Carbon cycle in the paleoenvironment: an abrupt increase of biogenic carbon in the end-Cretaceous atmosphere

Ryunosuke Kikuchi 1,2, Carla Sofia S. Ferreira 1, Romeu Gerardo Jorge 3,
1CERNAS, ESAC - Politécnico de Coimbra, Coimbra, Portugal; 2Faculty of Science & Technology, Ryukoku University, Otsu, Japan; 3Department of Environmental & Occupational Health Sciences, SEGMAZ, Vagos, Portugal
E-mail of the corresponding author: kikuchi@esac.pt

Abstract - A knowledge of what has happened in the past seems helpful in improving the predictability of the link between global-scale phenomena and the carbon cycle; this paper therefore attempts to reconstruct the end-Cretaceous carbon cycle (65 million years ago) by means of modeling. The performed simulation suggests that a great amount (130 gigatons at least) of biogenic carbon was rapidly injected into the atmosphere. Methane originating from gas hydrate (GH) is the most likely candidate for the input of biogenic carbon at the end of the Cretaceous period because it is considered that thick GH stability zones were damaged by perturbations associated with the Chixculub asteroid impact, and the vast amount of methane was released to the atmosphere as a gas blast. Though GH deposits are greater than other major reservoirs of carbon, these deposits are not commonly categorized as typical carbon reservoirs in terms of the global carbon cycle. How to integrate GH-related methane with well-known carbon reservoirs remains for a future study in order to improve the predictability of the future carbon cycle.

Keywords - carbon cycle, biogenic carbon, Cretaceous-Tertiary (K-T) boundary, extraterrestrial impact, mass extinction

Received: December 21, 2016 Accepted: January 4, 2017

1. Introduction

Carbon is stored in the biosphere within living or recently dead plants, animals and microorganisms in the ocean and on land; e.g. forests contain 86% of the planet’s carbon on top of the ground (cf. Rambler et al. 1989). Carbon is present in not only the biosphere but also the atmosphere, soil, oceans and crust – when the earth is viewed as a system, these components are referred to as carbon reservoirs because they act as storage houses for large amounts of carbon (review in ESSPs 2006). The major reservoirs shown in Table 1 are generally considered to be of great relevance to the overall carbon cycle. Current amounts of carbon in the major reservoirs are summarized in Table 1. Unlike the crust and oceans, most of the carbon in the terrestrial ecosystem exists in organic form (review in CCI 2016).

Any movement of carbon between these reservoirs is called a flow or flux. Carbon flows between the reservoirs in an exchange called the carbon cycle, which has slow and fast components (review in CCI 2016). The rate of change in atmospheric carbon depends, however, not only on human activities but also on biogeochemical and climatological processes and their interactions with the carbon cycle (Falkowski et al. 2000). Any change in the cycle that shifts carbon out of one reservoir puts more carbon in the other reservoirs. The earth’s carbon reservoirs naturally act as both sources (adding carbon to the atmosphere) and sinks (removing carbon from the atmosphere). If all sources are equal to all sinks, the carbon cycle can be said to be in equilibrium (or in balance) and there is no change in the size of the pools over time.

Great amounts of organic carbon are currently stored in the ecosystem (cf. Table 1), and this carbon is known to play a key role in determining whether or not biogenic carbon will be released into the atmosphere as carbon dioxide and/or methane under any given set of environmental variables; however, large uncertainties remain regarding the nature and magnitude of carbon cycles in the biosphere (BER 2016). Understanding the global carbon cycle requires new approaches which aim at linking global-scale climate phenomena with biogeochemical processes (BER 2016).

2. Scope and focus

It seems to be important to consider the earth’s history because a knowledge of what has happened in the past helps to improve the predictability of the link between
global-scale phenomena and the carbon cycle. The Cretaceous is usually noted for being the last portion of the "Age of Dinosaurs" (cf. Officer & Page 1996) and is defined as the period between 145.5 and 65.5 million years ago, the last period of the Mesozoic Era, following the Jurassic (cf. Zachos et al. 2001). K is actually the traditional abbreviation for the Cretaceous period, and T is the abbreviation for the Tertiary period; so the K-T boundary (~65 Ma) is the point between the Cretaceous and Tertiary periods. The K-T mass extinction is well known for the death of the dinosaurs, and this extinction wave is marked by a layer (i.e. K-T boundary) of clay and/or rock enriched with iridium (cf. Officer & Page 1996). The iridium enrichment at the K-T boundary provided the sole basis for the asteroid impact theory (Alvarez et al. 1980). Since the publication of the bolide impact hypothesis in 1980 (Alvarez et al. 1980), the public and a large number of scientists have come to believe that a meteorite caused the global extinction of the dinosaurs and many other groups at the end of the Cretaceous (Keller 2001). In the nearly four decades since the impact hypothesis was proposed, much evidence has been discovered that defies this simple cause-effect scenario (review in Schmitz 2011). Major mass extinctions in Earth's history are generally attributed to asteroid impacts (e.g. Chixulub impact, ~65 Ma) (Smit 1999), flood volcanisms (e.g. Deccan traps, ~65.4 Ma) (Hofmann et al. 2000) and associated environmental extremes such as impact blast, acid rain, metal pollution, global wildfires, tsunami, and earthquakes (Toon et al. 1997) (Keller 2003); whereas the then carbon cycle has not been sufficiently discussed. Therefore, this paper attempts to reconstruct the end-Cretaceous carbon cycle by means of modeling.

3. Basic information

Basic information is briefly presented first, followed by a description of modeling simulation.

3.1. Photosynthesis on end-Cretaceous land

It may be possible that a large extraterrestrial impact injects a vast amount of dust into the atmosphere, blocking out the sunlight to a level that is insufficient to allow photosynthesis which is linked with the food chain (Toon et al. 1982).

Research combining a field survey in the Chixulub ejecta layer with theoretical calculation indicates that very few of the particles are of the size that it would take to shut down photosynthesis for any significant length of time (Pope 2002).

Laser irradiation experiments also suggest that most of the SO$_4$ in the K-T impact vapor cloud may have been SO$_3$ (short-term residence in the atmosphere). Hence this sulfuric acid aerosol may not have been able to block the sunlight for a long time (Ohno et al. 2004).

Furthermore, the marine algal record – diatoms, dinoflagellates and coccolithophorids – does not support a K-T blackout (review in McLean 1991).

3.2. Biological effects associated with the K-T impact

Amphibians commonly breathe and drink through their skin; therefore, pollution, toxicants and acid rain have adverse effects on them. Furthermore, their eggs, which are without a protective shell, are vulnerable to pollutants and ultraviolet (UV) radiation (SERC 2005).

All the amphibians survived unaffected through the K-T boundary (Archibald 2002). A 100% survival rate seemingly proves that there were no adverse biological effects associated with UV radiation, acid rain and metal pollution.

3.3. Period

The end of the mass extinction wave is marked by a layer (e.g. K-T boundary) of clay/rock enriched with iridium (Officer & Page 1996). Measurement using a constant-flux proxy of sedimentation rate implies deposition of K-T clay in 10 ± 2 thousand years (Mukhopadhyay et al. 2001). It should be emphasized that an extremely rapid process of ecological turnover (vertebrate extinction in particular) is anticipated.

3.4. Carbon isotope

There are two stable isotopes of carbon, light $^{12}$C and heavy $^{13}$C, and this ratio is expressed in terms of delta notation ($\delta^{13}$C) (cf. Faure 1986). It is known that photosynthesis is accompanied by an isotopic fractionation which favors the fixation of $^{12}$C into plants; the mechanism for this fractionation is not well known (review in Brugnoli & Farquhar 2000). Since organisms preferentially take up light $^{12}$C and have a $\delta^{13}$C signature of about -25‰ (cf. Faure 1986), a negative $\delta^{13}$C shift isotopically indicates an input of light biogenic carbon.

4. Simulation run

There are fundamentally two types of carbon cycle – long-term carbon cycle (millions of years) and short-term carbon cycle (on a scale less than millions of years) (Berner 1999); as the K-T event occurred over a short period (see section 3.3), the latter cycle is applicable.

The traditional approach toward modeling the carbon cycle is the multi-box mass exchange method (review in Hoffert et al. 1981); however, a potential problem with this classical approach is that the reservoirs must truly be well-mixed or uniform in concentration, for the approximation to hold (Hoffert et al. 1981). Hence, a diffusion model (Siegenthaler & Oeschger 1987) was applied, and this model consists of (i) an atmospheric box coupled to (ii) a biospheric box (above-ground phase and soil phase) and (iii) an ocean box (surface phase and deep phase) (see Figure 1a).
4.1. Main parameters

A model simulation is combined with data obtained from the Deep Sea Drilling Project and the Ocean Drilling Program (review in Ivany & Salawitch 1993): (i) a 1.4 ‰ δ\(^{13}\)C value before the K-T boundary and a -0.4 ‰ δ\(^{13}\)C value afterwards are given by calculating the average paleoceanic δ\(^{13}\)C gradients between surface water and deep water; (ii) the negative degree of the planktonic δ\(^{13}\)C gradient provides a lower limit to the amount of isotopically light carbon that must be added on condition that near cessation of primary productivity is sufficient to bring its gradient value to zero; the limit value (-0.4 ‰) is therefore more realistic than zero for estimating the carbon amount; and (iii) normal factors (exchange frequency = 58.7 yr\(^{-1}\) and isotopic fraction for transfer = 1.0) were applied in this model simulation.

4.2. Results

A simulation run could not reconstruct the lower limit (a δ\(^{13}\)C gradient of -0.4 ‰) on the applied conditions because of the isotopic imbalance between \(^{12}\)C and \(^{13}\)C in each reservoir (Figure 1a); i.e., a negative excursion in δ\(^{13}\)C means that isotopically light carbon (e.g., biogenic carbon) was delivered to the K-T atmosphere. Taking the isotopic balance into account, the simulation results when carbon is supplemented (on biomass base) are illustrated in Figure 1b.

To put it differently, the performed simulation suggests that a great amount (1.3×10\(^{17}\) g at least) of isotopically light carbon (i.e., biogenic carbon) was injected to the end-Cretaceous atmosphere.

5. Consideration – sources of biogenic carbon

Statistics indicate that fossil fuel use accounts for annual emissions to the current atmosphere of ~5.5 GtC (Andres et al. 1996). The simulation results indicate an injection of 130–380 GtC (Figure 1b) into the then atmosphere, and this amount is too large to ignore as a margin of error.

The vital question in our understanding of the current state of the global carbon cycle is reflected in the missing sink – it is not known where about one-half of anthropogenic CO\(_2\) is going (cf. Moffat 1997); in contrast, comprehension of the end-Cretaceous carbon cycle may be reflected in the missing source – it is not known where the great amount of biogenic carbon suddenly came from.

5.1. Degassing from carbonate

Most carbonate is made by calcifying organisms and plankton (cf. Tucker & Wright 1990). The impact-induced release of CO\(_2\) from carbonate may be a possible source of the increased atmospheric carbon, but this CO\(_2\) degassing is quantitatively questionable from the viewpoints of thermodynamic equilibrium and kinetic effect because an experimental study (Agrinier et al. 2001) proves that reverse reaction (CO\(_2\) + CaO \(\leftrightarrow\) CaCO\(_3\)) occurs on a similar time scale (~100 s) to that of
direct decomposition; that is, the degassing CO\textsubscript{2} is again captured with hot CaO grains.

5.2. Deccan traps volcanism
As stated in section 2, the two events – the asteroid impact (~65 Ma) and Deccan traps volcanism (~65.4 Ma) – are very close on the geologic timescale, and perhaps are partially overlapped. There is a possibility that the vast delivery of biogenic carbon to the K-T atmosphere may have been associated with the Deccan traps volcanism.

However, flood basalts of the Deccan traps do not originate from a subduction zone (i.e. seafloor-altered basalts containing oceanic materials), and hence the released carbon (as CO\textsubscript{2}) was most likely isotopically heavier than or equivalent to atmospheric carbon (Ivany & Salawitch 1993). This implies that a main factor for the negative $\delta^{13}$C excursion in the K-T atmosphere was not the Deccan traps volcanism, but isotopically light biogenic carbon.

5.3. Marine carbon
On the hypothesis of a dramatic drop in the surface ocean pH (D’Hondt et al. 1994), it may be possible to consider the atmospheric input of marine carbon from the acidified ocean.

However, it is reported that the ocean acidification must have been local and not global (Toon et al. 1997), and a lithologic study at the Chicxulub impact site suggests that the rich amount of larnite grains ($\beta$-Ca\textsubscript{2}SiO\textsubscript{4}) contained in the impact plume must have been enough to neutralize acids (H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3}) produced after the K-T impact (Maruoka & Koeberl 2003).

5.4. Thermal pulse and global wildfire
It is reported that the boundary layers are enriched with soot, so this seems to be evidence that a global wildfire was ignited directly after the impact (e.g. Wolbach et al. 1990). A thermal pulse (~1,000°C) may have spread across the area of the impact and potentially a wide region, and its thermal energy may have been sufficient to ignite wildfires across the world (Kring & Durda 2002).

Atmospheric injection of photosynthetic carbon can be caused by biomass burning associated with global wildfires. If a lot of terrestrial vegetation was burned, a lot of charcoal would be expected on land. A field study shows that rocks laid down at the time contain little charcoal (Belcher et al. 2003). Furthermore, the morphology of the K-T soot (i.e. aciniform type) is more consistent with a source of pyrolysis of clay rather than combustion of biomass (Harvy 2004). That is, there were no wildfires after the Chicxulub impact.

5.5. Submarine methane hydrate
Gas hydrates (GH) are naturally occurring ice-like crystals that form at high pressure and low temperature in marine sediments (Matsumoto 2001). These hydrates are largely composed of methane and water, and are properly called methane hydrates (MH) (Matsumoto, 2001). The amount of methane (CH\textsubscript{4}) released from hydrate deposits is currently small (0.01 Gt per year) (IPCC 2001); however, methane is the most likely candidate for the carbon input at the end Cretaceous, and its source is probably gas hydrate for the following several reasons:

5.5.1. Carbon type, distribution, amount and dissociation
(i) Biogenic carbon – CH\textsubscript{4} originating in natural gas hydrate is predominantly biogenic, and its $\delta^{13}$C value is approximately -60% (Kvenvolden 1993).

(ii) Wide distribution – CH\textsubscript{4} hydrates have been inferred at more than 50 places throughout the world, and most of them occur at depths within 2.0-2.5 km of the sea level in the world’s continental margins (Kvenvolden 1993).

(iii) Storage amount – current estimates of CH\textsubscript{4} in the world’s gas hydrate deposits are in rough accord at about 10,000 Gt of carbon (Kvenvolden 1998), which is greater than other carbon reservoirs (cf. Table 1). Furthermore, CH\textsubscript{4} commonly pond and forms large deposits of free gas below a hydrate stability field, and the amount of this free gas is currently estimated at one-sixth to two-thirds of the total CH\textsubscript{4} trapped in the present hydrates (Hornbach et al. 2004).

(iv) Dissociation – since hydrates prevent sediment compaction, their dissociation related to climatic change has been suggested as an important factor in creating weak sediment layers, along which sediment failure can be triggered, after which the methane released from the hydrate reservoir into the water column and eventually into the atmosphere could contribute to further climate change (Kennett et al. 2003; and references therein).

5.5.2. Methane production in the Late Cretaceous
The potential for CH\textsubscript{4} production in the Late Cretaceous corresponds to the high volume of early Turonian organic carbon buried in marine basins worldwide (Raiswell 1998). For this reason, it can be considered that a large amount of CH\textsubscript{4} may have been trapped and concentrated in both the hydrate stability zone and the underlying free gas zone

5.5.3. GH stability in the Late Cretaceous oceans
The sea level was high (~150 m above the present sea level) (Hallam 1992); the average temperature in the Late Cretaceous oceans may have been 2 to 10 °C higher than that in modern oceans (Hallam 1992); and the geothermal gradient affecting the sub-bottom temperature may have been almost equal to the modern typical gradient of 0.035 °C/m (Max et al. 1999).

Considering the warm seawater, high sea level and the aforementioned geothermal gradient, the stability pattern of submarine gas hydrate in the Late Cretaceous oceans can be drawn on the basis of published data (see Figure 2). Hydrate in the lower part of the hydrate stability zone...
gas is sealed by the (HSZ) can block permeability and form an impermeable seal, trapping free gas below the HSZ.

It follows from Figure 2 that the HSF in the Late Cretaceous ocean would have been thinner (about half) than in the present day and free gas is sealed by the hydrate field. That is, it can be considered that the HSF in the late Cretaceous must have been sensitive to oceanic change.

![Figure 2](image)

**Figure 2.** Diagram of gas hydrate stability in the late Cretaceous oceans (redrawn from Max et al. 1999). Note: BHSF = base of hydrate stability field, BSR = bottom simulating reflections, and HSF = hydrate stability field.

### 5.5.4. Potential triggers of dissociation

As stated in section 5.5, the current amount of CH$_4$ released from hydrate deposits is small because methane hydrate is stable under low-temperature, high-pressure conditions even with an excess amount of free gas.

If a thick HSF is damaged by a tsunami-induced sea-level fall (Max et al. 1999) and/or earthquake (vibration) (Day 1999), there is a strong possibility that the HSF may be disrupted by the overpressure of free gas (1/6 to 2/3 of the total GH-related methane on the current basis, section 5.5.1 (iii)) resident below the hydrate field and/or this free gas may leak.

Furthermore, the following scenario is also possible: the BHSF probably becomes overpressurized because of the newly released gas, leading to a zone of weakness (i.e., low shear strength, where failure could be triggered by gravitational loading or seismic disturbances such as an earthquake and vibration), and submarine landslides (i.e., slumps) result in disruption of the GH deposit and vast release of CH$_4$ and free gas.

### 5.5.5. Diffusion in the atmosphere

In the Gulf of Mexico, CH$_4$ is aerobically oxidized before reaching the atmosphere (Kastner et al. 2005); however, large seeps are more efficient at transferring CH$_4$ to the atmosphere (Clark et al. 2003). The CH$_4$ release resulting from a breached trap (i.e. CH$_4$ hydrate) could be very rapid, causing a blast of gas (Dickens et al. 1997). It can therefore be inferred that the CH$_4$ released as blast gas was rapidly diffused in the end-Cretaceous atmosphere. General circulation also must have contributed to this diffusion.

### 6. Concluding remarks

The simulation performed for reconstructing the end-Cretaceous carbon cycle suggests a rapid and vast injection of biogenic carbon into the then atmosphere. Its carbon source is probably gas hydrate (GH) having a thick stability zone. It is considered that the thick GH stability zone was damaged by impact-induced events such as a sea-level fall and vibration (earthquake). This stability zone was disrupted by the overpressure of free gas, and a vast amount of methane was released to the atmosphere as a gas blast.

Though gas hydrate (GH) deposits are greater than other carbon reservoirs, these deposits are not commonly categorized as major reservoirs in terms of the global carbon cycle, because modern GH is stable, and the release amount of methane is quite small.

Most GH deposits naturally occur both at low temperatures and high pressure regimes in deep ocean. It is well known that heat-trapping CO$_2$ (i.e. greenhouse gas) emitted by human activities has raised the average global temperature over the past century. As climate change has warmed the Earth, most parts of world’s oceans have seen temperature rise (IPCC 2013). Since GH stability is sensitive to environmental perturbations (e.g. pressure and temperature), there is a possibility that a large amount of methane trapped in natural GH may be released to the atmosphere after a perturbation. What is even worse, methane produces 34 times as much warming as CO$_2$ over a 100-year period, and 72 times as much over a 20-year period (IPCC 2013). It should be noted that widely accepted models for carbon cycle omit oceanic GH and seafloor methane fluxes.

The following points remain for a future study: (i) whether or not there is any causal relationship between a rapid increase of atmospheric methane and the K-T mass extinction; and (ii) how to theoretically integrate GH-related methane with well-known carbon reservoirs in order to improve the predictability of the future carbon cycle.

### Public Interest Statement

The end-Cretaceous mass extinction (for example, the demise of the dinosaurs) has generated considerable public interest. The main problem is the issue of the selectivity of the mass extinction: that is, 55% of all species that are present below the boundary are not present above the line that divides the age of dinosaurs.
from the age of mammals (Archibald 2002). For the first step, it is important to know what happened directly and indirectly. Since it is hard to determine the then air quality on the basis of the fossil record, this study attempts to reconstruct the end-Cretaceous atmosphere by isotopic carbon balance.

Acknowledgments

Parts of this work were supported by Centro de Estudios de Recursos Naturais, Ambiente e Sociedade (CERNAS). The authors are grateful to Ms. C. Lentfer for English review.

References


http://dx.doi.org/10.1007/s003670050081

http://dx.doi.org/10.1126/science.277.5324.315

http://dx.doi.org/10.1126/science.291.5510.1952

http://dx.doi.org/10.1029/96RG03038


http://dx.doi.org/10.1016/0016-7037(90)90444-P

http://dx.doi.org/10.1038/srep01438

http://dx.doi.org/10.1130/0091-7613(1988)016<0641:CMFTOD>2.3.CO;2

http://dx.doi.org/10.1038/471573a

http://dx.doi.org/10.1111/j.1600-0889.1987.tb00278.x


http://dx.doi.org/10.1146/annurev.earth.27.1.75


http://dx.doi.org/10.1016/0016-7037(90)90444-P

http://dx.doi.org/10.1038/srep01438

http://dx.doi.org/10.1130/0091-7613(1988)016<0641:CMFTOD>2.3.CO;2


http://dx.doi.org/10.1038/471573a

http://dx.doi.org/10.1111/j.1600-0889.1987.tb00278.x


http://dx.doi.org/10.1146/annurev.earth.27.1.75


http://dx.doi.org/10.1016/0016-7037(90)90444-P

http://dx.doi.org/10.1038/srep01438

http://dx.doi.org/10.1130/0091-7613(1988)016<0641:CMFTOD>2.3.CO;2


http://dx.doi.org/10.1038/471573a

http://dx.doi.org/10.1111/j.1600-0889.1987.tb00278.x