Carbonation and the Urey Reaction

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Abstract

There are three major reservoirs for carbon in the Earth at the present time, the core, the mantle, and the continental crust. The carbon in the continental crust is mainly in carbonates (limestones, marbles, etc). In this paper we consider the origin of the carbonates. In 1952 Harold Urey proposed that calcium silicates produced by erosion reacted with atmospheric CO_2 to produce carbonates, this is now known as the Urey reaction. In this paper we first address how the Urey reaction could have scavenged a significant mass of crustal carbon from the early atmosphere. At the present time the Urey reaction controls the CO_2 concentration in the atmosphere. The CO_2 enters the atmosphere by volcanism and is lost to the continental crust through the Urey reaction. We address this process in some detail. We then consider the decay of the Paleocene-Eocene thermal maximum (PETM). We quantify how the Urey reaction removes an injection of CO_2 into the atmosphere. A typical decay time is 100,000 years but depends on the variable rate of the Urey reaction.

Introduction

The continental crust is a major reservoir for carbon in the Earth. A major question in geology is the origin of the carbon, principally in calcium carbonates. The first successful attempt to explain the origin of calcium carbonates (limestones, marbles) in the continental crust was given by Urey (1952). The basic equation he gave was of the form

$$\mathrm{CaSiO_3} + \mathrm{CO_2} \Leftrightarrow \mathrm{CaCO_3} + \mathrm{SiO_2} \qquad (1)$$

He proposed that atmospheric CO_2 combines with a calcium silicate to generate a calcium carbonate plus silica. A direct quote from his paper states: "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 presence of CO_2 was always kept at a low level by this reaction or similar reactions just as it is now."

In the current literature an expanded version of the Urey reaction is given (Blattler and Higgins 2017). In order to include the role of acid rain the Urey reaction takes the form

$$\begin{aligned}\mathrm{CaSiO_3} + 2\mathrm{CO_2} + \mathrm{H_2O} &\rightarrow \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-} + \mathrm{SiO_2} \\ &\rightarrow \mathrm{CaCO_3} + \mathrm{SiO_2} + \mathrm{CO_2} + \mathrm{H_2O}\end{aligned} \qquad (2)$$

The carbonation takes place when 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.

The three large reservoirs for carbon in the Earth at the present time are the core, mantle, and continental crust. We assume that the core is an isolated reservoir and neglect its role. About one per cent of the carbon in the Earth is in the continental crust. Wadepohl (1995) has given a comprehensive study of the composition of the continental crust with an emphasis on carbon. He gives an estimate for the total mass of carbon (c) in the continental crust (cc) at the present time (y) of ${}^{c}M_{ccp} = 4.2 \times 10^{7}$ Gt. Hayes and Waldbauer (2006) have reviewed the literature on carbon in the continental crust and suggest that it may be as high as ${}^{c}M_{ccp} = 10^{8}$ Gt. DePaolo (2015) gives a range of 6 to 7×10^{7} Gt. In this paper we take a representative value to be ${}^{c}M_{ccp} = 5 \times 10^{7}$ Gt. The mass of carbon in the ocean is about a factor of 10^{3} less than the mass of carbon in the continental crust (Houghton 2007).

Urey (1952, 1956) clearly recognized that the reaction he proposed would efficiently remove CO_2 from the Earth's atmosphere, but at that time little was known about the early atmosphere. 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 (a) at the present time (p) is ${}^{c}M_{ap} = 1.28 \times 10^{8}$ Gt. Scaling the atmospheric carbon masses to the overall masses of Venus and the Earth gives an estimate of the mass of carbon (c) in the early atmosphere (t=0) of the Earth. The estimated value is ${}^{c}M_{a0} = 1.57 \times 10^{8}$ Gt (Kasting and Ackerman 1986).

Carbon from the atmosphere to the continental crust

One hypothesis for the origin of the carbon in the continental crust is that it was extracted directly from the atmosphere relatively early in Earth's history. The estimated mass of carbon (c) in the early atmosphere (a) given above, ${}^{c}M_{a0} = 1.57 \times 10^{8}$ Gt, is substantially larger than the total estimated carbon in the continental crust given above, ${}^{c}M_{ccp} = 5 \times 10^{7}$ Gt. The hypothesis of direct extraction from the atmosphere has been discussed in some detail by Kramers (2002) and by Lowe and Tice (2004).

The basic hypothesis is that the mass flux of carbon from the atmosphere to the continental crust, ${}^{c}J_{a\text{-}cc}$, is controlled by the availability of calcium silicates. 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 silicate. In addition, the Earth must have had oceans in order for the acid rain to catalyze the Urey reaction between atmospheric CO_2 and the service deposits of calcium silicates. Little data are available for timing the initiation of the extraction of CO_2 from the atmosphere. We will assume that the process begins at a time t_0 after the early bombardment and the solidification of the magma ocean at about 4.4 Ga. We further assume that the Urey reaction extracted carbon from the atmosphere at a constant rate ${}^{c}J_{a\text{-}cc}$ until the concentration of CO_2 in the atmosphere was reduced to a very low level. During the time, $t_0 < t < t_0 + \tau_{a\text{-}cc}$, the Urey reaction extracts atmospheric carbon to the continental crust. We will specify the mass of carbon extracted from the atmosphere and obtain

$$ {}^{c}J_{a-cc} = \frac{{}^{c}M_{a0}}{\tau_{a-cc}} \tag{3} $$

We assume that the mass of carbon in the atmosphere ${}^{c}M_a$ decreases linearly in time from ${}^{c}M_{a0}$ to zero during the time period $\tau_{a\text{-}cc}$ and the mass of carbon in the continental crust increases linearly in time.

Assuming all the carbon in the continental crust ${}^{c}M_{ccp}$ was extracted from the atmosphere the dependence on time is given by

$$ {}^{c}M_{cc} = 0 \qquad 0 \le t \le t_0 $$

$$ {}^{c}M_{cc} = {}^{c}M_{ccp}\,[(t - t_0)/(\tau_{a\text{-}cc})] \qquad t_0 \le t \le t_0 + \tau_{a\text{-}cc} \tag{4} $$

$$ {}^{c}M_{cc} = {}^{c}M_{ccp} \qquad t_0 + \tau_{a\text{-}cc} \le t \le t_p $$

Taking ${}^{c}M_{ccp} = 5 \times 10^7$ Gt, $t_0 = 1$ Gyr, and $\tau_{a\text{-}cc} = 1$ Gyr, the dependence of ${}^{c}M_{cc}$ on t is given in Fig. 1. The required flux of carbon from the atmosphere to the continental crust is ${}^{c}J_{a\text{-}cc} = 50$ Mtyr^{-1}. It must be emphasized that the value of $\tau_{a\text{-}cc}$ is uncertain and the flux ${}^{c}J_{a\text{-}cc}$ is expected to have considerable variability in time. However it is quite clear that the extraction of carbon from the atmosphere to the continental crust would have been carried out early in Earth's history.

Removal of the volcanic addition of carbon to the atmosphere

When excess carbon in the atmosphere has been depleted by the Urey reaction an approximate steady-state balance is established between the volcanic input of carbon into the atmosphere and the extraction by the Urey reaction. We approximate this balance by the relation

$$ {}^{c}J_{a-cc} = \frac{{}^{c}M_{a}}{\tau_{u}} \qquad (5) $$

where ${}^{c}J_{a\text{-}cc}$ is the rate of volcanic input of carbon into the atmosphere. We assume that this extraction rate is constant and is proportional to the mass of carbon in the atmosphere ${}^{c}M_{a}$. The characteristic time τ_u takes account of the rate at which acid rain can interact with calcium silicate sediments, and although we assume that τ_u is constant it clearly can be a function of time.

A comprehensive model for the variability of atmospheric CO_2 over Phanerozoic times has been given by Berner and Kothavala (2001). This model, GEOCARB 3, is complex and involves both organic and inorganic processes. Transport of 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 Calderia, 1997). 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 Eq.(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 to the atmosphere of CO_2 in subduction zone volcanics (Frezzotti et al. 2011).

The present mass of carbon in the atmosphere is 860 Gt (400 ppmv CO_2), but this is not a quasi-equilibrium value because of the anthropogenic addition at high fluxes (3.5 Gtyr^{-1}). We will take the 1900 value of 650 Gt (300 ppmv CO_2) as the present equilibrium value. This is a typical value for the current glacial epoch (0 to 50 Ma). Values given by the GEOCARB 3 Model are generally consistent with observations (Royer 2014). Between 50 and 250 Ma the average values were about 3000 Gt. During the major glacial epoch between 250 and 350 Ma low observed values near 650 Gt are found. Between 350 and 550 Ma values were considerably higher, typically near 10,000 Gt. This variability reflects variations in both of the variables in Eq. (3), the volcanic flux ${}^{c}J_{a\text{-}cc}$ into the atmosphere and the characteristic time τ_u.

Carbon from the mantle to the continental crust

The second hypothesis for the origin of the carbon in the continental crust is that it comes from the mantle. If the volcanic flux of carbon out of the mantle at ocean ridges and hot spots exceeds the carbon lost to the mantle at subduction zones, the difference will be added to the continental crust. Some of the volcanic carbon input will enter the atmosphere and will be transferred to the continental crust through the Urey reaction. However, some will enter the oceans and will be converted directly to carbonates without entering the atmosphere.

Rates of carbon loss from the mantle by volcanism and lost by subduction will certainly vary over geologic time, but the variations are uncertain. Again, we assume that the plate tectonic processes required for carbon transfer began at a time t_0 after the solidification of the magma ocean at about 4.5 Ga. We further assume that the transfer of carbon out of the mantle has been at a constant rate ${}^{c}J_{m\text{-}cc}$ until the present time t_p. Assuming all the carbon in the continental crust has been extracted from the mantle, the dependence on time is given by

$$^{c}M_{cc} = 0 \qquad 0 \le t \le t_0$$
$$^{c}M_{cc} = {}^{c}M_{ccp}\,[(t - t_0)/(t_p - t_0)] \qquad t_0 \le t \le t_p + \tau_{a\text{-}cc} \tag{6}$$

The mass of carbon in the continental crust increases linearly in time over the period t_0 to t_p. The required flux of carbon from the mantle to the continental crust is given y

$$^{c}J_{m-cc} = \frac{^{c}M_{ccp}}{t_p - t_0} \tag{7}$$

Taking $^{c}M_{ccp} = 5 \times 10^{7}$ Gt, $t_0 = 1$ Gyr, and $t_p = 4.4$ Gyr the dependence of $^{c}M_{cc}$ on t is given in Fig 1. The required flux of carbon from the mantle to the continental crust is $^{c}J_{m\text{-}cc} = 14.7$ Mtyr^{-1}.

We next consider the estimate for the present loss of carbon from the mantle to the atmosphere. Dasgupta and Hirschmann (2010) have summarized the available data on the loss of carbon from the mantle to the surface reservoirs and give values in the range $^{c}J_{m\text{-}s} = 36 \pm 24$ Mtyr^{-1}. Just as carbon is lost from the mantle by volcanism, carbon is returned to the mantle by subduction. A detailed study of carbon fluxes at subduction zones has been given 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 due to subduction zone volcanism. They suggested that 24 ± 24 Mtyr^{-1} reach the mantle. Clearly it is quite possible that all the carbon in the continental crust could have come from the mantle. This conclusion was also given by Hayes and Waldbauer (2006).

In Fig. 1 we give examples of the two limiting cases, the carbon in continental crust comes entirely from the atmosphere and the carbon comes entirely from the mantle. In the first case the addition is early in time and in the second case it is more uniform in time. Observations of the mass of carbonates in the continental crust as a function of age could distinguish between the two cases, but the data are sparse. Observations of the mass of carbon in the atmosphere as a function of time could also be a constraint. An example given by Rye et al. (1995) utilizing studies of paleosols concluded that the mass of carbon in the atmosphere at 2.2 to 2.75 Ga was less than 10^5 Gt. The conclusion is that the extraction of a significant mass of carbon from the atmosphere to the continental crust was completed by t = 2 Gyr. However how large this mass was is uncertain.

PETM

The decay of the Paleocene-Eocene thermal maximum (PETM) can be used to quantitatively constrain the role of the Urey reaction. The PETM was a period of elevated global temperatures (4 to 5 degrees C) and high atmospheric CO_2 beginning at 56.3 Ma, the onset lasted less than 10 Kyr and the subsequent decay lasted about 100 Kyr (Mclnerney and Wing 2011). Storey et al. (2007) have made a strong case for associating the PETM with flood volcanism resulting from the opening of the north Atlantic.

Isotope studies have quantitatively documented the PETM. These studies have been reviewed by Gutjahr et al. (2017). These authors also provided estimates for the carbon content of the atmosphere during the PETM. They suggest that the background carbon mass in the atmosphere before and after the PETM was ${}^{c}M_{ab}$ = 1400 Gt and the peak mass of carbon was ${}^{c}M_{a0}$ = 3050 Gt.

We now carry out an 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 Eq. (5) to include the transient removal of carbon from the atmosphere and write

$$\frac{d\,{}^{c}M_{a}}{dt} = {}^{c}J_{(a-cc)b} - \frac{{}^{c}M_{a}}{\tau_{u}} \qquad (8)$$

From Eq. (5) the background mass of carbon in the atmosphere is given by

$$ {}^{c}M_{ab} = \tau_u \, {}^{c}J_{(a-cc)b} \qquad (9) $$

We prescribe an initial mass of carbon in the atmosphere at $t = 0$, ${}^{c}M_{a0}$ and solve Eq. (7) taking τ_u to be constant with the result

$$ {}^{c}M_{a} = ({}^{c}M_{a0} - {}^{c}M_{ab})e^{-t/\tau_u} + {}^{c}M_{ab} \qquad (10) $$

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.

We next obtain the dependence of atmosphere carbon mass on time during PETM based on the model dependence given in Eq. (10). Taking the values ${}^{c}M_{ab} = 1400$ Gt and ${}^{c}M_{a0} = 3050$ Gt with τ_u =100 kyr the model results are given in Figure 2.

We now return to Eq. (9). This result relates the background atmospheric carbon mass ${}^{c}M_{ab}$ to the background rate of volcanic input of CO_2 carbon into the atmosphere ${}^{c}J_{(a-cc)b}$ and the Urey reaction rate τ_u. During the PETM we have taken the background carbon mass ${}^{c}M_{ab} = 1400$ Gt. Taking $\tau_u = 100$ kyr we find from Eq. (9) that ${}^{c}J_{(a-cc)b} = 14$ Mtyr^{-1}. This is an independent determination of the volcanic flux of carbon into the atmosphere at that time. As discussed above we take the present equilibrium mass of carbon in the atmosphere to be ${}^{c}M_{ab} = 6500$ Gt. Assuming that ${}^{c}J_{(a-cc)b} = 14$ Mtyr^{-1} we require from Eq. (9) that $\tau_u = 50$ kyr. This is our estimated relaxation time for a carbon excursion today.

Discussion

Urey (1952) proposed the Urey reaction, Eq. (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 curst, taking the extraction rate ${}^{c}J_{a\text{-}cc}$ 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 Fig. 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 ${}^{c}J_{a\text{-}cc}$ 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.

Implications

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.

References

Berner, R. A., Caldeira, K. (1997) The need for mass balance and feedback in the geochemical carbon cycle. Geology 25, 955–956.

Berner, R. A., Kothavala, Z. (2001). GEOCARB III: A revised model of atmospheric CO_2 over Phanerozoic time. American Journal of Science 301, 182–204.

Blättler, C. L., Higgins, J. A. (2017). Testing Urey's carbonate–silicate cycle using the calcium isotopic composition of sedimentary carbonates. Earth and Planetary Science Letters 479, 241–251.

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

DePaolo, D. J. (2015). Sustainable carbon emissions: The geologic perspective. MRS Energy & Sustainability 2, E9.

Frezzotti, M. L., Selverstone, J., Sharp, Z. D., Compagnoni, R. (2011). Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. Nature Geoscience 4, 703–706.

Gutjahr, M., Ridgwell, A., Sexton, P. F., Anagnostou, E., Pearson, P. N., Pälike, H., Norris, R. D., Thomas, E., Foster, G. L. (2017). Very large release of mostly volcanic carbon during the Palaeocene–Eocene thermal maximum. Nature 548, 573–577.

Hayes, J. M., Waldbauer, J. R. (2006). The carbon cycle and associated redox processes through time. Philosophical Transactions of the Royal Society of London B: Biological Sciences 361, 931–950.

Houghton, R. A. (2007). Balancing the global carbon budget. Annual Review of Earth and Planetary Sciences 35, 313–347.

Kasting, J. F., Ackerman, T. P. (1986). Climatic consequences of very high carbon dioxide levels in the Earth's early atmosphere. Science 234, 1383–1386.

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 112, E3997–E4006.

Kramers, J. D. (2002). Global modelling of continent formation and destruction through geological time and implications for CO_2 drawdown in the Archaean eon. Geological Society, London, Special Publications 199, 259–274

Lowe, D. R., Tice, M. M. (2004). Geologic evidence for Archean atmospheric and climatic evolution: Fluctuating levels of CO_2, CH_4, and O_2 with an overriding tectonic control. Geology 32, 493–496.

McInerney, F. A., Wing, S. L. (2011). The Paleocene-Eocene thermal maximum: A perturbation of carbon cycle, climate, and biosphere with implications for the future. Annual Review of Earth and Planetary Sciences 39, 489–516.

Rye, R., Kuo, P.H. and Holland, H.D. (1995). Atmospheric carbon dioxide concentrations before 2.2 billion years ago. Nature, 378, 603-605.

Royer, D. L. (2014). Atmospheric CO_2 and O_2 during the Phanerozoic: Tools, patterns, and impacts. Treatise on Geochemistry, 2nd Edition. vol 6, pp 251-267.

Storey, M., Duncan, R. A., Swisher, C. C. (2007). Paleocene-Eocene thermal maximum and the opening of the northeast Atlantic. Science 316, 587–589.

Urey, H. C. (1952). On the early chemical history of the earth and the origin of life. Proceedings of the National Academy of Sciences 38, 351–363.

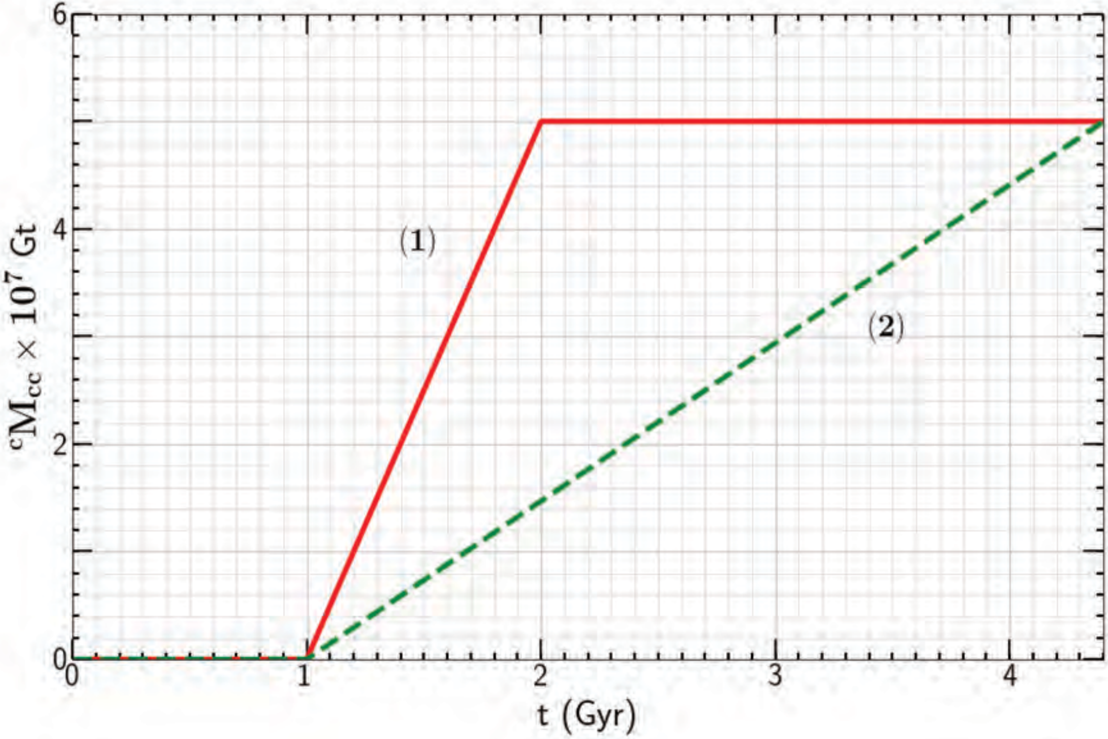
Urey, H. C. (1956). Regarding the early history of the earth's atmosphere. Geological Society of America Bulletin 67, 1125–1128.

Wedepohl, K. H., 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta 59 (7), 1217-1232.

Figure Captions

Figure 1. Dependence of the mass of carbon in the continental crust ${}^{c}M_{cc}$ on time. Two limiting models are given for adding the present mass ${}^{c}M_{ccp}$ = 5 x 10^7 Gt. 1) Addition from the atmosphere beginning at t_0 = 1 Gyr. All atmospheric carbon is transferred in $\tau_{a\text{-}cc}$ = 1 Gyr at a constant flux ${}^{c}J_{a\text{-}cc}$ = 50 Mtyr^{-1}. 2). Addition from the mantle beginning at t_0 = 1 Gyr. Carbon is added at a constant flux ${}^{c}J_{m\text{-}cc}$ = 14.7 Mtyr^{-1} to the present.

Figure 2: 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 given in Eq. (11) with ${}^{c}M_{ab}$ = 1400 Gt and ${}^{c}M_{a0}$ = 3050 Gt and τ_{u} = 100 kyr.



$^c M_{cc} \times 10^7$ Gt
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t (Gyr)
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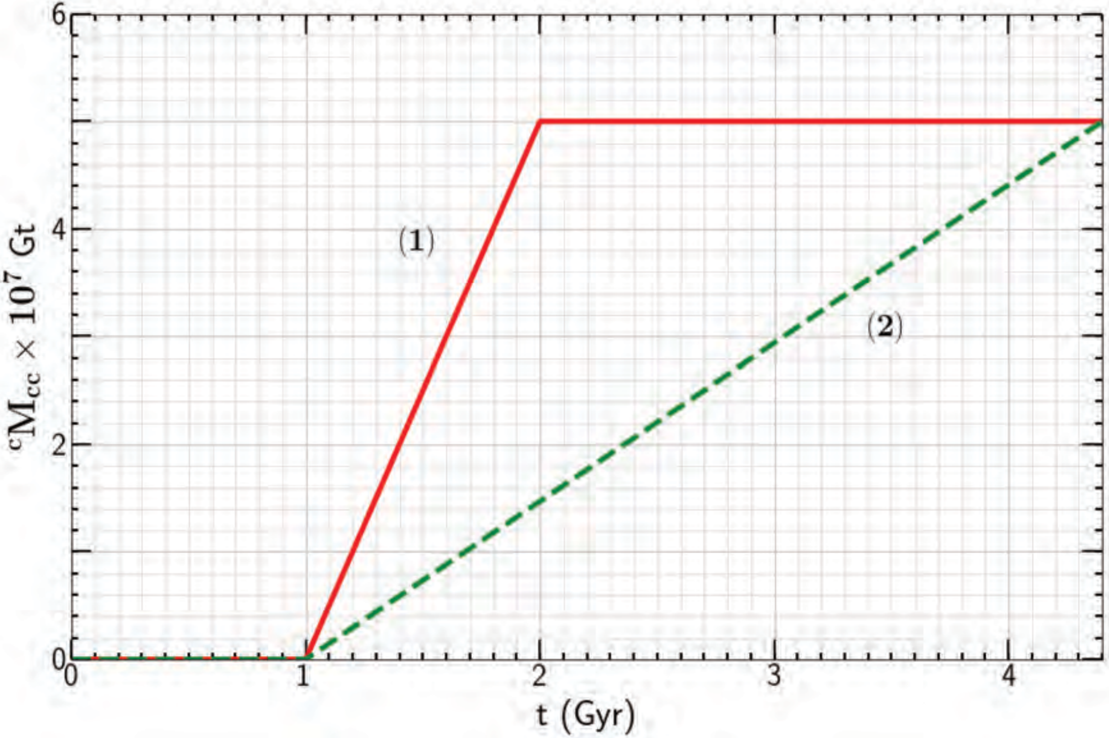

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