Eli Tziperman, EPS 231, Climate dynamics

### **Glacial cycles**

### EPS 231 Climate dynamics Eli Tziperman

Li T-inorman, EPS 231, Climate dynamics

### Observed glacial cycle characteristics





Last Glacial Maximum: 21 kyr ice sheet elevation 2–3 km sea level lower by 130 m



10 ka

Fig. 4. Thickness isopachs for the ICE-4G model for a sequence of times beginning at Last Glacial Maximum at 21 ka and ending at the present. The contour interval is 1 km.

SCIENCE • VOL. 265 • 8 JULY 1994

12 ka

Peltier 1994, Science

### Observed glacial cycle characteristics





Ice core taken out of drill, Byrd, Antarctica (L. Thompson) https://en.wikipedia.org/wiki/File:Icecore 4.jpg

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### Observed glacial cycle characteristics



Epica ice core

**Eight glacial cycles from an Antarctic ice core** 

EPICA community members, 2004



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### Observed glacial cycle characteristics



Deep sea core, past 5 M yrs Lisiecki and Raymo (2005) LR04 Benthic Stack https://en.wikipedia.org/wiki/Marine\_isotope\_stages

### Observed glacial cycle characteristics

Lisiecki, Lorraine E., and Maureen E. Raymo. "A Pliocene-Pleistocene stack of 57 globally distributed benthic δ180 records." Paleoceanography (2005)



Figure 4. Td<sup>18</sup>O stack constructed by the graphic correlation of 57 globally distributed benthic d<sup>18</sup>O records. The scale of the vertical axis changes across panels.

A Pliocene-Pleistocene stack of 57 globally distributed benthic D<sup>18</sup>O records

Characteristics of glacial cycles to be explained by a <sup>limate dynamics</sup> successful theory...

- 100 kyr time scale
- Saw-tooth structure: long glaciations (~90,000 yr), short deglaciations (10,000 yr)
- Transition from 41 kyr to 100 kyr glacial cycles ~800 kyr ago
- Atmospheric CO<sub>2</sub> variations during glacial cycles
- Global scale: both northern & southern hemispheres



### Glacial cycle mechanism ingredients

- 1. energy balance and albedo feedback
- 2. accumulation, ablation (mass balance) as a function of ice sheet height, equilibrium line
- 3. Milankovitch forcing
- 4. ice flow and Glenn's law
- 5. parabolic ice sheet profile
- 6. ice streams, calving
- 7. dust loading and enhanced ablation
- 8. temperature-precipitation feedback
- 9. shallow ice approximation
- 10.isostatic adjustment
- 11.geothermal heating

### equilibrium line, accumulation zone, ablation zone



http://www.snowballearth.org/slides/Ch10-7.gif

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### Milankovitch forcing

Proxy record: 41 kyr and 100 kyr oscillations<sup>231, Climate dynamics</sup>





http://deschutes.gso.uri.edu/~rutherfo/milankovitch.html



Milankovitch cycles over the past 1,000,000 years. Source: Global Warming Art

There seems to be a connection between glaciations & summer insolation at 65N.

Hays et al 1976: insolation is the "pacemaker" of glacial cycles. How does this work...?



https://www.people.fas.harvard.edu/~phuybers/Inso/index.html

Peter Huybers



https://www.people.fas.harvard.edu/~phuybers/Inso/index.html

Peter Huybers

#### Eli Tziperman, EPS 231, Climate dynamics Geometry for calculating insolation: Hartmann Appendix A



The averaged daily insolation, W, as a function of the longitude  $\lambda$  of Earth's orbit around the sun, measured from the vernal equinox, March 21st (June 21st is  $\lambda = 90^{\circ}$ ), obliquity  $\varepsilon$ , precession angle  $\tilde{\omega}$ , eccentricity e; S0 is the solar constant (1360 W/m<sup>2</sup>),  $\delta$  is the declination angle of the Sun (given by sin  $\delta = \sin \varepsilon \sin \lambda$ ),  $e = c/a = s(a^2 - b^2)^{1/2}/a$  is the eccentricity, a and b are the semi-major and semi-minor axes,  $\phi$  is the latitude, and h<sub>0</sub> is the hour angle at sunrise and sunset, given by  $\cosh_0 = -\tan\phi \tan \delta$ .



**Figure 2.** The orbital parameters of the Earth. Eccentricity *e* is defined as e = c/a, where *a* is the semimajor axis and *c* is the distance between the focus and the center of the ellipse. The semiminor axis *b* is then given by Pythagoras's theorem  $(a^2 = b^2 + c^2)$ , which gives  $b = a\sqrt{1 - e^2}$ . The current eccentricity value is e = 0.0167, which means that the Earth's orbit is very close to a circle. The tilt of the Earth's axis with respect to the orbital plane is the obliquity  $\varepsilon$  (current value is  $\varepsilon = 23.44^{\circ}$ ). This tilt implies that the Earth equatorial plane intersects with its orbital plane, the intersection defining the  $\gamma\gamma'$  line and the position of equinoxes and solstices. In the current configuration the Earth is closest to the Sun (perihelion) around January 3, just a few weeks after the Northern Hemisphere winter. This position, relative to the vernal equinox  $\gamma$ , is measured by the  $\tilde{\omega}$  angle.

#### Paillard 2001

## Milankovitch forcing: eccentricity iperman, EPS 231, Climate dynamics



Fig. 2.9. Spectrum of eccentricity.

https://www.ua-magazine.com/2022/04/16/astronomy-may-haveinfluenced-ancient-human-species-and-gave-rise-the-homo-sapiens/

### Milankovitch forcing: precession of orbit and of axis of rotation<sup>nics</sup>





https://commons.wikimedia.org/wiki/ File:Gyroscope\_precession.gif Rotational precession [left] and orbital precession [right]. [Robert Simmon / NASA; WillowW / Wikimedia Commons] downloaded from <a href="https://www.technologyshout.com/there-is-a-new-hypothesis-about-how-uranus-tilts-on-its-side-24/">https://www.technologyshout.com/there-is-a-new-hypothesis-about-how-uranus-tilts-on-its-side-24/</a>

Note speed of orbiting at different phases of cycle, due to Kepler's laws

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### Milankovitch forcing: precession<sup>ziperman, EPS 231, Climate dynamics</sup>



precession, through length of seasons."

https://commons.wikimedia.org/wiki/File:Precession-sphere-EN.svg

Earth axis

#### In-class workshop

back of the envelope calculation to show that in spite of the small eccentricity, the combined effect of eccentricity and precession on summer insolation is very significant

• Assume a (moderately large) Earth orbit eccentricity of 0.03

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[solution: presenter notes]

### Milankovitch forcing: obliquity<sup>i Tziperman, EPS 231, Climate dynamics</sup>



#### Muller & MacDonald 2002

Obliquity does affect the annual mean insolation at a given latitude, but not the global average. ➡ Antisymmetric effect on the N/S hemispheres. Larger obliquity leads to more radiation at the poles in summers, but still none at winter, so more generally high latitude annual insolation depends on obliquity.



Milankovitch forcing: combining precession, obliquity, eccentricity<sup>cs</sup>



June insolation different latitudes

Figure 1. Insolation time series at 65°N for 21 June (longitude measured from the vernal equinox is  $I = 90^{\circ}$ ) and at the equator for 21 March (the vernal equinox,  $I = 0^{\circ}$ ) [Laskar, 1990]. Note that the 21 March insolation (warm season in the equatorial Pacific) leads the insolation of 21 June (Northern Hemisphere (NH) summer solstice) at 65°N by 5 kyr. Milankovitch forcing: combining precession, obliquity, eccentricity<sup>ics</sup>

14 15 North Pole 65N 12 100 kyr 10 10 spectral power 8 6 5 4 2 0 0 0 0.02 0.04 0 0.02 0.06 0.04 0.06 18 35 65S equator 16 30 14 25 spectral power 5 & 0 C 20 15 6 10 4 5 2 0 0 0.02 0 0.04 0.06 0.02 0.04 0 0.06 frequency (cycles/kyr) frequency (cycles/kyr)

Fig. 2.14. Spectra of July insolation, at latitudes 90N, 65N, 0 and 65S.

July insolation power at different latitudes

#### Muller & MacDonald 2002

## notes: parabolic ice sheet (simple version only, 1-WH-lect\_08\_2001.pdf p 100 use next slide)



Distance, km

### Ice streams, calving, ablation



https://nsidc.org/support/faq/what-features-can-i-detect-rampamm-1-sar-image-mosaic-antarctica Rignot et al 2011

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## **Ablation**, ice flow Antarctic ice streams



https://www.jpl.nasa.gov/video/details.php?id=1015

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## **Ablation**, ice flow Antarctic ice streams



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# Greenland Calving event, "Chasing ice" film



https://www.youtube.com/watch?v=hC3VTgIPoGU
# Greenland Calving event, "Chasing ice" film



https://www.youtube.com/watch?v=hC3VTgIPoGU

# Ablation Calving: role of buoyancy forces



**Figure 2.** A selection of key calving styles: **(a)** rifting due to longitudinal extension, **(b)** collapse of overhang following undercutting by subaqueous melt, **(c)** buoyant calving: release of a protruding 'ice foot' below the waterline and **(d)** buoyant calving: uplift of a super-buoyant glacier tongue.

#### Temperature precipitation feedback



Figure 3. Temperature history according to calibrated isotope curve, corrected for elevation changes. The data have been smoothed with a 250-year triangular filter so that the effect of different elevation corrections, corresponding to different marginal retreat distances, can be seen.







Figure 5. Accumulation rate histories for different marginal retreat distances.



### isostatic adjustment



### Early glacial theories



Figure 1. The ice ages according to **Adhemar** [1842], Croll [1875], and Milankovitch [1941]. Adhemar was aware only of the precession of equinoxes, and he related the glacial ages to the lengths of the seasons. Croll benefited from the advances in astronomy and was aware of changes in the other astronomical parameters, though he could not compute the obliquity changes. In his view, the interglacial epoch is associated with small eccentricity and therefore with small precessional changes. **Milankovitch** was the first to integrate the effect of all astronomical parameters and to compute explicitly the insolation at the top of the atmosphere. He understood that summer, not winter, was the critical season. His insolation minima were associated with the major alpine glacier advances recorded by geological evidence.

### Early glacial theories



# Figure 9. Results from the **Calder [1974] model**. The threshold $i_0$ is equal to 502 W m<sup>2</sup>, and the ratio $k_A/k_M$ is chosen equal to 0.22. The forcing *i* is the summer solstice insolation at 65N [Laskar, 1990]. The result is very sensitive to these choices. The agreement with the record is quite poor, but this crude model still predicts the major transitions at the right time, a feature that many, more sophisticated models do not reproduce well. An isotopic record is given here for comparison [Bassinot et al., 1994b].

$$\frac{dV}{dt} = -k(i - i_0),$$

#### Early glacial theories



Figure 10. Same as Figure 9, but for the Imbrie and Imbrie [1980] model. The forcing *i* is the summer solstice insolation at 65N. The time constants are  $\tau_{\rm M}$ =42 kyr and  $\tau_{\rm A}$ =10 kyr.



dt 9

An Imbrie-like glacial theory Eli Tziperman, EPS 231, Climate dynamics



Figure 13. Same as Figure 9, but for Paillard's [1998] model. Threshold values are  $i_{0}=0.75$  and  $i_{1}=0$ . Time constants are  $\tau_{i}=10$  kyr,  $\tau_{G}=\tau_{g}=50$  kyr, and  $\tau_{F}=25$  kyr. A total of about 14 model parameters.

#### 100 kyr cycle as a nonlinear response to Milankovitch

Le-Treut and Ghil (1983): the 100 cycle as a difference tone of insolation's 19k and 23k frequencies, due to nonlinear glacial dynamics.

$$\frac{1}{109}kyr^{-1} = f_1 - f_2 = \frac{1}{19}kyr^{-1} - \frac{1}{23}kyr^{-1}$$



Fig. 10. Power spectrum of (a) simulated marine  $\delta^{18}$ 0 and (b) ice-core  $\delta^{18}$ 0 records. The periods associated with the labeled peaks in panel (b) are, from left to right, 109 kyr, 41 kyr, 23 kyr, 19 kyr, 14.7 kyr, 13 kyr, 11.5 kyr, 10.4 kyr and 9.5 ky (from [90]).

Then Rial (1999):  

$$\frac{1}{107}kyr^{-1} = \frac{1}{95}kyr^{-1} - \frac{1}{826}kyr^{-1}$$



late dynamics

Fig. 11. Model-simulated marine  $\delta^{18}0$  record; its power spectrum appears in Fig. 10a (from [90]).

imate dynamics

100 kyr cycle from orbitally-forced ice sheet models



#### Eli Tziperman, EPS 231, Climate dynamics 100 kyr cycle from toy "Earth system" models

Barry Saltzman: Carbon dioxide and the delta180 record of late-Quaternary climatic change: a global model (Clim Dyn, 1:77–85, 1987)  $\mathrm{d}X$  $= -\alpha_1 Y - \alpha_2 Z - \alpha_3 Y^2$ (17) $\overline{\mathrm{d}t^*}$ d(SL) dt  $\mathrm{d}Y$  $= -\beta_0 X + \beta_1 Y + \beta_2 Z - (X^2 + 0.004Y^2)Y + F_Y$ (18)  $\overline{\mathrm{d}t^*}$ H<sub>sw</sub> dZ(19) $=X-\gamma_2 Z$  $dt^*$ SL 500 400 100 300 200 Ø TIME (kYr B.P.) Orbitally-forced solution of the three-component dynamical system (17)-(19) in non-dimensional units, mu (solid curve), I\*

EQUATOR

POLE

(dotted), and theta\* (dashed)

1.Ø

Ø

Ø

# 100 kyr cycle from toy "Earth system" models

Barry Saltzman: Carbon dioxide and the delta180 record of late-Quaternary climatic change: a global model (Clim Dyn, 1:77–85, 1987)



Comparison of solution for atmospheric carbon dioxide concentration (solid) with the variations inferred by Shackleton and Pisias (1985) for core V19-30 (dashed).

# 100 kyr cycle from toy "Earth system" models

Barry Saltzman: Carbon dioxide and the delta180 record of late-Quaternary climatic change: a global model (Clim Dyn, 1:77–85, 1987)

A great fit to observations can be overdone...:

Comparison of solution for atmospheric carbon dioxide concentration (solid) with the variations inferred by Shackleton and Pisias (1985) for core V19-30 (dashed).



Unfortunately, the ice core record that came out soon after that, looks very different:





Interglacial, no ice, warm atmosphere, large accumulation.

Gildor and Tziperman, ~2000



Interglacial, no ice, warm atmosphere, large accumulation.

Land ice sheets grow, temperature decreases.

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Cooling leads to sea ice formation, ice albedo feedback causes switchlike rapid sea ice growth.



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Cold, dry, weak accumulation, ablation continues. Land ice retreats.

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Interglacial, no ice, warm atmosphere, large accumulation.

Land ice sheets grow, temperature decreases.

Cooling leads to sea ice formation, ice albedo feedback causes switchlike rapid sea ice growth.

Cold, dry, weak accumulation, ablation continues. Land ice retreats.

Sea ice melts, first slowly then again abruptly due to sea ice feedbacks. Back to initial state.

### Sea ice 'pancakes'



# Observational evidence for sea ice switch?

LGM: sea-ice cover

Mechanism predicts a hysteresis between sea ice & land ice



This mechanism, unlike many others, is falsifiable: need to examine phase between land ice & sea ice.

Currently, only sea ice proxy at a single time slice, LGM (21kyr) exists. (Anne de Vernal et al, 2000)



### Insolation-driven glacial hysteresis (Abe-Ouchi et al 2013)

A coupled ice-sheet climate model shows a hysteresis loop with insolation. When Insolation varies with Milankovitch forcing, this leads to glacial-like oscillations

This represents a case where there would have been no glacial oscillations without time-varying Milankovitch forcing.

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Fig 2b: Ice volume as a function of insolation. Showing hysteresis loop (upper branch in red, lower in blue), and model trajectory (black) for last 122 kyr under time-dependent Milankovitch insolation.



and model run for the last 400 kyrs (1e).

This represents a case where there would have been no glacial oscillations without time-varying Milankovitch forcing.

#### Milankovitch forcing:

### Variations in the Earth's Orbit: Pacemaker of the Ice Ages

For 500,000 years, major climatic changes have followed variations in obliquity and precession.

J. D. Hays, John Imbrie, N. J. Shackleton 1977

"pacemaker" = nonlinear phase locking?

First: analysis of phase locking of fireflies

# Eli Tziperman, EPS 231, Climate dynamics Three "successful" glacial models: 1

Saltzman, Hansen and Maasch, 1984: glacial cycles are due to the interaction of land ice, ice shelves and deep ocean temp.

$$\frac{d\xi'}{dt} = a_0\xi' + a_1(1 - a_2\chi')\chi' - a_3\theta' + F_{\xi} + R_{\xi}, \quad (1)$$

$$\frac{d\chi'}{dt} = b_0\xi' + b_1(1 - b_2\chi' - b_3\chi'^2 - b_4\xi'^2)\chi' - b_5\theta' + F_{\chi} + R_{\chi}, \quad (2)$$

$$\frac{d\theta'}{dt} = c_0\xi' + c_1\chi' - c_2\theta' + F_{\theta} + R_{\theta}, \quad (3)$$
\*1.0
$$\frac{d\theta'}{500} + \frac{\xi}{300} + \frac{\xi}{300} + \frac{\xi}{200} + \frac{\xi}{100} + \frac{\xi$$

# Three "successful" glacial models: 2

Paillard 1998: 3 steady states, one equation, transition between steady states based on Milankovitch forcing.

Glacial cycles are due to jumps between steady states (of THC?) forced by Milankovitch



# Three "successful" glacial models. 3

Gildor and Tziperman 2000: "sea ice switch": land ice grows during warm periods (small sea ice cover) and retreats during cold periods (large sea ice cover);



(Ashkenazy & Tziperman 2004)

### Why is it so `simple' to fit glacial ice Volume? Climate dynamics

**The question** (Saltzman, Hansen & Maasch 1984): "How does small amplitude periodic forcing control phase in a complex nonlinear oscillatory system, and is there a good physical interpretation for this phase locking phenomenon?"





**The answer: It's "nonlinear phase locking":** (Hyde&Peltier 1987; Gildor&Tziperman 2000; Ashkenazy&Tziperman 2004)

1665, Christiaan Huygens, Dutch mathematician, astronomer and physicist. While working on design of precise pendulum clocks, suitable for determination of a ship coordinates in the sea, he observed and described synchronization of two clocks placed on a common support. http://www.agnld.uni-potsdam.de/~mros/synchro.html

#### Eli Tziperman, EPS 231, Climate dynamics

### Examples of nonlinear phase locking: 1/3

Moon always faces Earth: makes one rotation around its axis for every rotation around Earth.



NASA, https://www.cronodon.com/PlanetTech/mercury.html



The planet Mercury turns three times for every two orbits around the Sun, this is a 2:3 nonlinear resonance

- Coincidences? No... It's nonlinear phase locking/ nonlinear resonance aided by tidal friction.
- > Linear resonance: 1:1 ratio between forcing and response;
- > Nonlinear resonance: p:q ratio with p,q any integers.

Eli Tziperman, EPS 231, Climate dynamics EXamples of nonlinear phase locking: 2/3

### Crowd synchrony on the Millennium Bridge

Footbridges start to sway when packed with pedestrians falling into step with their vibrations. (Strogatz et al 2005)



Eli Tziperman, EPS 231, Climate dynamics Eli Tziperman, EPS 231, Climate dynamics



 $\theta_1 = \omega_1 + K_1 \sin(\theta_2 - \theta_1)$  $\dot{\theta}_2 = \omega_2 + K_2 \sin(\theta_1 - \theta_2)$  $\omega_1 = \omega_2$ : two run together, side by side

Two "coupled" runners in a circular stadium

 $0 < |\omega_1 - \omega_2| < K_1 + K_2$ : run @ same speed, but separated by a constant distance (Strogatz 94)





1.50

1.25

### Another demonstration of nonlinear phase locking



https://www.youtube.com/watch?v=W1TMZASCR-I Alireza Bahraminasab

### Another demonstration of nonlinear phase locking



https://www.youtube.com/watch?v=W1TMZASCR-I Alireza Bahraminasab

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### Phase locking of glacial cycles





# Why has it been so simple to fit SPECMAP?

Because glacial cycles are phase locked to Milankovitch forcing, and so are the models; **not** because the model's mechanism is correct...

Try to better understand nonlinear phase locking...

# Phase locking: the mechanism



#### **Required ingredients:**

Nonlinear oscillator(s): that can change its frequency as function of its amplitude);

Dissipation: "erases" memory of initial conditions & enables phase locking (radiative cooling in atm, glacial basal friction, ocn viscosity...)

Tziperman, Raymo, Huybers, Wunsch 2006
Eli Tziperman, EPS 231, Climate dynamics

### Phase between Milankovitch and ice volume

"Recent well dated proxies show that the phase of Milankovitch forcing during the terminations of 18 kyr BP and 135 kyr BP are not the same..." [Gallup et al, Science 2002]



Perhaps Milankovitch forcing doesn't *have* to be the same during all terminations even if Milankovitch forcing paces the cycles?

# Phase between Milankovitch forcing and glacial terminations

phases during a model run forced by 65N July radiation:

And by a pure 40 kyr sine wave insolation curve



Phase of Milankovitch forcing is not the same during different terminations, due to the irregular structure of the Milankovitch forcing. Still, Milankovitch forcing sets time of terminations via phase locking! Tziperman, Raymo, Huybers, Wunsch 2006

#### The 41Ky problem and integrated insolation

#### The 41Ky problem

Imbrie et al (1992), Muller and MacDonald (2001), Nisancioglu (2004), and many others



Peter Huybers



ablation is known to be correlated with PDD



assuming insolation determines surface ice temperature, define summer energy similarly to PDD,

Summer Energy = 
$$\sum_{i} \beta_{i} W_{i} \begin{cases} \beta_{i} = 0 \text{ if } W_{i} \leq \tau \\ \beta_{i} = 1 \text{ if } W_{i} > \tau \end{cases}$$

#### Peter Huybers

#### In class workshop

Do we expect the insolation threshold to be larger or smaller for a warmer climate?

Eli Tziperman, EPS 231, Climate dynamics Summer energy is strongly correlated with Positive degree days and insolation, but maximum summer insolation is not!



Peter Huybers

Eli Tziperman, EPS 231, Climate dynamics Summer energy is strongly correlated with Positive degree days and insolation, but maximum summer insolation is not!



Peter Huybers

#### Eli Tziperman, EPS 231, Climate dynamics Milankovitch forcing: precession+eccentricity

#### **In-class workshop**

Use Kepler's laws to explain *qualitatively* why the integrated summer insolation above a threshold is expected to be independent of precession

Kepler Laws:

- (1) planets move in elliptical orbits with the Sun as a focus,
- (2) a planet covers the same area of space in the same amount of time no matter where it is in its orbit

#### Kepler's Second Law

A planet sweeps out equal areas in equal intervals of time



Eli Tziperman, EPS 231, Climate dynamics Summer intensity and duration



Summer duration & intensity are anti-correlated: just when Earth is closest to the sun during summer, summertime is the shortest (Kepler\*). When intensity is integrated over the summertime, precession-related changes in duration and intensity nearly balance one another, and the obliquity component is dominant. (\*) a line connecting a planet & the sun sweeps out equal areas during equal intervals of time, due to angular momentum conservation

f2

f3



Eli Tziperman, EPS 231, Climate dynamics Early Pleistocene summer energy and the rate of ice-volume change



**High threshold:** integrated insulation=peak summer intensity, precession dominates; **Low threshold:** obliquity dominates.

**Cold climate:** need a high threshold for representing melting temperature; **Warm climate:** need only a low threshold.

→ Relevant to the mid-Pleistocene transition from 41kyr to 100kyr ??

### Glacial CO<sub>2</sub> variations



notes The ocean carbonate system

$$\rm CO_2(g) \rightleftharpoons \rm CO_2(aq),$$

#### $CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$

 $H_2CO_3^* (\equiv CO_2^*) \equiv CO_2(aq) + H_2CO_3.$ 

#### $\mathrm{CO}_2(\mathbf{g}) \rightleftharpoons \mathrm{H}_2\mathrm{CO}_3^*.$

 $H_2CO_3^* \rightleftharpoons H^+ + HCO_3^ HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}.$ 

 $\mathrm{CO}_2(\mathbf{g}) \rightleftharpoons \mathrm{H}_2\mathrm{CO}_3^*.$ 

#### $H_2O \rightleftharpoons H^+ + OH^-$

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$$
  
 $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}.$ 

$$\mathrm{CO}_2(\mathbf{g}) \rightleftharpoons \mathrm{H}_2\mathrm{CO}_3^*.$$

$$CO_{2}(g) \rightleftharpoons H_{2}CO_{3}^{*}.$$

$$K_{H} \equiv K_{0}(T, S, p) = \frac{[H_{2}CO_{3}^{*}]}{[CO_{2}(g)]}$$

$$K_{1}(T, S, p) = \frac{[H^{+}][HCO_{3}^{-}]}{[H_{2}CO_{3}^{*}]}$$

$$HCO_{3}^{-} \rightleftharpoons H^{+} + CO_{3}^{2^{-}}.$$

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→ 6 unknown  $[CO_2(g)], [H_2CO_3^*], [OH^-], [H^+], [HCO_3^-], [CO_3^{2-}], and only four equations$ 

Charge conservation (alkalinity)

Carbonate alkalinity  $Alk_C$ 

$$Alk = \left[\mathrm{HCO}_{3}^{-}\right] + 2\left[\mathrm{CO}_{3}^{2-}\right] + \left[\mathrm{OH}^{-}\right] - \left[\mathrm{H}^{+}\right]$$

*T*, *S*, *p*: the ocean temperature, salinity, and pressure where the carbonate system is solved.

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plus the carbonate equations

$$K_{\mathrm{H}} \equiv K_0(T, S, p) = \frac{\left[\mathrm{H}_2 \mathrm{CO}_3^*\right]}{\left[\mathrm{CO}_2(\mathrm{g})\right]}$$

T, S, p: the ocean temperature, salinity, and pressure where the carbonate system is solved.

$$K_1(T, S, p) = \frac{\left[\mathrm{H}^+\right] \left[\mathrm{HCO}_3^-\right]}{\left[\mathrm{H}_2\mathrm{CO}_3^*\right]}$$
$$K_2(T, S, p) = \frac{\left[\mathrm{H}^+\right] \left[\mathrm{CO}_3^{2-}\right]}{\left[\mathrm{HCO}_3^{2-}\right]}$$

 $K_w(T, S, p) = \left[\mathrm{H}^+\right] \left[\mathrm{OH}^-\right]$ 

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► 6 unknown  $[CO_2(g)], [H_2CO_3^*], [OH^-], [H^+], [HCO_3^-], [CO_3^{2-}], and six equations$ 

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The next slide shows these to be small at the oceanic pH range

T, S, p: the ocean temperature, salinity, and pressure where the carbonate system is solved.

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#### Carbonate system solution



# Figure 5.3: The solution of the carbonate system,

showing the concentration of carbonate species as a function of pH for a fixed alkalinity.

# Figure 5.4: The response of pH and carbonate ion to CO<sub>2</sub> increase.

The solution of the carbonate system for a fixed alkalinity as in Figure 5.3, showing the ocean pH (blue) and the carbonate ion  $CO_3^{2-}$  concentration (red) as a function of atmospheric  $CO_2$ .



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#### **In-class workshop**

Solve for  $HCO_3^-$ ,  $CO_3^{2-}$  and  $H^+$  using the approximate equations.

For the values of pH at present/near future:

 $\left[\mathrm{HCO}_{3}^{-}\right], \left[\mathrm{CO}_{3}^{2-}\right] \gg \left[\mathrm{H}^{+}\right], \left[\mathrm{OH}^{-}\right], \left[\mathrm{H}_{2}\mathrm{CO}_{3}^{*}\right].$ 

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So that

$$Alk_{C} = [HCO_{3}^{-}] + 2[CO_{3}^{2-}] + [OH^{-}] - [H^{+}]$$
$$C_{T} = [HCO_{3}^{-}] + [CO_{3}^{2-}] + [H_{2}CO_{3}^{*}].$$

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$$C_{T} = \left[\mathrm{HCO}_{3}^{-}\right] + \left[\mathrm{CO}_{3}^{2-}\right] + \left[\mathrm{H}_{2}\mathrm{CO}_{3}^{*}\right].$$

➡ only 5 unknowns (OH<sup>-</sup> drops out) & the eqns become

$$K_{H} = \frac{\left[H_{2}CO_{3}^{*}\right]}{\left[CO_{2}(g)\right]},$$

$$K_{1} = \frac{\left[HCO_{3}^{-}\right]\left[H^{+}\right]}{\left[H_{2}CO_{3}^{*}\right]},$$

$$K_{2} = \frac{\left[CO_{3}^{2-}\right]\left[H^{+}\right]}{\left[HCO_{3}^{-}\right]},$$

$$Alk_{C} = \left[HCO_{3}^{-}\right] + 2\left[CO_{3}^{2-}\right],$$

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$$\left[\mathrm{HCO}_{3}^{-}\right] = 2\mathrm{C}_{\mathrm{T}} - \mathrm{Alk}_{\mathrm{C}},$$

and can be solved as

$$\begin{bmatrix} CO_3^{2-} \end{bmatrix} = Alk_C - C_T.$$
$$\begin{bmatrix} H^+ \end{bmatrix} = K_2 \frac{2C_T - Alk_C}{Alk_C - C_T}$$
$$\begin{bmatrix} H_2CO_3^* \end{bmatrix} = \frac{K_2}{K_1} \frac{(2C_T - Alk_C)^2}{Alk_C - C_T}$$
$$\begin{bmatrix} CO_2(g) \end{bmatrix} = \frac{K_2}{K_1K_H} \frac{(2C_T - Alk_C)^2}{Alk_C - C_T}$$

$$K_{H} = \frac{\left[H_{2}CO_{3}^{*}\right]}{\left[CO_{2}(g)\right]},$$

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 $Alk_{C} = \left[\mathrm{HCO}_{3}^{-}\right] + 2\left[\mathrm{CO}_{3}^{2-}\right]$  $C_{T} = \left[\mathrm{HCO}_{3}^{-}\right] + \left[\mathrm{CO}_{3}^{2-}\right].$ 

For the values of pH at present/near future:  $[HCO_3^-], [CO_3^{2-}] \gg [H^+], [OH^-], [H_2CO_3^*].$ So that

$$Alk_{C} = \left[\mathrm{HCO}_{3}^{-}\right] + 2\left[\mathrm{CO}_{3}^{2-}\right] + \left[\mathrm{OH}^{-}\right] - \left[\mathrm{H}^{+}\right]$$
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$$\begin{bmatrix} CO_2(g) \end{bmatrix} = \frac{K_2}{K_1K_H} \frac{(2C_T - Alk_C)^2}{Alk_C - C_T}$$

what could be simpler 😳

$$K_{H} = \frac{[\Pi_{2} \oplus O_{3}]}{[OO_{2}(g)]},$$

$$K_{1} = \frac{[HCO_{3}^{-}][H^{+}]}{[H_{2}CO_{3}^{*}]},$$

$$K_{2} = \frac{[CO_{3}^{2-}][H^{+}]}{[HCO_{3}^{-}]},$$

$$Alk_{C} = [HCO_{3}^{-}] + 2[CO_{3}^{2-}],$$

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#### Response to warming



Figure 5.5: Response of the carbonate system to warming, as a function of the ocean temperature. The DIC and alkalinity are assumed fixed. (a) Reaction constants normalized by their values at 10 °C. (b) pH. (c) Atmospheric pCO<sub>2</sub>.

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$$[\mathrm{H}^+] = K_2 \frac{2C_T - Alk_C}{Alk_C - C_T}, \qquad [\mathrm{CO}_2(\mathrm{g})] = \frac{K_2}{K_1 K_H} \frac{(2C_T - Alk_C)^2}{Alk_C - C_T}.$$

 $K_1$ ,  $K_2$  and  $K_H$  all play a role, not only Henry's constant responsible for the dissolution of  $CO_2$ . In solution for the atmospheric  $CO_2$  concentration,  $K_2/(K_1K_H)$ , Henry's constant  $K_H$  decreases with temperature, while the other two increase. The ratio overall increases, leading to the increase in atmospheric  $CO_2$  with warming.
Finally, attempting to understand the glacial CO<sub>2</sub> problem using a box model



**Figure 1.** Schematic diagram of the three-box model of *Sarmiento and Toggweiler* [1984] and *Siegenthaler and Wenk* [1984].

Toggweiler 1999 model

### Finally, attempting to understand the glacial CO<sub>2</sub> problem using a box model

In the low-latitude surface box, assume that the upwelling nutrient flux is completely utilized by the biology. The downward carbon particulate flux (in moles of carbon) is then,

$$P_l = r_{c:p} \times T \times PO_{4,d}$$



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The deep box Dissolve Inorganic Carbon budget (  $\sum CO_2 \equiv C_T \equiv DIC \equiv Total CO_2$ )

$$\frac{d}{dt}(\Sigma CO_{2d}) = (f_{dh} + T)(\Sigma CO_{2h} - \Sigma CO_{2d}) + (P_l + P_h)$$



Toggweiler 1999

# blem using a box model

Figure 1. Schematic diagram of the three-box model of In the low-latitude surface Sarmiento and Toggweiler [1984] and Siegenthaler and Wenk lux is completely utilized by the biology. The downward carbon particulate flux (in moles of carbon) is then,

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$$\frac{d}{dt}(\Sigma CO_{2d}) = (f_{dh} + T)(\Sigma CO_{2h} - \Sigma CO_{2d}) + (P_l + P_h)$$



Assume a steady state and substitute  $P_l$ ,  $\Delta_{hd} = \Sigma CO_{2d} - \Sigma CO_{2h} = r_{c:p} \frac{T \times PO_{4d}}{f_{dh} + T} + \frac{P_h}{f_{dh} + T}$ small  $\Delta = d - h, s = d + h, \Rightarrow h = \frac{1}{2}(s - \Delta)$ 

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atmosphere  
() ()  
h T ()  
h T T T  
f<sub>hd</sub> 
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The sum of the two terms on the LHS (s) is the total CO<sub>2</sub> and is conserved  $\Rightarrow$  If the difference on the LHS ( $\Delta$ ) decreases, the surface value (h) increases  $\Rightarrow$  atmospheric CO<sub>2</sub> increases

$$f_{hd} \downarrow \Rightarrow \operatorname{CO}_{2(g)} \downarrow$$

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One indeed expects the mixing to be weaker in glacial times due to increased stratification then: as the surface temperature near Antarctica (h box) is as cold as today, but the deeper water being supplied by the NADW should be colder in glacial times. **Voila!** 



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#### Turns out this explanation contradicts proxy evidence of SO productivity, back to square 1



Eli Tziperman, EPS 231, Climate dynamics

Glacial cycles, summary

Features to be explained:

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- 100 kyr time scale
- Saw-tooth structure: long glaciations (~90,000 yr), short deglaciations (10,000 yr)
- The transition from 41 kyr to 100 kyr glacial cycles ~800 kyr ago
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- Likely a self-sustained oscillation that would have existed without Milankovitch and CO<sub>2</sub> variations
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Mechanism for glacial cycles is still unresolved, although this is the largest climate variability signal over the past 1 Myr; Mechanism for CO<sub>2</sub> variations also still not clear

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## The End