# Past transitions and perturbations in global carbon cycling

(what can we learn about Earth system function and the interpretation of paleoenvironmental proxies?)

Andy Ridgwell



# OR: Not the PETM (almost)



# There will be a 1 EUR fine for saying 'PETM' out loud



# Ocean carbon cycling



# Ocean carbon cycling



# What are the ocean carbon 'pumps'?















# Ocean carbon cycling











































# Modern vs. ancient carbon cycling



#### Early Earth: Low atmospheric $pO_2$





# [Best • Proxy • Ever]

1A

| 1<br>1s <sup>1</sup><br>hydrogen                 |   |   |  |   |  |  |  |   |  |   |  |  |  |   | <i>.</i> .   |   | 2<br>He<br><sup>1s<sup>2</sup></sup>  |
|--|---|---|--|---|--|--|--|---|--|---|--|--|--|---|--|---|---|
| 1.008<br>2                                       | $\frac{2A}{\Lambda}$  |   |  |   |  |  |  |   |  |   |  | 3A   | 4A   | 5A  | 6A   |   | 4.003   |
| Li Li  | Be  |   |  |   |  |  |  |   |  |   |  | B  | Č  | Ń   | Ŏ  | Ĕ   | Ne  |
| [He]2s <sup>1</sup><br>lithium<br><b>6.941</b>   | [He]2 <del>s<sup>2</sup></del><br>beryllium<br><b>9.012</b> |   |  |   |  |  |  |   |  |   |  | [He]2s <sup>2</sup> 2p <sup>1</sup><br>boron<br><b>10.81</b>                                     | [He]2s <sup>2</sup> 2p <sup>2</sup><br>carbon<br>12.01                                       | [He]2s <sup>2</sup> 2p <sup>3</sup><br>nitrogen<br>14.01  | [He]2s <sup>2</sup> 2p <sup>4</sup><br>oxygen<br>16.00                                   | [He]2s <sup>2</sup> 2p <sup>5</sup><br>fluorine<br><b>10.00</b>                 | [He]2s <sup>2</sup> 2p <sup>6</sup><br>neon<br>20.18  |
|  | 12  |   |  |   |  |  |  |   |  |   |  | 13   | 14   | 15  | 16   | 17  | 18  |
| Na   | Mg  |   |  |   |  |  |  |   |  |   |  |  | Si   | $\mathbf{P}$  | S  |   |   |
| [Ne]3s'<br>sodium<br><b>22.99</b>                | [Ne]3 <del>s'</del><br>magnesium<br>24.31                   | 3B  | 4B   | 5B  | 6B   | 7B   |  | —8B -   |  | 11B   | 12B  | aluminum<br>26.98  | silicon<br>28.09   | [NeJ3 <del>5</del> 3p <sup>o</sup><br>phosphorus<br><b>30.97</b>                                | sulfur<br>32.07  | [Ne]35 <sup>-</sup> 3p <sup>-3</sup><br>chlorine<br>35-45                       | [Ne]35-3p <sup>o</sup><br>argon<br>39.95  |
| 19   | 20  | 21  | 22   | <u>2</u> 3  | 24   | 25   | <u>2</u> 6   | 27  | 28   | 29  | _30  | 31   | 32   | 33  | 34   | 35  | 36  |
| K  | Ca  | Sc  |  | <b>V</b>  |  | Mn   | Fe   | Co  | Ni   | Cu  | Zn   | Ga   | Ge   | AS  | Se   | Br  | Kr  |
| potassium<br><b>39.10</b>                        | [Ar]45 <sup>-</sup><br>calcium<br><b>40.08</b>              | [Ar]4s <sup>-3d</sup><br>scandium<br>44.96                    | [Ar]45 <sup>-</sup> 30 <sup>2</sup><br>titanium<br><b>47.88</b>            | [Ar]4s=3d <sup>3</sup><br>vanadium<br><b>50.94</b>                              | chromium<br>52.00  | [Ar]4 <del>s<sup>2</sup></del> 3d <sup>3</sup><br>manganese<br><b>54.94</b>    | [Ar]4s <sup>-</sup> 3d <sup>o</sup><br>iron<br><b>55.85</b>                        | [Ar]4 <del>5'</del> 3d'<br>cobalt<br><b>58.93</b>                                     | [Ar]4s <sup>2</sup> 3d <sup>8</sup><br>nickel<br><b>58.69</b>                    | [Ar]4s <sup>1</sup> 3d <sup>10</sup><br>copper<br><b>63.55</b>                | [Ar]4s <sup>2</sup> 3d <sup>10</sup><br>zinc<br><b>65.39</b>             | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup><br>gallium<br><b>69.72</b>                  | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup><br>germanium<br>72.58                   | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup><br>arsenic<br>74.92                        | [Ar]45 <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup><br>selenium<br>7 <b>8.96</b>        | [Ar]45 <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup><br>bromine<br><b>79.90</b> | [Ar]45 <sup>-</sup> 3d <sup>10</sup> 4p <sup>6</sup><br>krypton<br><b>83.80</b>               |
| 37   | 38  | 39  | 40   | 41  | 42   | 43   | 44   | 45  | 46   | 47  | 48   | 49   | 50   | 51  | 52   | 5 <u>3</u>  | 54  |
| Kb   | Sr  |   | Zr   | Nb  | Mo   | TC   | Ru   | Rh  | Pd   | Ag  |  | ln   | Sn   | Sb  | Te   |   | Xe  |
| [Kr]5s <sup>1</sup><br>rubidium<br><b>85.4</b> 7 | [Kr]5s <sup>2</sup><br>strontium<br><b>87.62</b>            | [Kr]5 <sup>2</sup> 4d <sup>1</sup><br>yttrium<br><b>88.91</b> | [Kr]55 <sup>2</sup> 4d <sup>2</sup><br>zirconium<br><b>91.22</b>           | [Kr]5s <sup>1</sup> 4d <sup>4</sup><br>niobium<br><b>92.91</b>                  | [Kr]55 <sup>1</sup> 4d <sup>5</sup><br>molybdenum<br><b>95.94</b>                | [Kr]5s <sup>2</sup> 4d <sup>5</sup><br>technetium<br>(98)                      | [Kr]5s <sup>1</sup> 4d <sup>7</sup><br>ruthenium<br><b>101.1</b>                   | [Kr]5s <sup>]</sup> 4d <sup>8</sup><br>rhodium<br><b>102.9</b>                        | [Kr]4d <sup>10</sup><br>palladium<br><b>106.4</b>                                | [Kr]5s <sup>1</sup> 4d <sup>10</sup><br>silver<br><b>107.9</b>                | [Kr]55-4d <sup>10</sup><br>cadmium<br>112.4                              | [Kr]55 <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup><br>indium<br><b>114.8</b>                   | [Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup><br>tin<br><b>118.7</b>                  | [Kr]55€4d <sup>10</sup> 5p <sup>3</sup><br>antimony<br>121.8                                    | [Kr]5 <del>5<sup>2</sup>4d<sup>10</sup>5p<sup>4</sup></del><br>tellurium<br><b>127.6</b> | [Kr]55 <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup><br>iodine<br><b>126.9</b>  | [Kr]5s-4d <sup>10</sup> 5p <sup>6</sup><br>xenon<br>131.3                                     |
| 55   | _56   | _57   | 72   | 73  | 74   | 75   | 76   | 77  | 78   | 79  | _80  | 81   | 82   | 83  | _84  | 85  | 86  |
| Cs   | Ba  | La*   | Hf   | 'l'a  | W  | Re   | Os   | lr  | Pt   | Au  | Hg   | TI   | Pb   | Bi  | PO   | At  | Rn  |
| [Xe]6s <sup>1</sup><br>cesium<br><b>132.9</b>    | [Xe]6 <del>s<sup>2</sup></del><br>barium<br><b>137.3</b>    | [Xe]6 <sup>2</sup> 5d <sup>1</sup><br>lanthanum<br>138.9      | [Xe]6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>2</sup><br>hafnium<br>178.5    | [Xe]6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>3</sup><br>tantalum<br><b>180.9</b> | [Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>4</sup><br>tungsten<br><b>183.9</b> | [Xe]6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>5</sup><br>rhenium<br><b>186.2</b> | [Xe]6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>6</sup><br>osmium<br><b>190.2</b>      | [Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>7</sup><br>iridium<br><b>190.2</b>       | [Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>9</sup><br>platinum<br><b>195.1</b> | [Xe]6s <sup>1</sup> 4f <sup>14</sup> 5d <sup>10</sup><br>gold<br><b>197.0</b> | [Xe]6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup><br>mercury<br>200.5 | Xej6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>1</sup><br>thallium<br><b>204.4</b> | Xej6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>2</sup><br>lead<br><b>207.2</b> | Xej6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>3</sup><br>bismuth<br><b>208.9</b> | [Xe]6s 4f <sup>14</sup> 5d <sup>1U</sup> 6p <sup>4</sup><br>polonium<br>(200)            | [Xe]6s 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>5</sup><br>astatine<br>(210)   | <sup>[Xe]65<sup>2</sup>4f<sup>14</sup>5d<sup>10</sup>6p<sup>6</sup><br/>radon<br/>(222)</sup> |
| 87   | 88  | 89  | 104  | 105   | 106  | 107  | 108  | 109   | 110  | 111   | 112  |  |  |   |  |   |   |
| Fr   | Ra  | Ac~   | <b>R</b> f   | DD  | Sg   | Bh   | Hs   | Mt  | Ds   | Uuu   | Uub  |  |  |   |  |   |   |
| [Rn]7s<br>francium<br>(223)                      | [Rn]7 <del>s'</del><br>radium<br>( <b>226</b> )             | [Rn]7 <del>\$</del> 6d <sup>1</sup><br>actinium<br>(227)      | [Rn]7\$5f <sup>14</sup> 6d <sup>2</sup><br>rutherfordium<br>(2 <b>57</b> ) | [Rn]7\$5f <sup>14</sup> 6d <sup>3</sup><br>dubnium<br>( <b>260</b> )            | [Rn]7€5f <sup>14</sup> 6d <sup>4</sup><br>seaborgium<br>(263)                    | [Rn]7\$5f <sup>14</sup> 6d <sup>5</sup><br>bohrium<br>( <b>262</b> )           | [Rn]7\$ <sup>2</sup> 5f <sup>14</sup> 6d <sup>6</sup><br>hassium<br>( <b>265</b> ) | [Rn]7\$ <sup>2</sup> 5f <sup>14</sup> 6d <sup>7</sup><br>meitnerium<br>( <b>266</b> ) | [Rn]7\$5f <sup>14</sup> 6d <sup>9</sup><br>darmstadtium<br>(271)                 | (272)   | (277)  |  |  |   |  |   |   |



# [Best • Proxy • Ever]

1A

| 1<br>Is <sup>1</sup><br>hydrogen<br>1.008                               | 2A   |  |   |  |  |   |   |  |  |   |  | 3 4   | 4 A   | 5A  | 6A   | 74  | 2<br><b>He</b><br><sup>15<sup>2</sup></sup><br>helium<br>4.003   |
|---|--|--|---|--|--|---|---|--|--|---|--|---|---|---|--|---|--|
| 3<br><b>L1</b><br><sup>[He]2s<sup>1</sup><br/>lithium<br/>6.941</sup>   | 4<br>Be<br><sup>[He]2s<sup>2</sup><br/>beryllium<br/>9.012</sup>     |  |   |  |  |   |   |  |  |   |  | 5<br>B<br>[He]2s <sup>2</sup> 2p <sup>1</sup><br>boron<br>10.81     | 6<br>C<br>[He]2 <sup>2</sup> 2p <sup>2</sup><br>carbon<br>12.01   | <b>7</b><br><b>N</b><br><sub>[He]2s<sup>2</sup>2p<sup>3</sup><br/>nitrogen<br/><b>14.01</b></sub> | 8<br>0<br>(He]2 <sup>2</sup> 2p <sup>4</sup><br>oxygen<br>16.00  | 9<br>[He]2s <sup>2</sup> 2p <sup>5</sup><br>fluorine<br>19.00                                       | 10<br><b>Ne</b><br><sup>[Hej2\$2p<sup>6</sup><br/>псоп<br/>20.18</sup>   |
| 11<br>Na<br><sup>[Ne]35<sup>1</sup><br/>sodium<br/>22.99</sup>          | 12<br>Mg<br><sup>[Ne]35</sup><br>magnesium<br>24.31                  | 3B   | 4B  | _5B  | 6B   | 7B  |   | —8B -  |  | 11B   | 12B  | 13<br>Al<br><sup>[Ne]3\$3p<sup>1</sup><br/>aluminum<br/>26.98</sup> | 14<br>S1<br><sup>[Ne]3\$3p<sup>2</sup><br/>silicon<br/>28.09</sup>  | 15<br>P<br>[Ne]3\$ <sup>2</sup> 3p <sup>3</sup><br>phosphorus<br>30.97                            | 16<br>S<br><sup>[Ne]3s<sup>2</sup>3p<sup>4</sup><br/>sulfur<br/>32.07</sup>                                  | 17<br><b>Cl</b><br><sup>[Ne]3\$3p<sup>5</sup><br/>chlorine<br/>35.45</sup>                          | 18<br>Ar<br><sup>[Ne]3s<sup>2</sup>3p<sup>6</sup><br/>argon<br/><b>39.95</b></sup>                               |
| 19<br>K<br><sub>[Ar]45<sup>1</sup><br/>potassium<br/>39.10</sub>        | 20<br>Ca<br>[Ar]4 <sup>2</sup><br>calcium<br>40.08                   | 21<br>Sc<br>[Ar]4s <sup>2</sup> 3d <sup>1</sup><br>scandium<br>44.96             | 22<br>Ti<br>[Ar]4 <sup>2</sup> 3d <sup>2</sup><br>titanium<br>47.88                         | 23<br>V<br>[Ar]4s <sup>2</sup> 3d <sup>3</sup><br>vanadium<br>50.94                          | 24<br>Cr<br>[Ar]4s <sup>1</sup> 3d <sup>5</sup><br>chromium<br>52.00                           | 25<br>Mn<br>[Ar]4 <sup>2</sup> 3d <sup>5</sup><br>manganese<br>54·94                  | 26<br>Fe<br>[Arj4s <sup>2</sup> 3d <sup>6</sup><br>iron<br>55.85                              | 27<br>C0<br>[Ar]4 <sup>2</sup> 3d <sup>7</sup><br>cobalt<br><b>58.93</b>                     | 28<br><b>Ni</b><br><sub>[Ar]45<sup>2</sup>3d<sup>8</sup><br/>nickel<br/><b>58.69</b></sub> | 29<br>Cu<br>[Ar]4s <sup>1</sup> 3d <sup>10</sup><br>copper<br>63.55                           | 30<br>Zn<br><sup>[A7]45<sup>2</sup>3d<sup>10</sup><br/>zinc<br/>65.39</sup>          | $\underset{\substack{[Ar]4s^23d^{10}4p^1\\gallium}{69.72}}{31}$     | 32<br>Ge<br><sub>[Ar]45<sup>2</sup>3d<sup>10</sup>4p<sup>2</sup><br/>germanium<br/>72.58</sub>                | 33<br><b>AS</b><br>[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup><br>arsenic<br>74.92       | 34<br>Se<br>[Ar]4 <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup><br>sclenium<br>78.96                         | 35<br>Br<br>[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup><br>bromine<br>79.90                | 36<br>Kr<br><sup>[Ar]45<sup>2</sup>3d<sup>10</sup>4p<sup>6</sup><br/>krypton<br/>83.80</sup>                     |
| 37<br><b>Rb</b><br><sup>[Kr]55<sup>1</sup><br/>rubidium<br/>85.47</sup> | 38<br><b>Sr</b><br>strontium<br>87.62                                | $\underset{\substack{[Kr]5s^24d^1\\yttrium\\ 88.91}}{39}$                        | 40<br>Zr<br><sup>[Kr]55<sup>2</sup>4d<sup>2</sup><br/>zirconium<br/>91.22</sup>             | 41<br>Nb<br>[Kr]55 <sup>1</sup> 4d <sup>4</sup><br>niobium<br>92.91                          | 42<br><b>Mo</b><br><sup>[Kr]55<sup>1</sup>4d<sup>5</sup><br/>molybdenum<br/>95.94</sup>        | 43<br><b>Tc</b><br><sup>[Kr]5<sup>2</sup>4d<sup>5</sup><br/>technetium<br/>(98)</sup> | 44<br><b>Ru</b><br><sup>[Kr]5s<sup>1</sup>4d<sup>7</sup><br/>ruthenium<br/><b>101.1</b></sup> | 45<br><b>Rh</b><br><sup>[Kr]55<sup>1</sup>4d<sup>8</sup><br/>rhodium<br/><b>102.9</b></sup>  | 46<br>Pd<br><sub>[Kr]4d<sup>10</sup><br/>palladium<br/><b>106.4</b></sub>                  | 47<br>Ag<br>[Krj5s <sup>1</sup> 4d <sup>10</sup><br>silver<br>107.9                           | 48<br>Cd<br>[Kr]5 <sup>2</sup> 4d <sup>10</sup><br>cadmium<br>112.4                  | $\underset{{}_{IKr J5s^{2}4d}^{I0}5p^{1}}{Indium}_{114.8}$          | ${ {50 \atop {Sn}} \atop {}_{{}_{{}_{{}_{{}_{{}_{{}_{{}_{{}_{{}_$   | 51<br>Sb<br><sup>[Kr]5s<sup>2</sup>4d<sup>10</sup>5p<sup>3</sup><br/>antimony<br/>121.8</sup>     | 52<br><b>Te</b><br><sup>[Kr]55<sup>2</sup>4d<sup>10</sup>5p<sup>4</sup><br/>tellurium<br/><b>127.6</b></sup> | 53<br>I<br>[Kr]5 <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup><br>iodine<br>126.9                   | 54<br>Xe<br><sup>[Kr]5s<sup>2</sup>4d<sup>10</sup>5p<sup>6</sup><br/>xenon<br/>131.3</sup>                       |
| 55<br>Cs<br>[Xej6d<br>cesium<br>132.9                                   | 56<br><b>Ba</b><br><sup>[Xe]6<sup>2</sup><br/>barium<br/>137.3</sup> | 57<br>La*<br><sup>[Xe]62<sup>5</sup>5d<sup>1</sup><br/>lanthanum<br/>138.9</sup> | 72<br>Hf<br><sup>[Xe]6<sup>2</sup>4f<sup>14</sup>5d<sup>2</sup><br/>hafnium<br/>178.5</sup> | 73<br>Ta<br><sup>[Xe]6<sup>2</sup>41<sup>14</sup>5d<sup>3</sup><br/>tantalum<br/>180.9</sup> | 74<br>W<br><sup>[Xej624f<sup>14</sup>5d<sup>4</sup><br/>tungsten<br/>183.9</sup>               | 75<br><b>Re</b><br><sup>[Xe]624f<sup>145d5</sup><br/>rhenium<br/>186.2</sup>          | 76<br>OS<br>(Xej6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>6</sup><br>osmium<br>190.2            | 77<br>Ir<br><sub>[Xe]6s<sup>2</sup>4i<sup>14</sup>5d<sup>7</sup><br/>iridium<br/>190.2</sub> | 78<br>Pt<br>[Xe]6 <sup>3</sup> 4f <sup>14</sup> 5d <sup>9</sup><br>platinum<br>195.1       | $\begin{matrix} 79 \\ Au \\ {}_{[Xe]6s^{1}4f^{14}5d^{10}} \\ {}_{gold} \\ 197.0 \end{matrix}$ | 80<br>Hg<br>[Xej6 <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup><br>mercury<br>200.5 | $[1]_{\substack{x_{ej6}^{2}4t^{14}5d^{10}6p^{1}\\thallium\\204.4}}$ | 82<br><b>Pb</b><br><sub>xej6<sup>2</sup>4f<sup>14</sup>5d<sup>10</sup>6p<sup>2</sup><br/>lead<br/>207.2</sub> | 83<br>B1<br><sub>Xej6241</sub> <sup>145d106p3</sup><br>bismuth<br>208.9                           | 84<br>Po<br><sub>[Xe]65<sup>2</sup>41<sup>14</sup>5d<sup>10</sup>6p<sup>4</sup><br/>polonium<br/>(209)</sub> | 85<br>At<br><sub>Xej6\$4f</sub> <sup>14</sup> 5d <sup>10</sup> 6p <sup>5</sup><br>astatine<br>(210) | 86<br><b>Rn</b><br><sub>[Xe]65<sup>2</sup>4f<sup>14</sup>50<sup>10</sup>6p<sup>6</sup><br/>radon<br/>(222)</sub> |
| 87<br>Fr<br><sup>[Rn]7§</sup><br>francium<br>(223)                      | 88<br><b>Ra</b><br>[Rn]7 <sup>2</sup><br>radium<br>(226)             | 89<br>Ac~<br>[Rn]7\$661<br>actinium<br>(227)                                     | 104<br><b>Rf</b><br>[Rn]7\$5f <sup>14</sup> 6d <sup>2</sup><br>rutherfordium<br>(257)       | 105<br>Db<br>(Rn]7 <sup>2</sup> 55 <sup>14</sup> 6d <sup>3</sup><br>dubnium<br>(260)         | 106<br><b>Sg</b><br>[Rn]7 <sup>2</sup> 55 <sup>14</sup> 6d <sup>4</sup><br>seaborgium<br>(263) | 107<br>Bh<br>[Rn]7 <sup>2</sup> 5f <sup>14</sup> 6d <sup>5</sup><br>bolhrium<br>(262) | 108<br>HS<br>[Rn]7 <sup>2</sup> 5f <sup>14</sup> 6d <sup>6</sup><br>hassium<br>(265)          | 109<br>Mt<br>[Rn]7 <sup>2</sup> 5f <sup>14</sup> 6d <sup>7</sup><br>meitnerium<br>(266)      | 110<br>DS<br>[Rn]7\$5f <sup>14</sup> 6d <sup>9</sup><br>darmstadtium<br>(271)              | 111<br>Uuu<br>(272)   | 112<br><b>Uub</b>  |   |   |   |  |   |  |





Ridgwell and Arndt [submitted]

#### Ocean Carbon Cycling and Models

! calculate carbonate alkalinity loc ALK DIC = dum ALK & & - loc H4BO4 - loc OH - loc HPO4 - 2.0\*loc PO4 - loc H3SiO4 - loc NH3 - loc HS & & + loc H + loc HSO4 + loc HF + loc H3PO4 ! estimate the partitioning between the aqueous carbonate species loc zed = ( & (4.0\*loc ALK DIC + dum DIC\*dum carbconst(icc k) loc ALK DIC\*dum carbconst(icc k))\*\*2 + & 4.0\*(dum carbconst(icc k) - 4.0)\*loc ALK DIC\*\*2 & loc conc HCO3 = (dum DIC\*dum carbconst(icc k) -& )\*\*0.5 loc zed)/(dum carbconst(icc k) - 4.0) loc conc CO3 = & & (& loc ALK DIC\*dum carbconst(icc k) - dum DIC\*dum carbconst(icc k) - & 4.0\*loc ALK DIC + loc zed & & ) & & / (2.0\*(dum carbconst(icc k) - 4.0))loc conc CO2 = dum DIC - loc ALK DIC + & & (& loc ALK DIC\*dum carbconst(icc k) - dum DIC\*dum carbconst(icc k) - & & 4.0\*loc ALK DIC + loc zed & & & ) & & / (2.0\*(dum carbconst(icc k) - 4.0))loc H1 = dum carbconst(icc k1)\*loc conc CO2/loc conc HCO3 loc H2 = dum carbconst(icc k2)\*loc conc HCO3/loc conc CO3















www.seao2.info/misc\_harvard2014.html



### Not the PETM ...



### Not the PETM ....





# CaCO<sub>3</sub> cycling through time



#### Major changes in plankton assembledge Dinoflagellates \_\_\_\_\_ Acritarchs Diatoms Coccolithophorids Radiolaria Foraminifera Neoproterozoic Mesoproterozoic Period Era Κ Cm С Ng Pg J Ρ D S 0 Т Paleoproterozoic Cenozoic Mesozoic Paleozoic Eon Phanerozoic Archean **Proterozoic** 300 1000 2000 2500 3500 400 500 1500 3000 0 100 200 Time (Ma)

# CaCO<sub>3</sub> cycling through time



# CaCO<sub>3</sub> cycling through time




# What do we not 'have' prior to about ~180 Ma?







3500







decreasing calcification rates (% compared to Preindustrial conditions)





Pandolfi et al. [2011] (Science)









#### Major changes in plankton assembledge





#### Major changes in plankton assembledge Dinoflagellates Acritarchs Diatoms Coccolithophorids Radiolaria Foraminifera Neoproterozoic Mesoproterozoic Period <mark>Ng Pg</mark> Era <sup>Cenozoir</sup> Κ С Cm J Ρ D S 0 т Cenozoic Mesozoic Paleozoic Paleoproterozoic Eon Phanerozoic **Proterozoic** Archean 300 1000 400 500 1500 2000 2500 3000 3500 100 200 0 Time (Ma)

Planktic carbonate production and 'ballasting'

Compilation of sediment trap observations: depths >= 2000 m (to exclude hydrodynamically distorted fluxes and relationships) and differentiated by basin: cyan == Atl, yellow == Ind, green == Pac, magenta == SO.

[Wlison et al., 2012; GBC 26, doi:10.1029/2012GB004398]



## CaCO<sub>3</sub> cycling through time: Planktic carbonate production and 'ballasting'



Spatial distribution of carrying capacity (ballasting) coefficients calculated using geographically weighted regression analysis for CaCO<sub>3</sub>.

Wilson et al. [2012]





# (warm == stratified) && (stratified == anoxic) == .true. ???

('stratified' || 'sluggish' || 'stagnant' )

























### Not quite PETM ...



Planktic foraminiferal  $\delta^{13}$ C from early Eocene Tanzania



Open ocean  $\delta^{13}C_{\text{DIC}}$  adjacent to modern Tanzania



Planktic foraminiferal  $\delta^{13}$ C from early Eocene Tanzania

# Open ocean $\delta^{\mbox{\tiny I3}}C_{\mbox{\tiny DIC}}$ adjacent to modern Tanzania



# Open ocean $\delta^{\mbox{\tiny I3}}C_{\mbox{\tiny DIC}}$ adjacent to modern Tanzania





modern Tanzania early Eocene Tanzania 90 -90-0 0 -90 -90 -260 -180 100 180 0 0 Ocean depth (km) 2-2 3-3 blue == model  $\delta^{13}C_{DIC}$ 4 4 (Eocene config) 5-5 -1.0 0.0 2.0 3.0 -1.0 0.0 2.0 3.0 1.0 1.0  $\delta^{13} C_{\text{DIC}}$  (‰)  $\delta^{13} \overline{C}_{DIC}$  (‰)

Planktic foraminiferal  $\delta^{13}$ C from

Open ocean  $\delta^{13}C_{DIC}$  adjacent to

#### More, not-the-PETM ...







Ridgwell et al. [in prep]



Ridgwell et al. [in prep]




























# Modern Pacific zonal $\delta^{13}C_{(DC)}$ profile



increasing fractionation between  $pCO_2$  and  $[CO_2]$  with decreasing temperature towards to poles





















Contours of carbon release vs. source isotopic signature for a global -4‰ carbon isotopic excursion. Contours differ according to the initial mean global  $\delta^{13}$ C.

Ridgwell and Arndt [submitted]









In the Rothman et al. [2003] model, the RDOC reservoir is assumed to have been at least 10 times the size of the inorganic (ocean DIC + atmospheric  $pCO_2$ ) reservoir. For a modern DIC + pCO2reservoir of 39,000 PgC, this mean 390,000 PgC of DOC – more than 500 times larger than modern). For a higher late Precambrian DIC reservoir, the minimum DOC reservoir becomes  $1.6 \times 10^6$  PgC, equivalent to concentration of a little over 1000 mgC per L of seawater and becoming the third most dominant dissolved species in the ocean after CI<sup>-</sup>.





#### A DOC-dominated carbon cycle?





#### Sexton et al. [2011]

In the Eocene hyperthermal RDOC hypothesis, difficulties include envisioning a sufficiently stratified deep ocean (even when ignoring the lack of any evidence for widespread anoxia) that could partition RDOC away from the upper ocean and destruction by oxidation/photodedregation.





One possibility might be a biotic change that resulted in a drastic reduction in RDOC production. Notably: the (modern) decay time of RDOC – ca. 10 kyr – is consistent with the time-scale of PETM onset.



# models ...

! calculate carbonate alkalinity

loc\_ALK\_DIC = dum\_ALK &
& - loc\_H4BO4 - loc\_OH - loc\_HPO4 - 2.0\*loc\_PO4 - loc\_H3SiO4 - loc\_NH3 - loc\_HS &
& + loc H + loc HSO4 + loc HF + loc H3PO4

! estimate the partitioning between the aqueous carbonate species

```
loc zed = ( \&
& (4.0*loc ALK DIC + dum DIC*dum carbconst(icc k) -
loc ALK DIC*dum carbconst(icc k))**2 + &
& 4.0*(dum carbconst(icc k) - 4.0)*loc ALK DIC**2 &
& )**0.5
              loc conc HCO3 = (dum DIC*dum carbconst(icc k) -
loc zed)/(dum carbconst(icc k) - 4.0)
loc conc CO3 = \&
& (&
   loc ALK DIC*dum carbconst(icc k) - dum DIC*dum carbconst(icc k) - &
&
    4.0*loc ALK DIC + loc zed &
&
& ) &
\& / (2.0*(dum carbconst(icc k) - 4.0))
loc conc CO2 = dum DIC - loc ALK DIC + &
& ( &
& loc ALK DIC*dum carbconst(icc k) - dum DIC*dum carbconst(icc k) - &
& 4.0*loc ALK DIC + loc zed &
& ) &
\& / (2.0*(dum carbconst(icc k) - 4.0))
loc H1 = dum carbconst(icc k1)*loc conc CO2/loc conc HCO3
loc H2 = dum carbconst(icc k2)*loc conc HCO3/loc conc CO3
```







www.seao2.info/misc\_harvard2014.html





#### cGENIE ClimaTea 2014 version: README

Andy Ridgwell

April 23, 2014

 To get an exact (read-only) copy of the ('mu □n' development branch)cGENIE source code used for the ClimaTea presentation – in linux, (ideally from your home directory) type: svn co https://svn.ggy.bris.ac.uk/subversion/genie/tags/cgenie.Harvard2014
 --username=genie-user cgenie.muffin NOTE: All this must be typed continuously on ONE LINE, with a S PACE before '--username',

and before 'cgenie'. You will be asked for a password – it isg3n1e-user.

2. You need to set a couple of environment variables – the coniller name, netCDF library name, and netCDF path. These are specified in the fileuser.mak (genie-main directory). If the cgenie code tree (cgenie.muffin) and output directory (cgenie output) are installed anywhere other than in your account HOME directory, paths specifying this will have to be edited in: user.mak anduser.sh (genie-main directory). Installing the model code under the default directory name (cgenie.mu□n) in your HOME directory is hence by far the simplest and avoids incurring additional/unnecessary pain (configuration complexity) ...

You will also need to have installed or linked to an appropriate FORTRAN compiler and netCDF library (built with the same FORTRAN compiler). The GNU FORT RAN compiler (gfort) version 4.4.4 or later is recommended. The netCDF version needs to be 4.0 (more recent versions require a little work-around, not documented here ...).

3. To test the code installation – change directory tocgenie.muffin/genie-main and type: make testbiogem

This compiles a carbon cycle enabled configuration of GENIE and runs a short test, comparing the results against those of a pre-run experiment (also downloaded alongside the model source code). It serves to check that you have the software environment correctly configured. If you are unsuccessful here ... double-check the software and directory environment settings in user.mak (or user.sh) and for a netCDF error, check the value of theNETCDF DIRenvironment variable. (Refer to the User Manual for addition fault-finding tips.) If environment variables are changed: before re-trying the test, you will need to type:

make cleanall

That is is for the basic installation. To run the model it is a simple matter of calling the 'runmuffin.sh' shell script fromgenie-main and supplying a couple of parameter values, e.g.:

./runmuffin.sh cgenie.eb\_go\_gs\_ac\_bg.worjh2.ANTH / EXAMPLE.worjh2.Caoetal2009.SPIN 10000

Refer to thecGENIE User manualfor more information regarding installing, running, and analyzing model output, and cGENIE Examplesfor more information on this specific example.<sup>1</sup> Also read the cGENIE README

Highly recommended ... is in order to have a working appreciation of the structure of the model and output, plus the format of the model output and how to visualize it – to read through:

http://www.seao2.info/cgenie/labs/EC4.2013/GEOGM1110andM1404.2013-14.cGENIE\_LAB.0000.pdf

(which serves as a basic introduction to the model and how to use it).



# models ...

|   | Fil                  | e Edit Plot Window Help           |                    |  |                           |
|---|----------------------|-----------------------------------|--------------------|--|---------------------------|
|   |                      |                                   |                    |  |                           |
|   |                      | 🧠 <new plot="" window=""> 🗸</new> |                    |  | , 💌 🔛                     |
|   | Cre                  | eate Plot                         |                    |  | Remove Remove All Hide CD |
|   |                      | Datasets & Variables              |                    | 🔏 ocn_PO4 in fields_biogem_3d (872)  |                           |
|   |                      | Name                              |                    | File Edit Plot Window Help   | <u>^</u>                  |
|   |                      | 🖃 🛅 fields_biogem_3d (872).nc     | fields_biogem_3    |  |                           |
|   |                      | 🙆 bio_fpart_CaCO3                 | particulate flux - | Plot 1: ocn_PO4  |                           |
|   |                      |                                   | particulate flux - | dissolved phosphate (PO4)  | );                        |
|   |                      | io_fpart_POP                      | particulate flux - |  |                           |
|   |                      | in bio_fpart_ash                  | particulate flux - |  | double                    |
|   |                      | bio_fpart_det                     | particulate flux - |  |                           |
|   |                      | bio_rpartnorm_CaCO3               | export-normalize   |  |                           |
|   |                      | bio_partnorm_ach                  | export-normalize   |  |                           |
| ■ 1:almond.ggy,bris.ac.uk - mushroom@almond - SSH Secure Shell  |                      | bio_partnorm_det                  | export-normalize   |  |                           |
| File Edit View Window Help  |                      | Carb H                            | carbonate chemi    |  |                           |
| 🔛 🎒 💁 🖳 📕 🗱 🛱 🦰 構 💋 🎾 🦓 🛷 🎌   |                      | carb_RF0                          | carbonate chemi    |  |                           |
| Filename for restart input : atchem   |                      | CO2                               | carbonate chemi    |  |                           |
| Filename for restart output : atchem  |                      | 🤤 carb_conc_CO3                   | carbonate chemi    |  |                           |
| Initialisation of ATCHEM module complete  |                      | - Carb_conc_HCO3                  | carbonate chemi    |  |                           |
| ·····   |                      | carb_dCO3_arg                     | carbonate chemi    |  |                           |
| Check for weightings from genie atm = 0.99999999999999  |                      | 🙋 carb_dCO3_cal                   | carbonate chemi    |  |                           |
| Check for weightings from genie ocn = 0.99999999999999  |                      | carb_fug_CO2                      | carbonate chemi    |  |                           |
| *****   |                      | carb_ohm_arg                      | carbonate chemi    |  |                           |
| Initialisation complete, simulation starting  |                      | carb_ohm_cal                      | carbonate chemi    |  |                           |
| ***************************************   |                      | gnd_A                             | ocean cell surfac  |  |                           |
| do the looping  |                      | grid_do                           | arid definition    |  |                           |
| model vear * nCO2(uatm) d13CO2 * AWO(Sv) ice(%) <sst> <sss> * «DTC»)</sss></sst>  | (uM) <alk>(uM)</alk> | ging_over                         | land-sea mask      |  |                           |
|   |                      | arid topo                         | ocean depth        | dissolved phosphate (PO4) (mol kg-1)   |                           |
| >>> SAVING BIUGEN TIME-SERIES 0 year 0.50 285.160 -6.812 17.359 0.211 1.393 34.901 2242.<br>temp / min = 0.2713E+03 (19.36, 8) / max = 0.2774E+03 (27.20, 8)                | .457 2363.077        | misc_pH                           | ocean pH           |  |                           |
| sal / min = 0.3488E+02 ( 6,18, 8) / max = 0.3496E+02 ( 19,36, 8)  |                      | misc_rCaCO3toPOC                  | CaCO3 to POC r     | 0 2.01E-07 4.02E-07 6.03E-07 8.04E-07 1.005E-06 1.206E-06 1.407E-08 1.806E-08 1.806E-08 2.01E-08 |                           |
| DIC / min = 0.2203E-02 (34,12, 8) / max = 0.2249E-02 ( 4,16, 7)<br>DIC 13C / min = 0.3334E+00 ( 4.16, 7) / max = 0.8790E+00 (35,12, 8)                                      |                      | 🔄 misc_rPO4toCa                   | PO4:Ca ratio (oc   | Aitolf projection centered on 0.0°E Data Min = 4.12629E-09, Max = 1.71647E-06                    |                           |
| DIC_14C / min =1917E+00 (4,16, 7) / max = 0.1239E+01 (35,12, 8)   |                      | misc_rho                          | ocean density      | Array(c) SCAR Contours Man Mice  |                           |
| P04 / min = 0.1968E-05 (36,19, 8) / max = 0.2203E-05 (4,16, 7)  |                      | - 🙆 ocn_ALK                       | alkalinity (ALK)   | Array(s) sow concours map mist.  |                           |
| ALK / min = 0.2363E-02 (4,16, 7) / max = 0.2365E-02 (21,22, 8)  |                      | - 🙋 ocn_Ca                        | dissolved calcium  | Min.: 0E-06 Max.: 2.01E-06 Fit to Data Center on 0 Always Fit Units: mol kg-1 🗸                  |                           |
| DOM_C / nin = $3166E-07$ (17,25, 6) / max = $0.1155E-04$ (31,20, 8)   |                      | ocn_DIC                           | dissolved inorgar  | Color Table: Table rainbow_diff PAL-2 V, Invert Table Scaling Factor: 10^ 0 🗘                    |                           |
| DOM_C_14C / min =1000E+20 (1,13, 1) / max =2505E+02 (21,25, 4)  |                      | ocn_DOM_C                         | dissolved organic  | Invalid/Missing: Gray V, Outlier Shape: Triangle V Divisions, Major: 10 🗘, Minor: 2 🖒            |                           |
| DOM_P / min =3006E-09 (17,25, 6) / max = 0.1090E-06 (31,20, 8)  |                      | ocn_DOM_P                         | dissolved organic  | Scale Caption: Default Other SCALE CAPTION   |                           |
| CFC11 / min = 0.0000E+00 (1, 3, 2) / max = 0.000E+00 (1, 3, 2)  |                      | ocn_mg                            | dissolved Magne    |  |                           |
| CFC12 / min = 0.0000E+00 (1, 3, 2) / max = 0.0000E+00 (1, 3, 2)   |                      |                                   | dissolved oxyger   |  |                           |
| ng / min = 0.5281E-01 ( 0,33, 8) / max = 0.5283E-01 (19,35, 8)<br>>>> SAVING BIOGEN TIME-SLICE @ year 0.5000000000000   |                      |                                   | salinity           |  |                           |
| >>> SAVING BIOGEM TIME-SERIES @ year 1.50 295.241 -7.277 17.955 2.247 3.545 34.901 2240.  | .918 2363.122        |                                   | temperature        | [lon][lat][vert]   |                           |
| <pre>temp / min = 0.2712E+03 (19.36, 8) / max = 0.2831E+03 (27,20, 8)<br/>sal / min = 0.3483E+02 (25,21, 8) / max = 0.3516E+02 (19.36, 8)</pre>                             |                      | phys u                            | ocean velocity - u |  |                           |
| DIC / min = 0.2168E-02 (31,19, 8) / max = 0.2258E-02 ( 4,16, 7)   |                      | phys_v                            | ocean velocity - v | [lon][lat][vert]   |                           |
| DIU_13U / min = 0.2156E+00 ( 4,16, 7) / max = 0.1296E+01 (34,11, 8)<br>DIC 14C / min =5418E+00 ( 4.16, 7) / max = 0.2424E+01 (34,11, 8)                                     |                      | phys_w                            | ocean velocity - w | v [lon][lat][vert]   |                           |
| P04 / min = 0.1736E-05 ( 3,16, 8) / max = 0.2288E-05 ( 4,16, 7)   |                      |                                   |                    |  |                           |
| 02 / min = 0.1543E-03 ( 4,16, 7) / max = 0.3343E-03 (13,29, 8)<br>ALK / min = 0.2362E-02 (10.34, 8) / max = 0.2369E-02 (18.36, 8)   |                      |                                   | jim o              | al- Dhaidh ()  | ×                         |
| DOM_C / min =1272E-06 (17,25, 6) / max = 0.1772E-04 (31,20, 8)  |                      |                                   | Date Of            |  | 2                         |
| $DOM_{C} = \frac{130}{120} / \min =1000E+20 (1,12, 1) / \max = 0.6137E+01 (27,16, 1)$ $DOM_{C} = \frac{140}{120} / \min =1000E+20 (1,12, 1) / \max = 0.3613E+02 (27,16, 1)$ |                      |                                   |                    |  |                           |
| DOM_P / min =1200E-08 (17,25, 6) / max = 0.1672E-06 (31,20, 8)  |                      |                                   |                    |  |                           |
| Ca / min = 0.1024E-01 (25,21, 8) / max = 0.1028E-01 (18,36, 8)  |                      |                                   |                    |  |                           |
| CFC12 / min = 0.0000E+00 (1, 3, 2) / max = 0.0000E+00 (1, 3, 2)<br>CFC12 / min = 0.0000E+00 (1, 3, 2) / max = 0.0000E+00 (1, 3, 2)  |                      |                                   |                    |  |                           |
| Mg / min = 0.5276E-01 (25,21, 8) / max = 0.5296E-01 (18,36, 8)  | 016 0060 147         |                                   |                    |  |                           |
| >>> SAVING BIUGEN TIME-SERIES @ year 2.50 302.269 -7.580 17.161 4.377 5.279 34.901 2240.<br>temp / min = 0.2712E+03 (19,36, 8) / max = 0.2857E+03 (31,20, 8)                | .016 2363.147        |                                   |                    |  |                           |
| sal / min = 0.3479E+02 (25,21, 8) / max = 0.3526E+02 (19,36, 8)   |                      |                                   | -                  |  |                           |
| DIU / min = 0.2143E-02 (31,19, 8) / max = 0.2265E-02 ( 4,16, 7)<br>DIC 13C / min = 0.1340E+00 ( 4.16, 7) / max = 0.1540E+01 (22,25, 8)                                      |                      |                                   |                    |  |                           |
| DIC_14C / min =8203E+00 ( 4,16, 7) / max = 0.3046E+01 (11,27, 8)  |                      |                                   |                    |  |                           |
| P04 / min = 0.1575E-05 ( 3,16, 8) / max = 0.2352E-05 (26,29, 7)<br>02 / min = 0.1463E-03 ( 4.16, 7) / max = 0.3331E-03 (13,30, 8)   |                      |                                   |                    |  |                           |
| ALK / min = 0.2360E-02 (25,21, 8) / max = 0.2371E-02 (18,36, 8)   |                      |                                   | <b>v</b>           |  |                           |

🍰 D

\_ = X

Remove All Hide CDL

# models ...



Simulation running. You can change what the map or graph display using the drop-down lists.

# Thanks to:

Jamie Wilson & Steve Barker, Eleanor John, Paul Pearson [Cardiff] Patricia Sanchez-Baracaldo, Sandra Arndt, Daniela Schmidt [Bristol] Ellen Thomas [Yale] The Royal Society, Natural Environmental Research Council, EU ERC



