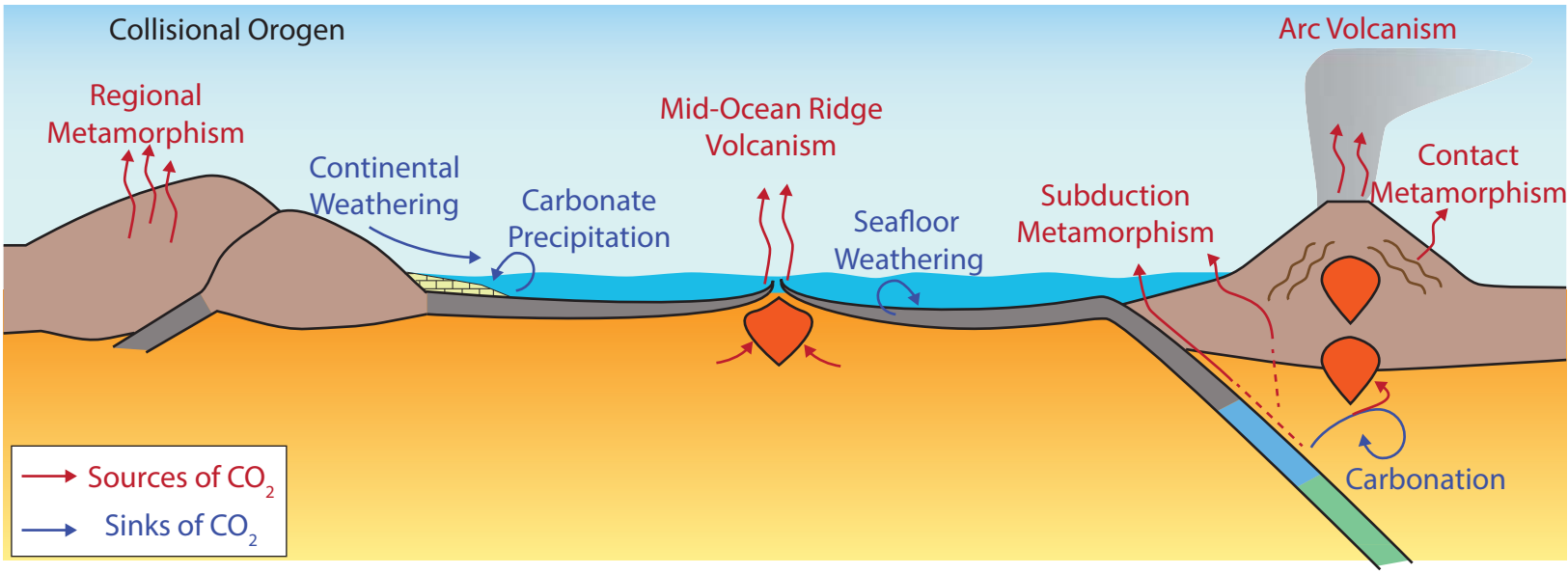

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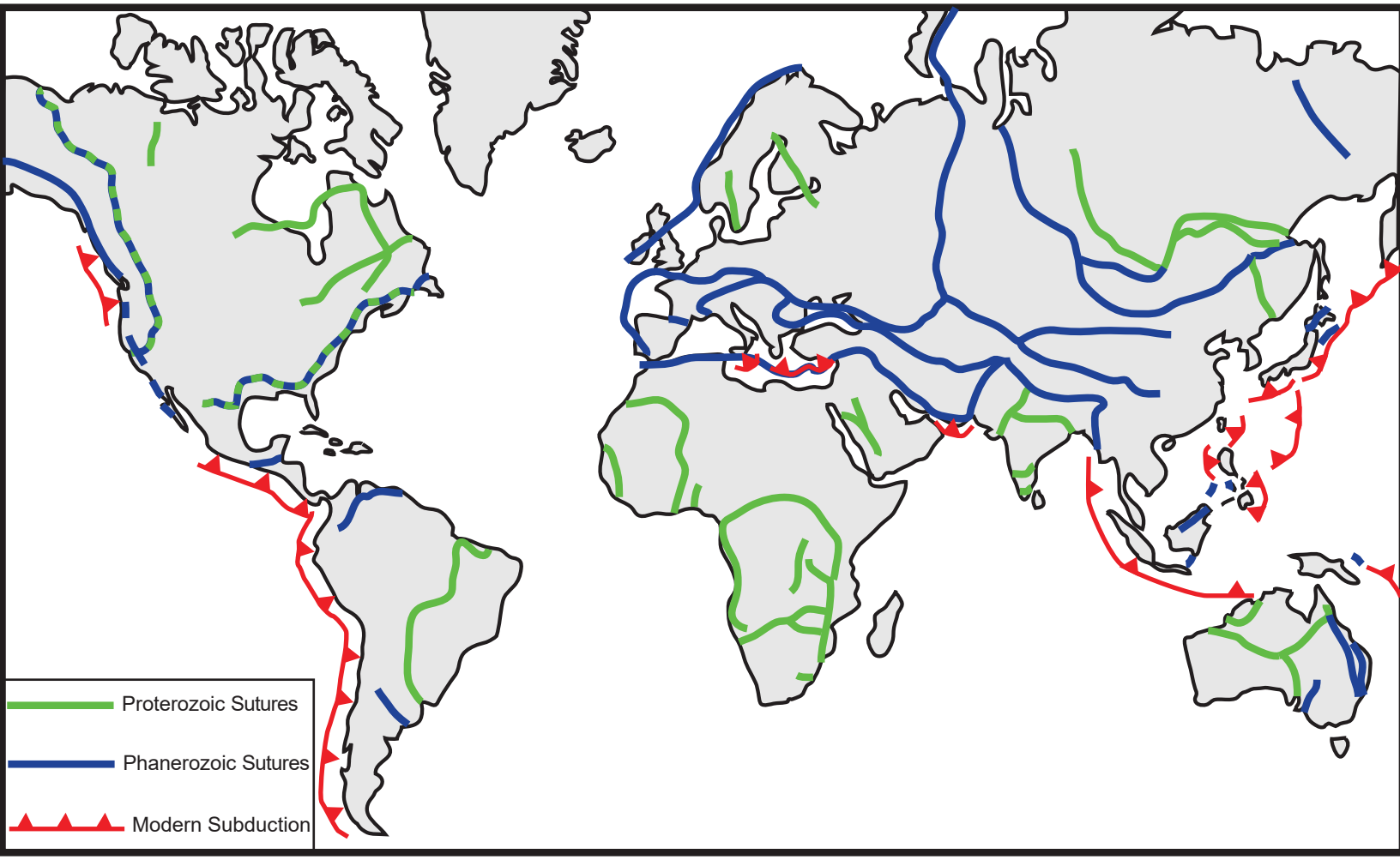

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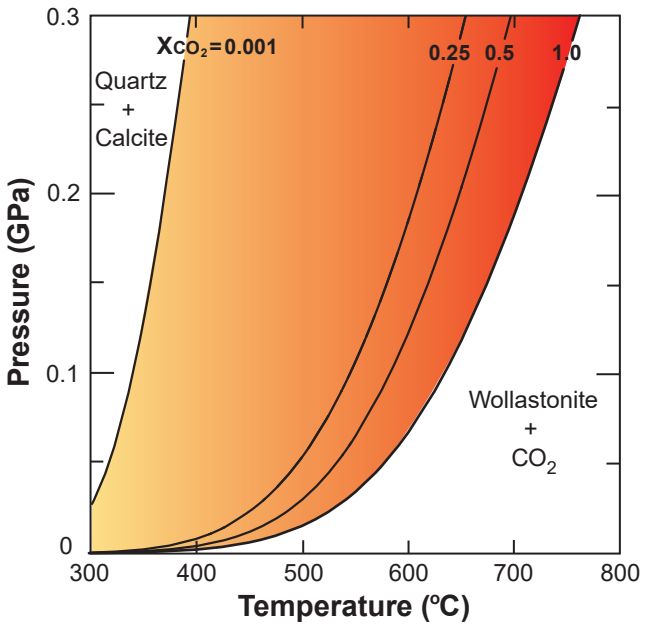

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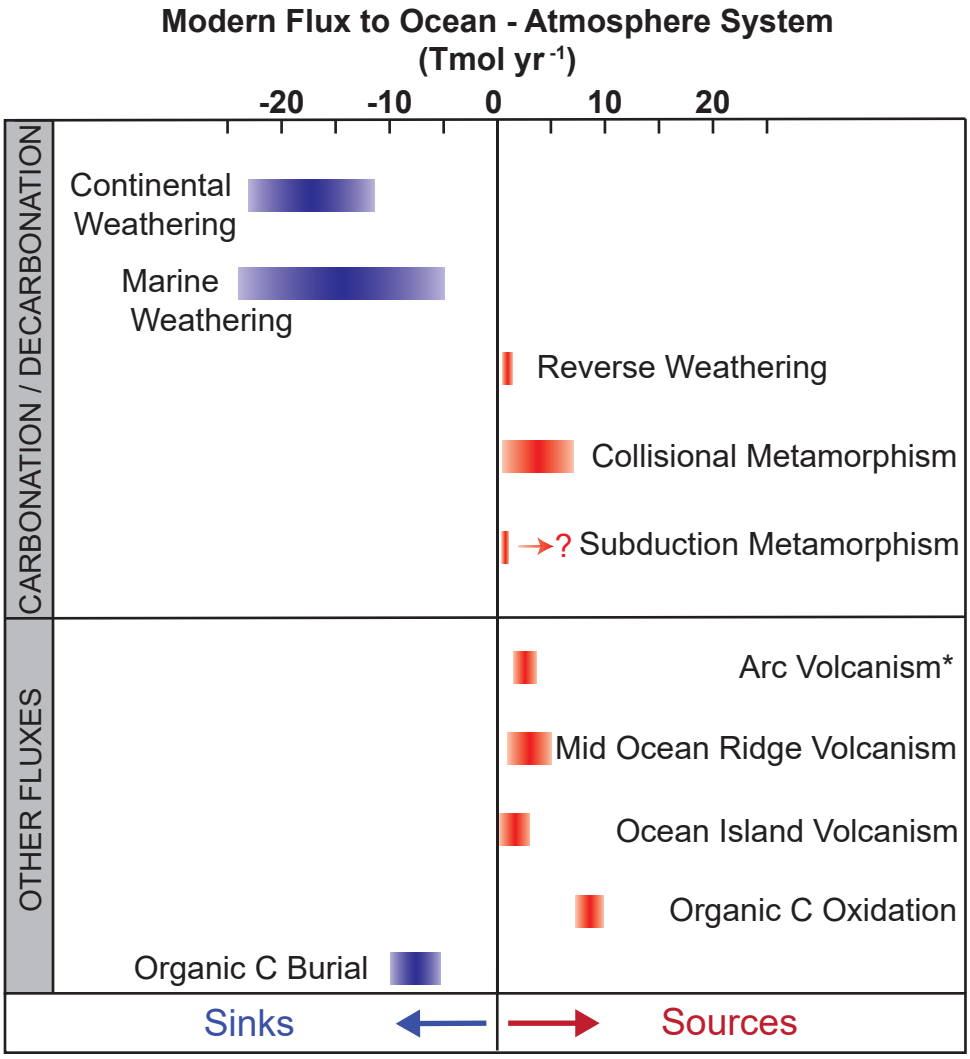

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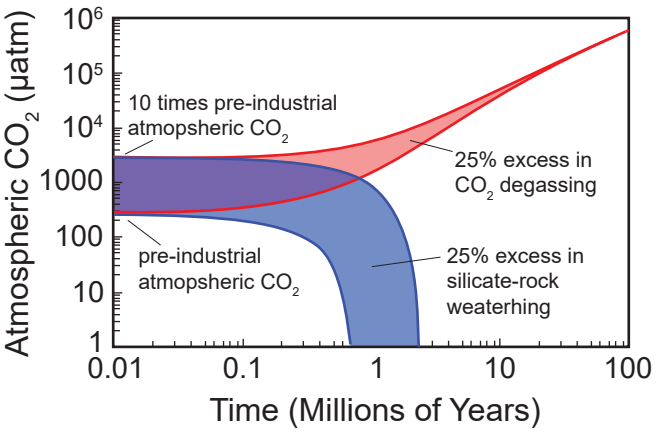

Figure 6