On the Role of the Urey Reaction in Extracting Carbon From the Earth's Atmosphere and Adding It to the Continental Crust

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Urey (1952a,b, 1956) introduced the Urey reaction to explain the origin of carbonates in the continental crust. The reaction extracts CO_2 from the atmosphere in acid rain that reacts with calcium silicates, the products are transported to the oceans where organic and inorganic processes results in the deposition of calcium carbonates. The origin of the CO_2 can be (1) the early atmosphere and (2) the mantle. The reaction removes almost all the atmospheric CO_2 that survived the formation of the Earth. If surface volcanism introduces more CO_2 than is lost by subduction, the CO_2 entering the atmosphere will be lost to the continental crust by the Urey reaction. Studies of carbon fluxes between surface reservoirs have demonstrated the importance of the Urey reaction in controlling the concentration of CO_2 in the atmosphere. At the present time the only surface reservoir with a large mass of carbon is the continental crust. In order to quantify the rate at which the Urey reaction removes CO_2 from the atmosphere we utilize data from the Paleocene-Eocene thermal maximum (PETM). This was a period of elevated global temperatures ($\Delta T = 4 - 5°C$) at 56 Ma attributed to a pulse of volcanism and associated CO_2 in the north Atlantic. We utilize the decay time of this thermal anomaly to quantify the rate at which CO_2 is extracted from the atmosphere by the Urey reaction.

Keywords: Urey reaction, carbon, continental crust, atmosphere, early Earth

1. INTRODUCTION

We first give a brief introduction to the distribution of carbon in the Earth. In doing this we will utilize the concept of carbon reservoirs. In some cases the definition of a carbon reservoir is well-defined. The Earth's atmosphere is an example. Carbon in the atmosphere is primarily in CO_2 and its concentration is relatively uniform. In other cases the definition of a carbon reservoir is arbitrary. The Earth's mantle is an example. The relatively uniform composition of mid-ocean ridge basalts (including CO_2) is taken as evidence of a near-uniform upper mantle reservoir. However, the variability of ocean-island and hot-spot basalts is evidence for a complex heterogeneous lower-mantle.

Houghton (2007) considered the present distribution of carbon in near-surface reservoirs including the atmosphere, oceans, ocean sediments, vegetation and soil, and fossil fuels. However, the near-surface reservoirs contain only a small fraction of the carbon in the Earth. The major reservoirs for carbon at the present are the core, the mantle, and the continental crust. It is generally accepted that a large fraction of the carbon resides in the core reservoir. Both during early core

formation and accretion, and during core formation after the moon-forming giant impact, carbon in the solid Earth was largely partitioned into the core. Dasgupta (2013) estimates that the mass of carbon in the core is $^cM_c = 4.44 \times 10^9$ Gt (1 Gt $= 10^{12}$ kg) but there is certainly a large error bar. We suggest that a reasonable estimate for the present mass of carbon in the core is $^cM_c = (4 \pm 2) \times 10^9$ Gt.

A number of authors have studied the global carbon flux at mid-ocean ridges. These values can be used to estimate the composition of carbon in the mantle source region. Michael and Graham (2015) give a mass fraction $^cC_m = (34 \pm 20) \times 10^{-6}$ and Rosenthal et al. (2015) give a value $^cC_m = (75 \pm 40) \times 10^{-6}$. We suggest that a reasonable estimate for the composition of carbon in this source region is $^cC_m = (5 \pm 2.5) \times 10^{-5}$. Assuming the entire mantle to have this concentration, the mass of carbon in the mantle is $^cC_m = (2 \pm 1) \times 10^8$ Gt.

The third large reservoir for carbon at the present time is the continental crust. About 1% of the carbon in the Earth is in the continental crust; a large fraction of this carbon is in carbonates (limestones, marble, etc.) Wedepohl (1995) has given a comprehensive review of the composition of the continental crust with an emphasis on carbon. He gives a total carbon mass in the continental crust $^cM_{ccp} = 4.2 \times 10^7$ Gt. Of this total he attributes about 80% to sediments, almost entirely in carbonates. Hayes and Waldbauer (2006) have reviewed the literature on carbon in the crust and have given a range of masses and gave a preferred total carbon mass $^cM_{ccp} = 10^8$ Gt. In this paper we will accept the value given by Wedepohl (1995) as a representative value for the present mass of carbon in the continental crust $^cM_{ccp} = 4.2 \times 10^7$ Gt, but suggest that a reasonable range of acceptable values is $^cM_{ccp} = 2 \times 10^7 - 2 \times 10^8$ Gt.

A list of the estimated present masses of carbon in the reservoirs we consider is given in **Table 1**. The estimated total mass of carbon in all of the reservoirs is $^cM = 4.68 \times 10^9$ Gt. With the mass of the Earth, 5.97×10^{24} kg, the concentration of carbon in the bulk Earth by mass is about 0.1%. These values are consistent with previous estimates (Dasgupta, 2013; DePaolo, 2015). We do not give error bars because the uncertainties of some values are difficult to specify.

A large fraction of the carbon in the surface reservoirs is in the continental crust, ~99.99%. Much of this carbon is in the carbonates (limestones, marbles). Some 20–30% of the sediments in the continental crust are carbonates, independent of age (Mackenzie and Morse, 1992). Urey (1952a,b, 1956) proposed that a reaction between atmospheric CO_2 and calcium silicate was a major source of carbon in the continental crust. This reaction is now known as the Urey reaction. The principal purpose of this paper is to evaluate the role of the Urey reaction in terms of our present knowledge of the distribution of carbon in the Earth.

Two sources of the carbon in the continental crust are available. The first of these is the atmosphere. Today the atmosphere has very little carbon in it, however the atmosphere of Venus has a large mass of carbon as CO_2. It is quite possible that the early Earth also had a very high concentration of CO_2, the Urey reaction could have removed a significant fraction of this

TABLE 1 | Masses of carbon in the Earth's carbon reservoirs considered in this paper (1 Gt $= 10^{12}$ kg).

Reservoir	Mass of carbon Gt	References
Core	4×10^9	Dasgupta, 2013
Mantle	2×10^8	This paper
Continental crust	4.2×10^7	Wedepohl, 1995
Oceans	3.8×10^4	Houghton, 2007
Atmosphere	8.5×10^2	NOAA, 2017
Total	4.24×10^9	

carbon to the continental crust. The second source of the carbon in the continental crust is the mantle. If the flux of carbon out of the mantle in surface volcanism exceeds the loss of carbon in subduction, the mantle could have lost carbon to the continental crust. The Urey reaction could have played an important role in this process.

2. THE UREY REACTION

Urey (1952a,b, 1956) introduced the Urey reaction to explain the origin of calcium carbonates (limestones, marbles) in the continental crust. The basic reaction combines atmospheric CO_2 with a calcium silicate to generate a calcium carbonate plus silica. In order to include the role of acid rain in the process we write the Urey reaction in the form

$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$$
$$\rightarrow CaCO_3 + SiO_2 + CO_2 + H_2O \quad (1)$$
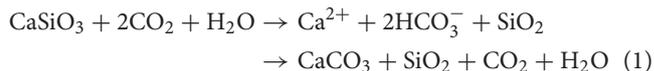
The aqueous products are removed by calcium carbonate precipitation. Carbon dioxide (carbonic acid) in acid rain dissolves calcium silicate (wollastonite) sediments to give calcium, bicarbonate, and silica. The resulting calcium and bicarbonate ions flow in rivers to the oceans where either organic or inorganic precipitation produces the calcium carbonate. Blättler and Higgins (2017) have considered Urey's carbonate-silicate cycle in some detail utilizing measured calcium isotope ratios.

The role of the Urey reaction in maintaining a low concentration of CO_2 in the Earth's atmosphere was explicitly stated by Urey (1952b). "As carbon dioxide was formed it reacted with silicates to form limestone. Of course the silicates may have been a variety of minerals but the pressure of CO_2 was always kept at a low level by this reaction or similar reactions just as it is now."

Although the mass of carbon in the atmosphere today is small (~ 850 Gt), the mass may have been much higher in the past. One of the major differences between Venus and the Earth is atmospheric composition. The atmospheric pressure on Venus is about a factor of 100 greater than the atmospheric pressure on Earth and is 96% carbon dioxide. The mass of carbon in the Venus atmosphere is $^cM_{ap} = 1.28 \times 10^8$ Gt. Scaling the atmospheric carbon masses to the overall masses of Venus and the Earth gives an estimate of the mass of carbon in the early

atmosphere of the Earth. The estimated value is $^cM_{ap} = 1.57 \times 10^8$ Gt (Kasting and Ackerman, 1986).

Another major difference between the Earth and Venus is the giant impact that is hypothesized to have been responsible for the origin of the moon. During the final stages of the Earth's accretion, a collision between the Earth and an astronomical body about the size of Mars occurred 20–100 Myrs after the origin of the solar system. A detailed review of the influence of this collision on the first several hundred million years of Earth evolution has been given by Zahnle et al. (2007). The intensity of the collision melted and vaporized significant fractions of the Earth and the incoming body. Some fraction of the incoming body (and some fraction of the Earth) subsequently accreted and cooled to form Earth's moon. It is estimated that the hot silicate atmosphere cooled and condensed over about a thousand years. A global magma ocean cooled and solidified much more slowly, possibly over tens of millions of years. Sleep and Zahnle (2001) and Sleep et al. (2011, 2014) have proposed that a substantial fraction of the CO_2 in the atmosphere was absorbed by the solid surface crust of the global magma ocean. Episodic foundering subduction of this dense crust transported the carbon into the Earth's mantle, removing CO_2 from the atmosphere.

An alternative to the mechanism proposed by Sleep and Zahnle (2001) is that carbon was directly transferred to the mantle during accretion (Li et al., 2016) or that carbon was transferred by tectonic processes during the Hadean. Shaw (2008) has provided a comprehensive review of CO_2 evolution in the Hadean to the early Proterzoic.

An important question concerning carbon is the origin of the carbon in the continental crust. One hypothesis is that they were extracted from the atmosphere by the Urey reaction relatively early in the Earth's history. This hypothesis was put forward by Kramers (2002) and by Lowe and Tice (2004). It should be noted that the potential mass of carbon in the early atmosphere, 1.57×10^8 Gt, is substantially larger than the estimated present mass of carbon in the continental crust $^cM_{ccp} = 4.2 \times 10^7$ Gt. Thus, a substantial fraction of the carbon in the continental crust could have been transferred from the atmosphere.

In order for the Urey reaction to extract CO_2 from the atmosphere the early Earth must have had continental crust in order to generate surface deposits of calcium silicates. In addition the Earth must of had oceans in order for the acid rain to catalyze the Urey reaction between atmospheric CO_2 and the surface deposits of calcium silicates. Little data is available for timing the initiation of the extraction of CO_2 from the atmosphere. We will assume that the process began at a time t_0 after the solidification of the magma ocean at about 4.5 Ga. We further assume that the Urey reaction extracted carbon from the atmosphere at a constant rate $^cJ_{a-cc}$ until the concentration of CO_2 in the atmosphere was reduced to a very low level. The rate of loss of carbon from the atmosphere is given by

$$\frac{d\,^cM_a}{dt} = -\,^cJ_{a-cc}. \tag{2}$$

We require $^cM_a = \,^cM_{a0}$ at $t = t_0$ and obtain

$$^cM_a = \,^cM_{a0} - \,^cJ_{a-cc}(t - t_0) \tag{3}$$

This transport is completed at $t = \tau$ when $^cM_a = 0$ where

$$\tau = t_0 + \frac{^cM_{a0}}{^cJ_{a-cc}} \tag{4}$$

Taking $^cM_{a0} = 1, 2,$ and 3×10^7 Gt we give the dependence of the carbon flux $^cJ_{a-cc}$ on the flux time $\tau - t_0$ in **Figure 1**. Combining Equations (3) and (4) we find the time dependence of the mass of carbon in the atmosphere

$$^cM_a = \,^cM_{a0}\left(1 - \frac{t - t_0}{\tau - t_0}\right) \tag{5}$$

for the period $t_0 < t < t_0 + \tau$. For $t_0 + \tau < t < t_0 + t_p$, we have added $^cM_{a0}$ to the continental crust.

Again taking $^cM_{a0} = 1, 2,$ and 3×10^7 Gt we give the mass of carbon in the continental crust $^cM_{cc}$ as a function of time t in **Figure 2** for $t_0 = 1$ Gyr and $\tau = 1$ and 3 Gyr. Carbon is lost from the atmosphere to the continental crust after plate tectonics provides the calcium silicate required for the Urey reaction to proceed.

In discussing the role of the Urey reaction we focus our attention on its role in the generation of carbonate sediments in the continental crust. Above we discussed how it could be directly responsible for the extraction of primordial CO_2 from the atmosphere. We now turn our attention to its indirect role in the addition of carbon from the mantle into the continental crust. Carbon is extracted from the mantle by volcanism and is returned to the mantle by subduction. If the rate of addition exceeds the rate of loss then the difference may be responsible for the origin of a large fraction of the carbon in the continental crust. Order of magnitude estimates of this process given by Hayes and Waldbauer (2006) demonstrated the plausibility of this mechanism.

A comprehensive model for the variability of atmosphere CO_2 over Phanerozoic times has been given by Berner and Kothavala (2001). This model, GEOCARB III, is complex and involves both organic and inorganic processes. Transport of
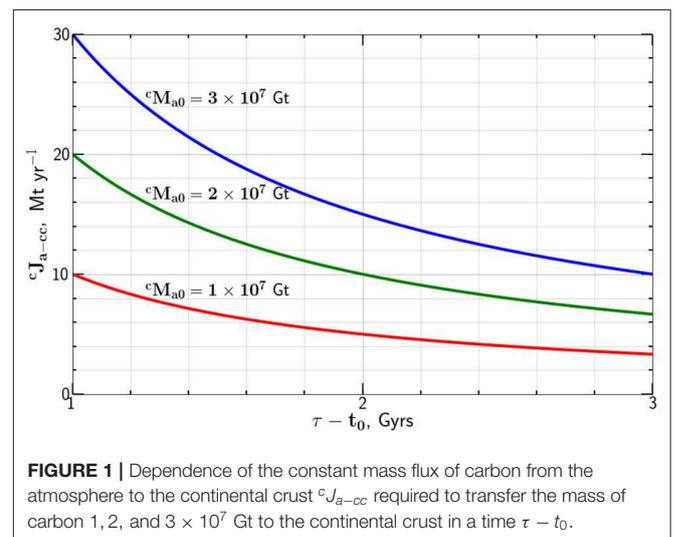
FIGURE 1 | Dependence of the constant mass flux of carbon from the atmosphere to the continental crust $^cJ_{a-cc}$ required to transfer the mass of carbon 1, 2, and 3×10^7 Gt to the continental crust in a time $\tau - t_0$.

FIGURE 2 | Dependence of the mass of carbon in the atmosphere ^cM_a on time t for $t_0 = 1$ Gyr, $\tau = 1$ and 3 Gyr, and $^cM_{a0} = 1, 2, 3 \times 10^7$ Gt.
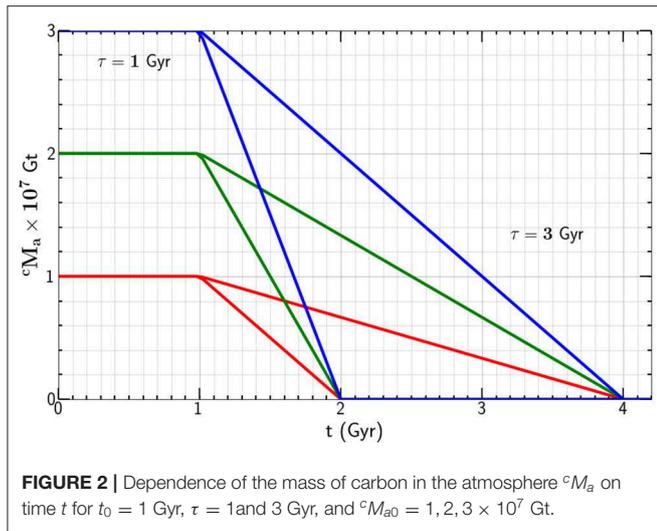
carbon between the atmosphere, oceans, and continental crust is quantified on the million year time scale. The balance is dominated by the exchange of carbon between carbonates in the continental crust and carbon in the surficial reservoirs (oceans and atmosphere) and organic carbon (Berner and Caldeira, 1997). This exchange occurs through the Urey reaction given in Equation (1). When erosion is high, the Urey reaction extracts CO_2 from the atmosphere adding carbonates to the continental crust. High erosion rates are associated with low sea level and large continental areas. When erosion is low, the Urey reaction operates in the opposite direction (from right to left in Equation 1) with carbonates decomposing to give CO_2. An example of this metamorphic process is the subduction of carbonate sediments and the generation and return of CO_2 to the atmosphere in subduction zone volcanics (Frezzotti et al., 2011).

We will next provide estimates for the rate at which surface volcanism transfers carbon from the mantle to the surface reservoirs. Volumetrically, surface volcanism is dominated by mid-ocean ridge volcanism. A number of authors have studied the global carbon flux from the mantle at mid-ocean ridges. Some studies involve direct measurements of CO_2 concentrations and others utilize correlations with other elements, such as barium. Hayes and Waldbauer (2006) summarized the early literature and gave a mid-ocean ridge global carbon flux $^cJ_{m-a} = 12$ Mtyr^{-1}. Dasgupta and Hirschmann (2010) summarized the available data and gave a global carbon flux $^cJ_{m-a} = 36 \pm 24$ Mtyr^{-1}. Michael and Graham (2015) obtained an estimate of the carbon flux from mid-ocean ridges using measurements of CO_2/Ba ratios with published compilations of trace elements. They suggest that the global flux of carbon out of the mantle at mid-ocean ridges is $^cJ_{m-a} = 34 \pm 20$ Mtyr^{-1}. Rosenthal et al. (2015) used CO_2/Ba and CO_2/Nb systematics and conclude that the global flux of carbon is $^cJ_{m-a} = 50 \pm 30$ Mtyr^{-1}. Chavrit et al. (2014) carried out CO_2 vesicularity measurements on some 400 mid-ocean ridge glasses. These results were interpreted to give a global carbon flux $^cJ_{m-a} = 10 \pm 3.4$ Mtyr^{-1}. Since not all CO_2 would be expected to be in cavities, the actual carbon flux would be expected to be somewhat higher. Based on these previous

studies we suggest that a reasonable choice for the carbon flux from the mantle at mid-ocean ridges is $^cJ_{m-a} = 36 \pm 24$ Mtyr^{-1}.

Flux estimates of carbon in ocean island basalts and hot spot volcanics have been reviewed by Hayes and Waldbauer (2006). Volumetrically this volcanism is about 10% of the mid-ocean ridges volcanism but some of this volcanism may be tapping a primitive lower mantle reservoir with higher concentrations of carbon. Considering the uncertainties we will neglect this source of carbon to the atmosphere in our modeling.

Just as carbon is lost from the mantle at mid-ocean ridges, carbon is returned to the mantle at subduction zones. A detailed study of carbon fluxes at subduction zones has been carried out by Kelemen and Manning (2015). These authors suggest that the downward flux of carbon at global subduction zones is 53 ± 13 Mtyr^{-1}. However, a substantial fraction of this carbon never makes it to the mantle. Carbon is returned to the oceans and atmosphere in subduction zone volcanism. Kelemen and Manning (2015) estimate the loss of carbon due to subduction zone volcanics is in the range 30 ± 12 Mtyr^{-1}. Taking the difference of these values, the present subduction flux of carbon to the mantle is $^cJ_{sp} = 24 \pm 24$ Mtyr^{-1}. Dasgupta and Hirschmann (2010) have also provided a comprehensive study of carbon subduction and conclude that $^cJ_{sp} = 36 \pm 12$ Mtyr^{-1} reach the mantle. An earlier review of carbon subduction was given by Hayes and Waldbauer (2006). These authors concluded that the input flux of carbon is 36 ± 12 Mtyr^{-1} and that the flux to the mantle is $^cJ_{sp} = 27 \pm 9$ Mtyr^{-1}.

We obtain an estimate for the net flux of carbon from the mantle required to produce a large mass of carbon in the continental crust assuming that this flux $^cJ_{m-cc}$ has been a constant during the period $t_p - t_0$ to t_p (present time). We use the relation

$$^cJ_{m-cc} = \frac{^c\Delta M_{m-cc}}{t_p - t_0} \tag{6}$$

Taking the carbon mass transported from the mantle to the continental crust $^c\Delta M_{m-cc} = 1, 2,$ and 3×10^7 Gt we give the dependence of the carbon flux $^cJ_{m-cc}$ on the flux time $t_p - t_0$ in **Figure 3**. The results are essentially identical to those given in **Figure 1** for the transfer from the atmosphere. This is not surprising since Equation (6) is basically the same as Equation (3).

The time dependence of the mass $^cM_{m-cc}$ transferred from the mantle to the continental crust is given by

$$^cM_{m-cc} =^c \Delta M_{m-cc} \frac{t - t_p}{t_p - t_0} \tag{7}$$

Again taking $^c\Delta M_{m-cc} = 1, 2,$ and 3×10^7 Gt we give the dependence of the mass of carbon added to the continental crust $^cM_{a-cc}$ as a function of time t in **Figure 4** for $t_0 = 1.4$ Gyr.

When excess CO_2 in the atmosphere has been depleted by the Urey reaction an approximate steady state balance is established between the volcanic input of CO_2 and extraction by the Urey reaction. It has been argued by many authors that this balance is
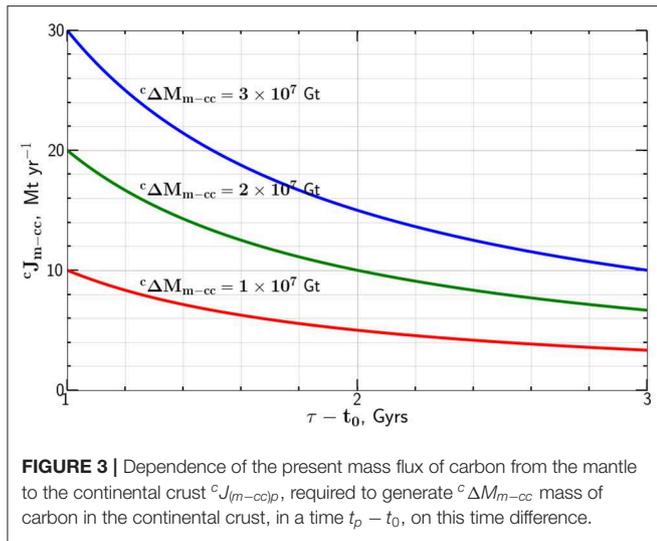
FIGURE 3 | Dependence of the present mass flux of carbon from the mantle to the continental crust $^cJ_{(m-cc)p}$, required to generate $^c\Delta M_{m-cc}$ mass of carbon in the continental crust, in a time $t_p - t_0$, on this time difference.
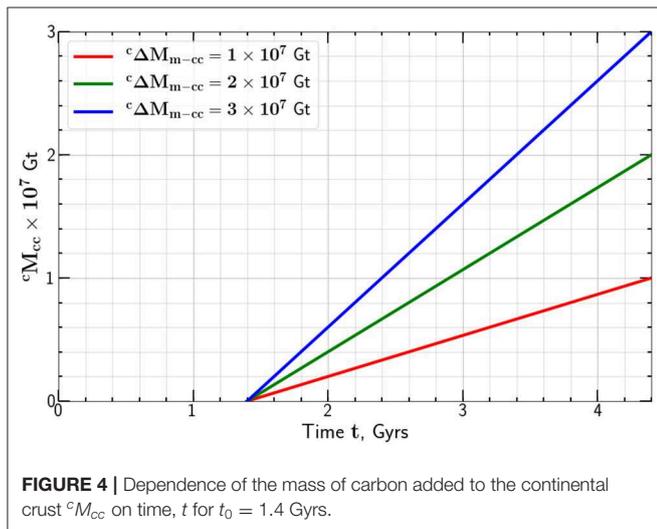
FIGURE 4 | Dependence of the mass of carbon added to the continental crust $^cM_{cc}$ on time, t for $t_0 = 1.4$ Gyrs.

controlled by the Urey reaction. We approximate this balance by the relation

$$^cJ_{a-cc} = \frac{^cM_a}{\tau_{a-cc}} \qquad (8)$$

where $^cJ_{a-cc}$ is the rate of volcanic input of carbon into the atmosphere. We assume that the extraction rate is proportional to the mass of carbon in the atmosphere ^cM_a. The rate at which the Urey reaction rate processes carbon τ_{a-cc} takes account of the rate at which acid rain can interact with calcium silicate sediments, clearly τ_{a-cc} can be a function of time.

3. PETM

As a further test of our approach to the use of the Urey reaction to explain variations in atmospheric CO_2 concentrations we will consider the Paleocene-Eocene thermal maximum (PETM). This was a period of elevated global temperatures that occurred at about 56 Ma. The elevated temperatures are attributed

to increased concentrations of CO_2 and possibly methane in the atmosphere. The maximum increase in global surface temperatures is in the range $4 - 5°C$ and the period of excess temperatures lasted some 10^6 yrs. The occurrence of this period of high atmospheric CO_2 and temperatures was first documented by Kennett and Stott (1991) from an observation of large carbon and oxygen isotope ratios in an ocean drilling core.

A comprehensive review of the subsequent studies of this event was given by McInerney and Wing (2011). By the time this review paper was published some 400 research papers on a wide variety of aspects of PETM were included. The onset of the period of high atmosphere CO_2 and temperature was dated at 56.3 Ma, the onset lasted <10 ka, and the subsequent decay lasted some 120–220 ka. Observational data used to constrain the structure of the thermal pulse involves a variety of isotope measurements in drilling cores. One example is the temporal dependence of the observed $\delta^{13}C$ anomaly in a drilling core (Cui et al., 2011). A second example is the use of boron isotope data as a proxy for seawater (Gutjahr et al., 2017). Jones et al. (2013) have carried out a detailed study of the warming associated with the PETM. They conclude that the global mean surface anomaly is in the range 4–5°C.

Several sources of the carbon associated with the PETM have been proposed. These include methane clathrates and melting of permafrost. Storey et al. (2007) have made a very strong case for associating the PETM with the flood basalt volcanism resulting from the opening of the north Atlantic. This volcanism is documented in east Greenland and the Faroe Islands. The earliest of these flood basalts have an age of 56.1 ± 0.5 Ma. We support the hypothesis that a substantial fraction of the carbon responsible for the PETM was CO_2 entering the atmosphere from these flood basalts.

Studies of isotopic anomalies associated with the PETM systematically show a rapid increase at about 55.8 Ma with a subsequent decay of the anomaly over about 10^5 yrs. There is considerable scatter between drill sites. As an example of an isotopic anomaly we give data from the Deep Sea Drilling Project (DSDP) site 401 in the northeast Atlantic Ocean (Gutjahr et al., 2017). A strong negative carbon isotope anomaly was found in foraminifera *Morozovella subbotinae*. The observed $\delta^{13}C$ anomaly is given as a function of time t_{PETM} relative to the onset of the anomaly in **Figure 5**.

Gutjahr et al. (2017) have carried out an extensive modeling study using the available isotope data to provide estimates for the carbon generated during the PETM. We will utilize these values and take the total carbon added to the Earth's surface to be 12,000 Gt. Before and after the PETM we take the background carbon mass in the atmosphere to be $^cM_{ab} = 1,400$ Gt and the peak mass of carbon in the atmosphere during the PETM to be $^cM_{a0} = 3,050$ Gt.

We now carry out an approximate analysis of the decay of the PETM due to the loss of CO_2 from the atmosphere by the Urey reaction. We extend the balance given in Equation (8) to include the transient removal of carbon from the atmosphere and write

$$\frac{d^cM_a}{dt} = {}^cJ_{(a-cc)b} - \frac{^cM_a}{\tau_{a-cc}} \qquad (9)$$
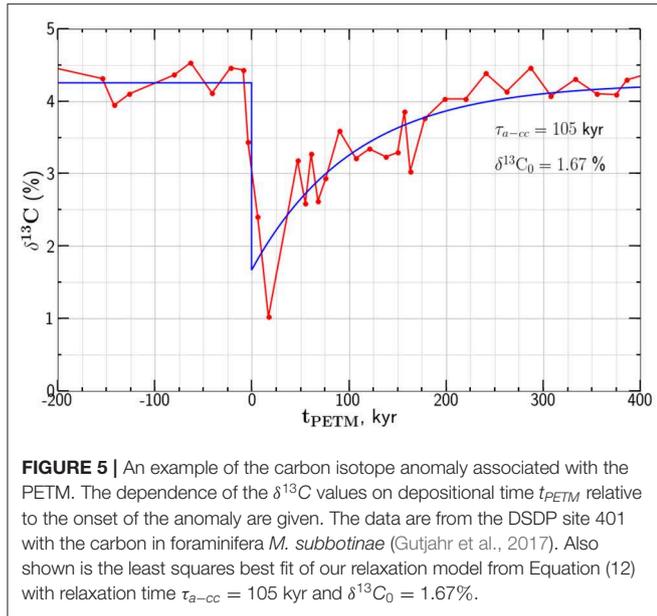
FIGURE 5 | An example of the carbon isotope anomaly associated with the PETM. The dependence of the $\delta^{13}C$ values on depositional time t_{PETM} relative to the onset of the anomaly are given. The data are from the DSDP site 401 with the carbon in foraminifera M. subbotinae (Gutjahr et al., 2017). Also shown is the least squares best fit of our relaxation model from Equation (12) with relaxation time $\tau_{a-cc} = 105$ kyr and $\delta^{13}C_0 = 1.67\%$.

From Equation (8) the background mass of carbon in the atmosphere is given by

$$^{c}M_{ab} = \tau_{a-cc} \, ^{c}J_{(a-cc)b} \tag{10}$$

We prescribe an initial mass of carbon in the atmosphere at $t = 0$, $^{c}M_{a0}$, with $^{c}M_{a0} > {}^{c}M_{ab}$ and solve Equation (10) taking τ_{a-cc} to be constant with the result

$$^{c}M_a = (^{c}M_{a0} - {}^{c}M_{ab})e^{-t/\tau_{a-cc}} + {}^{c}M_{ab} \tag{11}$$

The excess mass of carbon in the atmosphere $^{c}M_{a0} - {}^{c}M_{ab}$ decays exponentially as the Urey reaction extracts carbon from the atmosphere.

In order to estimate the value of the characteristic decay time τ_{a-cc} we assume that the negative carbon isotope anomaly is proportional to the mass of carbon in the atmosphere and write Equation (11) as

$$\delta^{13}C = \delta^{13}C_b - (\delta^{13}C_b - \delta^{13}C_0)e^{-t_{PETM}/\tau_{a-cc}} \tag{12}$$

where $\delta^{13}C_b$ is the background isotope ratio before and after PETM and $\delta^{13}C_0$ is the minimum isotope ratio prescribed at $t = 0$. Taking $\delta^{13}C_b = 4.25\%$ the dependence of $\delta^{13}C$ on t_{PETM} from Equation (12) is compared with the isotope anomaly values given in **Figure 5**. The least squares fit of the exponential decay to the data points in given taking $\tau_{a-cc} = 105$ kyr and $\delta^{13}C_0 = 1.67\%$.

We next use this value of τ_{a-cc} to obtain the dependence of atmosphere carbon mass on time during PETM based on the model dependence given in Equation (11). Taking the values $^{c}M_{ab} = 1,400$ Gt and $^{c}M_{a0} = 3,050$ Gt as given by Gutjahr et al. (2017) with $\tau_{a-cc} = 105$ kyr the model results are given in **Figure 6**.

We now return to Equation (10). This result relates the background atmospheric carbon mass $^{c}M_{ab}$ to the background
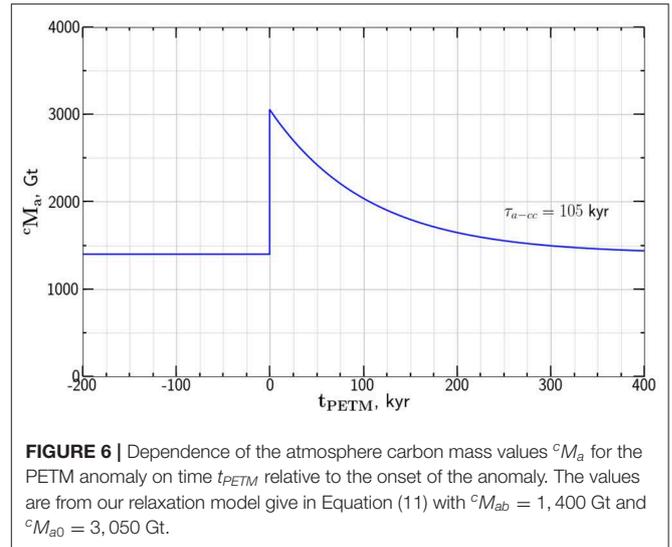
FIGURE 6 | Dependence of the atmosphere carbon mass values $^{c}M_a$ for the PETM anomaly on time t_{PETM} relative to the onset of the anomaly. The values are from our relaxation model give in Equation (11) with $^{c}M_{ab} = 1,400$ Gt and $^{c}M_{a0} = 3,050$ Gt.

rate of volcanic input of CO_2 carbon into the atmosphere $^{c}J_{(a-cc)b}$ and the Urey decay time τ_{a-cc}. During the PETM we have taken the background carbon mass $^{c}M_{ab} = 1,400$ Gt. Taking $\tau_{a-cc} = 105$ kyr we find from Equation (12) that $^{c}J_{(a-cc)b} = 13$ Mtyr^{-1}. This is an independent determination of the volcanic flux of carbon into the atmosphere. In **Figure 4** we gave volcanic the flux required to generate a specific mass of carbon in the continental crust

4. DISCUSSION

Urey (1952a) proposed the Urey reaction, Equation (1) to explain the origin of carbonates in the continental crust. He argued that the reaction would essentially remove all CO_2 from the atmosphere. It is now accepted that in analogy to Venus, there may have been a large mass of carbon in the Earth's early atmosphere, as much as 10^8 Gt. However, only a fraction of this may have survived the moon forming impact. We give a very simplified model for the extraction of carbon from the atmosphere to the continental crust, taking the extraction rate $^{c}J_{a-cc}$ to be constant. There are basically no constraints on the variation of this rate with time. If a significant fraction of the carbon in the continental crust was extracted from the atmosphere, it is likely that it occurred early in Earth's history as illustrated in **Figure 1**.

The Urey reaction also controls the equilibrium mass of carbon in the atmosphere after the removal of any large initial concentration. The input of carbon to the atmosphere is from volcanism and we show that the equilibrium mass of carbon in the atmosphere $^{c}M_{ab}$ is proportional to the rate of volcanic injection $^{c}J_{a-cc}$ divided by a characteristic Urey time τ_u. We quantify the value of τ_u by studying the observed relaxation of the Paleocene-Eocene thermal maximum, which occurred at 56 Ma, and the relaxation time is about $\tau_u = 10^5$ yrs.

We also give a simplified model for the extraction of carbon from the atmosphere to the continental crust. If the volcanic

loss of carbon from the mantle by volcanism exceeds the return of carbon by subduction, the difference is added to the continental crust. If the volcanic carbon enters the oceans organic precipitation creates carbonates. If the volcanic carbon enters the atmosphere it enters the continental crust by the Urey reaction. Current estimates of carbon fluxes from and to the mantle are sufficient to have produced all the carbon in the continental crust. At the present time it is not possible to quantify the relative importance of carbon addition to the continental crust from the early atmosphere and the mantle.

We have addressed two major questions concerning carbon in the atmosphere in this paper. The first is the origin of the carbon in the continental crust. We conclude that it is possible the carbon could have been extracted either from the early atmosphere or from the mantle over a longer period of time. Studies of the concentration of carbon in the atmosphere and continental crust over geologic time are required and should receive a high priority.

The second question we have addressed is the relaxation of injections of carbon into the atmosphere back to equilibrium values. We quantify this by studying the Paleocene-Eocene thermal maximum (PETM). This has obvious implications for the recovery from the process of anthropogenic injection of carbon into the atmosphere. We find the relaxation time to be about 50,000 yrs.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the manuscript/supplementary files.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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