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"Clumped isotopes" of atmospheric trace gases

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Thanks to: Magdalena Hofmann, Dipayan Paul, Elena Popa

Overview

Traditional vs. clumped isotope signatures

Processes affecting clumped isotope anomalies

Applications to atmospheric research

The MAT 253 Ultra instrument at Utrecht University

Outlook

Use of isotope measurements

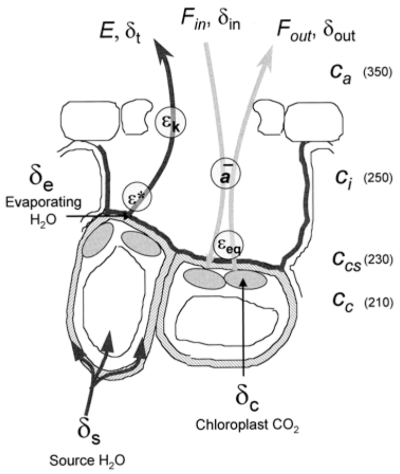
Additional (not always) independent observables

But also additional unknowns

(e.g. ^{18}O exchange with leaf water)

“Second order” isotope effects sometimes less affected

→ e.g. clumped isotopes



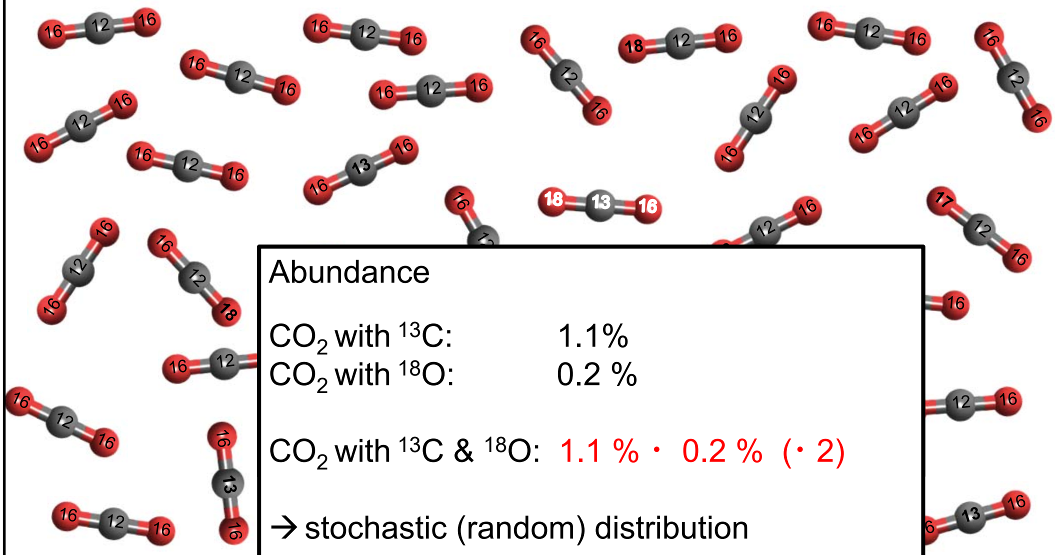
Gillon and Yakir, Plant Phys, 2000

“Clumped isotopes”

Molecules with multiple heavy isotopes

CO_2:	$^{13}C^{18}O^{16}O$	$^{12}C^{18}O^{18}O$
CH_4:	$^{13}CH_3D$	$^{12}CHD_2$
N_2O:	$N^{15}N^{18}O$	$^{15}N^{15}N^{16}O$
O_2:	$^{17}O^{18}O$	$^{18}O^{18}O$
N_2:	$^{15}N^{15}N$	

Abundance of clumped isotopes



Abundance

CO_2 with ^{13}C: 1.1%
CO_2 with ^{18}O: 0.2 %

CO_2 with ^{13}C & ^{18}O: 1.1 % · 0.2 % (· 2)

→ stochastic (random) distribution

almost, but not precisely

Notation

Traditional δ values for CO_2

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{VPDB}} - 1 \right) \qquad \delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{VSMOW}} - 1 \right)$$

Analogous definition

$$\delta^{47} = \left(\frac{\left(\frac{^{13}C^{18}O^{16}O}{^{12}C^{16}O^{16}O}\right)_{sample}}{\left(\frac{^{13}C^{18}O^{16}O}{^{12}C^{16}O^{16}O}\right)_{reference}} - 1 \right)$$

Clumped isotope signature

$$\Delta_{47} \approx \left(\frac{\left(\frac{^{13}C^{18}O^{16}O}{^{12}C^{16}O^{16}O}\right)_{sample}}{\left(\frac{^{13}C^{18}O^{16}O}{^{12}C^{16}O^{16}O}\right)_{randomized\ sample}} - 1 \right)$$

Deviation from random isotope distribution

independent of “bulk” isotopic composition

What affects a clumped isotope signature?

Thermodynamic equilibrium

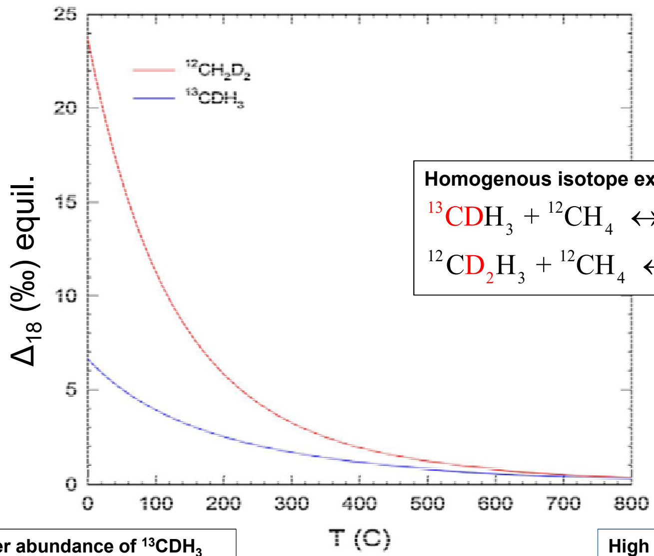
→ T information

Non-equilibrium processes, e.g.

- Diffusion
- Chemical reactions
- Substrates (acetate-methyl vs. CO_2/H_2 for CH_4)
- Biology/reversible reactions

Statistics

Temperature dependency of $^{13}CDH_3$ abundance



Homogenous isotope exchange reactions

$$^{13}CDH_3 + {}^{12}CH_4 \leftrightarrow {}^{13}CH_4 + {}^{12}CDH_3$$

$$^{12}CD_2H_3 + {}^{12}CH_4 \leftrightarrow {}^{12}CDH_3 + {}^{12}CDH_3$$

Low T: Higher abundance of $^{13}CDH_3$
Due to higher bond strength of doubly substituted isotopologue.

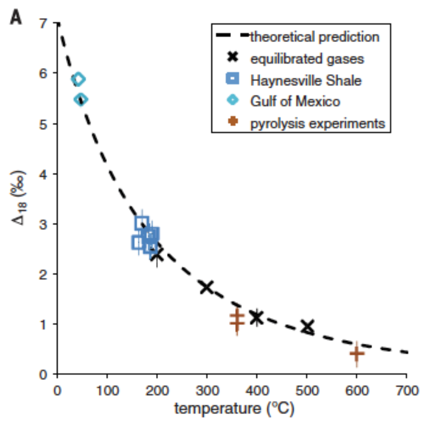
High T: Stochastic composition
^{13}C and ^{D} are randomly distributed within all CH_4 isotopocules.

→ Clumped isotope thermometer

Young et al., 2016

Clumped isotope thermometer – and deviations

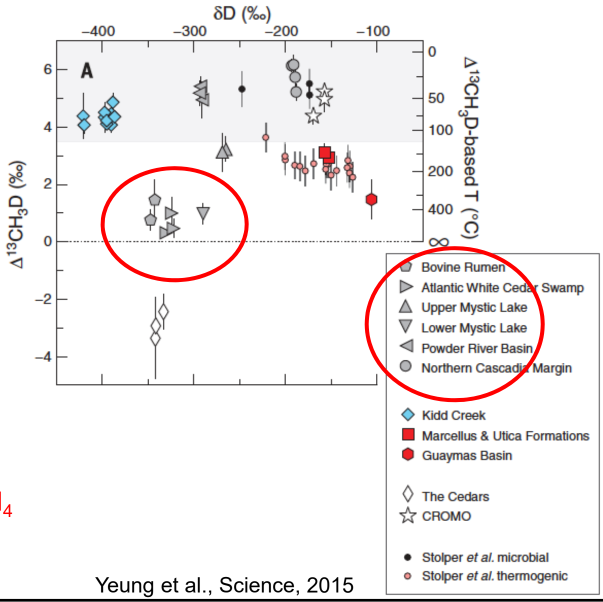
Formation temperature of CH_4



Δ_{18}: Primarily ^{13}C-D clumping in CH_4

Stolper et al., Science, 2014

Biological (kinetic) processes



Yeung et al., Science, 2015

Kinetics

Whenever "clumped" isotope effect is NOT the sum of the individual isotope effects

$$\varepsilon_{1,2} \neq \varepsilon_1 + \varepsilon_2$$

→ change in clumped isotope signal

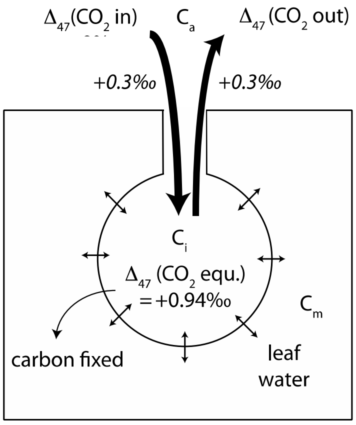
$$\varepsilon = \frac{k_{heavy}}{k_{light}} - 1$$

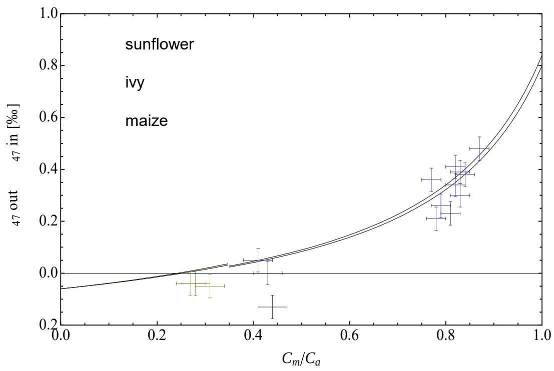
Example: Isotope fractionation in diffusion of CO_2 in air:

	Fractionation
$^{13}C^{16}O^{16}O$	-4.4 ‰
$^{12}C^{18}O^{16}O$	-8.7 ‰
sum	-13.1 ‰
$^{13}C^{18}O^{16}O$	-12.8 ‰

difference + 0.3 ‰

Thermodynamics and diffusion: Photosynthetic CO_2





$\otimes_{47}$ signal independent of ™18O of H_2O

Overall effect: Photosynthesis lowers $\otimes_{47}$ of atmospheric CO_2

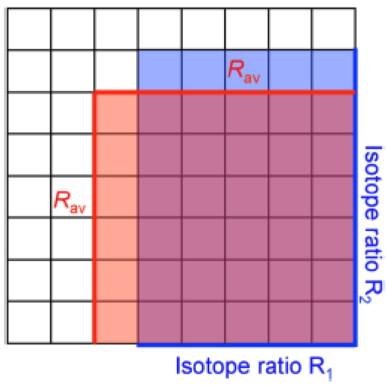
Hofmann et al., in prep, 2016

Statistics

Two indistinguishable atoms (e.g. $^{18}O^{18}O$, $^{12}CH_2D_2$)
→ fundamental issue with definition of Δ

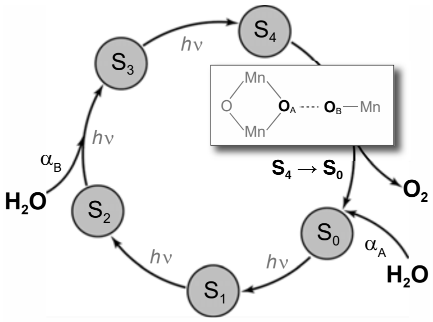
$$\Delta_{36} \approx \left(\frac{\left(\frac{^{18}O^{18}O}{^{16}O^{16}O}\right)_{sample}}{\left(\frac{^{18}O^{18}O}{^{16}O^{16}O}\right)_{randomized\ sample}} - 1 \right)$$

Product of individual abundances

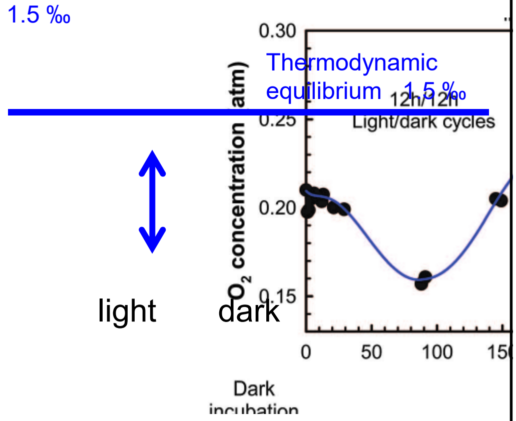


→ not known for indistinguishable atoms
→ Assign average value
→ Error!! Negative clumping signal

O_2 from photosynthesis



Starting atmospheric O_2
> 1.5 ‰



Photosynthetic O_2
<< 1.5 ‰

O_2 formation at the oxygen evolving complex

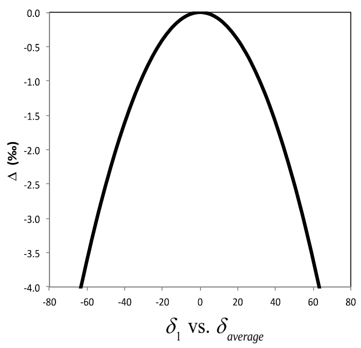
(5-step Kok cycle for the H_2O splitting reaction
$2H_2O + 4\ h\nu \rightarrow O2 + 4\ H^+ + 4\ e^-$)

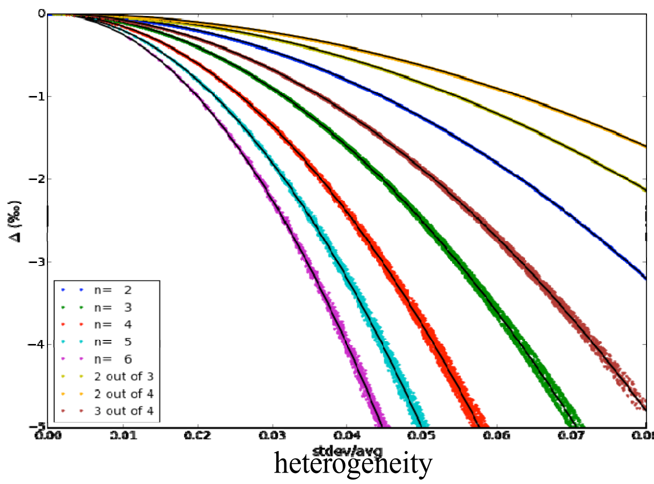
Yeung et al., Science, 2015

Statistical negative clumped isotope anomalies

Applicable to all systems with indistinguishable atoms!

Information on heterogeneity of isotopic pools





Yeung et al results:
$\Delta_{obs} \approx -1.5$ ‰
$\delta_{heter} \approx 50$ ‰

Röckmann et al. 2016

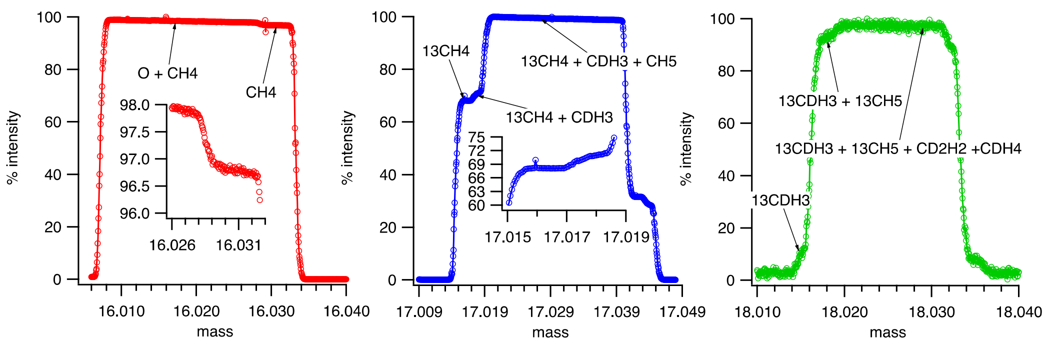
Measurement difficulties – abundance / precision

Isotopocule	Abundance
$^{13}C^{18}O^{16}O$	4.6 * 10^{-5}
$^{12}C^{18}O^{18}O$	4.4 * 10^{-6}
$^{13}CH_3D$	6.6 * 10^{-6}
$^{12}CHD_2$	1.4 * 10^{-7}
$^{15}N^{15}N^{16}O$	1.4 * 10^{-5}
$^{14}N^{15}N^{18}O$	1.6 * 10^{-5}
$^{18}O^{18}O$	4.4 * 10^{-6}
$^{17}O^{17}O$	1.4 * 10^{-7}

Measure these low abundances to better than
10^{-3} – 10^{-5}
1‰ – 0.01‰
precision

Measurement difficulties – mass resolution

Isotopocule	Mass	Isotopocule	Mass	ΔM
$^{13}CH_3D$	18.041	$^{12}CHD_2$	18.044	0.003



The MAT Ultra IRMS at Utrecht University

MAT 253 ULTRA
Double focusing machine (electrostatic + magnetic)
Mass resolution up to 40.000! Resolves e.g. $^{14}N_2$, $^{12}C^{16}O$, $^{12}CH_4$
- High sensitivity with electron multipliers
- Many double and potentially multiple substituted molecules

Achieved in first weeks

CO_2 :	^{13}C – ^{18}O clumping	Δ_{47} = 0.02 ‰
	^{18}O – ^{18}O clumping	Δ_{48} = 0.03 ‰
O_2 :	^{17}O – ^{18}O clumping	Δ_{35} = 0.03 ‰
	^{18}O – ^{18}O clumping	Δ_{36} = 0.03 ‰
	^{17}O – ^{17}O clumping	Δ_{34} = 0.1 ‰
CH_4 :	^{13}C – D clumping	coming next

Outlook

Applications to atmospheric sciences

CH_4: → Formation temperatures of methane
→ thermogenic versus biogenic sources
→ fundamental origin of Arctic methane

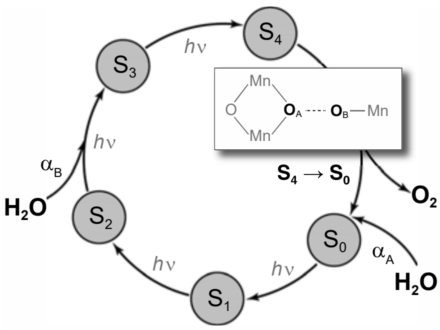
CO_2: → constraints on photosynthesis?

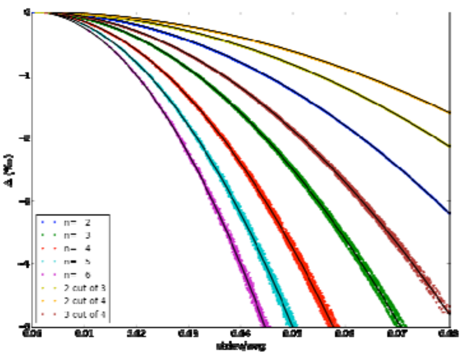
O_2: → tracer for oxidative processes?

N_2O: → production pathways: nitrification – denitrification

Challenge for atmospheric measurements: large samples needed !

Explanation: different O sources in photosystem II





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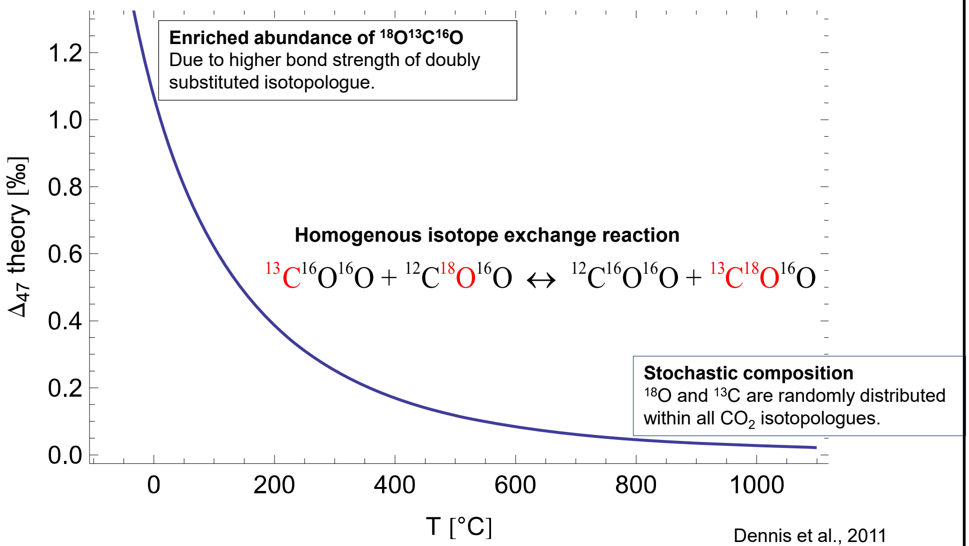
Yeung et al., Science, 2015

Temperature dependency of $^{18}O^{13}C^{16}O$ abundance



Dennis et al., 2011

→ Clumped isotope thermometer