Supplementary Material

Supplementary information 1: Carbon-alkalinity-calcium deep time box model

This model is designed to track the transfer of atmospheric and marine carbon over geological time, while including explicit representation of the calcium and alkalinity cycles and how they control carbonate deposition. The biogeochemical system is taken largely from the work of Walker and Kasting (1992), with some additions from Rampino and Caldeira (2005), Payne and Kump (2007) and Clarkson et al. (2015), with the underlying hydrological model from Sarmiento and Toggweiler (1984).

1. Model structure

The model we use is slightly modified from the model of Dal Corso et al. (2020). For this work we remove the Hg cycle and add a simple Ca cycle. All other model processes remain identical. For convenience we reproduce the model derivation here. The model has three ocean boxes: surface (s), high-latitude (h) and deep (d). As in Sarmiento and Toggweiler (1984) the surface box is 100 m deep and occupies 85% of the ocean surface, whereas the high-latitude box is 250 m deep and represents 15% of the ocean surface. Each ocean box includes the same biogeochemical species, and a thermohaline circulation mixes the boxes in the order s, h, d. The upper boxes exchange with the atmosphere, which is a single box. As well as transfer fluxes between ocean and atmosphere boxes, biogeochemical fluxes of weathering, degassing and burial operate between the surface system and crust. The model schematic is shown in figure 1 below.
**Figure S1. Model schematic.** Concentrations of modelled species are tracked in boxes representing the atmosphere (a), surface ocean (s), high-latitude ocean (h) and deep ocean (d). Exchange between boxes via air-sea exchange and circulation and mixing are shown as dashed arrows. Biogeochemical fluxes between the hydrosphere and continents/sediments are shown as solid arrows. See text for full details of fluxes.

## 2. Model species

Model species are shown in table S1 below.

<table>
<thead>
<tr>
<th>Description</th>
<th>Name</th>
<th>Exists in</th>
<th>Size at present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface ocean water</td>
<td>$W_s$</td>
<td>Surface Ocean</td>
<td>$3.07 \times 10^{16}$ m$^3$</td>
</tr>
<tr>
<td>High-latitude water</td>
<td>$W_h$</td>
<td>High Latitude</td>
<td>$1.35 \times 10^{16}$ m$^3$</td>
</tr>
<tr>
<td>Deep water</td>
<td>$W_d$</td>
<td>Deep ocean</td>
<td>$1.35 \times 10^{18}$ m$^3$</td>
</tr>
<tr>
<td>Atmospheric CO$_2$</td>
<td>$CO_{2a}$</td>
<td>Atmosphere</td>
<td>$5 \times 10^{16}$ mol C</td>
</tr>
<tr>
<td>Surface ocean DIC</td>
<td>$DIC_s$</td>
<td>Surface Ocean</td>
<td>$6 \times 10^{16}$ mol C *</td>
</tr>
<tr>
<td>High-latitude DIC</td>
<td>$DIC_h$</td>
<td>High Latitude</td>
<td>$3 \times 10^{16}$ mol C *</td>
</tr>
<tr>
<td>Deep ocean DIC</td>
<td>$DIC_d$</td>
<td>Deep ocean</td>
<td>$3 \times 10^{18}$ mol C*</td>
</tr>
<tr>
<td>Surface ocean alkalinity</td>
<td>$ALK_s$</td>
<td>Surface Ocean</td>
<td>$6 \times 10^{16}$ mol CaCO$_3$ equiv. *</td>
</tr>
<tr>
<td>High-latitude alkalinity</td>
<td>$ALK_h$</td>
<td>High Latitude</td>
<td>$3 \times 10^{16}$ mol CaCO$_3$ equiv. *</td>
</tr>
<tr>
<td>Deep ocean alkalinity</td>
<td>$ALK_d$</td>
<td>Deep ocean</td>
<td>$3 \times 10^{18}$ mol CaCO$_3$ equiv. *</td>
</tr>
<tr>
<td>Surface ocean calcium</td>
<td>$CAL_s$</td>
<td>Surface Ocean</td>
<td>$3.1 \times 10^{17}$ mol Ca</td>
</tr>
</tbody>
</table>
High-latitude calcium $C_{AL_h}$
Deep ocean calcium $C_{AL_d}$

*starting values chosen close to equilibrium values, model equilibrates to DIC $\approx 2$ mM and ALK $\approx 2.2$ mM, roughly approximate to the modern ocean. Other values follow Sarmiento and Toggweiler (1984) and Lenton et al., (2018).

3. Model fluxes
Model fluxes, with equations and present values are shown in table S2 below. Transfer fluxes follow a simple concentration relationship, air sea exchange follows Walker and Kasting (1992), carbonate burial (net accumulation) follows Rampino and Caldeira (2005) and all other fluxes are chosen from recent carbon cycle models (Lenton et al., 2018). Degassing shown in figure S1 sums carbonate and organic carbon degassing.

<table>
<thead>
<tr>
<th>Description</th>
<th>Name</th>
<th>Equation</th>
<th>Size at present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer fluxes</td>
<td>$\text{tran}_{ij}$</td>
<td>$C_{i,f,circ}$</td>
<td>Multiple</td>
</tr>
<tr>
<td>Air sea exchanges</td>
<td>$f_{\text{airsea}}$</td>
<td>$A_j M_{\text{atm}} \left( pCO_{2a} - pCO_{2j} \right) / \tau_{oa}$</td>
<td>Multiple</td>
</tr>
<tr>
<td>Silicate weathering</td>
<td>$f_{\text{sitw}}$</td>
<td>$k_{basw} f_{\text{bas}} + k_{\text{granw}} f_{\text{gran}}$</td>
<td>$8 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Carbonate weathering</td>
<td>$f_{\text{carbw}}$</td>
<td>$k_{\text{carbw}} f_{\text{carb}}$</td>
<td>$8 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Oxidative weathering</td>
<td>$f_{\text{oxidw}}$</td>
<td>$k_{\text{oxidw}} (RO_2)^{0.5}$</td>
<td>$7.75 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Carbonate degassing</td>
<td>$f_{\text{ccdeg}}$</td>
<td>$k_{\text{ccdeg}}$</td>
<td>$8 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Organic carbon degassing</td>
<td>$f_{\text{ocdeg}}$</td>
<td>$k_{\text{ocdeg}}$</td>
<td>$1.25 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Marine carbonate burial</td>
<td>$f_{\text{mccb}}$</td>
<td>$k_{\text{mccb}} (\Omega - 1)^{1.7} / \Omega$</td>
<td>$16 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Marine organic C burial</td>
<td>$f_{\text{mocb}}$</td>
<td>$k_{\text{mocb}}$</td>
<td>$4.5 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Land organic C burial</td>
<td>$f_{\text{locb}}$</td>
<td>$k_{\text{locb}}$</td>
<td>$4.5 \times 10^{12}$ mol C yr$^{-1}$</td>
</tr>
<tr>
<td>Evaporite dissolution</td>
<td>$f_{\text{evapdis}}$</td>
<td>$k_{\text{evapdis}}$</td>
<td>Varied in experiments</td>
</tr>
<tr>
<td>Evaporite deposition</td>
<td>$f_{\text{evapdep}}$</td>
<td>$k_{\text{evapdep}}$</td>
<td>Varied in experiments</td>
</tr>
</tbody>
</table>

4. Non-flux calculations
Atmospheric CO$_2$ volume ratio:
where $CO_{2a}$ is atmospheric CO2 in moles, and $CO_{2a_0}$ is this value at present day.

**Global average surface temperature:**

\[
GAST = 288 + k_{clim} \left( \log\left( \frac{CO_{2ppm}}{280} \right) \right) \log(2)
\]

where $k_{clim}$ is climate sensitivity to doubling CO2. Low-latitude surface temperature ($T_s$) is assumed to scale by $\frac{2}{3}$ times global temperature change, and both high-latITUDE ($T_h$) and deep ocean ($T_o$) temperature are assumed to follow global temperature change.

**Carbonate speciation:**

Effective equilibrium constants are calculated following Walker and Kasting (1992), after Broecker and Peng (1982). These consider only temperature dependencies, omitting those on pressure and salinity.

\[
K_{carb} = 5.75 \times 10^{-4} + 6 \times 10^{-6} (T_j - 278)
\]

\[
K_{CO_2} = 0.035 + 0.0019 (T_j - 278) \text{ PAL m}^3 \text{mol}^{-1}
\]

Dissolved carbon species are then calculated following Walker and Kasting (1992):

\[
[HC\mathord{O}_3^-]_j = DIC_j - \sqrt{\frac{DIC_j^2 - ALK_j (2DIC_j - ALK_j)(1 - 4K_{carb})}{1 - 4K_{carb}}}
\]

\[
[CO_3^{2-}]_j = \frac{ALK_j - [HC\mathord{O}_3^-]_j}{2}
\]

\[
pCO_2_j = \frac{K_{CO_2} [HC\mathord{O}_3^-]^2}{[CO_3^{2-}]} \]

**Calcium carbonate saturation state:**

\[
\Omega_j = \frac{[Ca]_j [CO_3^{2-}]_j}{K_{sp}}
\]

where $\Omega_j$ is the CaCO3 saturation state in box $j$ and $K_{sp}$ is the solubility product. $[Ca]$ and $[CO_3^{2-}]$ are concentrations.

**Terrestrial chemical weathering**

Temperature dependence of basalt and granite weathering:
Temperature dependence of carbonate weathering:

\[ f_{T_{\text{bas}}} = e^{0.0608(GAST - 288)(1 + 0.038(GAST - 288))^{0.65}} \]

\[ f_{T_{\text{gran}}} = e^{0.0724(GAST - 288)(1 + 0.038(GAST - 288))^{0.65}} \]

Weathering constants:

\[ k_{\text{basw}} = 2.4 \times 10^{12} \text{ mol yr}^{-1} \]

\[ k_{\text{granw}} = 5.6 \times 10^{12} \text{ mol yr}^{-1} \]

5. Fixed parameters

Fixed parameters are shown in table S3.

<table>
<thead>
<tr>
<th>Description</th>
<th>Name</th>
<th>Size at present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermohaline speed</td>
<td>( f_{\text{circ}} )</td>
<td>20 Sv</td>
</tr>
<tr>
<td>Relative area of low-latitude surface ocean</td>
<td>( A_s )</td>
<td>0.85</td>
</tr>
<tr>
<td>Relative area of high-latitude surface ocean</td>
<td>( A_h )</td>
<td>0.15</td>
</tr>
<tr>
<td>Present day moles of atmospheric CO2</td>
<td>( M_{\text{atm}} )</td>
<td>( 5 \times 10^{16} \text{ mol C} )</td>
</tr>
<tr>
<td>Timescale parameter for gas exchange</td>
<td>( \tau_{\alpha} )</td>
<td>10 years</td>
</tr>
<tr>
<td>Long-term climate sensitivity</td>
<td>( k_{\text{clim}} )</td>
<td>5 K</td>
</tr>
<tr>
<td>Calcium carbonate solubility product</td>
<td>( K_{sp} )</td>
<td>0.8 mmol^{2} kg^{-2} *</td>
</tr>
<tr>
<td>Present day CaCO3 saturation state</td>
<td>( \Omega_0 )</td>
<td>3</td>
</tr>
</tbody>
</table>

*chosen within ocean range (0.43-1.15) (Zeebe and Wolf-Gladrow, 2001) to achieve reasonable DIC and ALK at present. Other parameters follow Walker and Kasting (1992), Sarmiento and Toggweiler (1984), Clarkson et al. (2015). Long-term climate sensitivity (Lunt et al., 2009) is larger than equilibrium climate sensitivity (ECS), and appears to be around 5K during the Phanerozoic (Mills et al., 2019).

6. Differential equations

The following equations track the 11 non-water species from table 1.

Atmospheric CO2:

\[ \frac{d(CO_2)}{dt} = -f_{\text{airsea}} - f_{\text{airsea}} + f_{\text{ccdeg}} + f_{\text{oceq}} + f_{\text{oxid}} - f_{\text{loch}} - f_{\text{carb}} - 2f_{\text{silw}} \]

Low-latitude surface ocean DIC
\[
\frac{d(DIC_s)}{dt} = f_{\text{air sea}} + tran_{DIC_{ds}} - tran_{DIC_{sh}} + 2f_{\text{carbw}} + 2f_{\text{silw}} - f_{\text{mccb}} - f_{\text{mocb}}
\]

High-latitude surface ocean DIC

\[
\frac{d(DIC_h)}{dt} = f_{\text{air sea}h} + tran_{DIC_{sh}} - tran_{DIC_{hd}}
\]

Deep ocean DIC

\[
\frac{d(DIC_d)}{dt} = tran_{DIC_{hd}} - tran_{DIC_{ds}}
\]

Low-latitude surface ocean alkalinity

\[
\frac{d(ALK_s)}{dt} = tran_{ALK_{ds}} - tran_{ALK_{sh}} + 2f_{\text{carbw}} + 2f_{\text{silw}} - 2f_{\text{mccb}}
\]

High-latitude surface ocean alkalinity

\[
\frac{d(ALK_h)}{dt} = tran_{ALK_{sh}} - tran_{ALK_{hd}}
\]

Deep ocean alkalinity

\[
\frac{d(ALK_d)}{dt} = tran_{ALK_{hd}} - tran_{ALK_{ds}}
\]

Low-latitude surface ocean Ca

\[
\frac{d(ALK_s)}{dt} = tran_{CAL_{ds}} - tran_{CAL_{sh}} + f_{\text{carbw}} + f_{\text{silw}} - f_{\text{mccb}} + f_{\text{evap dis}} - f_{\text{evap dep}}
\]

High-latitude surface ocean Ca

\[
\frac{d(ALK_h)}{dt} = tran_{CAL_{sh}} - tran_{CAL_{hd}}
\]

Deep ocean Ca

\[
\frac{d(ALK_d)}{dt} = tran_{CAL_{hd}} - tran_{CAL_{ds}}
\]

7. Model solution

The model is solved in MATLAB using the ODE15s variable-order method for stiff systems.

Code is available on request to BJWM.

8. References


