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Stable Isotopes as tools in Process Studies

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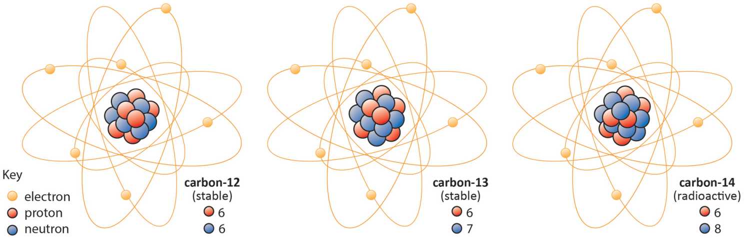
Definition

Isotopes

'Atoms of the same element but with a different mass number (...) are called isotopes. For most practical purposes the isotopes of a given element behave the same chemically.'
Alonso and Finn, Physics, 1970



Terminology

^{12}C	^{13}C	^{14}C
12.00000	13.00335	14.00324
98.89%	1.11%	ppt
		$t_{1/2}$ 5730y

$$\delta^{13}C = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample} - \left(\frac{^{13}C}{^{12}C}\right)_{std}}{\left(\frac{^{13}C}{^{12}C}\right)_{std}} \cdot 1000 \quad / ‰$$

$$\left(\frac{^{13}C}{^{12}C}\right)_{PDB} = 0.0112372$$

The standard for carbon isotope ratios is a fossil lime rock of Belemnitella americana from the Pee-Dee-Formation in South Carolina, USA (PDB)

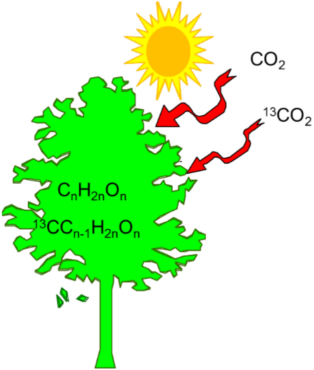
Why do we measure isotopes?

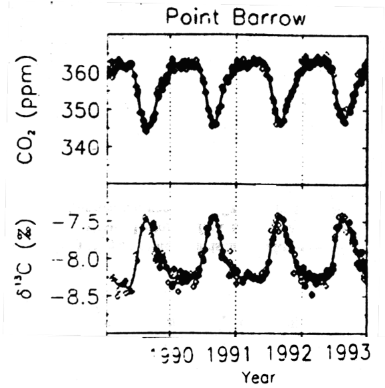
Small differences in nuclear masses do not change general behavior

BUT

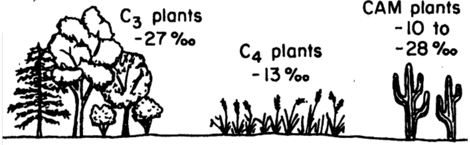
- physical and chemical effects cause slight differences in the isotope distribution in the nature
- small variations in isotope distribution are fingerprints for those effects which are often preserved

Discrimination of ^{13}C during carbon fixation





Boutton, 1991



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Science-Based Forensic Applications of Stable Isotopes

(Chesson et al., 2014)

- **Nonspatial Applications of Stable Isotope Analysis**
  - Synthetic Drugs
    - Amphetamine-type stimulants
    - Performance-enhancing steroids
  - Manufactured Explosives
    - Peroxide-based explosives
    - An industrial explosive: ammonium nitrate
    - A military-grade explosive: pentaerythritol tetranitrate
  - Packaging Materials
  - Crude Oils and Petroleum Products
- **Spatial Applications of Stable Isotope Analysis**
  - Water Isotopes and the Isoscapes Foundational Approach
  - Waters, Beverages, and the Isoscapes Potential
- **Plant-Related Forensic Applications of Stable Isotope Analysis**
  - Economic Adulteration of Foods
  - Food Origin Authentication
  - Controlled Substances Produced from Plants
    - Cocaine and heroin
    - Marijuana
  - Wood and other Plant Product Isotope Records
    - Arson – isotopic comparisons
    - Flavor compounds – adulteration detection
    - Plant and wood products – geographical region of origin
- **Human-Related Forensic Applications of Stable Isotope Analysis**
  - Dietary Patterns
  - Spatial Patterns
    - Body water, geography, and metabolism
    - Carbonates and phosphates in teeth and bones
    - Proteins in bone and hair
  - Provenancing Unidentified Homicide Victims
  - Human Diseases
- **Animal-Related (Nonhuman) Forensic Applications of Stable Isotope Analysis**
  - Animal Migration and Movement
  - Provenance of Trade Goods
- **Archaeological and Gem Origin Investigations Utilizing Stable Isotope Analysis**
  - Sculpture Source: Monuments, Statues, and Artifacts
  - Gem Origins
    - Rubies and sapphires
    - Emeralds
    - Diamonds

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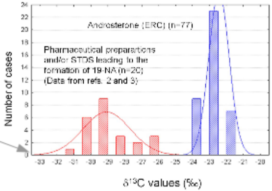

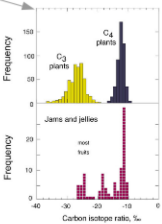

Science-Based Forensic Applications of Stable Isotopes

(Chesson et al., 2014)

Nonsp
Synt
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Ar
A
Pack
Cruc
Spatia
Wate
Wate
Plant-I
Ecor
Fooc
Cont
Cc
M
Woo
Ar
Fl
Pl
Humar
Dieta
Spat
Bc
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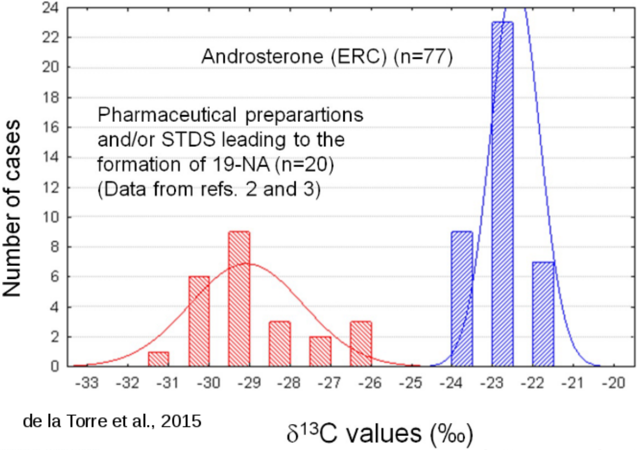
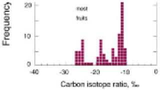


de la Torre et al., 2015



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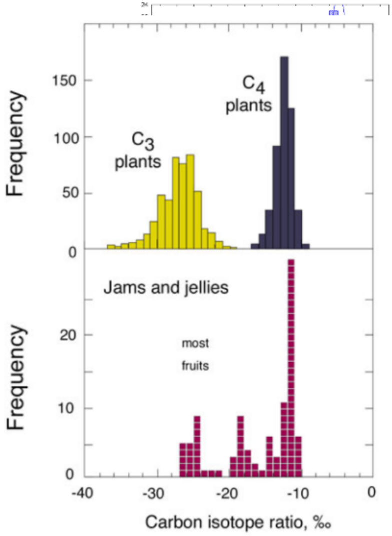

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Atmospheric 'Forensic'

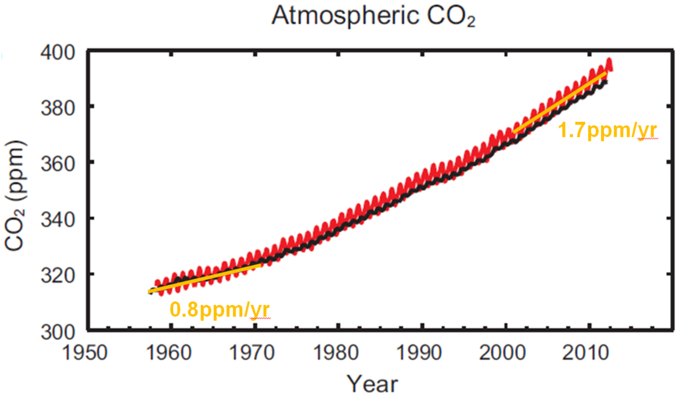
Atmospheric CO_2

- CO_2 concentration increased globally by about 100ppm over the last 250 years $\rightarrow$ human activities
- how can we be sure this increase comes from anthropogenic activities?

One piece of evidence:
$^{13}C/^{12}C$ isotope measurements

Long Term Observations: The Keeling Curve

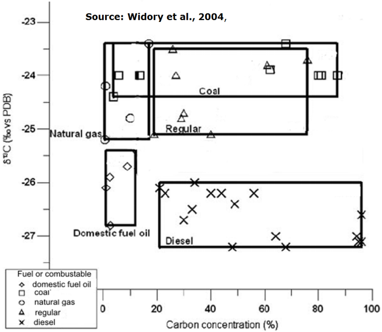
CO_2 concentration at Mauna Loa Observatory



IPCC 2013

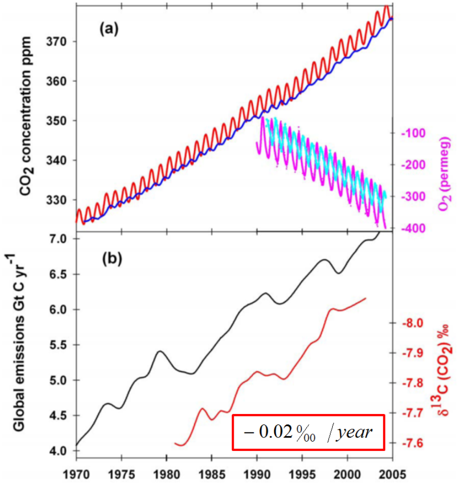
Superimposed Isotopic Fractionation

- Continuous Decrease in δ Value due to Fossil Fuels Combustion
  -0.025 ‰



- Seasonal Variation due to the biospheric carbon
  $\pm$ 0.005‰

Addition of a Stable Isotope Fingerprint to the Collection of Evidence



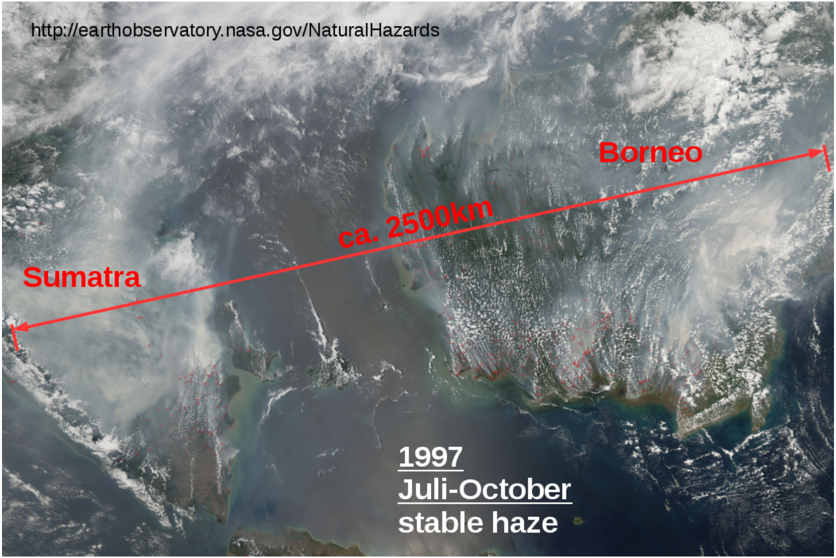
Conclusion:

observed trends are in line with understanding of total emissions from fossil fuel sources and their $\delta^{13}C$

$\rightarrow$ anthropogenic activities

increase atmospheric CO_2

Haze Dome over South-East Asia



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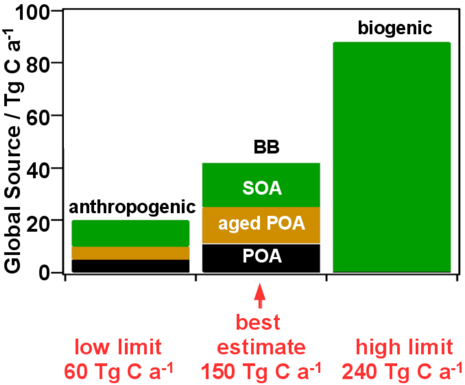
Biomass Burning (BB) Impact on Troposphere

BB: largest source of primary fine carbonaceous particles



Hallquist et al., ACP, 2009

Levoglucosan

the specific molecular marker used in CMB receptor models

- BB unique source
- high emission factors
- stable???

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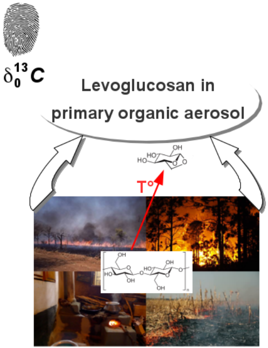
Isotopic 'Hydrocarbon clock'



$$\delta^{13}C = \left(\frac{[^{13}C]_{sampl}/[^{12}C]_{sampl}}{[^{13}C]_{std}/[^{12}C]_{std}} - 1\right) \cdot 1000\,‰$$

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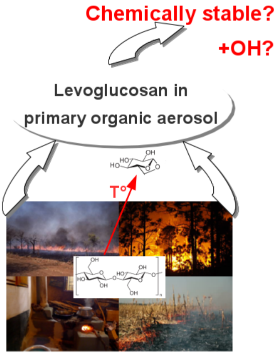
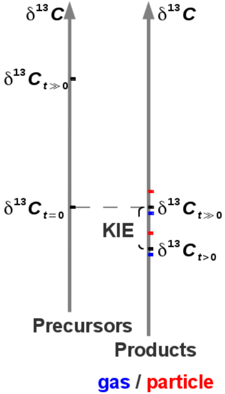


$$KIE = \frac{^{12}k}{^{13}k}$$



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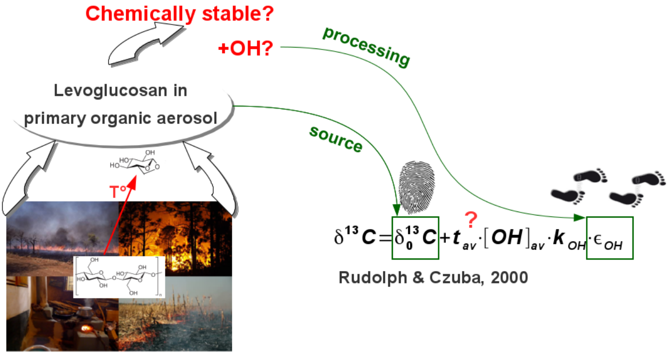


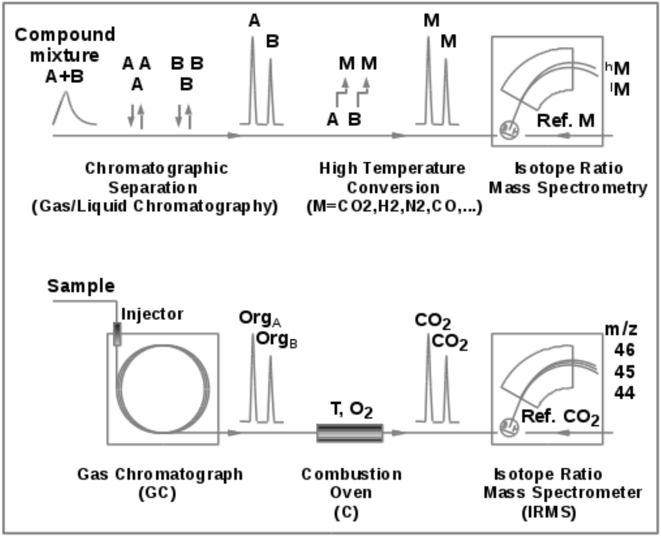
$$\delta^{13}C = \delta_0^{13}C + t_{av} \cdot [OH]_{av} \cdot k_{OH} \cdot \epsilon_{OH}$$

$$\epsilon = (KIE - 1) \cdot 1000 ‰$$

Objectives

- compound specific isotopic measurements of levoglucosan for
  - laboratory samples → kinetic isotope effect (KIE) of the oxidation reaction
  - source/ambient aerosol
- information on origin and pathways of the probed air masses for the ambient samples
- can this analysis give insight into aerosol
  - sources?
  - processing?

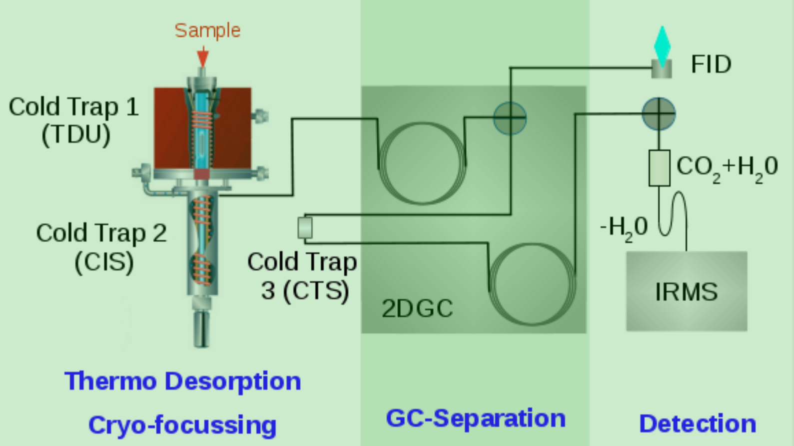
Compound Specific Measurements of Stable Isotopic Composition



Setup for compound specific isotopic analyses of levoglucosan

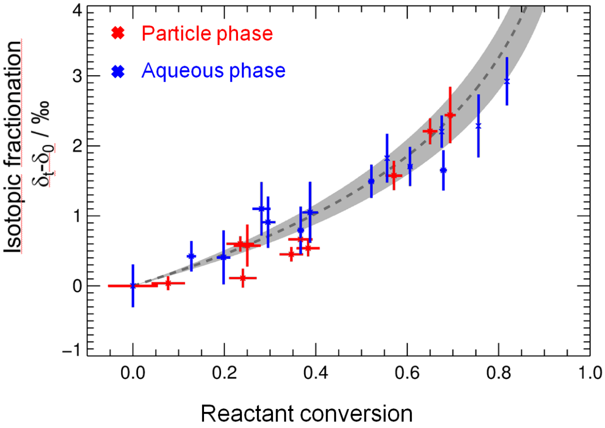
Liquid Extraction / Thermal Desorption 2 Dimension Gas Chromatography

Isotope Ratio Mass Spectrometry LE/TD-2DGC-IRMS



Sang et al., EST, 2012

Levoglucosan isotopic fractionation at different extent of processing



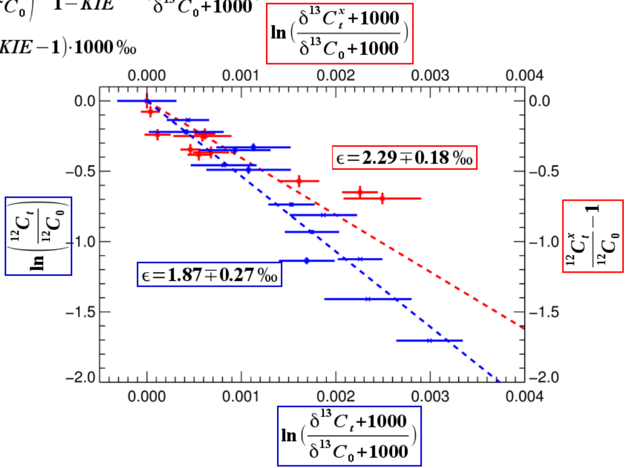
- for both samples δ^{13}C increases with processing
- $\rightarrow$ chemical degradation

Sang et al., GRL, 2016

Deriving KIE from experimental data

$$\ln\left(\frac{^{12}C_t}{^{12}C_0}\right)=\frac{KIE}{1-KIE}\cdot\ln\left(\frac{\delta^{13}C_t+1000}{\delta^{13}C_0+1000}\right)$$

$$\epsilon=(KIE-1)\cdot 1000\,‰$$



similar KIE for levoglucosan oxidation by OH radicals

- aerosol particles
- in aqueous solution

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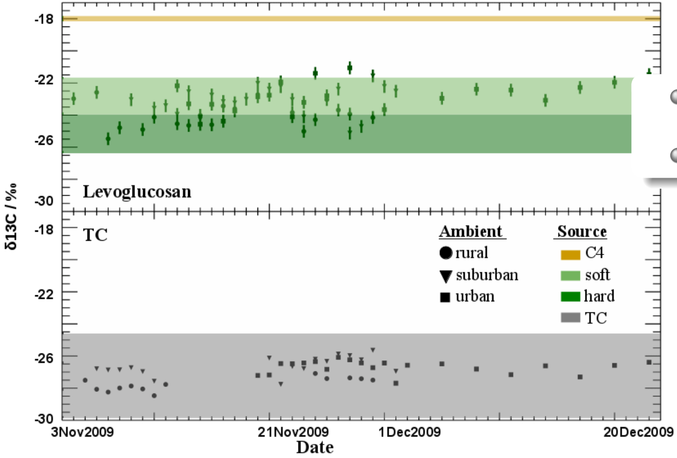
Levoglucosan δ^{13}C in ambient vs. source aerosol



- higher variability for levoglucosan ⇔ TC
- 2 hypotheses???

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Mixing or Aging?

- Mixing?
  - 50% C4 plant contribution
- Aging?

FLEXPART 6.2

- Lagrangian particle dispersion model
- backwards simulations, 3 days $\Leftrightarrow$ lifetime
  - source region
  - pathawys of sampled air parcels
- ECMWF data
  - 1° horizontal resolution
  - 91 vertical levels
  - 1 hour time resolution

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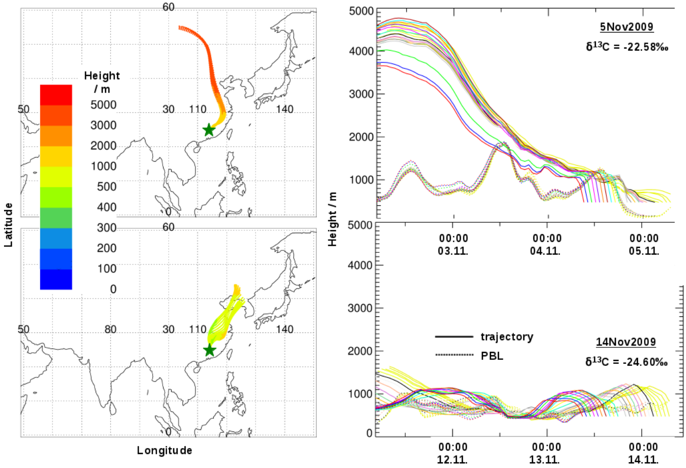
Selected 3-days back trajectories



- NO mixing BUT aging
- t_{av} ⇔ hours above PBL, during day
- t_{av} is 'reduced' by passing PBL 'two-endpoint' mixing
  $c \ll c_{PBL}$
  $V \gg V_{PBL}$

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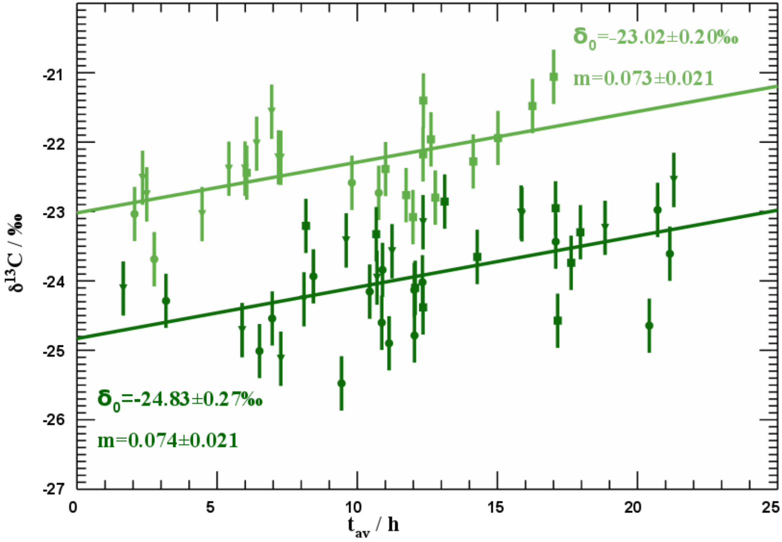
Levoglucosan δ^{13}C in ambient aerosol vs. t_{av} and source regions



What can we learn...?

$\delta = \delta_0 + t_{av} * [OH] * k_{OH} * \varepsilon$

$m = 3600. * [OH] * k_{OH} * \varepsilon$

	Source $\delta^{13}C$ ‰	$\delta_0{}^{13}C$ ‰	[OH] molec cm^{-3}	ε (KIE) ‰
Softwoods	- 22.8 ± 0.99 (Sang et al., EST, 2012)	- 23.02	~3*10^6 ↑ ε = 2.22‰ k_{OH} = 2.66*10^{-12} molec cm^{-3} s^{-1} (Sang et al., GRL, 2016)	(ε_{pred} = 2.77-5.77 Rudolph, 2007) ε = 2.43-7.31 ↑ [OH] = 1 - 3*10^6 molec cm^{-3}
Hardwoods & grasses	- 24.8 ± 1.45	- 24.83		

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Conclusions

- compound specific isotopic measurements of levoglucosan for laboratory samples and source/ambient aerosol
- information on origin and pathways of the probed air masses
- can this analysis give insight into aerosol sources and processing?

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LE/TD-2DGC-IRMS

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derive kinetic information on levoglucosan chemical degradation

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30 h free tropospere ⇔ up to 70% degradation