

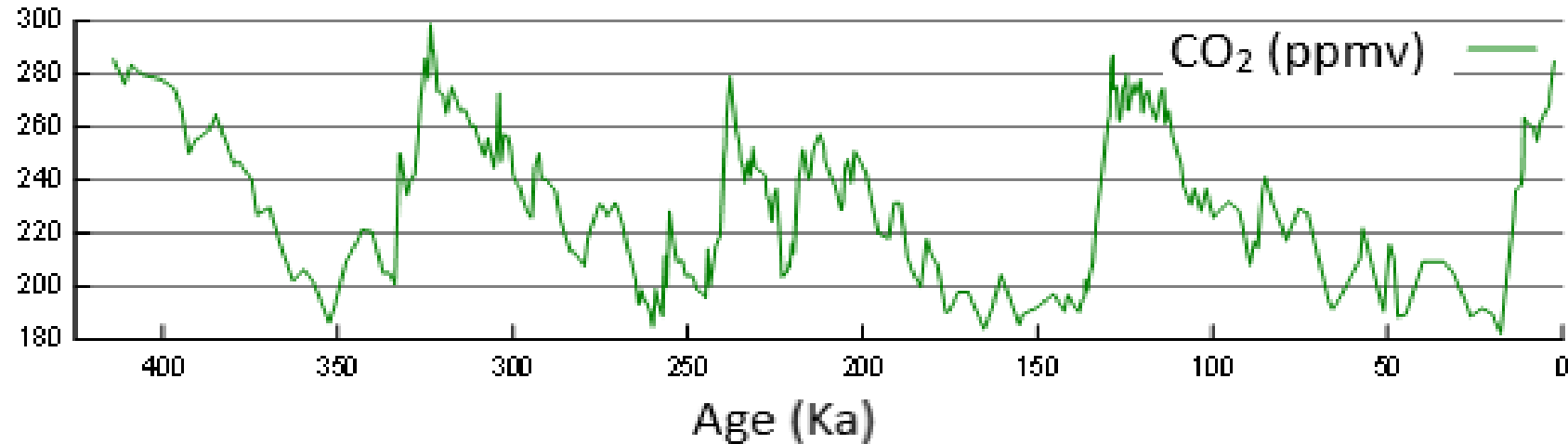
Increase in CO<sub>2</sub>  
during the Last Termination  
explained by  
a new inorganic carbon cycle.

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# The Problem



*Figure 1 - showing CO<sub>2</sub> level during the last four glacial cycles. Adapted from Ref.1*

When each of the last glacial periods ended, the concentration of CO<sub>2</sub> in the atmosphere increased abruptly by about 40%.

The oceans hold roughly 60 times more carbon than the atmosphere. Carbon in the oceans would also have increased by 40%, since the carbon in the oceans and the atmosphere are in balance.

The source of this global increase in carbon has remained unresolved for almost 40 years.

Here, using modern chemistry, I will show that the additional carbon came from dissolution of calcium carbonate on the sea bed.

# The Chemistry of Silicate Weathering

It is generally believed that the weathering of silicate rocks draws down carbon dioxide from the atmosphere. That belief originated in 1845 with a paper by Jack Joseph Ebelmen. At that time carbon dioxide was thought to be an acid and was, in fact, called carbonic acid. However, CO<sub>2</sub> is actually drawn down from the atmosphere by dissolving in rain.



When that happens it reacts with the rainwater to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>).



Carbonic acid is weak acid which only partly reacts with water to form hydronium and bicarbonate ions.



Most rocks, both silicate and carbonate are considered insoluble, but their solubility increases in the presence of acid e.g. wollastonite (CaSiO<sub>3</sub>) reacts as follows:

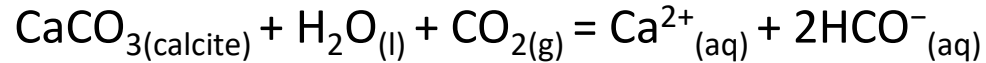


This last reaction, R6, proceeds to the right almost to completion since  $K_w = 10^{-14}$ . Then, because of Le Chatelier's Principle R5 will also proceed to the right in order to restore the lost OH<sup>-</sup> ions. That will cause R4 to proceed to the right in order to restore the lost SiO<sub>3</sub><sup>2-</sup>, which increases the solubility of the CaSiO<sub>3</sub>.

So, carbon dioxide is drawn down out of the atmosphere by R1 – R3, but the weathering of rocks, R4 – R6 does not include carbon ions. The weathering is caused by the hydronium ions, and the bicarbonate is a “spectator” ion.

# The Chemistry of Carbonate Weathering

In 1965 Garrels (Ref. 6) wrote the classic equation for the weathering of calcium carbonate as:



where  $_{(\text{g})}$  is a gas,  $_{(\text{l})}$  is a liquid and  $_{(\text{aq})}$  is an aqueous solute.

However, it is written as a “**go to completion**” reaction where all reactants are consumed, which is wrong. What really happens is a series of **equilibrium** reactions similar to those for carbonate weathering:



In those two reactions (1) & (2)  $\text{CO}_2$  is dissolved in rainwater which becomes acidic (i.e. contains hydronium ions ( $\text{H}_3\text{O}^+$ )).



In reaction (5) the hydronium ions from the rain neutralises the hydroxyl ions. Le Chatelier's Principle then means that reactions (4) and then (3) proceed to the right to replace the  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  respectively, making the calcite more soluble.

# *The Results of Weathering*

- Silicate weathering does not affect the amount of carbon in the Atmosphere-Ocean system and so can have no effect on climate.
- Carbonate weathering, on the other hand, adds carbon, in the form of bicarbonate ions, to the system . This increase in DIC leads eventually to increased atmospheric CO<sub>2</sub>, which will have an an on the climate.
- Thus, when atmospheric CO<sub>2</sub> increases, rainfall becomes more acidic, carbonate weathering increases, DIC in the aquasphere and oceans increases causing atmospheric CO<sub>2</sub> to increase in a positive feedback loop.
- Moreover, the increased atmospheric CO<sub>2</sub> will lead to ocean acidification, and to the lysocline shoaling. This will release more inorganic carbon into the ocean adding to the positive feedback loop.

# The Chemistry of Carbonate Production

Carbonate in the ocean, which provides a major sink for the overall carbon system, are produced by biotic activity, and not by chemical precipitation.

Therefore, the solubility index of calcium carbonate does not control the rate at which calcium carbonate is formed. It only controls the rate at which calcium carbonate dissolves.

Since solubility is increased by acidity, the depth of the lysocline is affected by the pH of the seawater.

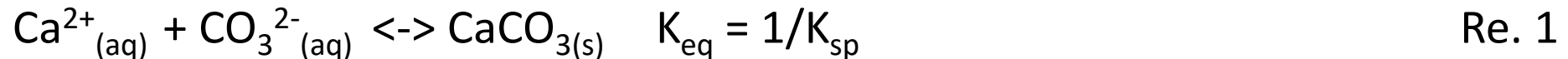
Respiration of benthic biota creates  $\text{CO}_2$  which reacts with the seawater to produce hydronium ions and reduce the pH of the seawater.

The rate at which carbonate is formed depends on the availability of nutrients, e.g. iron.

The formation of calcium carbonate is normally written as a reaction which “goes to completion” and where  $\text{CO}_2$  is produced:



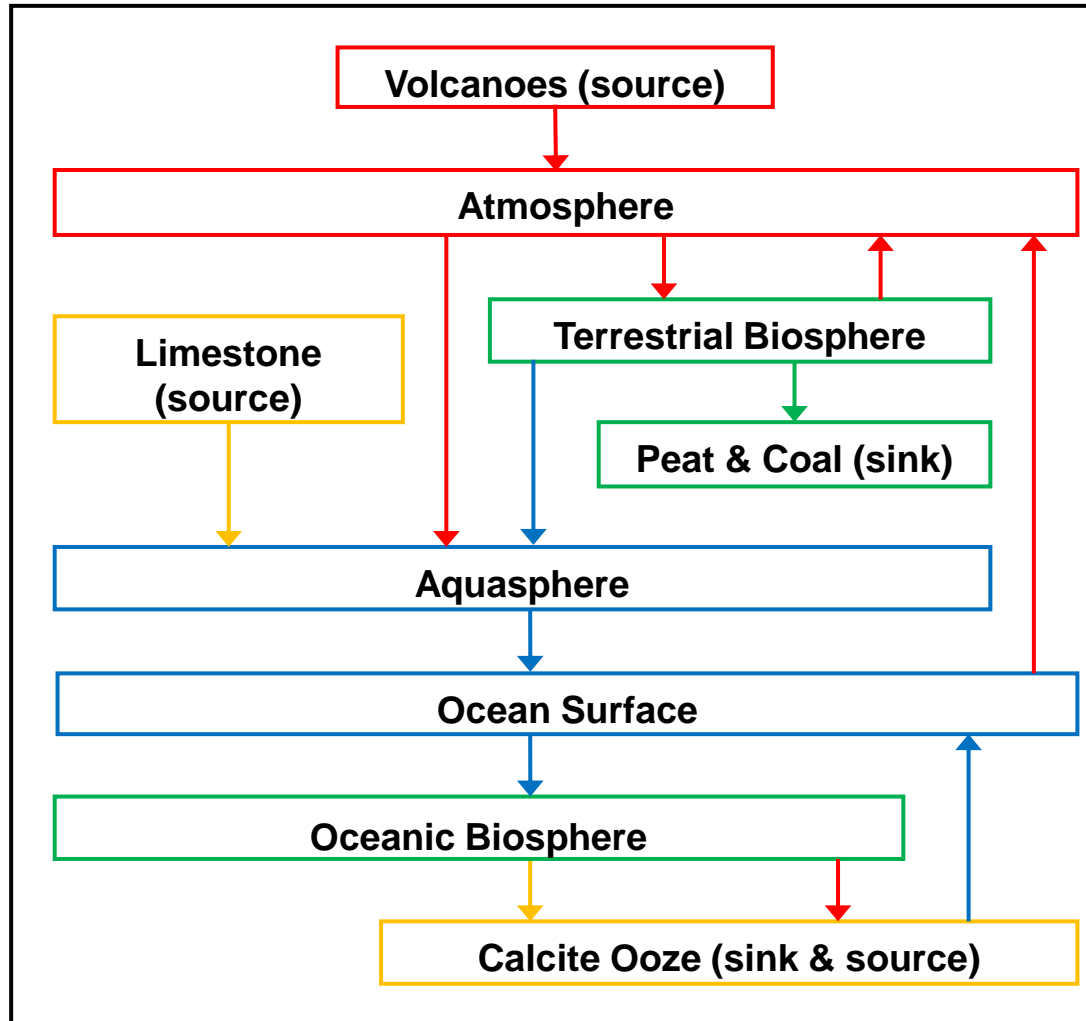
The formation of calcium carbonate is actually an equilibrium reaction ...



... in which no  $\text{CO}_2$  is generated by the formation of  $\text{CaCO}_3$ .

Since  $\text{CaCO}_3$  is formed biologically in the oceans, the nocturnal emissions of  $\text{CO}_2$  from coral reefs are the result of normal respiration, not the creation of Eq. 1.

# The New Inorganic Carbon System



Here, the inorganic carbon cycle is shown as an open flow system with sources and sinks, rather than as a closed flow system, i.e. a cycle. (Ref. 8, p.25)

Reservoirs and flows shown in red are  $\text{CO}_2$ , shown in yellow are  $\text{CaCO}_3$ , shown in green are  $\text{CH}_2\text{O}$ , and shown in blue are DIC.

The sources correspond to flows out of the lithosphere, and the sinks to flows into the lithosphere in carbon cycle diagrams.

As in conventional systems, carbon enters the atmosphere-ocean system from volcanoes and leaves as carbonate sediments on the ocean floor.

Here, limestone rocks provide an additional source of inorganic carbon caused by carbonate weathering.

What is not shown is a sink caused by silicate weathering, since that does not exist.

Peat and coal act as an organic carbon sink.

# The Aquasphere

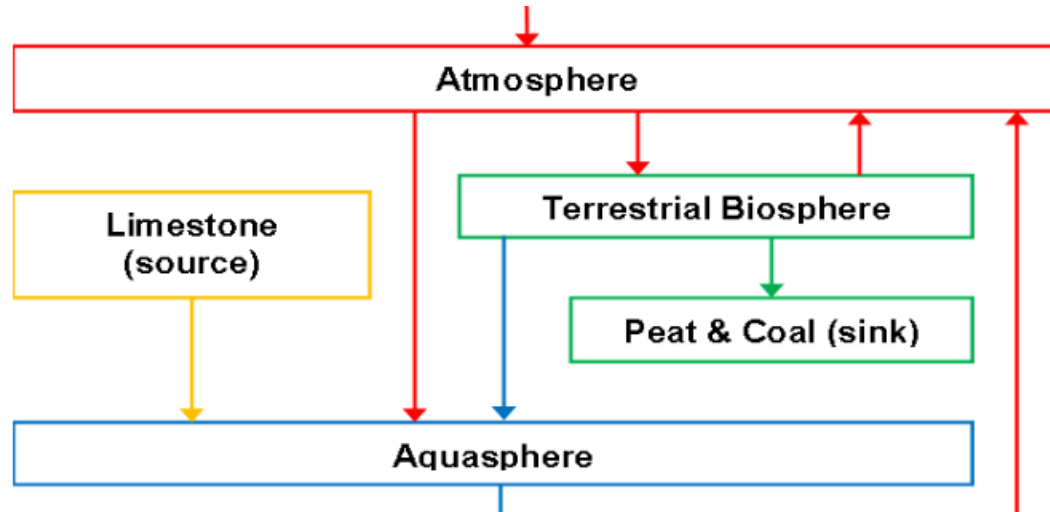
- The Earth System is composed of four great realms:
  - the Atmosphere, the Hydrosphere, the Lithosphere, and the Biosphere.
- Here, the Hydrosphere is divided into two carbon reservoirs: the Oceans and the Aquasphere.
- The Aquasphere consists of rain, ground water, steams, lakes and rivers.
- Carbon exists in the aquasphere as dissolved inorganic carbon (DIC), i.e. aqueous carbon dioxide, carbonic acid, bicarbonate ions, and carbonate ions.
- **DIC = aqueous  $\text{CO}_2 + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$**
- (The Aquasphere may be the remaining missing carbon sink. In the annually produced Global Carbon Budget there has been a budget imbalance of  $0.3 \text{ GtC yr}^{-1}$  [Ref. 3]. The three reservoirs considered there are Atmosphere, Ocean, and Land. Could it be that inclusion of the Aquasphere would produce a balance?)



# *Rain is part of the Aquasphere*

- It is important to realise that rain is part of the aquasphere, and not of the atmosphere.
- The atmosphere is gaseous, and carbon exists there as carbon dioxide.
- The aquasphere is liquid, and carbon exists there as dissolved inorganic carbon (DIC).
- Rain is liquid, and carbon exists there as dissolved inorganic carbon.
- Therefore, from the perspective of the carbon system, rain is part of the aquasphere, not the atmosphere.

# Carbon into the Aquasphere



- The biosphere respire most of that carbon back into the atmosphere as carbon dioxide gas, but some of that carbon is respired into the aquasphere by dissolving in ground water and increasing its acidity.
- What is not respired goes on to form peat and coal.
- Carbon dioxide is drawn down from the atmosphere into the aquasphere by dissolving in rain and forming carbonic acid.
- Carbon dioxide is also drawn down from the atmosphere into the biosphere by photosynthesis to form organic carbon.
- Limestone rocks are weathered by the acidic water in the aquasphere and add calcium and carbonate ions to it.
- Weathering of silicates rocks neither adds nor removes carbon from the aquasphere!

# *The Last Glaciation*

During the last glaciation, when the ice sheets grew, they would have dammed rivers and prevented the weathering of carbonate rocks.

This would have decreased the flow of DIC from the aquasphere into the oceans.

Assuming that productivity of the oceanic biosphere remained constant, carbonate sediments would have continued to form at the previous rate.

This would have resulted in a decrease in oceanic DIC, since input would no longer be balanced by output.

Then, since oceanic DIC decreased, oceanic dissolved CO<sub>2</sub> decreased. Oceanic CO<sub>2</sub> and atmospheric CO<sub>2</sub> are in equilibrium so atmospheric CO<sub>2</sub> would also have decreased.

This decrease in atmospheric CO<sub>2</sub> concentration would cause ocean basicification, the opposite of ocean acidification.

The basicification would increase carbonate sedimentation and further decrease oceanic DIC.

This would lead to less CO<sub>2</sub> entering the atmosphere from the ocean surface and the decrease in atmospheric CO<sub>2</sub> which occurred. See Fig. 2.

# Atmospheric CO<sub>2</sub> and Sea-level

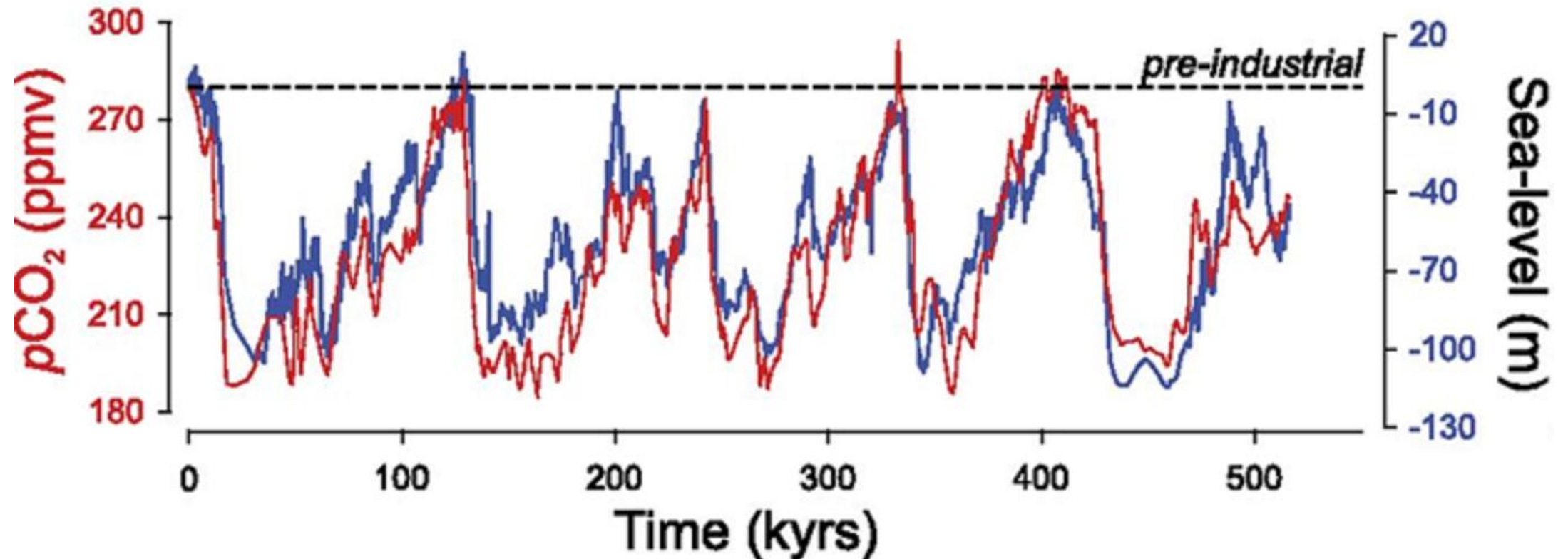


Figure 2 – Showing the correlation between atmospheric CO<sub>2</sub> and sea-level, which supports but does not prove that rising sea level causes the lysocline to shoal. Adapted from Ref. 4.

# *The Last Termination*

During the last terminations, when ice sheets melted and sea level rose, assuming the depth from the surface of the ocean to the CCD was unchanged, then the lysocline would have shoaled.

The shoaling would have weathered the sediments, which had been created during the glaciation, adding DIC to the oceans and increasing aqueous CO<sub>2</sub>.

This increase in oceanic aqueous CO<sub>2</sub>, which equivalates with the atmosphere, explains both the source and the cause of the increased atmospheric CO<sub>2</sub> during glacial terminations.

The weathered carbonate was laid down during the glaciation and would be up to 100 ka old. Therefore it would be depleted in <sup>14</sup>C, which could explain the Mystery Interval named by Broecker and Barker, 2007: Ref 5).

The second source of <sup>14</sup>C depleted carbon would arise from rivers to the oceans as the ice sheets melted and the rivers became undammed.

In the future, when the Greenland and West Antarctic ice sheets melt as a result of anthropogenic global warming, the lysocline will shoal and produce an additional increase in atmospheric CO<sub>2</sub>.

Moreover, ocean acidification will also cause the lysocline to shoal, also producing more oceanic DIC and consequently more atmospheric CO<sub>2</sub>.

If atmospheric CO<sub>2</sub> passes a tipping point, then a positive feedback loop may arise with atmospheric CO<sub>2</sub> causing the lysocline to shoal and the lysocline shoaling causing atmospheric CO<sub>2</sub> to rise, as may have occurred during the PETM.

# *Paleo-Eocene Thermal Maximum*

Around 55 Ma ago global temperatures rose by at least 5°C, which was accompanied by a diminution of all large land-based species.

The lysocline shoaled as the result of an increase in atmospheric CO<sub>2</sub>, but the source of that trigger is not yet known.

Here, I suggest that there was an under-sea extension of the Ayrshire coalfield into the Firth of Clyde.

The volcanic activity, when the North Atlantic opened heated that coalfield producing CH<sub>4</sub>.

That would explain the “large decrease in the <sup>13</sup>C/<sup>12</sup>C ratio of marine and terrestrial carbonates” [Ref.2: Pagani, et al. 2006) during the PETM.

The CH<sub>4</sub> oxidised to CO<sub>2</sub> and caused ocean acidification which was the trigger for the shoaling of the lysocline.

The shoaling of the lysocline, i.e. weathering of carbonate sediments, would have caused ocean acidification, DIC to increase, and atmospheric CO<sub>2</sub> to rise.

Increased atmospheric CO<sub>2</sub> would have caused more ocean acidification resulting in a tipping point being passed where shoaling of the lysocline became part of a positive feedback loop that led to a runaway increase in CO<sub>2</sub> and global temperatures.

Could the current increase in anthropogenic CO<sub>2</sub> lead to a similar runaway event?

# Summary

CO<sub>2</sub> is drawn down from the atmosphere by rain into the aquasphere

Silicate weathering does not draw down CO<sub>2</sub> from the atmosphere.

Carbonate weathering adds DIC to the aquasphere, which carries the DIC to the ocean surface.

Deep-sea ocean sediments can be weathered by sea level rise.

Ocean carbonate sediments can also be weathered by seawater which has had its pH lowered by CO<sub>2</sub> from the respiration of benthic biotic material.

These ideas need to be explored further, because they imply that there are positive feedbacks in the system of which we are currently unaware.

# References

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