

## Past atmospheric composition

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#### **Scope** - Interpreting ice core records of CO<sub>2</sub> using:

- Models of bubble trapping
- Box models of the carbon cycle
- Additional observations (isotopes of carbon: <sup>13</sup>C and <sup>14</sup>C)



## Outline

- Background
- Retrospective
- Current problems





## Section 1: Background





Black = pre-industrial carbon stocks and annual fluxes Red = anthropogenic (2000-2009) carbon stocks and fluxes (IPCC 2013)



Emissions – fossil fuel and land use change Partitioning – atmosphere, land and oceans

Understand past to predict future, incl. feedbacks



#### Box model of the global carbon cycle



CSIRO box diffusion model (Enting and Lassey, 1993) Model C, <sup>13</sup>C and <sup>14</sup>C:

<sup>13</sup>C: stable isotope, useful to distinguish uptake by the land and oceans (uptake by the land has a stronger preference for <sup>13</sup>C than does uptake by the ocean)

<sup>14</sup>C: radioactive isotope, useful for calibrating models. Variations in <sup>14</sup>C are both natural (cosmic ray flux in stratosphere) and anthropogenic (nuclear weapons tests in 1950s and 60s; fossil fuel emissions are <sup>14</sup>C free)

Approx. 99% of atmospheric  $CO_2$  is <sup>12</sup>C, 1% is <sup>13</sup>C and 1 in  $10^{12}$  is <sup>14</sup>C. Isotopes are usually described in terms of ratios to <sup>12</sup>C.



#### Trapping of air into bubbles in ice





## Section 2: Retrospective



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#### Ice core records of CO $_2$ and $\delta^{13}\text{CO}_2$





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#### **Quantify measured changes with model**



Enting and Mansbridge (1987): ice core  $CO_2$ and history of biotic  $CO_2$  releases from ecosystem modelling are inconsistent with any linear time-invariant model of ocean uptake of  $CO_2$  Enting (1992): Allowing for  $CO_2$ -enhanced growth increases the discrepancy. The proposed explanation – the early increase in  $CO_2$  reflects a recovery from a perturbation associated with the Little Ice Age



#### Little Ice Age

- Little Ice Age = period of reported low temperatures in Europe
- Law Dome ice core record defines Little Ice Age decrease in CO<sub>2</sub>.
- Coinciding increase in  $\delta^{\rm 13}{\rm C}$ , although data is sparse



Law Dome ice core  $\rm CO_2$  and  $\delta^{13}\rm C$  record



### Little Ice Age

- With the box diffusion model, we tested the effect of lower temperatures on the land or ocean exchange
- Dotted lines show temperature-dependent ocean exchange (decrease in both  $\rm CO_2$  and  $\delta^{13}\rm C)$
- Dashed lines show temperaturedependent land exchange (decrease in  $CO_2$  and increase in  $\delta^{13}C$ ).
- Conclude significant cooling of terrestrial biomes was the dominant cause of the low CO<sub>2</sub> levels







#### Kalman filter double deconvolution

Double deconvolution – invert  $CO_2$  and  $\delta^{13}C$ measurements for net land and ocean fluxes, using carbon cycle model for isotopes (gross fluxes).

Kalman filter - statistical method, using a state space model. Observations are processed sequentially. Allows estimation of uncertainties.

=> Estimate net fluxes with uncertainties, analysis of the statistics tells you about variability.

Trudinger, Enting et al. (JGR-Atmospheres, 2002a, 2002b)



#### **1940s flattening in CO<sub>2</sub>**

- Flattening in CO<sub>2</sub> in 1940s
- If this were due to terrestrial exchange or fossil emissions, expect corresponding peak in d13C – don't see one
- Double deconvolution suggests a predominantly ocean cause for flattening.

Trudinger, Enting et al. (JGR-Atmospheres, 2002a, 2002b)





#### **Bubble trapping in ice – statistical modelling**



Percolation model from lattice statistics – connected clusters in a lattice.

Points = interstitial cavities in which air is trapped (bubbles)

Bonds (either connected or broken) = connecting pathways that are closed as firn compacts.

1.0 (c) 0.9 0.8 0.7 Proportion trapped 0.6 0.5 0.4 0.3 0.2 0. 0.55 0.60 0.65 0.45 0.50 0.40 Closure probability C

Monte Carlo simulations, showing proportion of trapped bubbles vs bondclosure probability

Enting (1985, 1986, 1987, 1993)

#### **Diffusion in firn**



CSIRO firn model used in many studies to date firn air, provide corrections for isotopes (due to gravity and diffusion), quantify age spread in firn and ice, reconstruct atmospheric histories (synthesis inversion).

#### **Bubble trapping in the CSIRO firn model**



Trapping modelled deterministically. Trapping = fn(open/closed porosity) Open/closed porosity = fn(density)

Trudinger, Enting et al. (1997, 2013)





#### Quantify age distribution at different sites

Depths with mean age of 1940 (ice for DE08-2 and firn for others)

Width depends on snow accumulation rate, depth of firn column, overlap of diffusion and trapping.





# What CO<sub>2</sub> variability do we expect to see at DSS (Law Dome)?

Constant Temperature anomaly (°C) Moberg 0.5 Jones Mann 0.0 Trudinger et al. (2012, AGU Fall Meeting) -0.5 -1.01000 1200 1400 1600 1800 Year SCCM (Simple Carbon-Climate Model) (temperature dependent land fluxes) 290 290 CO<sub>2</sub> (ppm) CO<sub>2</sub> (ppm) 285 285 0.08 DSS Greens fn. 0.06 280 280 Density 0.04 275 275 0.02 0.00 -20 0 -40 20 270 270 Years 1200 1600 1200 1400 1600 1800 1000 1400 1800 1000 -6.2<sub>E</sub> -6.2 F δ<sup>13</sup>CO<sub>2</sub> (permil) δ<sup>13</sup>CO<sub>2</sub> (permil) -6.3Ē -6.3 -6.4 -6.4Firn diffusion and -6.5 -6.5 trapping model -6.6 -6.6 -6.7 -6.7 1600 1000 1200 1400 1600 1800 1000 1200 1400 1800



1.0

## Section 3: Current problems



#### New CO<sub>2</sub> ice core records



CH<sub>4</sub> shows good agreement between WAIS and Law Dome. WAIS CO<sub>2</sub> is higher than Law Dome, and does not show the 1600 dip.



#### New ice core CO<sub>2</sub> records

-100

v

0

DML age distribution

DSS age distribution

-200

Rubino, Etheridge, Trudinger et al. (in prep)

New measurements at DML are consistent with DSS (including the dip at 1600) when age distributions are taken into account



Fractional contribution

0.07

0.05

0.03

a)

b)

100

Atmospheric reconstruction

DSS data





285

280

275

270

277 275

273

271

269

#### New information on pore close-off

#### Xray imaging of firn





Pore space

### Simulated flow field

#### Freitag et al. (2002)

Pore space

Freitag et al. (2004)



#### New information on pore close-off

We have known for years that firn has seasonal density layers, which affect diffusion and trapping, however recent evidence shows

- Layers with lower density near the surface become higher density layers at depth (Freitag et al., 2004; Gregory et al., 2014).
- Impurities in firn have a significant impact on densification (Horhold et al., 2012; Freitag et al., 2013)
- Lower accumulation-rate sites generally have coarser grained firn, and close-off at lower open porosity, than higher accumulationrate sites which generally have finer-grained layers (Gregory et al., 2014)

Next generation firn models will need to consider these effects e.g. 3D lattice-Boltzmann model of air flow (Courville et al., 2010); stochastic parameterisation of closed porosity (Mitchell et al., 2015)



#### **Two unsolved problems**

- Confirm features and fill in gaps in history of  $CO_2$  and  $\delta^{13}C$  over last 1000 years, esp. 1600s, 1940s flattening: [New DSS ice core, precise, high resolution measurements – measure everything we can to understand diffusion and trapping.
- Understanding of bubble trapping: New measurements. Next generation model of diffusion and trapping (statistical? lattice model? impurities? firn microstructure?)



# Thank you

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