A discussion of the mechanism involved in marine carbon storage and hypothesis's that account for variations in atmospheric CO_2 between glacial and interglacial periods

Context:

Earth's climate system receives its energy from the Sun. Consequently, the Earth's radiation balance and mean temperature is determined by its absorption of solar radiation (Haigh, 2007). This solar forcing of the climate (Jager, 2005, Shopov, 2013) is subject to variations that can cause instances of global climate change. One such variation is that referred to as the Milankovitch cycle whereby the Earth's orbit around the sun is subject to change. A combination of a change in the obliquity of Earth's axis, the eccentricity of Earth's orbit and the precession (wobble) alter the seasonal and latitudinal solar radiation or insolation the planet receives (IPPC, 2007). Analysis suggest that low insolation during summer months in the Northern Hemisphere eventually causes a build up of winter snow year on year, taking the first steps in creating an ice sheet and subsequently the Ice Age (IPPC, 2007). Further studies show that carbon dioxide (CO_2) concentrations in the atmosphere are lower during glacial periods and higher during interglacial periods (fig. 1). This variation sees the removal of nearly 80 - 100ppm of CO2 from the atmosphere under full glacial conditions (Sarmiento & Gruber, 2006). Ice core data shows that CO2 concentrations in the atmosphere follow temperature change in the Antarctica, therefore positive CO2 feedbacks within the climate system amplify the Milankovitch cycles to create glacial cycles (IPPC, 2007, Sigman & Boyle, 2000)

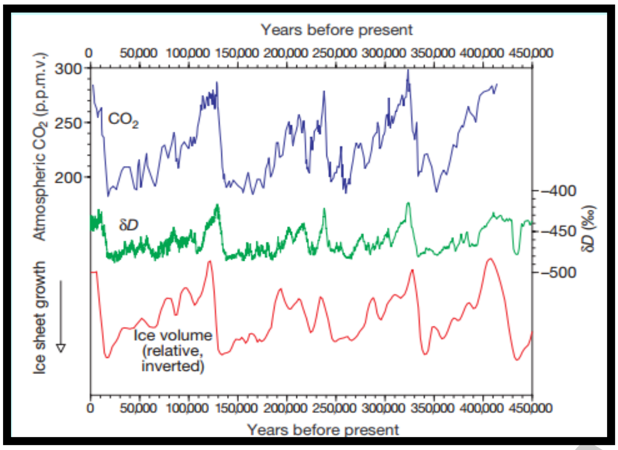

Fig.1 Ice sheet growth and CO2 atmospheric concentrations, Source: Sigman & Boyle, 2000

The Carbon Cycle:

Carbon, the building block of life on Earth is cycled through different reservoirs such as the atmosphere, ocean, biosphere and rocks. The exchange between each reservoir, which can be on short to long timescales, is referred to as the carbon cycle (NASA, 2011) and this is what controls the distribution of CO2 throughout Earth's systems (fig. 2)

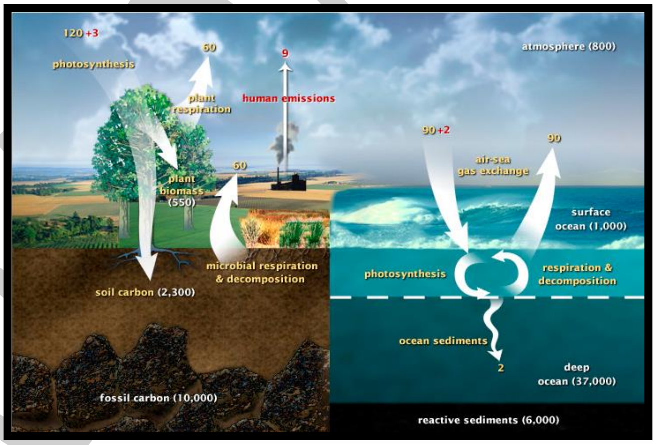

Fig. 2 The Carbon Cycle, Source NASA, 2011

Consideration of the timescales involved in carbon exchanging from one reservoir to the other (Fig.3) and the variation of atmospheric CO2 by nearly 100ppm between glacial (G) and interglacial (IG) periods, Broecker concluded that changes in the CO2 storage of the oceans corresponded best with past CO2 variability. Particularly given the fact the atmosphere, terrestrial zone and surface ocean together account for less than 10% of the inorganic storage ability of the deep ocean (Sigman & Boyle, 2000) .

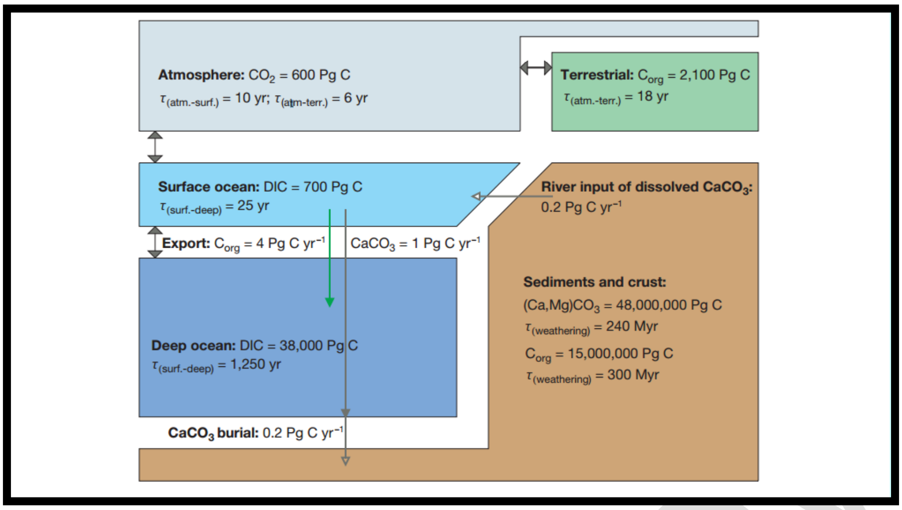

Fig. 3 View of fluxes and reservoirs (pre-industrial) Holocene carbon cycle Source Sigman & Boyle, 2000

During the Ice Ages, ice sheets kilometres thick dominated the Northern Hemisphere reducing the terrestrial's carbon storage capabilities (Sigman & Boyle, 2000). Sea levels had fallen by 125m exposing continental shelves and weathering removed the carbon stored in these zones to the ocean and atmosphere (Sigman & Boyle, 2000). Consequently, during the Ice Age the terrestrial zone became a source of CO2, proven by Carbon-13 isotope data taken from the oceans (Sarmiento & Gruber, 2006). For this reason the deep ocean, as the largest reservoir of CO2 with timescales similar to documented CO2 variations provide the best starting point in explain past climate change.

The Marine Carbon Cycle: Mechanisms that sequester CO2 into the oceans:

Physical Processes at the Surface Ocean - Temperature and Salinity:

An exchange between atmospheric and oceanic CO2 takes places when the partial pressure (pCo2) in the surface ocean is not in equilibrium with atmospheric pCO2 (Goosse et al, 2015). An area of ocean can be supersaturated, meaning pCO2 is higher in seawater and a positive flux takes place from the ocean to the atmosphere, undersaturated zones are the opposite (Goosse et al, 2015). In addition the pCO2 of surface water is controlled by the salinity, temperature and the oceans chemical composition, such as Dissolved Inorganic Carbon (DIC) and Alkalinity (ALK), (Sigman & Boyle, 2000, Broecker & Henderson, 1998). As a result, the pCO2 of surface water is never constant and its interaction with the deep ocean is consistently being 'reset' (Sigman & Boyle, 2000).

G/IG Variations: Co2 is more soluble in cold water, as a result during glacial periods more atmospheric CO2 is sequestered into the surface ocean. However, the deep reservoir, 25 times that of the atmosphere and surface ocean together, has a mean temperature of 2 degrees, and would not have become much colder during the Ice Age (Sigman & Boyle, 2000). This then places a limit on the amount of CO2 sequestering from surface ocean into the deep ocean (Sigman & Boyle, 2000). Furthermore, as in all Earth's systems, feedbacks exist. Consequently, during glacial periods more fresh water is trapped in ice thereby increasing the salinity of the ocean which in turn makes CO2 less soluble. Therefore, estimates suggest that colder waters sequestered about 30ppm of atmospheric CO2; conversely increased salinity sequestered about 6.5ppm of oceanic CO2 to the atmosphere (Sigman & Boyle, 2000). Moreover, terrestrial CO2 exchanges to the ocean of about 500Pg C would leave a balance of 8.5ppm of atmospheric CO2 being sequestered by the ocean as a result of cooler temperatures and increased salinity during the glacial period (Sigman & Boyle, 2000). For this reason, Broecker and Henderson (1998) conclude that "*even if both bottom water and intermediate water were cooled to their maximum extent during the glacial periods, this could not produce sufficient drawdown of CO2*" (p459).

Physical Processes – The Inorganic Carbon Cycle & Ocean Circulation

Atmospheric CO2 exchange into the oceans, react with water to form carbonic acid (H2CO3); a weak acid it 'dissociates' to form bicarbonate (HCO3) and carbonate ions (CO2/3), the sum of which is referred to as DIC – Dissolved Inorganic Carbon (Goosse et al, 2015). Bicarbonate and carbonate are the dominant species, with the former making up to 90% of DIC and the latter about 10%, with a small remainder left as carbonic acid, 0.5% (Goosse et al, 2015). In addition, the fluxes between the atmosphere and ocean are determined by the availability of carbonate ions (CO2/3) which in turn influences the Alkalinity (ALK) of the ocean (Goosse et al, 2015). ALK measures the acidity of the ocean. The dissociation of carbonic acid (dissolved CO2) lowers the pH of the ocean and if the ALK decreases carbonic acid and bicarbonate will come to dominate, increasing CO2 in the surface ocean (Goosse et al, 2015). For this reason DIC and its relationship with ALK is an important factor to be considered when seeking to understand the mechanisms that sequester CO2 into the oceans.

G/IG Variations: A physical form of CO2 sequestering thought to amplify the orbital cycles is the solubility pump which transfers DIC to the deep ocean. DIC is most prevalent in colder waters, colder waters are denser and for this reason the solubility pump forces this DIC rich (and nutrient rich Nitrogen/Phosphorus) water to the deep oceans, thus sequestering CO2 from the atmosphere (MIT, 2009). Conversely, a feedback exists' that returns this sequestered CO2 to the atmosphere by a processes know as upwelling. By upwelling, this nutrient rich DIC, releases sequestered CO2 back to the atmosphere, increasing atmospheric CO2 (Sigman & Boyle, 2000).

However, where this DIC and nutrient rich water upwelled to the surface during glacial periods, particularly in the high latitudes, are cited as areas of high productivity of the biological pump which in turn stems 'the leak' of sequestered CO2 by upwelling (Sigman et al, 2010). The net effect sees CO2 sequestered back into the deep ocean at high latitudes during glacial periods due to a high performing biological pump (Sigman & Boyle, 2000). In addition, models predict a decline in the North Atlantic Deep water ocean circulation during the glacial period, depicting a atmospheric CO2 sequestration of 15ppm into the ocean (Rahmstorf, 2002).

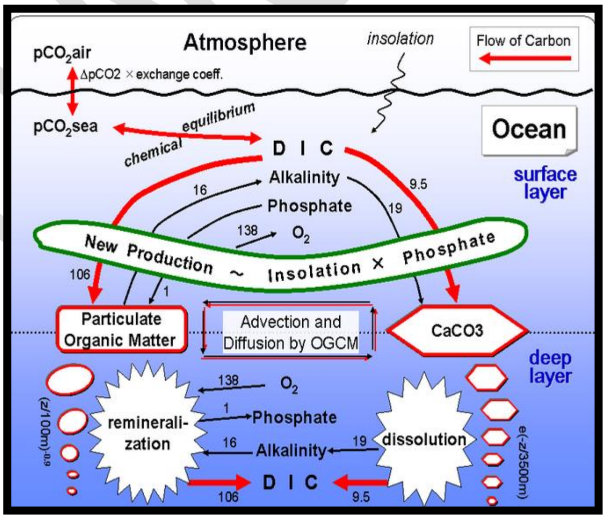

Fig. 4 DIC - biogeochemical processes, Source http://www.mri-jma.go.jp/Project/1-21/1-21-1/carbon_ocean-en.htm

Biological Processes – Biological Pump & Phytoplankton:

DIC and ALK is also influenced by biological processes such as the biological pump (fig. 5) and the counter-carbon pump. The biological pump involves the fixation of CO2 by phytoplankton through photosynthesis to form organic matter (Goosse et al, 2015). Some of these particles & organism, or particulate organic carbon (POC) is exported into deeper waters (Kohfeld & Ridgwell, 2013), where its remineralises (convert from organic to inorganic) into DIC and subsequently allows for more CO2 to be taken in at the surface ocean (Sigman et al, 2010, Kohfeld & Ridgwell, 2013). In addition, storage of CO2 in the deep ocean "*reduces the burial of calcium carbonate in seafloor sediments and thus makes the global ocean more alkaline, which increases the solubility of CO2 in sea water, further lowering (atmospheric) CO2*" (Sigman et al, 2010, p47)

G/IG Variations: A highly productive biological pump during the glacial is cited as having a positive feedback effect on atmospheric CO2. Phytoplankton fixation of CO2 also requires nutrients such as nitrogen (N) and phosphorus (P) which are naturally limited. McElroy (1983) depict an increase in ocean nutrients at low latitudes as possible ways in which increased biological pump activity at low latitudes could further sequester CO2 to the oceans (Sigman & Boyle, 2000). Increase nutrients are believed to be the result of increased C/N/P rich water upwelling, a consequence of cooler waters during glacial periods taking in more CO2 combined with the physical processes of the solubility pump. An increase in oceanic nutrient content of 30 % could increasing CO2 solubility and CO2 sequestration to the deep ocean during glacial periods by as much as 30-/+45 ppm (Sigman & Boyle, 2000). A second hypothesis proposes iron fertilization, an important factor for N2 fixation (Sigman & Boyle, 2000) of marine biota as a result of increased atmospheric dust during the glacial period (Kohfeld et al, 2005) with some estimates predicting a 20ppm sequestration of atmospheric CO2 to the oceans.

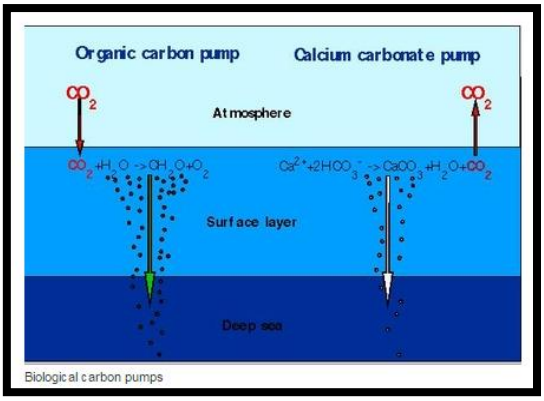

Fig. 5 Calificication in the ocean, Source AWI
http://www.awi.de/en/research/research_divisions/biosciences/marine_biogeosciences/research_thees
/calcification/

Biological & Chemical Processes – CaCO3, Calcification and Ocean Alkalinty:

Different species use the imported atmospheric CO2 to form calcium carbonate shells (CaCO3). It acts as a counter-pump to the other biological pump as its production increases CO2 transfer from the sea to the atmosphere. The carbonate pump is often "*counter-intuitive....the precipitation of carbonate carbon drives an increase in ocean pCO2, and with it, an increase in atmospheric CO2 concentration. Conversely, dissolution of CaCO3 drives a pCO2 (and atmospheric CO2) decrease*" (Ridgwell & Zeebe, 2005). Very little dissolution of CaCO3 occurs in the water column, most CaCO3 sinks to the seafloor. A third of CaCO3 is exported from the surface ocean to the ocean floor, and half of this CaCO3 is buried (Sarmiento & Gruber, 2004). On short-time scales this seems minimal, yet on longer-timescales, for example greater than a century, this CaCo3 burial is a crucial component of marine carbon storage (Goosse et al, 2015, Sarmiento & Gruber, 2004). The rate of CaCO3 sedimentation is compensated for by CaCO3 river input (Goosse et al, 2015). CaCO3 production, addition by weathering and removal by biogenic precipitation and burial of CaCO3 also influences DIC and ALK, ALK being increased to in the former and decreased in the latter (Sigman & Boyle, 2000).

G/IG Variations: Two hypotheses exist which refer to the possible link with CaCO3 and its impact on ALK. The coral reef hypothesis depicts a scenario whereby during the glacial period the continental self and coral reefs on it are exposed, now subject to weathering and providing fewer shallow water regions for CaCO3 to settle (build coral) subsequently increases ALK. Increased ALK in the ocean causes a decrease in

Atmospheric CO2 (Sigman & Boyle, 2000) in addition to more DIC containing carbonate CO3 and as dissolved CO2; therefore lowing atmospheric pCO2 (Sigman et al, 2010). Furthermore this increase in ALK drives deep ocean carbonate ions concentration up – and in turn the saturation horizon will deepen (Goosse et al, 2015), shoaling the lysocline, increasing seafloor CaCO3 burial and lowering atmospheric CO2 concentrations in the long-term (Sigman & Boyle, 2000, Sigman et al, 2010). An increase of Ca2/3 weathering on land would equate to 25ppm of a decrease in atmospheric CO2, deepening the Lysocline by over 1000m (Sigman & Boyle, 2000). However, data collected from the seafloor does not show any indication of such a deepening of the Lysocline and thus the hypothesis has been invalidated by Sigman & Boyle (2000).

The rain-ratio; a ratio between CaCO3 and organic carbon leaving the surface ocean area that receives light. A decrease in the ratio of CaCO3/Corg in the low latitudes causes a decrease in atmospheric CO2 [ALK high in surface ocean = enhanced CO2 solubility], (Sigman & Boyle, 2000). If CaCO3 transfer to deeper ocean is more than Corg, than ALK will decline (decreased pH/ore acidic) over a timescale of 5-/+10 kyr which feedbacks into the system as a rise in atmospheric CO2 (Sigman & Boyle, 2000). Conversely, if Corg production increases and CaCo3 remains static, increase the DIC deep reservoir and can lower atmospheric CO2 by 50ppm, with a 50% increase in Corg production accounting for a 80ppm reduce in atmospheric CO2 (Sigman & Boyle, 2000).

Discussed separately – hypothesis fall short of explaining variation:

The mechanism discussed all have a role to play in the CO2 variations observed between glacial and interglacial periods. Substantial changes can occur through the calcification processes associated with CaCO3 precipitation and dissolution, also through the strength of the biological pump. However, no single mechanism can account for the 80 to 100ppm variation in atmospheric CO2.

> *"Thus, despite the continuing lure to researchers of a single and conceptually elegant explanation, it has become increasingly clear that the observed glacial interglacial variability in CO2 must result from a combination of processes operating in conjunction [but not necessarily in phase or even in sign]*, (Köhler and Fischer, 2006 cited by Kohfeld & Ridgwell, 2013, p263).

The Role of The Southern Ocean in CO2 Glacial/Interglacial CO2 variations:

Reducing atmospheric CO2 – the glacial period:

> *"The modern Southern Ocean releases deeply sequestered CO2 to the atmosphere. Growing evidence suggests that the Southern Ocean CO2 'leak' was stemmed during ice ages, increasing ocean CO2 storage. Such a change would also have made the global ocean more alkaline, driving additional ocean CO2 uptake"* (Sigman et al, 2010)

Focusing on high latitudinal surface oceans such as the southern ocean and the corresponding marine carbon cycle mechanisms and proposed feedbacks as discussed seem to offer a more compounded explanation of CO2 variations between glacial and interglacial periods. High latitude oceans take in more CO2 then low latitude oceans, and low latitudes tend to export CO2 towards the high latitudes who tend to transport that CO2 to its interior (Sarmiento & Gruber, 2006). Once such 'Southern Ocean' hypothesis put forward by Sigman & Boyle (2000) and Sigman et al (2010) propose increased 'nutrient utilization' by phytoplankton as the cause of the decreased atmospheric CO2 recorded in Antarctic ice core records. A highly productive biological pump has been shown to efficiently sequester CO2 into deep ocean storage (Fig. 4).

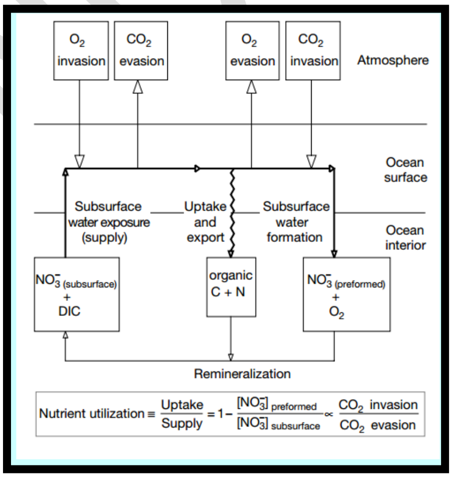

Fig. 4 "The effect on atmospheric CO2 of the biological pump in a region of deepocean ventilation. Deep water is nutrient- and CO2-rich because of the lower-latitude biological pump, which sequesters both nutrients and inorganic carbon in the ocean interior" Source Sigman & Boyle 2000, p.865

The Southern Ocean, a circulation apart of the THC 'outcrops' at the subpolar region in the Antarctic, having ventilated a large proportion of the oceans deep interior and carrying with it deep water rich in C/N/P, upwells and feeds the biological pumps (Sigman & Boyle, 2000, Sigman et al 2010). In addition, iron fertilisation sourced from atmospheric dust (known to increase during glacial periods) and/or melting during summer of sea ice would also add to the productivity to the biological pump. This has two effects; increased exports of organic carbon to the interior and lessening the rate at which CO2 can escape at the surface (Sigman & Boyle, 2000). In addition, increased sea-ice cover in the Antarctic region is also included as a mechanism whereby a stemming the Southern Ocean (CO2) leak is possible (Sigman et al, 2010). The southern ocean represents a meeting point between surface ocean and deep DIC storage, "*the closure of this window has a large impact on atmospheric CO2*" (Sarmiento & Gruber, 2006, p440). In addition, as already referred to above; "*changes in the low latitudes are much less effective in changing atmospheric CO2, since changes in this reservoir tend to be compensated by equilibration with the deep ocean... This is not the case for high latitude changes, so that any change in high-latitude pCO2 leads to nearly corresponding changes in atmospheric CO2*" (Sarmiento & Gruber, 2006, p. 441).

Additionally, as already discussed changes in the biological pump will impact on ALK. Imbalances between ALK inputs and removal forces the CaCO3 cycle to react and equalize itself by either shoaling or deepening of the lysocline so that the mean ALK will be brought back to equilibrium thereby impacting atmospheric/oceans CO2 transfers (Sarmiento & Gruber, 2006). A study by Toggweiler (1999) found that the there was a physical and chemical separation between the Southern Ocean and the NADW/AABW during the last glacial maximum (Sarmiento & Gruber, 2006). A model carried out by Toggweiler (1999) illustrated a 60ppm drop in atmospheric CO2 because of reduced bottom ocean ventilation and CaCO3 compensation in reaction to ALK changes.

In conclusion it seems "*the most promising explanations for the bulk of the pCO2 decrease involve ocean biogeochemistry and its interaction with the ocean's physical circulation*" (Sigman et al, 2010).

Increasing atmospheric CO2 – the interglacial period:

Quantifying the increase in CO2 is not a simple process given some ice cores not suitable for investigating the increase in CO2 because of chemical reactions (Antarctica) and that "*some CO2 records, especially those from Greenland ice cores, are compromised by the* *production of CO2 by chemical reactions between impurities in the ice*" (Monnin et al, 2001, p.112). The fasted warming event in Antarctic began at about 18,000 years ago coincide with the Heinrich Event "*in the North Atlantic....This event is characterized by debris-bearing icebergs, freshening of polar North Atlantic surface waters, an abrupt decrease in North Atlantic subsurface water formation, and circum North-Atlantic cooling*" (Sigman et al, 2010, p53). Although the Heinrich event is thought a consequence of initial Antarctic warming brought on by some orbital forcing and an increase in Carbon export from the ocean, similar to what happen during the Younger Dryas interval (Sigman et al, 2010). Although data shows the warming is Antarctic led, two hypothesis exist; firstly, when a melt beings in the North Hemisphere the fresh-water flow into the Atlantic shutdowns the existing THC in-turn creating a 'density vacuum' causing the overturning of Antarctic deep waters to rush in and consequently release sequestered CO2 (Sigman et al, 2010); Secondly the initial warming in the Antarctic melts sea-ice and subsequently releases sequestered CO2 (Sigman et al, 2010).

Two studies carried out on ice cores both conclude that warming is 'Southern Ocean' led highlighting the dominance of this high latitude region in controlling CO2 variations between glacial and interglacial. Additionally; "*from 15.4 to 13.8 ky B.P. (interval II), CO2 rises from 219 to 231 ppmv at a rather constant rate of 8 ppmv/ky before a rapid increase of 8 ppmv within three centuries at 13.8 ky*" (Monnin et al, 2001, p. 113), corresponds to the fast warming in the Northern Hemisphere which is most likely linked with the formation of North Atlantic Deep Water (NADW), the result of a sudden CO2 increase caused by a changing thermohaline circulation. This changing THC highlights the power role the oceans place in climate change. Similarly, Caillon et al (2003) study agrees and in support of Petit et als (1999) assessment that; "*CO2 may be controlled in large part by the climate of the southern ocean. Although there is not yet clear support for this assertion (through models, for example), a delay of about 800 years seems to be a reasonable time period to transform an initial Antarctic temperature increase into a CO2 atmospheric increase through oceanic processes.*"

Conclusion:

This discussion's objective was to cover some of the main mechanisms that account for atmospheric CO2 sequestration into the ocean. In reality however linear processes and closed systems rarely exist and instead inter-dependant and open systems flourish. This in turn makes it harder for scientists to decipher the workings and feedbacks that take place within the Earths System. Deciphering the causes of CO2 variations in Earth climate history is an ongoing process thus leaving us in the present with only 'known-known's' that do effect CO2 but to what degree is yet unclear. Therefore;

> *"The most viable hypotheses for the cause of glacial/interglacial CO2 change involve the extraction of carbon from the surface ocean by biological production, either at low or high latitudes, necessarily allied with changes in the marine calcium carbonate budget" (Sigman & Boyle, 2000)*

Bibliography:

Broecker, W. S., Henderson, G. M., (1998), The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO2 changes, *Paleoceanography*, 13, pp. 352±364

Caillon,N., Severinghaus, JP. Jouzel, J., Barnola, J.M., Kang, J., Lipenkov, V.Y. (2003), Timing of Atmospheric CO2 and Antarctic Temperature Changes Across Termination III, Science, VOL 299 pp. 1728 – 1731

Goosse H., P.Y. Barriat, W. Lefebvre, M.F. Loutre and V. Zunz, (date of view). Introduction to climate dynamics and climate modeling. [Online], Available at http://www.climate.be/textbook.

Haigh, J.D (2007), The Sun and the Earth Climate, Living Reviews in Solar Physics, Vol. 4, Issue. 2

IPPC, Fourth Assessment Report, (2007), Climate Change 2007: Working Group I: The Physical Science Basis, [online], Available at https://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch6s6-4.html

Jager, C. DE, (2005), Solar Forcing of Climate 1 : Solar Variability, Space Science Reviews, 120, pp. 197 – 241

Kohfeld, K., Ridgwell, A., (2013) Glacial-Interglacial Variability in Atmospheric CO2, [online] Available at file:///C:/Users/sinead/Downloads/Kohfeld-2013-Glacial-Interglacial-Variability.pdf

Köhler, P., and H. Fischer (2006), Proposing a mechanistic understanding of changes in atmospheric CO2 during the last 740 000 years, Climate Past Discussions, 2, 1–42.

MIT, (2009), Oceans and Climate, [Online], Available at http://oceans.mit.edu/

Monnin,E., Indermuhle,A., Da¨llenbach, A., Fluckiger, J., Stauffer, B., Stocker,T.F., Raynaud, D., Barnola, J.M. (2001) Atmospheric CO2 Concentrations over the Last Glacial Termination, Science, 291, 112, pp 112 – 114

NASA, (2011), The Carbon Cycle, [online] available at http://earthobservatory.nasa.gov/Features/CarbonCycle/

Petit, J.R J. Raynaud, J.D, Barkov, B., Barnola, J.M, Basile, I., Bende, M., Chappellaz, J., Delaygue, D.J., Delmotte, M., Kotlyakov,V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pe´pin, L., Ritz, C., Saltzmank, E., Stievenard, M., (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature 399, 429

Rahmstorf, S., (2002), Ocean circulation and climate during the past 120,000 years, Nature 419, 207-214

Ridgwell, A., and R. E. Zeebe (2005), The role of the global carbonate cycle in the regulation and evolution of the Earth system, Earth Planet. Sci. Lett., 234, 299–315

Sarmiento, J.L., Gruber, N., (2006) Ocean Biogeochemical Dynamics - Chapter 9: Calcium Carbonate Cycling by Princeton University Press September 10, 2004 [online] available at http://www.ocquim.qui.ufba.br/Livro%20Sarmiento%20e%20Gruber/Ocean%20Biogeochemistry%20Dynamics/Ch9-CaCO3_text.pdf

Sigman, D. M. & Boyle, E. A. Glacial/interglacial variations in atmospheric carbon dioxide. Nature 407, 859–869 (2000).

Sigman, D. M., Hain, M.P., Haug, G.H., (2010), The polar ocean and glacial cycles in atmospheric CO2 concentration, Nature, Vol 466j1 July 2010

Toggweiler, J. R. (1999), Variation of atmospheric CO2 by ventilation of the ocean's deepest water, Paleoceanography, 14(5), 571–588.