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Potential origins of 400–500 kyr periodicities in the ocean carbon cycle: A box model approach

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[1] Cenozoic proxy records of both the isotopic composition of dissolved inorganic carbon in the oceans (δ13C_{DIC}) and deep ocean carbonate preservation show significant periodicities in the range 400–500 kyr. Sensitivity analysis of the ocean carbon cycle to potential variability on this timescale in patterns of global oceanic primary productivity and/or continental weathering fluxes is performed using a 7 box ocean-atmosphere model. The data constraints imposed by Plio-Pleistocene proxy records of δ13C_{DIC}, carbonate preservation, and atmospheric pCO2 variability allow different scenarios to be evaluated. Forcing with the global oceanic primary production ratio of inorganic and organic carbon leads to the relative phases of response most consistent with the proxy data. However, only when changes also occur in total marine primary production can the observed relative amplitudes of δ13C_{DIC} and pCO2 variability also be reproduced. This scenario is consistent with oscillations between a highly productive, coccolithophore-rich global ocean and a less productive, diatom-rich one. Such oscillations have been proposed to originate from the orbital eccentricity cycle leading to changes in seasonality and thus silica utilization in the Southern Ocean. However, the period of response in model δ13C_{DIC} is always close to that of the forcing function used, and thus a significant discrepancy remains between the orbital eccentricity cycle period of 413 kyr and the observed ∼500 kyr δ13C_{DIC} periodicity seen in the Pleistocene.


1. Introduction

[2] The study of paleoceanographic proxies in Cenozoic sediment core records has revealed the existence within the ocean-climate system of periodic variability longer than the characteristic glacial-interglacial cycles of 10–100 kyr [Bickert et al., 1993; Herbert, 1997; Imbrie et al., 1992, 1993; Keigwin and Boyle, 1985; Raymo et al., 1997, 2006; Wang et al., 2004]. Perhaps the most widely recognized such periodicity occurs in the carbon isotopic composition of foraminiferal calcite (δ13C_{calcite}), a proxy for the isotopic composition of the dissolved inorganic carbon (DIC) in the surrounding seawater (δ13C_{DIC}). Strong periodicities in the range 400–500 kyr are present in Plio-Pleistocene planktic and benthic δ13C_{calcite} records from every major ocean basin [Bickert et al., 1993; Mix et al., 1995b; Tiedemann et al., 1994; Venz and Hodell, 2002; Wang et al., 2004]. Miocene [Woodruff and Savin, 1991] and Oligocene [Palike et al., 2006] δ13C_{calcite} records have been shown to also contain a significant ∼400 kyr periodicity suggesting that some form of 400–500 kyr δ13C_{DIC} cycles persist across at least the past 35 Myr. Such periodicities are not unique to δ13C_{DIC} and records of sedimentary carbonate content, which relates to deep ocean carbonate preservation, from both the Miocene [Moore et al., 1982] and Cretaceous [Herbert et al., 1986] also show ∼400 kyr cycles.

[3] Statistically robust identification of individual periodicities in the 400–500 kyr range within Plio-Pleistocene proxy records is often difficult due to the relatively large cycle and record duration ratio. However, high-resolution δ13C_{calcite} records do yield significant results and the 5 Myr duration ODP Site 1143 benthic δ13C_{calcite} record from the South China Sea is reproduced here [Tian et al., 2002, 2006; Wang et al., 2003, 2004] (Figure 1). The dominant > 100 kyr period in the record evolves from ∼413 kyr in the Pliocene to ∼500 kyr in the Pleistocene with spectral analysis of the whole record showing an averaged peak at 468 ka [Wang et al., 2004] (Figure 1c). In lower resolution or shorter records, observation in the time domain, with all periods < 350 kyr removed, allows identification of potential 400–500 kyr “cycles.” Applying this treatment to an Indian Ocean composite Grain Size Index (GSI) record, another proxy for carbonate preservation, shows a series of ∼500 kyr “cycles” over the past 1.5 Myr [Bassinot et al., 1994] (Figure 2). The record of atmospheric pCO2 over the last 0.8 Myr from a composite of Antarctic ice core records [Lüthi et al., 2008;
Petit et al., 1999] is dominated by \(~100\) kyr glacial and interglacial variability but also shows a single \(> 350\) kyr “cycle” with a maxima at \(\sim 0.4\) Ma (Figure 2). It therefore appears that some component of \(400–500\) kyr variability is present in most aspects of the global carbon cycle over the late Mesozoic and Cenozoic. Prior to the Pleistocene, the dominant period seen in most records is consistently \(400–413\) kyr, but both the \(\delta^{13}C_{\text{DIC}}\) and carbonate preservation cycles appear to “stretch” toward \(\sim 500\) kyr over the past 2 Ma.

[4] Within the Pleistocene, major shifts in the mode of glacial-interglacial behavior have been proposed to be preceded by, or associated with, maxima in the \(\sim 500\) kyr \(\delta^{13}C_{\text{DIC}}\) cycle [Wang et al., 2003, 2004]. The last major such shift occurred with the emergence of the dominant \(~100\) kyr glacial cycles during the Middle Pleistocene Transition (0.5–1.2 Ma) [Head and Gibbard, 2005] (Figure 2). Modeling studies suggest this transition may also constitute a fundamental change in the relationship between climatic and carbon cycle variables [Kohler and Bintanja, 2008]. The transition coincides with a significant negative excursion in mean ocean \(\delta^{13}C_{\text{DIC}}\) that may constitute a \(\sim 500\) kyr cycle minima [Wang et al., 2004] or a one-off perturbation related uniquely to the climatic transition itself [Hoogakker et al., 2006; Raymo et al., 1997].

[5] The \(400–500\) kyr periodicities seen in carbon cycle proxies are not so clearly manifested in records of past climatic variability [Herbert, 1997; Rial, 2004]. The Oligocene ODP Site 846 \(\delta^{18}O_{benthic}\) record, a proxy for global ice volume and deep water temperature, does show significant variance at \(\sim 405\) kyr [Palike et al., 2006]. However, the persistence of the \(400–500\) kyr carbon cycle peri-
[61x111]odicities into the ice-free world of the Cretaceous [Herbert et al., 1986; Herbert, 1997] suggests that the processes driving the cycles are not directly related to fluctuations in ice volume. No significant periodicity in the 400–500 kyr range is present in the ODP 1143 δ¹⁸O_benthic record over the past 5 Myr [Wang et al., 2004] (Figure 1b).

[6] Understanding the origin of the observed 400–500 kyr carbon cycle periodicities is an important first step toward elucidating the apparently complex and evolving relation-

Figure 2. (a) GSI composite [Bassinot et al., 1994], composite Antarctica pCO₂ record [EPICA Community Members, 2004], ODP Site 1143 δ¹⁸O_benthic and δ¹³C_benthic [Wang et al., 2004], and orbital eccentricity [Berger and Loutre, 1991] over the past 1.5 Myr. (b) Gaussian filtering around 0 kyr⁻¹ using a 0.0029 kyr⁻¹ bandwidth filter (removing all periods < 350 kyr) of the ODP Site 1143 δ¹³C_benthic, Antarctica composite pCO₂, GSI composite, and eccentricity data over the past 1.5 Myr.
ship between the carbon cycle and climate on these timescales. The orbital eccentricity cycle modulation of the precession cycle has a period of 413 kyr [Berger and Loutre, 1991] and is the most obvious external origin for the observed variability. Previous modeling studies have demonstrated that the carbon cycle tends to amplify long period components of the orbital forcing [Palike et al., 2006], potentially explaining the relatively large response to a relatively weak 413 kyr orbital forcing. The orbital variations could potentially influence the carbon cycle through either changes in midlatitude and high-latitude seasonality and hence primary production regimes or through the global hydrological cycle leading to variability in the weathering fluxes of productivity-limiting nutrients, DIC and Alkalinity (ALK) into the global ocean. The present study does not investigate the direct influence of insolation variations but evaluates, using a simple ocean-atmosphere box model, whether these potential response mechanisms within the carbon cycle could produce the variability observed in the proxy records.

[7] The 400–500 kyr timescale of interest here falls between the geological (>1 Myr) and glacial-interglacial (10–100 kyr) timescales and is close to the residence time of DIC in the oceans [Berner and Berner, 1987]. On the geological timescale the global mean surface temperature is primarily controlled by the level of atmospheric pCO2, determined in turn by the balance between volcanic and metamorphic degassing of carbon into the atmosphere and its removal through the weathering of silicate rocks [Berner et al., 1983; Li et al., 2009; Raymo and Ruddiman, 1992]. This weathered inorganic carbon reaches the ocean and ultimately forms new carbonate sediments. These processes are sufficiently slow however that on glacial-interglacial timescales the coupled ocean-atmosphere system behaves almost as a “closed” system with respect to DIC and ALK [Archer et al., 2000]. Glacial-interglacial variability in atmospheric pCO2 is thought to be caused by either the transfer of DIC to/from different parts of the closed system or through changes in the organic carbon (Corg) cycle [Archer and Maier-Reimer, 1994; Archer et al., 2000; Imbrie et al., 1993; Sigman and Boyle, 2000]. The Corg cycle may not be considered closed on even the glacial-interglacial timescale as the size of the terrestrial biosphere is dynamic, leading to changes in both mean ocean δ13C_DIC and pCO2 [Crowley, 1995; Shackleton, 1977]. It is thus possible that both open and closed system variability in both the inorganic and organic carbon cycles may play a role in the observed 400–500 kyr cycles and the model presented here includes first-order treatments of these processes.

[8] Numerical reconstructions on the Cenozoic timescale of global riverine fluxes of weathered inorganic carbon, ALK and productivity limiting nutrients are at present limited. Therefore, the approach taken here is to evaluate a wide range of forcing function amplitudes as a first attempt to constrain likely system sensitivity to each forcing. The effect on model output of the parameters used to define the box model itself is also considered. Finally, to evaluate the various scenarios, model output for deep ocean δ13C_DIC (hereafter “δ13C_DIC”) mean ocean carbonate ion concentration ([CO3^2-]_mean, a proxy for carbonate preservation), and atmospheric pCO2 is compared to available proxy data over the past 5 Myr. This period is selected, rather than a longer interval further back in time, due to the availability of multiple proxy constraints in the same interval allowing the evaluation of the relative phases of the variables as well as their periods and amplitudes. Three constraints are evaluated from this data comparison: (1) the amplitudes of periodic variability in δ13C_DIC and pCO2 (carbonate preservation output cannot be quantitatively compared to the proxy data); (2) the observed period of variability in δ13C_DIC, pCO2 and carbonate preservation; and (3) the relative phases of the response in δ13C_DIC, pCO2 and carbonate preservation.

2. Model Description

[9] Ocean-atmosphere box models simplify the complex 3-D dynamics of the global ocean and atmosphere into a series of finite “boxes” between which certain quantities, such as heat, or DIC, are advected. Such models possess the significant advantage of being able to simulate millions of years in a matter of minutes using a standard desktop computer. Many studies exist using box models to investigate first-order processes in the oceanic carbon cycle on glacial-interglacial [Michel et al., 1995; Toggweiler, 1999, 2008] and longer timescales [Hoogakker et al., 2006; Palike et al., 2006]. The present study adapts the C++ box modeling tool BoxKIT [Paillard, 1995] to the study of the 400–500 kyr cycles through the incorporation of key open system processes in both the inorganic and organic carbon cycles. The closed system model used to represent the ocean-atmosphere system is based closely on that of an existing 7 box ocean model [Toggweiler, 1999] (Figure 3).

[10] Closed system box models on the glacial-interglacial timescale are able to reproduce to the first order several key features of climate on this timescale [Toggweiler, 1999]. However, the open system carbon cycle processes relevant to the longer timescales of interest here are relatively poorly understood in comparison to the closed system ones and only first-order parameterizations are appropriate. In the case of the DIC and ALK cycles, the present study closely follows the approach of Toggweiler [2008]. However, in order to develop a plausible treatment of δ13C_DIC it is essential to also include some treatment of the organic carbon cycle on the same timescale. This is achieved by parameterizing the sedimentation of Corg as a function of primary productivity in the surface boxes such that model δ13C_DIC remains within the bounds implied by δ13C_benthic records over the past 5 Myr.

[11] The governing equations for each ocean box of the model may be summarized as

\[ V_i \frac{dX_i}{dt} = \sum_j A_{ij} + \sum_j P_{ij} + F \]  

(1)

Where \( V \) is the volume of box \( i \), \( X \) is a model variable, \( A \) are the advected terms and \( P \) are the remineralization terms (Figure 3). The advection and remineralization regimes are defined as by Toggweiler [2008]. \( F \) are the various open system fluxes, as defined in sections 2.1 and 2.2. Not all combinations of boxes and variables require all terms to be

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included. For example, in the case of the concentration of DIC in the low-latitude surface box the governing equation reduces to

\[
V_L \frac{d[DIC]_L}{dt} = M_L([DIC]_L - [DIC]_L) + FWEATH^{DIC}
\]  

The calculation of the \(d^{13}C_{DIC}\) terms and the atmospheric parameters, such as \(p_{CO_2}\), is somewhat more complex and is explained in Appendix A.

2.1. Open System Processes: Inorganic Carbon and Alkalinity

2.1.1. Volcanic-Metamorphic Input of Carbon

[12] The principle external source of inorganic carbon to the ocean-atmosphere system on the timescales of interest is from the volcanic and metamorphic outgassing of CO\(_2\). Parameterization of this flux is achieved through the addition of a fixed input of 160,000 mol C s\(^{-1}\) of DIC [Marty and Tolstikhin, 1998] directly to the surface ocean box. While this flux should strictly speaking enter the atmosphere, the mixing time between the atmosphere and surface ocean is sufficiently short compared to the other model processes that it can be neglected.

2.1.2. Continental Weathering of DIC and ALK

[13] On geological timescales the rate of weathering of continental silicate rocks (equation (3)) is thought to be a function of mean surface temperature and therefore the baseline level of atmospheric \(p_{CO_2}\) [Berner et al., 1983; Walker et al., 1981]. The riverine fluxes of weathered DIC and ALK (equations (4) and (5)) arising from silicate weathering are therefore parameterized as a linear function of \(p_{CO_2}\) [Walker et al., 1981].

\[
CaSiO_3 + 2CO_2 + 2H_2O \rightarrow 2HCO_3^- + 2H^+ + Ca^{2+} + SiO_2^{2-}
\]  

(3)

\[
FSIL^{DIC} = k_{sil} + \left(1/\tau_{sil}\right)p_{CO_2}
\]  

(4)

\[
FSIL^{ALK} = 2(k_{sil} + \left(1/\tau_{sil}\right)p_{CO_2})
\]  

(5)

For each mole of DIC added to the global ocean through silicate weathering, one mole of inorganic carbon is correspondingly removed from the atmospheric box (equation (3)). Thus, silicate weathering leads to the net transfer of ALK but not DIC into the ocean-atmosphere system. This leads to an increase in oceanic carbonate sedimentation which acts to remove both ALK and DIC from the system [Berner et al., 1983]. At equilibrium, the net loss of DIC from this process balances the volcanic-metamorphic degassing flux.

[14] The values of the constants \(k_{sil}\) and \(\tau_{sil}\) are taken as 62,300 mol C s\(^{-1}\) and 0.012 s ppmV mol C\(^{-1}\), respectively, after Toggweiler [2008]. This equates to a 1/e folding time for the weathering feedback of 500 kyr and on timescales exceeding this, the atmospheric \(p_{CO_2}\) returns to a fixed value.

---

**Figure 3.** Schematic diagram of the 7 box ocean-atmosphere model and the additional open system fluxes (bold type) used in the present study. The 7 box model is based closely on that of Toggweiler [2008]. The dashed gray box represents the “closed” ocean-atmosphere system.
equilibrium value. Antarctic \( p_{\text{CO}_2} \) records show a decrease in mean value of up to 22 ppmV over the past 0.61 Myr, suggesting that while the system is indeed closely buffered by \( p_{\text{CO}_2} \), small imbalances in the open system fluxes do exist on this timescale [Zeebe and Caldeira, 2008]. Such a secular decrease in mean \( p_{\text{CO}_2} \) may be represented in the model using a linear variation in the \( k_{\text{sed}} \) term.

[15] The weathering of continental carbonate rocks (equation (6)) also depends on global surface temperature and is parameterized similarly to the silicate process (equations (7) and (8)) but without the fixed component terms [Toggweiler, 2008].

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} \quad (6)
\]

\[
\text{FCARB}_{\text{DIC}} = (1/\tau_{\text{carb}})p_{\text{CO}_2} \quad (7)
\]

\[
\text{FCARB}_{\text{ALK}} = (2/\tau_{\text{carb}})p_{\text{CO}_2} \quad (8)
\]

In contrast to silicate weathering, carbonate weathering leads to the net transfer of ALK and DIC to the ocean-atmosphere system in the same ratio (2:1) as it will be eventually removed during carbonate sedimentation. As such, on timescales exceeding that of the carbonate compensation feedback, carbonate weathering has no effect on the feedback between \( p_{\text{CO}_2} \) and weathering.

[16] The fluxes of weathered DIC and ALK arising from equations (4) and (7) (for DIC) and (5) and (8) (for ALK) are added directly to the low-latitude surface ocean box. The value of the constant \( \tau_{\text{carb}} \) is taken as 0.0030 s ppmV mol \( C^-1 \) after Toggweiler [2008].

### 2.2. Organic Carbon Cycle Processes

[18] The silicate weathering and carbonate compensation feedbacks alone ensure that the DIC and ALK systems will always return to an equilibrium state. At this equilibrium, \( \left[ \text{CO}_3^{2-} \right]_{\text{deep}} \) will exceed \( \left[ \text{CO}_3^{2-} \right]_{\text{target}} \) by an amount sufficient for the net output of DIC to balance the long-term input from the volcanic-metamorphic degassing flux [Toggweiler, 2008]. This is not, however, the case for the \( 13C_{\text{DIC}} \) system as the \( 13C_{\text{DIC}} \) composition of the volcanic input flux is taken as being fixed at −5.0‰ [Kump and Arthur, 1999] and the \( 13C_{\text{DIC}} \) associated with the DIC in the silicate and carbonate weathering input fluxes is taken as 0.0‰ [Kump and Arthur, 1999]. The majority of the carbonate sedimentation flux is made up of surface dwelling foraminifera and coccolithophores. The \( 13C_{\text{DIC}} \) of the \( \text{CaCO}_3 \) sedimentation flux is thus set to be the \( 13C_{\text{DIC}} \) value of the low-latitude surface ocean box. This assumes that the bulk calcite sedimentation output flux is in isotopic equilibrium with DIC in the low-latitude surface box which typically has values in the range 1.0–2.0‰. Therefore, unless there is an additional output flux of more isotopically depleted material mean ocean \( 13C_{\text{DIC}} \) will drift toward more negative values.

[19] Records of deep Pacific Ocean benthic \( 13C_{\text{calcite}} \) over the past 5 Myr show that average values on the Myr timescale remain in the range −0.1 to +0.1‰ [Mix et al., 1995a; Wang et al., 2004] demonstrating that any such drift is very small in amplitude. This effective buffering of \( 13C_{\text{DIC}} \) must arise from the marine production and sedimentation of \( \text{C}_{\text{org}} \), with an isotopic composition taken in the model as −23.0‰. The primary source of oceanic \( \text{C}_{\text{org}} \) is direct fixation of DIC though primary productivity, with a much smaller component arising through riverine input of weathered terrestrial organic material [Hedges et al., 1997]. The vast majority of the \( \text{C}_{\text{org}} \) present in the surface ocean is then remineralized within the subsurface ocean leaving only a small sedimentation flux of ~0.15 GtC yr\(^{-1}\) in the modern case [Hedges et al., 1997]. The dominance of the primary productivity source for marine \( \text{C}_{\text{org}} \) suggests that the first-order parameterization of the \( \text{C}_{\text{org}} \) sedimentation flux is as a function of primary productivity. A simple linear function is used in the first instance:

\[
F_{\text{org}} = k_{\text{org}}P_{\text{surface}} \quad (11)
\]

The residence time of \( \text{C}_{\text{org}} \) (400 – 600yr) [Raymond and Bauer, 2001] is substantially shorter than that of DIC or the period of the 400–500 kyr cycles. Thus, the organic sedimentation flux is assumed to have a negligible effect on
surface ocean DIC concentrations. The effect of temporally variable in the isotopic fraction between inorganic and organic carbon [Rau et al., 1991] is also assumed to be negligible on this timescale. The value of $k_{org}$ is selected as 0.009 such that, for all forcing parameters used, the equilibrium value of $\delta^{13}C_{DIC}$ lies in the range consistent with the observed mean over the past 5 Myr in benthic $\delta^{13}C_{calcite}$.

3. Model Runs

3.1. Scenarios PRP, TP, WEATH, and PRP/TP

[20] The global balance in marine primary production between siliceous (principally diatom) and calcareous (principally coccolithophore) phytoplankton could change according to either seasonality (as the two groups tend to live at different latitudes) [Rickaby et al., 2007] or the relative supply of silica and ALK to the global ocean [Wang et al., 2004]. In either case, changes will occur in the global ratio of CaCO$_3$/C$_{org}$ of the material entering the biological pump. Due to the different $\delta^{13}C$ values of carbon in biogenic calcite and organic matter, this could plausibly lead to fluctuations in mean ocean $\delta^{13}C_{DIC}$ [Hoogakker et al., 2006; Wang et al., 2004]. The “Production Ratio Parameter hypothesis” (PRP) states that variations in the global CaCO$_3$/C$_{org}$ value for material entering the biological pump accounts for the observed 400–500 kyr periodicities. BoxKIT treats phosphate as the sole limiting nutrient for primary productivity using a Michaelis-Menten function. Therefore, the PRP scenario is investigated through direct forcing of the CaCO$_3$/C$_{org}$ value associated with primary productivity in all surface boxes. The Holocene global average CaCO$_3$/C$_{org}$ value is taken as 0.27 and forcing amplitudes in the range 0.00–0.35 are explored.

[21] Changes in the supply to the ocean of productivity-limiting nutrients, such as phosphate, may lead to changes in total primary productivity without necessarily changing the value of CaCO$_3$/C$_{org}$. The strength of the biological pump is related to the ultimate burial flux of both C$_{org}$ and CaCO$_3$ so variations in total productivity may also affect the mean ocean $\delta^{13}C_{DIC}$ [Keir, 1992; Sigman and Boyle, 2000]. The “Total Productivity” hypothesis (TP) states that variations in total marine primary productivity account for the observed 400–500 kyr periodicities. TP is investigated through forcing of the mean ocean phosphate concentration, [P]. The Holocene value for [P] is taken as 2.35 $\mu$mol L$^{-1}$ and forcing amplitudes in the range 0.00–0.65 $\mu$mol L$^{-1}$ are explored. Scenarios PRP and TP are not mutually exclusive and a series of runs involving the superposition of the two forcing mechanisms both in-phase (such that high CaCO$_3$/C$_{org}$ values are coincident with high total productivity) and in antiphase (such that low CaCO$_3$/C$_{org}$ values are coincident with high total productivity) with one another was also performed.

[22] Changes in the fluxes of weathered inorganic carbon and ALK have the potential to affect mean ocean $\delta^{13}C_{DIC}$ without directly affecting primary productivity because such changes can change the oceanic DIC/ALK ratio and the sedimentation flux of CaCO$_3$ [Clark et al., 2006; Hoogakker et al., 2006; Raymo et al., 1997]. The “Weathering Hypothesis” (WEATH) states that variations in the flux of weathered inorganic carbon and ALK can account for the observed 400–500 kyr periodicities. WEATH is investigated by forcing variability in the silicate weathering constant $k_{sil}$. The modern value of $k_{sil}$ is taken as 62,300 mol C s$^{-1}$ [Toggweiler, 2008] and forcing amplitudes in the range 0–26,000 mol C s$^{-2}$ are investigated.

[23] None of the above scenarios is dependent on the presence of glacial-interglacial cycles in climate or global ice volume. They thus all provide mechanisms consistent with the apparent persistence of the 400–500 kyr cycles across the late Mesozoic and Cenozoic greenhouse to icehouse transition. Model runs were also performed using an additional linear trend in $k_{sil}$ to simulate the effect of a long-term Cenozoic decrease in $pCO_2$. A trend of 0.01 mol s$^{-1}$ yr$^{-1}$ in $k_{sil}$ leads to a decrease of ~15 ppmV Myr$^{-1}$ in $pCO_2$. No significant difference in the amplitude or phase of the periodic response in $\delta^{13}C_{DIC}$, $pCO_2$ and $[CO_3^{2-}]_{mean}$ occurs provided that mean $pCO_2$ does not differ from the equilibrium value by more than ~50 ppmV in which case the model equilibrium $\delta^{13}C_{DIC}$ moves outside of the ~0.1 to 0.1‰ range defined by benthic $\delta^{13}C_{calcite}$ data for the past 5 Myr. This suggests that the model output of interest here is insensitive to drift in the mean $pCO_2$ level on the Pleistocene timescale [Zeebe and Caldeira, 2008] but that this effect may become significant on the Cenozoic timescale.

3.2. Evaluating Model Sensitivity to Forcing Function Periods and Amplitudes

[24] In each simulation the model is initially spun up from the Holocene initial conditions of Toggweiler [2008] for 1.5 Myr, by which time equilibrium in $\delta^{13}C_{DIC}$, $pCO_2$ and $[CO_3^{2-}]_{mean}$ is attained. After this spin-up phase, forcing functions are activated, such that there is no discontinuity in the forced parameters. The forcing functions consist of one or more of the open system process parameters, as described above, being varied with a sinusoidal forcing function across a period of 3 Myr.

[25] Selection of both the period and amplitude to use for the forcing functions is not trivial. The dominant periodicity in the 400–500 kyr range observed in $\delta^{13}C_{calcite}$ records evolves within single downcore records across the past 5 Myr [Wang et al., 2004]. Furthermore, different proxies and different core locations yield differing dominant periodicities within the 400–500 kyr range. The variation between cores is potentially related to age model uncertainties as $\delta^{13}C_{calcite}$ is not generally used as a tuning target in the creation of sediment core age models. However, the variation within single records, particularly the lengthening of dominant period toward ~500 kyr in the Pleistocene, which is seen in multiple proxies, is likely to be a real feature of the system.

[26] To explore model sensitivity to the period of the forcing, a set of initial experiments was performed using different forcing periodicities across the range 100–750 kyr. The results of these sensitivity tests are presented in full in Appendix B. A simple one to one relationship between the period of response and the forcing period used is observed but the choice of forcing period also affects the amplitude of periodic response in the parameters of interest. This effect is, however, relatively small for forcing periods in...
For simplicity, a single forcing period of 500 kyr is used in all subsequent model runs. Robust proxy records at an appropriate resolution over the past 5 Myr of the global ocean production ratio of CaCO_3/Corg, total primary productivity or riverine fluxes of weathered inorganic carbon and ALK do not at present exist. Therefore, experiments using a wide range of forcing function amplitudes for these variables were undertaken. Determining the mean values to use for each forcing variable presents a further difficulty. The Holocene appears to represent a maximum or near maximum in the Pleistocene ~500 kyr \( \delta^{13}C_{\text{DIC}} \) cycle (Figures 1a and 2b). However, Holocene conditions do not necessarily correspond to a maximum in each of the potential forcing parameters. It is therefore necessary to experiment with a range of mean values for each forcing. In the case of a higher (lower) than Holocene long-term mean value, the amplitude of variability is defined such that the modern value represents a minima (maxima) in the forcing cycle. The results of these sensitivity tests are presented in full in Appendix B. The approach taken is to use the better constrained Holocene values as the long-term mean in each case but to limit the range of forcing amplitudes used such that the uncertainty arising from this choice of mean forcing value on the amplitude of response in \( \delta^{13}C_{\text{DIC}} \) and \( pCO_2 \) is < 0.05‰ and < 5 ppmV, respectively.

4. Results

In each model run, the values of \( \delta^{13}C_{\text{DIC}} \), \( pCO_2 \) and \([CO_3^{2-}]_{\text{mean}}\) initially approach their respective equilibrium values during the spin-up phase (Figure 4). For the Holocene initial conditions used here, the long-term equilibrium values of \( \delta^{13}C_{\text{DIC}} \) and \( pCO_2 \) are 0.06‰ and 236 ppmV, respectively. \([CO_3^{2-}]_{\text{mean}}\) is used as a qualitative proxy for ocean average carbonate preservation, such that when \([CO_3^{2-}]_{\text{mean}}\) is at a maximum, carbonate preservation (dissolution) is at a maximum (minimum). After the spin-up phase and the activation of the forcing functions, sinusoidal behavior is exhibited by \( \delta^{13}C_{\text{DIC}} \), \( pCO_2 \) and \([CO_3^{2-}]_{\text{mean}}\). The model output is saved every 10 kyr throughout each 3Myr run and used to determine the periods and relative phases of the \( \delta^{13}C_{\text{DIC}} \), \( pCO_2 \) and \([CO_3^{2-}]_{\text{mean}}\) response and the amplitudes of the \( \delta^{13}C_{\text{DIC}} \) and \( pCO_2 \) response, as shown in Figure 4. The relative phase of the responses is

![Figure 4](image-url)
4.1. Amplitudes of Response for the PRP, TP, and WEATH Scenarios

[29] The uncertainties in the results are directly linked to both the uncertainties in the numerical values used within the parameterization of each scenario (Appendix B) and the assumptions in the model itself. Accurate modeling of past values for $^{13}\text{C}_{\text{DIC}}$, $p\text{CO}_2$ and $[\text{CO}_3^2]_{\text{mean}}$ is not realistic given these limitations. However, first-order results regarding the sensitivity and phase of response to the various forcing mechanisms are significant against the parameterization uncertainties.

4.2. Periods of Response for the PRP, TP, and WEATH Scenarios

[32] The spectral properties of the $^{13}\text{C}_{\text{DIC}}$ and $p\text{CO}_2$ output arising from model runs using forcing periods of 500 kyr were analyzed using the Analyseries software [Paillard et al., 1996]. For forcing with PRP, TP, WEATH or antiphase PRP/TP the resultant output in both variables showed a single dominant periodicity at $500 \pm 10$ kyr (the resolution of the spectral analysis method used) in every simulation. In the case of the in-phase PRP/TP runs the dominant period of the resultant cycles in $^{13}\text{C}_{\text{DIC}}$ in every simulation remained $500 \pm 10$ kyr. However, for the $p\text{CO}_2$ response a second significant spectral peak, arising through frequency doubling is seen for $R_{\text{amp}}$ values exceeding $0.025\%$ ppmV$^{-1}$. In the run with a $\text{CaCO}_3/\text{C}_{\text{org}}$ forcing amplitude of 0.1 and a $[\text{P}]$ forcing amplitude of 0.4 $\mu\text{mol L}^{-1}$, corresponding to near maximal $R_{\text{amp}}$, the 250 kyr period shows more spectral power than the 500 kyr one.

4.3. Relative Phases of Response for the PRP, TP, and WEATH Scenarios

[33] The phase relations of the model $^{13}\text{C}_{\text{DIC}}, [\text{CO}_3^2]_{\text{mean}}$ and $p\text{CO}_2$ responses differ significantly for the different forcing scenarios (Figure 7). For PRP, the forcing leads both $p\text{CO}_2$ and carbonate dissolution by $355 \pm 5^\circ$ and $^{13}\text{C}_{\text{DIC}}$ by $260 \pm 5^\circ$. In this scenario, high CaCO$_3$/C$_{\text{org}}$ occurs near synchronously with high $p\text{CO}_2$, consistent with the relative effects of carbon drawdown during photosynthesis and degassing during calcification. High CaCO$_3$/C$_{\text{org}}$ leads to the removal of ALK from the surface to the deep ocean leaving the parts of the ocean in which carbonate sedimentation does not occur relatively depleted in ALK. Thus, average ocean carbonate preservation is minimal at times of maximal CaCO$_3$/C$_{\text{org}}$. The lead of CaCO$_3$/C$_{\text{org}}$ over $^{13}\text{C}_{\text{DIC}}$ arises as whenever CaCO$_3$/C$_{\text{org}}$ exceeds the equilibrium value, higher deep ocean ALK leads to more CaCO$_3$ sedimentation (in relation to that of C$_{\text{org}}$) and a reduction of $^{13}\text{C}_{\text{DIC}}$.

[34] For TP, the forcing leads $p\text{CO}_2$ by $160 \pm 5^\circ$, carbonate dissolution by $240 \pm 5^\circ$ and $^{13}\text{C}_{\text{DIC}}$ by $70 \pm 5^\circ$. High total primary productivity leads to drawdown of CO$_2$ into the biological pump (reducing atmospheric $p\text{CO}_2$), increased dissolution in the subsurface ocean and enhanced C$_{\text{org}}$ sedimentation (in relation to CaCO$_3$) leading to enhanced mean ocean $^{13}\text{C}_{\text{DIC}}$. 
For WEATH, the forcing leads $p$CO$_2$ by 220 ± 5°, dissolution by 310 ± 5° and $\delta^{13}$C$_{DIC}$ by 240 ± 5°. The WEATH phase lags arise through the long time constant of the silicate weathering feedback. When $p$CO$_2$ exceeds the long-term equilibrium value, silicate weathering acts to lower it again adding ALK to the global ocean and thus increasing both carbonate preservation and CaCO$_3$ sedimentation (relative to that of $C_{org}$) which, in turn, increases $\delta^{13}$C$_{DIC}$. Because the carbonate sedimentation feedback is relatively fast compared to the silicate weathering one, the $\delta^{13}$C$_{DIC}$ response is close to being in-phase with $p$CO$_2$. The 90° phase lag of dissolution behind $p$CO$_2$ arises whenever, $p$CO$_2$ is greater than (lower than) the long-term equilibrium value, $[CO_3^{2-}]_{mean}$ increases (decreases).

In the PRP/TP scenarios, the relative phase of the $\delta^{13}$C$_{DIC}$, $p$CO$_2$ and carbonate dissolution responses depends on the relative amplitudes of the two forcing parameters. In the case of in-phase PRP/TP forcing it is seen that the lead of the $\delta^{13}$C$_{DIC}$ response over $p$CO$_2$ is in the range 90–150° for the entirety of the phase space, excepting those runs in which frequency doubling was observed in $p$CO$_2$, in which case calculation of an instantaneous lead/lag is impossible. The magnitude of the phase lag approaches ~90° as either forcing amplitude approaches zero and increases with the amplitudes of both forcing functions. The carbonate dissolution response remains close to in-phase with the $p$CO$_2$ response, as in the PRP scenario. In the case of antiphase forcing with PRP/TP, the phase lag between $\delta^{13}$C$_{DIC}$ and $p$CO$_2$ is always 90±10° regardless of the forcing amplitudes used and carbonate dissolution again remains close to in-phase with the $p$CO$_2$ response.

5. Discussion

5.1. Proxy Constraint on the Amplitude of Response in $\delta^{13}$C$_{DIC}$ and $p$CO$_2$

The three proxy records used for comparison with the model output are the ODP Site 1143 benthic $\delta^{13}$C$_{calcite}$
The ODP 1143 $\delta^{13}C_{\text{calcite}}$ record shows considerable temporal variability in amplitude between individual 400–500 kyr cycles. However, Gaussian filtering using a 350 kyr bandwidth filter demonstrates that the amplitude of variability in the $>350$ kyr range always lies within the range 0.05–0.15‰ over the past 5 Myr (Figure 1a). The same filter applied to the Antarctic $pCO_2$ record demonstrates that the amplitude of variability in the $>350$ kyr range over the past 0.8 Myr is $<10$ ppmV (Figure 2b). The relatively short duration of the $pCO_2$ record limits the potential for comparison of the two records. However, the apparent absence of significant 400–500 kyr periodicity from proxy records of Pliopleistocene equatorial Pacific sea surface temperature [Dekens et al., 2008; Lawrence et al., 2006] suggests there is no clear reason to suppose the amplitude of $pCO_2$ variability at these periods to be greater prior to 0.8 Ma. Interestingly, certain extratropical sea surface temperature records do show evidence for variability on these timescales but this is believed to be related to subtropical front movement and decoupled from $pCO_2$ variability [Bard and Rickaby, 2009]. If the 10 ppmV value from the Antarctica record is taken as a best guess upper bound to the Pliopleistocene $pCO_2$ cycle amplitude and using the range of $\delta^{13}C_{\text{DIC}}$ cycle amplitudes from the ODP 1143 $\delta^{13}C_{\text{calcite}}$ record, the range of minimum acceptable values for model $R_{\text{amp}}$ is $0.005–0.015$‰ ppmV$^{-1}$.

All of the scenarios experimented with here are capable of generating periodic response of 0.05–0.15‰ amplitude in $\delta^{13}C_{\text{DIC}}$. However, it is a pronounced feature of the model output that most scenarios also predict relatively large amplitude cycles at the same period in
pCO₂ ~ they have relatively low R_{amp} values (Figure 5). Both the PRP (R_{amp} = 0.003\% ppmV⁻¹) and WEATH (R_{amp} = 0.005\% ppmV⁻¹) scenarios produce unacceptably large amplitude pCO₂ variability across the entire observed range of δ¹³C_{DIC} cycle amplitudes. The TP scenario (R_{amp} = 0.011\% ppmV⁻¹) provides the closest match to the observed relative amplitudes but even this cannot reproduce the upper end δ¹³C_{DIC} cycle amplitudes without also generating pCO₂ response > 10 ppmV.

[40] Much of both the in-phase and antiphase PRP/TP phase spaces have R_{amp} values > 0.005\% ppmV⁻¹ (Figure 6). However, in the antiphase case values are always lower than for TP alone (R_{amp} = 0.011\% ppmV⁻¹) and only a small subset of the region with R_{amp} > 0.005\% ppmV⁻¹ is consistent with a pCO₂ response of < 10 ppmV. For the in-phase case these two regions are broadly coincident and of all the scenarios evaluated here, only in-phase PRP/TP is able to produce the entire observed range of δ¹³C_{DIC} amplitudes without also generating pCO₂ response > 10 ppmV.

5.2. Proxy Constraint on the Phase of the Response

[41] Comparison in the time domain of the > 350 kyr period component of the ODP 1143 δ¹³C_{calcite}, Antarctic composite pCO₂ and Indian Ocean GSI records over the past 1.5 Myr demonstrates irregular “pseudocycles” with a period of 500 ± 100 kyr in all records (Figure 2b). The pCO₂ record and dissolution index are close to being in phase over the past 0.8 Myr, suggesting that the longer GSI record may be used as a first-order guide to the relative phase of δ¹³C_{DIC} and pCO₂ over the past 1.5 Myr. Over this period, the δ¹³C_{DIC} cycles lead carbonate dissolution (and by inference pCO₂) by 90–150° (Figure 7). The uncertainties involved in correlating the various age models for the proxy data sets is of the order of 5–10 kyr and would not change the first-order relationships between the variables.

[42] Of the single forcing function scenarios, PRP provides a lead of δ¹³C_{DIC} over pCO₂ and carbonate dissolution of ∼90°, consistent with the proxy data (Figure 7). TP provides the same lead of δ¹³C_{DIC} over pCO₂ but carbonate dissolution is in near antiphase with pCO₂. WEATH provides δ¹³C_{DIC} response close to in-phase with pCO₂ and both leading dissolution by ∼90°. In the PRP/TP scenario (both in-phase and in antiphase) the relative phase criteria are always met. Therefore, the forcing scenarios most consistent with the phase constraints are the PRP and PRP/TP scenarios.

[43] The phases of the δ¹³C_{DIC}, pCO₂ and carbonate preservation responses in relation to the forcing functions used are also very different for the three scenarios. This is not however used as a discriminating test due to the difficulty of directly relating the phase of the forcing parameters used in the model to a proxy or orbital variable.

5.3. Proxy Constraint on the Period of the Response

[44] The model does not generate significant phase modulation and to generate a 500 kyr periodicity requires a 500 kyr forcing function. The frequency-doubling behavior seen for pCO₂ at high R_{amp} values in the PRP/TP scenario is the only exception to this. As such behavior is associated exclusively with very low amplitudes of model pCO₂ response it is unlikely that even the availability of longer proxy records will allow its evaluation. As such, this aspect of model output is not considered useful for the discrimination of different hypotheses.

[45] A significant discrepancy therefore exists between the observed Pleistocene ~500 kyr periodicity and the proposed origin of the forcing in the orbital eccentricity cycle at 413 kyr. The middle-late Pleistocene is uniquely characterized by the ~100 kyr mode of glacial-interglacial climate variability and it is possible that this relatively high amplitude periodicity interferes with the last two δ¹³C_{DIC} and carbonate preservation cycles such that the apparent periodicity is greater than a “true” underlying period at 413 kyr. Within such an interpretation, the proposed global negative δ¹³C_{DIC} shift during the Middle Pleistocene Transition [Raymo et al., 1997] may act to enhance the “natural” δ¹³C_{DIC} cycle minima (Figure 2).

5.4. Evaluating the Different Scenarios

[46] Of the proxy data constraints presented here only the amplitude of the δ¹³C_{DIC} cycles, as inferred from δ¹³C_{benthic}, is comparable to model output across more than 1.5 Myr. Taking this constraint alone, any of the investigated forcing mechanisms is capable of generating the appropriate amplitude of δ¹³C_{DIC} response. However, if it is assumed that the amplitude of observed > 350 kyr band variability seen in pCO₂ and the in-phase relationship seen between carbonate dissolution and pCO₂ over the past 0.8 Myr are representative of longer-term variability, then the scenarios may be discriminated between at quite a fine level.

[47] The two most useful constraints used for evaluating the different scenarios are “the relative amplitude constraint”: δ¹³C_{DIC} cycles of amplitude 0.05–0.15 % should be generated without the amplitude of pCO₂ variability exceeding 10 ppmV and “the relative phase constraint”: the δ¹³C_{DIC} cycles should lead the pCO₂ cycles by 90–150° and the carbonate dissolution cycles should be close to in-phase with pCO₂.

[48] The WEATH scenario fails both the phase and amplitude constraints and is therefore rejected. Furthermore, the sensitivity of the model output to changes in the system parameters is substantially greater when forced with WEATH than with the biological parameters. Thus, more detailed investigation of the role played by the weathering of inorganic material requires better data constraints before it can be further evaluated.

[49] The TP scenario fulfills the amplitude constraint but fails the phase constraint. In contrast, the PRP and antiphase PRP/TP scenarios fulfill the phase constraint but fail the amplitude constraint. It is likely, however, that the amplitude constraint is more sensitive than the phase constraint to both the model parameters and the limited availability of pCO₂ data. Thus, if a single forcing parameter is sought as the origin of the 400–500 kyr periodicities, the PRP scenario is favored.

[50] Of all the scenarios investigated here, only the in-phase PRP/TP scenario fulfills both constraints simultaneously. The subset of the in-phase PRP/TP phase space consistent with both the amplitude and phase constraints is broadly defined by the forcing amplitudes.
of CaCO3/Corg > 0.02 and |P| > 0.1 μmol L⁻¹. Thus, the minimum forcing values needed to satisfy the constraints are relatively small, representing variability of 7 and 4%, respectively, from the Holocene mean values. Significantly, the model is relatively insensitive to parameter choice and initial conditions when forced with the biological component of the carbon cycle (Appendix B). As the proxy data constraints are met using a fairly wide range of forcing functions in the PRP/TP space, the model suggests that changes in inorganic weathering of DIC and ALK are not necessary to explain the observed periodicities in the carbon cycle.

[51] The model results suggest that the relatively low amplitude of pCO₂ variability and hence climatic response in the 400–500 kyr band may arise from the counterbalance on the global scale of high relative carbonate (principally coccolithophore as opposed to diatom) production with high total marine productivity. This is consistent with both previous modeling studies [Barker et al., 2006] and observations that carbonate dissolution, which is close to in-phase with the forcing functions for the in-phase PRP/TP scenario (Figure 7) is broadly in-phase with Pleistocene coccolithophore bloom productivity [Rickaby et al., 2007]. The origins of secular variability in coccolithophore productivity across the Pleistocene have been proposed to relate to variations in silica leakage from the high-latitude Southern Ocean [Barker et al., 2006; Matsumoto et al., 2002; Rickaby et al., 2007]. In such a scenario, the global ocean oscillates between states of intense low-latitude coccolithophore and polar diatom productivity (high total primary productivity) and periods of diatoms blooming at low latitudes but limited high-latitude diatom productivity (low total primary productivity) [Rickaby et al., 2007].

[52] The ultimate origin of this variability has been proposed to be the orbital eccentricity cycle and its effect on seasonality and thus silica utilization in the Southern Ocean [Brzezinski et al., 2002; Matsumoto et al., 2002; Matsumoto and Sarmiento, 2008]. Across the middle-late Pleistocene the available proxy data seems to support this, with the eccentricity minima at ~0.4 Ma coinciding with the carbonate dissolution and coccolithophore bloom production maxima [Rickaby et al., 2007] (Figure 2b). However, when evaluated over the past 1.5 Myr, the difference in dominant period between the eccentricity and various proxy records means that no clear phase relationship is discernible (Figure 2b). Furthermore, comparison between the ODP 1143 δ¹³Ccalcite and eccentricity records over the past 5 Myr again yields no clear phase relationship (Figure 1a).

[53] One possible explanation for this is that the eccentricity cycle interacts with the carbon cycle on this timescale not through seasonality but through changes in the weathered fluxes of silica and ALK to the global ocean [Wang et al., 2004]. This latter mechanism may well involve a significant and temporally variable phase lag between changes in eccentricity and the subsequent availability of the nutrients in the global ocean. The present model results support the viability of a mechanism such as silica leakage in generating the observed δ¹³CDIC cycles but the absence of phase modulation behavior suggests that, if orbital eccentricity is the ultimate origin of the cycles, then the relationship between eccentricity and the availability of nutrients in the ocean must be nondirect and temporally variable.

5.5. Limitations of the Model

[54] The present study constitutes very much a first attempt toward sensitivity analysis of the long-term ocean carbon cycle to open system forcing. It clearly demonstrates the viability of fluctuations in CaCO3/Corg and total primary productivity as causes of the observed δ¹³CDIC cycles. However, significant limitations in the availability of data to both parameterize and test the model prevent more accurate treatment of the problem. The future development of globally averaged (stacked) Pli–Pleistocene proxy records, such as has now been done for δ¹³Ccalcite for the late Pleistocene [Oliver et al., 2009] would greatly aid future model-data comparisons of this type.

[55] The most significant source of likely error in the model itself is likely to be in the parameterization of the Corg cycle. In order for δ¹³Corg to remain buffered within the observed limits, it is necessary that the Corg cycle remains closely coupled to the inorganic one on the timescales of interest. More sophisticated treatment involving both inputs of weathered terrestrial Corg and the role played by Corg in sediment surface chemistry may well reveal behavior beyond the scope of the present model and allow direct comparison of model output with carbonate preservation records. Also, an entirely alternative origin for the δ¹³CDIC cycles may be long-term fluctuations in the size of the terrestrial biosphere, an option not investigated here. A more realistic implementation of primary productivity would account for spatial variability in the CaCO3/Corg production and rain rate ratios. The incorporation of shallow water carbonate sedimentation and dissolution would be a useful refinement to the model and allow the evaluation of the role played by the expansion of coral reefs in the Pleistocene.

[56] A more general additional source of uncertainty arises from the fact that riverine fluxes are not in a true steady state on the glacial-interglacial timescale [Vance et al., 2009]. It is plausible that the change from ~413 to ~500 kyr δ¹³CDIC cycles observed over the Pli–Pleistocene may arise from the interaction between a single, eccentricity driven periodicity and the superimposed glacial-interglacial variability. The absence of glacial-interglacial dynamics and the change in their mode across the Middle Pleistocene Transition may thus explain the inability of the present model to generate phase modulation.

6. Conclusions

[57] A 7 box ocean-atmosphere model was adapted to include the processes necessary to study the ocean carbon system on > 100 kyr timescales and then used to undertake sensitivity analysis of various hypothetical origins of the observed 400–500 kyr periodicities present in the Cenozoic ocean carbon cycle. The model is able to produce appropriate amplitude cycles in δ¹³CDIC when forced by periodic changes in the oceanic production ratio of CaCO3/Corg, the weathering flux of continental inorganic carbon or total ocean primary productivity.
[58] In model runs using only one of the above forcing mechanisms, only forcing with the global production ratio of $\frac{CaCO_3}{C_{org}}$ is able to reproduce the observed phase relationship between $\delta^{13}C_{DIC}$, carbonate preservation and $pCO_2$ over the past 1.5 Myr. However, the use of such forcing to reproduce the observed amplitude of $\delta^{13}C_{DIC}$ variability leads to larger amplitudes $pCO_2$ cycles than is consistent with available data. Forcing of the model with both the global production ratio of $CaCO_3/C_{org}$ and total primary productivity is able to replicate both the relative amplitudes and phases of response. This suggests that the relatively low amplitude of $pCO_2$ and hence climatic response in the 400–500 kyr band arises from the counter-balance on the global scale of high relative carbonate (principally coccolithophore as opposed to diatom) production with high total marine productivity.

[59] The simple model investigated here demonstrates that relatively small variations in the relative and total availability of different nutrients in the global ocean could account for the 400–500 kyr $\delta^{13}C_{DIC}$ periodicity. It cannot, however, explain any degree of phase modulation between the forcing and response. If the ultimate origin of the $\delta^{13}C_{DIC}$ cycles is orbital eccentricity then a significant discrepancy remains between the eccentricity period of 413 kyr and the observed ∼500 kyr $\delta^{13}C_{DIC}$ periodicity seen in the Pleistocene.

Appendix A: Model Calculation of $\delta^{13}C_{DIC}$ and $pCO_2$

[60] The $\delta^{13}C_{DIC}$ terms are calculated using $X_t = \delta^{13}C_{DIC} \times [DIC]_t$, and $F = \delta^{13}C_{DIC} (\text{flux}) \times F_{\text{carbon}}$ in equation (1). In the latter expression, $\delta^{13}C_{DIC} (\text{flux})$ is the isotopic composition of the open system flux (e.g., sedimentation) and $F_{\text{carbon}}$ is the flux of carbon (either DIC or $C_{org}$) in mol s$^{-1}$. The atmospheric $pCO_2$ value is computed as a secondary way by subtracting the amount of DIC in each ocean box from the total amount in the entire system at that time. The total amount of DIC in the system at time T (DIC$_{t-T}$) is evaluated based on the initial condition starting mean ocean [DIC] value ([DIC]$_{t=0}$) and the open system fluxes using $\text{DIC}_{t-T} = [\text{DIC}]_{t=0} V_{\text{total}} + \int_{t=0}^{T} (F^{\text{IN}} - F^{\text{OUT}}) dt$. The atmospheric $\delta^{13}C$ value is computed in an analogous way using $X_{t=0} = \delta^{13}C_{DIC}_{t=0} \times [DIC]_{t=0} \text{ in place of DIC}_{t=0} \text{ ($\delta^{13}C_{DIC}$)}$ is set to be 0.0% and $F^{\text{IN/OUT}} = \delta^{13}C_{DIC} (\text{flux}) \times F_{\text{carbon}}$ in place of $F^{\text{IN/OUT}}$.

Appendix B: Model Sensitivity to Variations in the Mean Forcing Function Values and Periods

[61] Initial model experiments in which the forcing period for PRP, TP and WEATH forcing was varied across the range 100–750 kyr show a linear scaling of the period of response in $\delta^{13}C_{DIC}$, $\text{[CO}_2\text{]}_{\text{mean}}$ and $pCO_2$. However, the amplitude of $\delta^{13}C_{DIC}$ and $pCO_2$ response is also dependent on the period of forcing used. This dependence produces an uncertainty in the amplitude of $\delta^{13}C_{DIC}$ response of 0.03% in the case of the TP scenario and < 0.005% for both the PRP and WEATH scenarios for forcing periods in the range 400–500 kyr. The uncertainty in $pCO_2$ response for the same period range is 5 ppmV for WEATH and < 1 ppmV for PRP and TP. These uncertainties, excepting the effect on $pCO_2$ with WEATH, are relatively small compared to the variations caused by the different forcing amplitudes experimented with.

[62] In all three of the PRP, TP and WEATH scenarios, the use of the Holocene value as the mean for the forced parameter leads to a strong linear correlation between the amplitude of forcing and the amplitude of responses in $\delta^{13}C_{DIC}$ and $pCO_2$. In contrast, use of mean values either above or below the modern value show a nonlinear response principally due to the retention of the modern boundary condition-tuned value of $k_{\text{org}}$. Mean forcing values in the range 0.14 – 0.41 for $CaCO_3/C_{org}$ 1.35 – 3.35 µmol L$^{-1}$ for $F_{\text{PRP}}$ and 40,000 – 100,000 mol C s$^{-1}$ for $F_{\text{all}}$ were investigated. For amplitudes up to 0.35 for $CaCO_3/C_{org}$, 0.65 µmol L$^{-1}$ for $F_{\text{PRP}}$ and 26,000 mol C s$^{-1}$ for $F_{\text{all}}$ the uncertainty in $\delta^{13}C_{DIC}$ response arising from the choice of mean forcing value used is < 0.05‰. For the same forcing amplitudes the uncertainty in $pCO_2$ response arising from the choice of mean forcing value used is 2, 5, and 5 ppmV, respectively.

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