Increase in CO_2 during the Last Termination explained by a new inorganic carbon cycle.

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The Problem

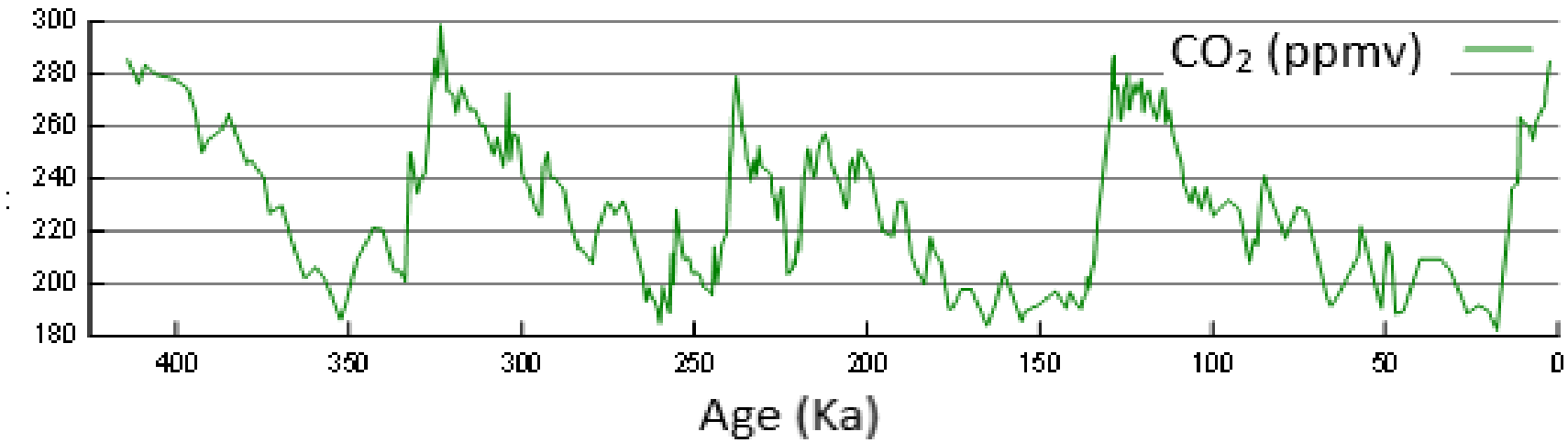

Figure 1 - showing CO2 level during the last four glacial cycles. Adapted from Ref.1

When each of the last glacial periods ended, the concentration of CO_2 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.

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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_2 is actually drawn down from the atmosphere by dissolving in rain.

$CO_{2(g)} <-> CO_{2(aq)}$ $K_{eq} = K_H$ Henry's constant R1

When that happens it reacts with the water to form carbonic acid (H_2CO_3).

$CO_{2(aq)} + H_2O_{(l)} <-> H_2CO_{3\,(aq)}$ $K_{eq} = K_0$ R2

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

$H_2CO_3 + H_2O <-> H_3O^+ + HCO_3^-$ $K_{eq} = K_{a1}$ the first acidity constant of H_2CO_3 R3

Most rocks, both silicate and carbonate are considered insoluble, but their solubility increases in the presence of acid, e.g.

$CaSiO_3 <-> Ca^{2+} + SiO_3^{2-}$ $K_{eq} = K_{sp}$ the solubility product of $CaSiO_3$
R4

$SiO_3^{2-} + H2O <-> HSiO_3^- + OH^-$ Keq = Kb1 the first basicity constant of the base SiO_3^2 R5

$H_3O^+ + OH^- <-> H_2O$ Keq = 1/Kw the ionic product of water R6

The last reaction , R6, proceeds to the right almost to completion since Kw = 10^{-14}. Then, because of Le Chatelier's Principle R5 will also proceed to the right in order to restore the lost OH^- ions. That will cause R4 to proceed to the right in order to restore the lost SiO_3^{2-}, and so increase the solubility of the $CaSiO_3$.

So, the 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 are spectator ions.

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The Chemistry of Carbonate Weathering

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

$$CaCO_{3(calcite)} + H_2O_{(l)} + CO_{2(g)} = Ca^{2+}{}_{(aq)} + 2HCO^{-}{}_{(aq)}$$

where $_{(g)}$ is a gas, $_{(l)}$ is a liquid and $_{(aq)}$ is an aqueous solute, but is wrong because it is a "go to completion" reaction where all reactants are consumed.

What really happens is series of equilibrium reactions similar to those for carbonate weathering:

$$CO_{2(g)} + H_2O_{(l)} \text{ <-> } H_2CO_{3(aq)} \qquad K_{eq} = K_H \qquad (1)$$

$$H_2CO_{3(aq)} + H_2O_{(l)} \text{ <-> } H_3O^{+}{}_{(aq)} + HCO_3^{-}{}_{(aq)} \qquad K_{eq} = K_{a1} \qquad (2)$$

In those two reactions CO_2 is dissolved typically in rainwater which becomes acidic (i.e. contains hydroniun ions (H_3O^+)).

$$CaCO_{3(calcite)} \text{ <-> } Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \qquad K_{eq} = K_{sp} \qquad (3)$$

$$CO_3^{2-}{}_{(aq)} + H_2O \text{ <-> } HCO_3^{-}{}_{(aq)} + OH^{-}{}_{(aq)} \qquad Keq = Kb1 \qquad (4)$$

$$OH^{-}{}_{(aq)} + H_3O^{+}{}_{(aq)} \text{ <-> } 2H_2O_{(l)} \qquad Keq = Kw \qquad (5)$$

In R. (5) the acid from the rain neutralises the hydroxyl ions. Le Chatelier's Principle then means R. (4) and R. (3) proceed to the right to replace the OH^- and CO_3^{2-} making the calcite more soluble.

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The Results of Weathering

- Silicate weathering does not control 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 to the system in the form of bicarbonate ions and will have an effect on the climate.
- Thus, when atmospheric CO_2 is increased, the climate warms and rainfall increases, carbonate weathering also will increase.
- That will lead to further increase in carbon dioxide, creating a positive feedback loop.
- Moreover, the increased atmospheric CO_2 will lead to ocean acidification, and the lysocline shoaling. This will release more carbon into the ocean creating and an additional positive feedback loop. .

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The Chemistry of Carbonate Production

Carbonate sediments in the ocean, which provide 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.

The rate at which it forms 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 CO_2 is produced:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

The formation of calcium carbonate is actually an equilibrium reaction …

$$Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \leftrightarrow CaCO_{3(s)} \qquad K_{eq} = 1/K_{sp}$$

… in which no CO_2 is generated by the formation of $CaCO_3$.

Since $CaCO_3$ is formed biologically in the oceans, the nocturnal emissions of CO_2 from coral reefs are the result of normal respiration.

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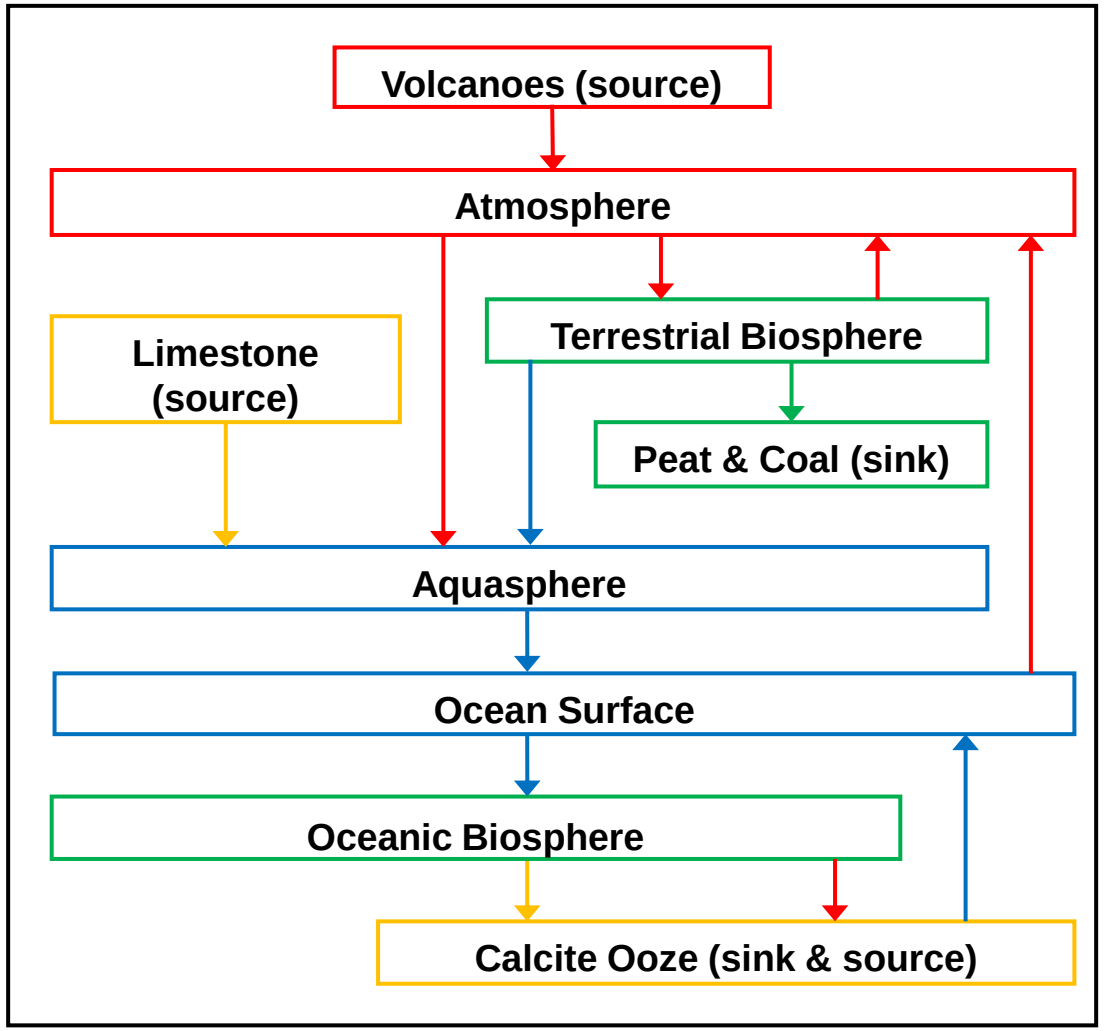
The New Inorganic Carbon System



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 CO_2, shown in yellow are $CaCO_3$, shown in green are CH_2O, and shown in blue are DIC.

The sources correspond to flows out of the lithosphere, and the sinks to flows into the lithosphere in a 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.

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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 CO_2 + H_2CO_3 + HCO_3^- + 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 GtC yr^{-1} [Ref. 3]. The three reservoirs considered are Atmosphere, Ocean, and Land. Could it be that inclusion of he Aquasphere would produce a balance?)

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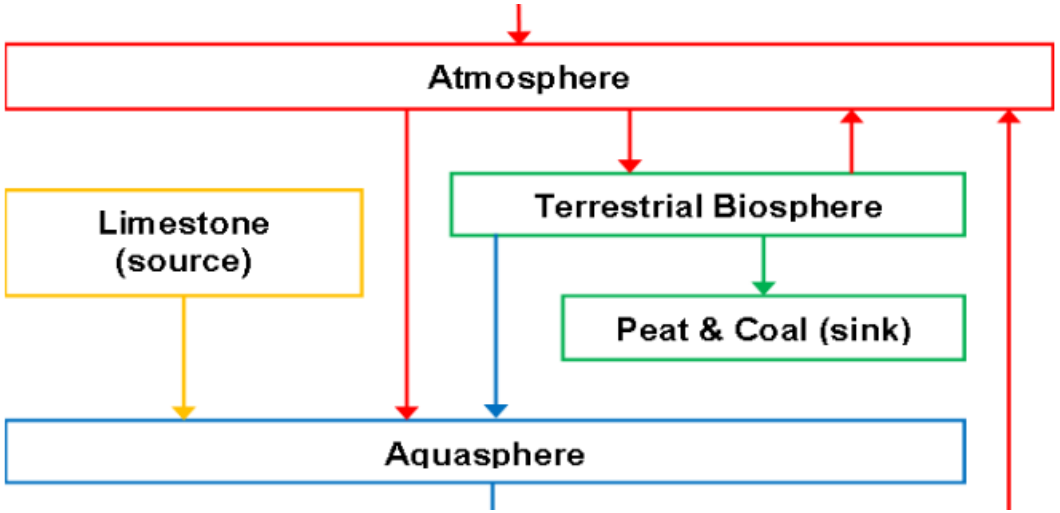
Rain is part of the Aquasphere

- **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



- **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.**
- **The biosphere respires 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 increasing its acidity.**
- **What is not respired goes on to form peat and coal.**
- **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!**

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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_2 decreased. Oceanic CO_2 and atmospheric CO_2 are in equilibrium so atmospheric CO_2 would also have decreased.

This decrease in atmospheric CO_2 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_2 entering the atmosphere from the ocean surface and the decrease in atmospheric CO_2 which occurred. See Fig. 2.

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Atmospheric CO_2 and Sea-level

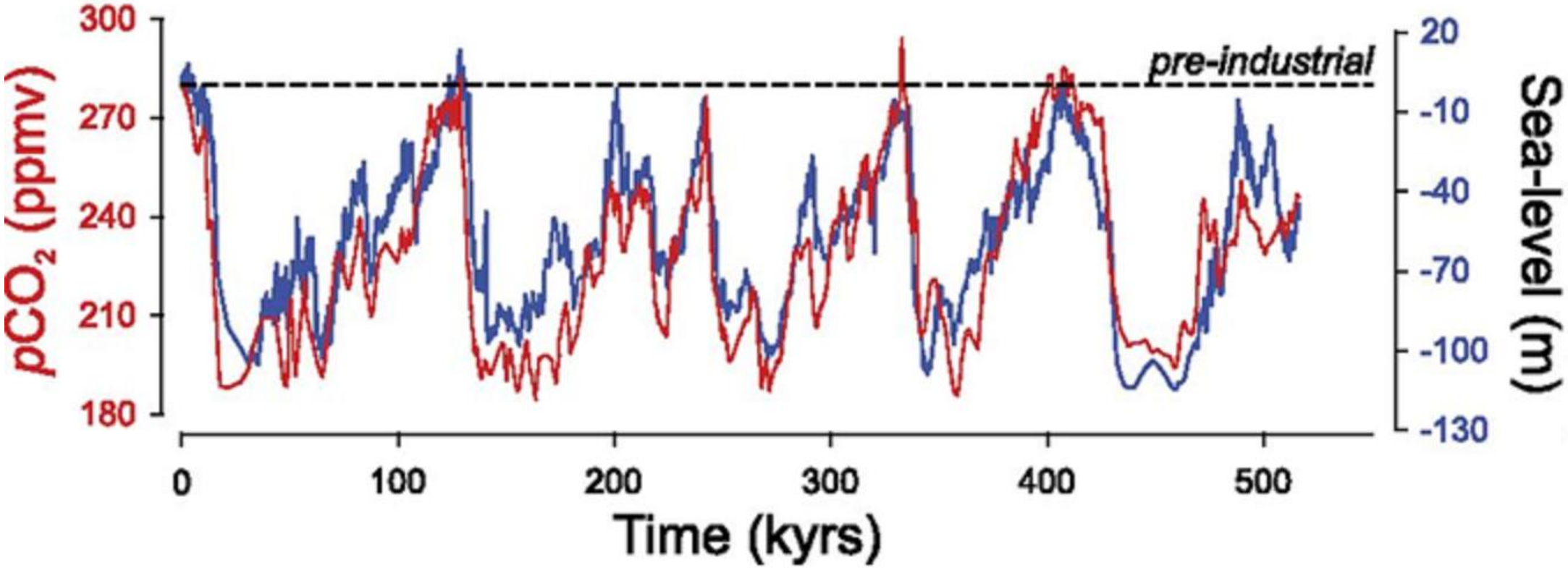

Figure 2 – Showing the correlation between atmospheric CO_2 and sea-level, which supports but does not prove that rising sea level causes the lysocline to shoal. Adapted from Ref. 4.

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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_2.

This increase in oceanic aqueous CO_2, which equivalates with the atmosphere, explains both the source and the cause of the increased atmospheric CO_2 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 ^{14}C, which could explain the Mystery Interval named by Broecker and Barker, 2007: Ref 5).

The second source of ^{14}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_2.

Moreover, ocean acidification will also cause the lysocline to shoal, also producing more oceanic DIC and consequently more atmospheric CO_2.

If atmospheric CO_2 passes a tipping point, then a positive feedback loop may arise with atmospheric CO_2 causing the lysocline to shoal and the lysocline shoaling causing atmospheric CO_2 to rise, as may have occurred during the PETM.

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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_2, 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_4.

That would e explain the "large decrease in the $^{13}C/^{12}C$ ratio of marine and terrestrial carbonates" [Ref.2: Pagani, et al. 2006) during the PETM.

The CH_4 oxidised to CO_2 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_2 to rise.

Increased atmospheric CO_2 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_2 and global temperatures.

Could the current increase in anthropogenic CO_2 lead to a similar runaway event?

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References

1. By Vostok-ice-core-petit.png: NOAA derivative work: Autopilot (talk) - Vostok-ice-core-petit.png, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=10684392
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