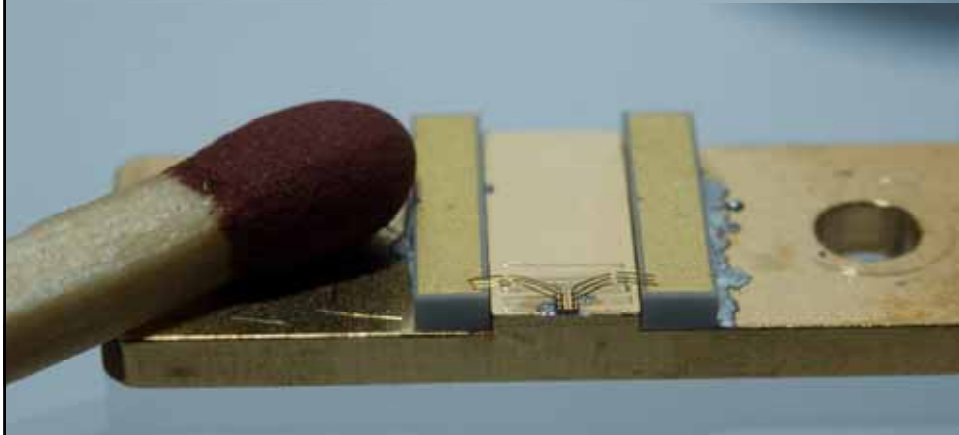


# High precision isotope ratio analysis of CO<sub>2</sub> and N<sub>2</sub>O using quantum cascade laser absorption spectroscopy



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## Far-field measurements @ empa



NABEL



GAW  
WCC CO, O<sub>3</sub>, CH<sub>4</sub>



AGAGE  
Advanced Global Atmospheric Gases Experiment

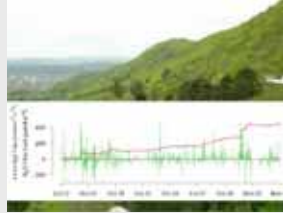
ICCLSW, Sept. 2008; EMM



## Near-field measurements @ empa



Neftel et al. Tellus B (2007)



Eugster et al. BGS (2007)



Mohn et al. Biore. Techn. (2007)



Hugener et al. JESH (2008)



Mohn et al. JMS (2005)



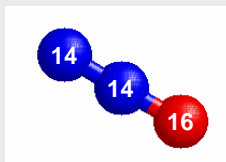
Heeb et al. EST (2008)

IOCLSW, Sept. 2008, EMM



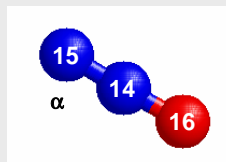
## N<sub>2</sub>O isotopomers

446



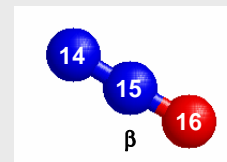
0.99

546



0.0036  
natural abundance

456



0.0036

$$\delta^{15}\text{N}^\alpha = \left( \frac{^{15}\text{N}^\alpha, \text{s} / ^{14}\text{N}, \text{s}}{^{15}\text{N}^\alpha, \text{ref} / ^{14}\text{N}, \text{ref}} - 1 \right) \cdot 1000\text{‰}$$

$$\text{SP} = \delta^{15}\text{N}^\alpha - \delta^{15}\text{N}^\beta$$

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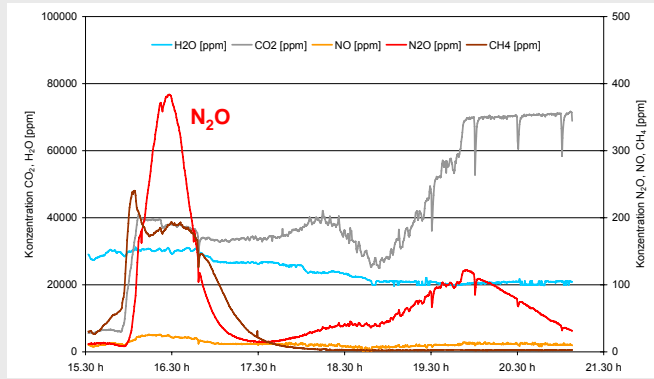


## N<sub>2</sub>O site preference during (de)nitrification



Sutka, A&EM, 2006

Nitrification **SP ~ 33 ‰**  
 $\text{NH}_3 \rightarrow \text{NO}_3^-$   
 Denitrification **SP ~ 0 ‰**  
 $\text{NO}_3^- \rightarrow \text{N}_2$   
 Anammox  
 $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

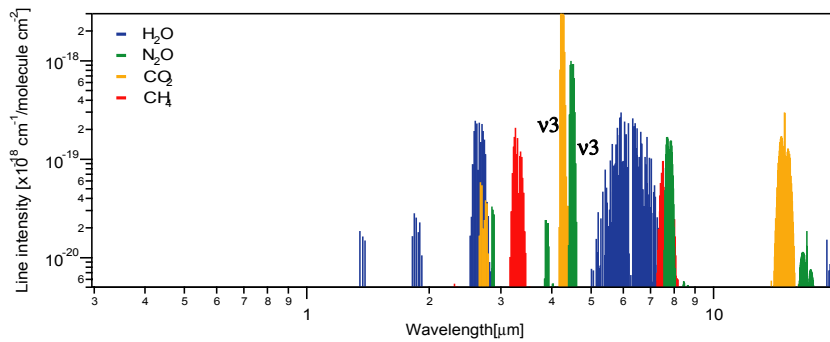


IOCLSW; Set

Salzgeber, Emmenegger et al. Water Res, submitted

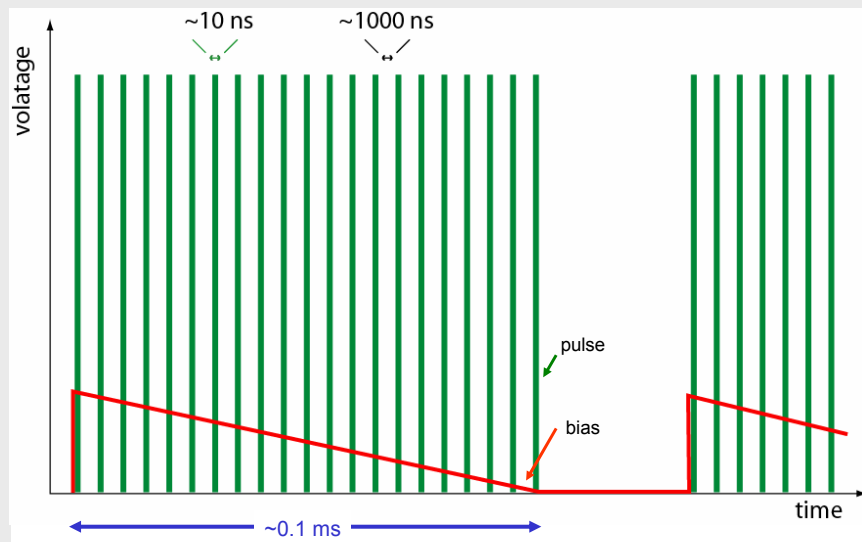


## Line intensities in the infrared



IOCLSW; Sept. 2008; EMM

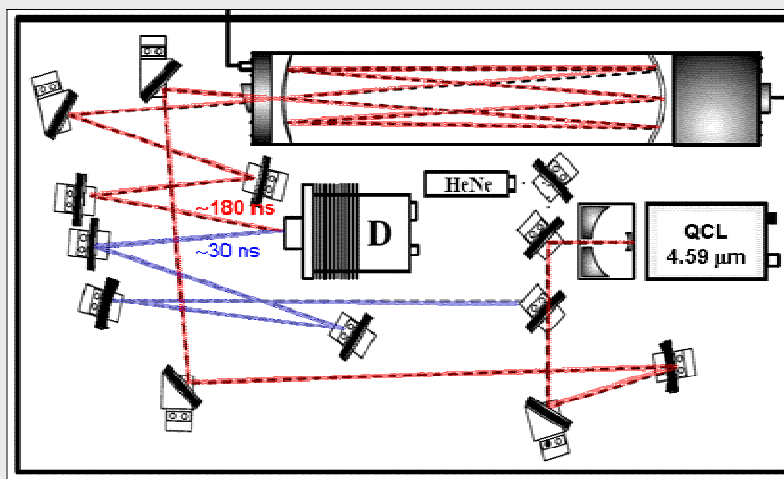
## Measurement of spectra @ 10 kHz



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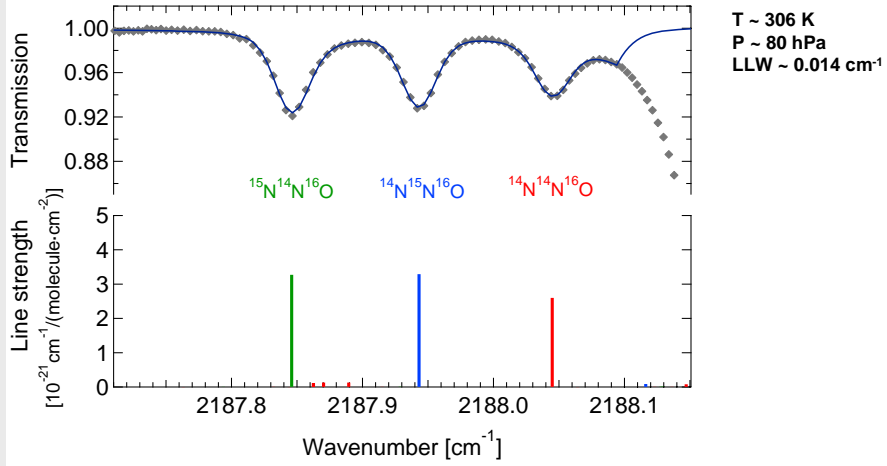
## Pulse normalization



ICCLSW, Sept. 2008, EMM

Tuzson et al. Infrared Phys. Techn. (2007)  
EMPA  
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## Absorption spectrum measured with QCLAS

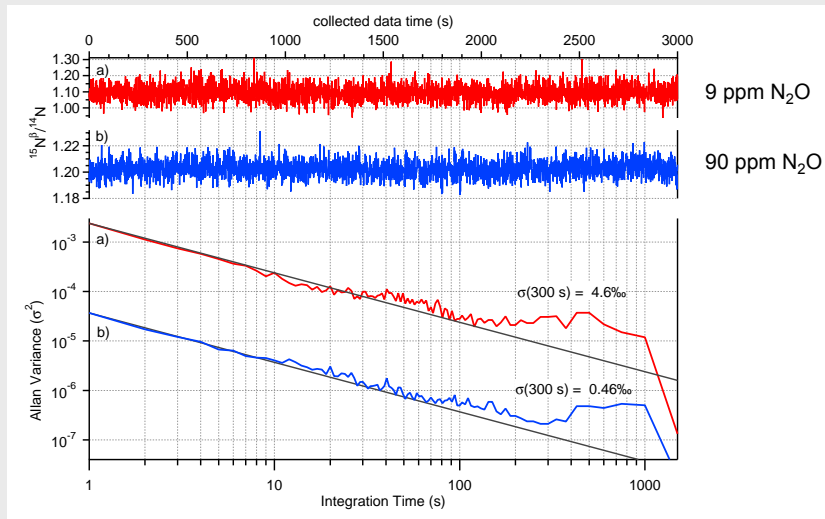


Wächter et al. Optics Express (2008)

IQCLSW, Sept. 2008; EMM



## Allan variance

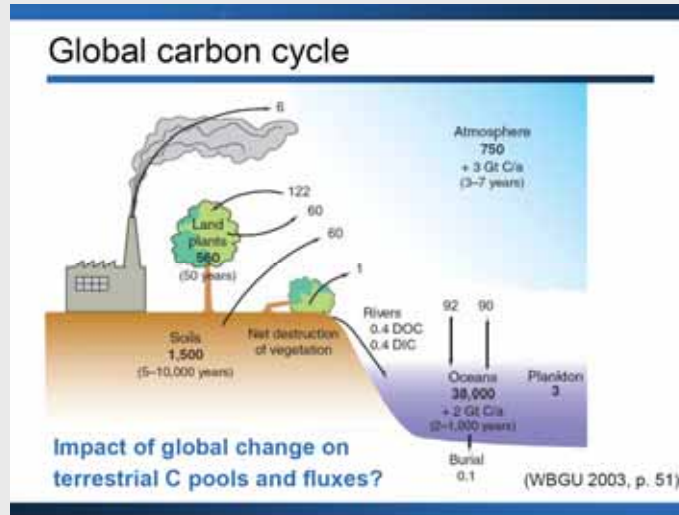


Wächter et al. Optics Express (2008)

IQCLSW, Sept. 2008; EMM



## Understanding the global carbon cycle

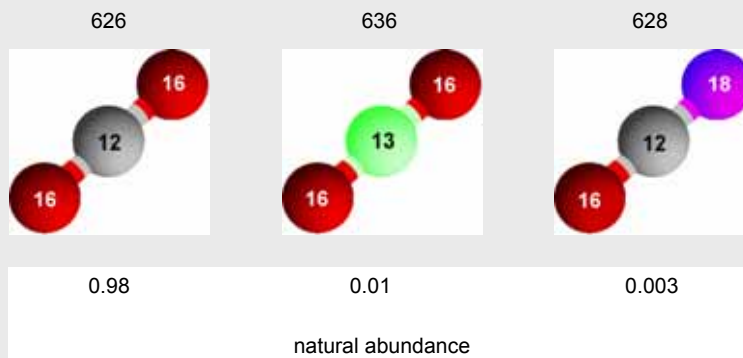


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## CO<sub>2</sub> isotopologues

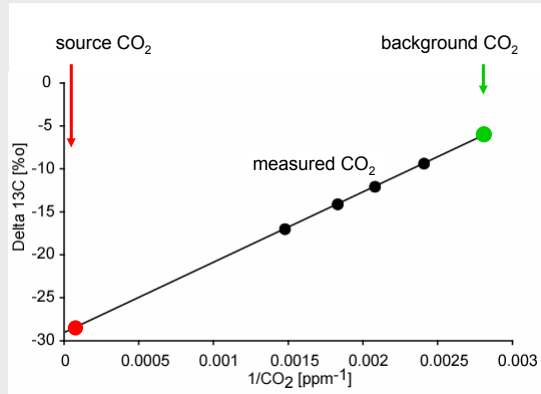
$$\delta^{13}\text{C} = \left( \frac{\alpha_{13,s} / \alpha_{12,s}}{\alpha_{13,\text{ref}} / \alpha_{12,\text{ref}}} - 1 \right) \cdot 1000\text{‰}$$



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## Keeling Plot



$$C_a = C_b + C_s \quad (1)$$

$$\delta^{13}C_a * C_a = \delta^{13}C_b * C_b + \delta^{13}C_s * C_s \quad (2)$$

$$\delta^{13}C_a = C_b (\delta^{13}C_b - \delta^{13}C_s) * (1/C_a) + \delta^{13}C_s \quad (3)$$

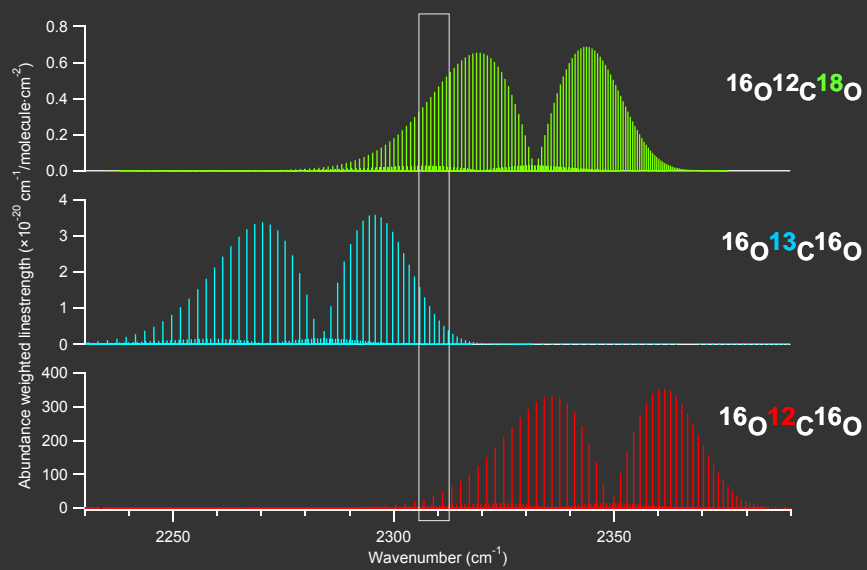
$$y = \frac{m}{x} + b$$

C. D. Keeling, 1958

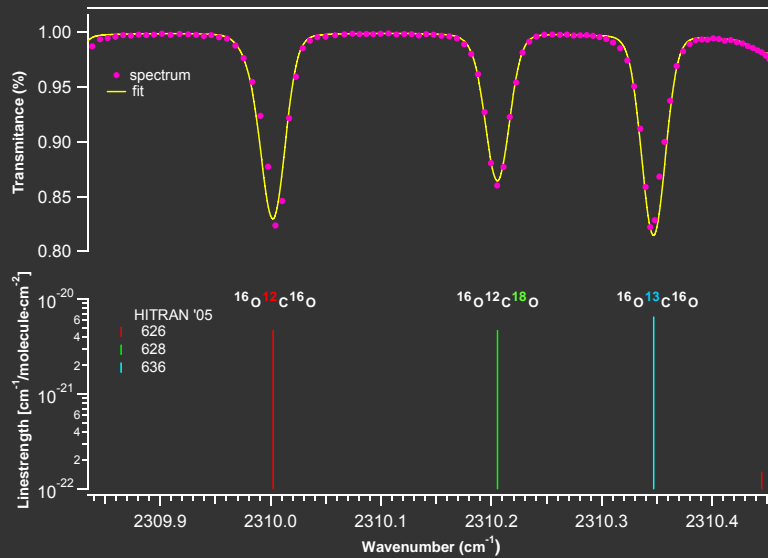
IOCLSW, Sept. 2008, EMM

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## Choice of spectral window



## Measurement and simulation



Infr. Phys. & Techn. (2008)

## Temperature dependence

$$I(\nu) = I_0(\nu) \cdot e^{-\alpha(\nu)LPC}$$

$$\alpha(\nu) = N \cdot S(T) \cdot g(\nu, \nu_0, T, P)$$

$$S(T) = S(T_0) \frac{T_0}{T} \exp\left[\frac{E''}{kT_0} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

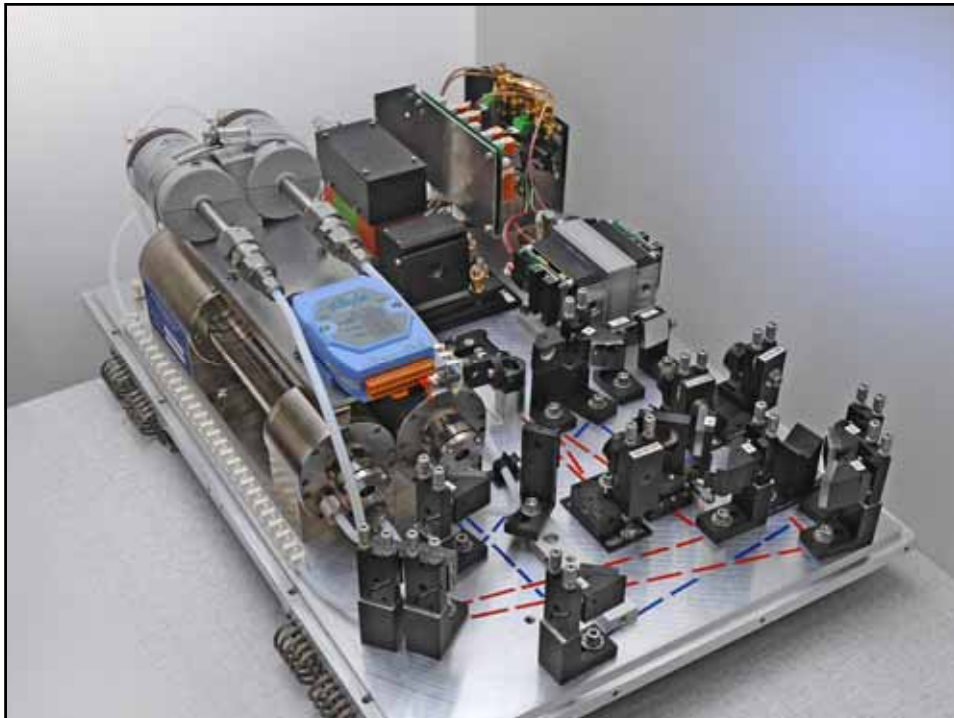
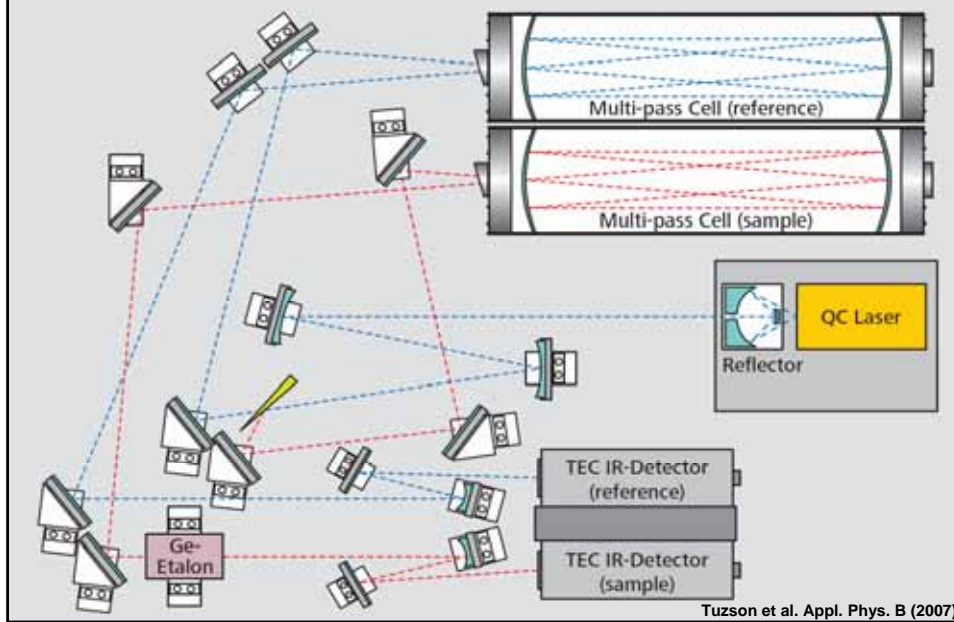
$$\Delta\delta = \frac{\Delta E''}{kT^2} \cdot \Delta T = 0.01\% \text{ mK}^{-1}$$

I: Light Intensity  
 $\nu$ : wavelength  
 $\alpha$ : absorption coeff.  
 LPC: pathlength, pressure, concentration  
 $g$ : line profile function  
 $N$ : number of molecules  
 $T_0$ : 296 K (Hitran)  
 $S$ : line strength  
 $E''$ : lower state energy  
 $k$ : Boltzmann

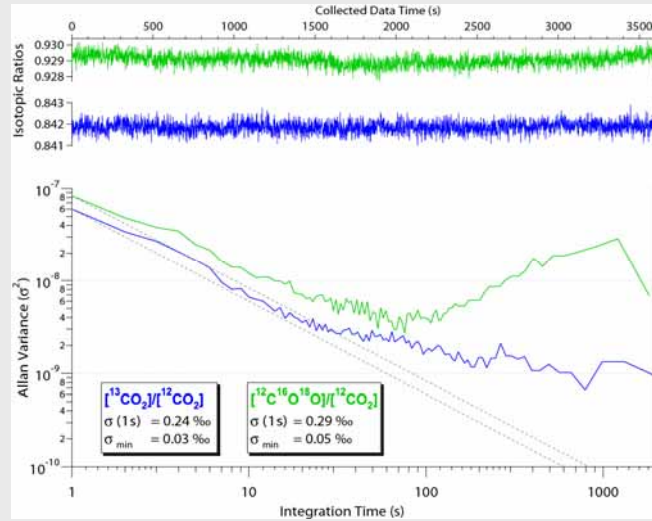
IQCLSW, Sept. 2008; EMM



## Optical layout for CO<sub>2</sub> isotopologues



## Instrument for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in $\text{CO}_2$

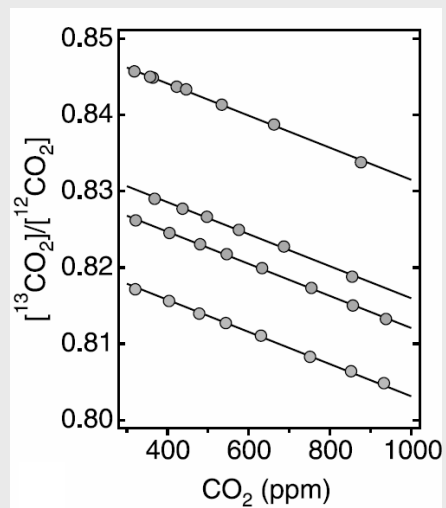
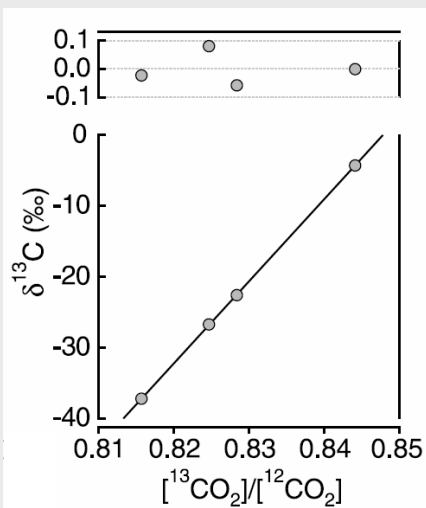


Tuzson et al. Appl. Phys. B (2007)



ICLWS, Sept. 2008, EMM

## Calibration procedure

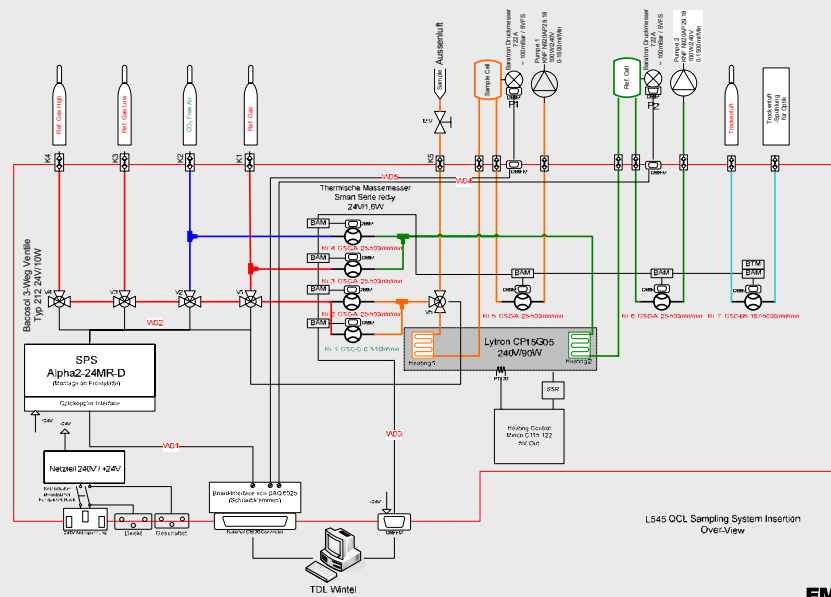


ICLWS, Sept. 2008, EMM

Tuzson et al. Appl. Phys. B (2007)



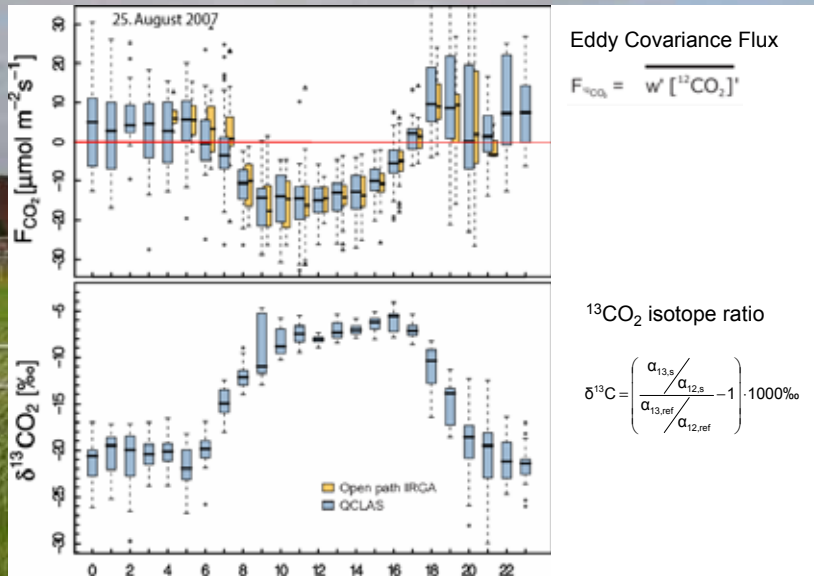
# Sampling system



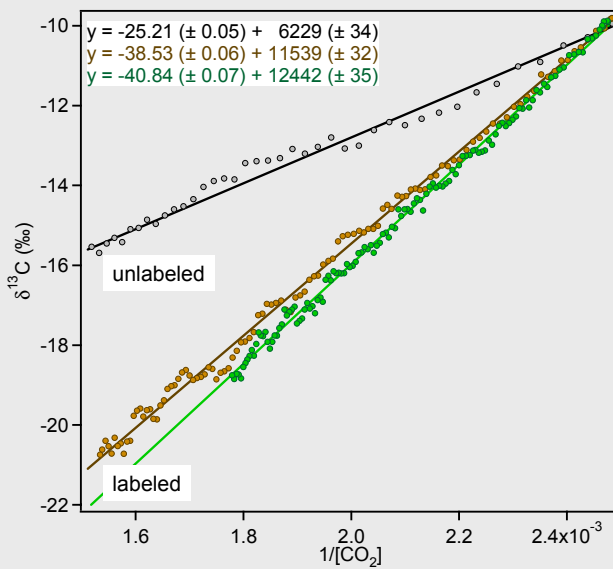
IQCLSW; Sept. 2008; EMM



## Field measurements



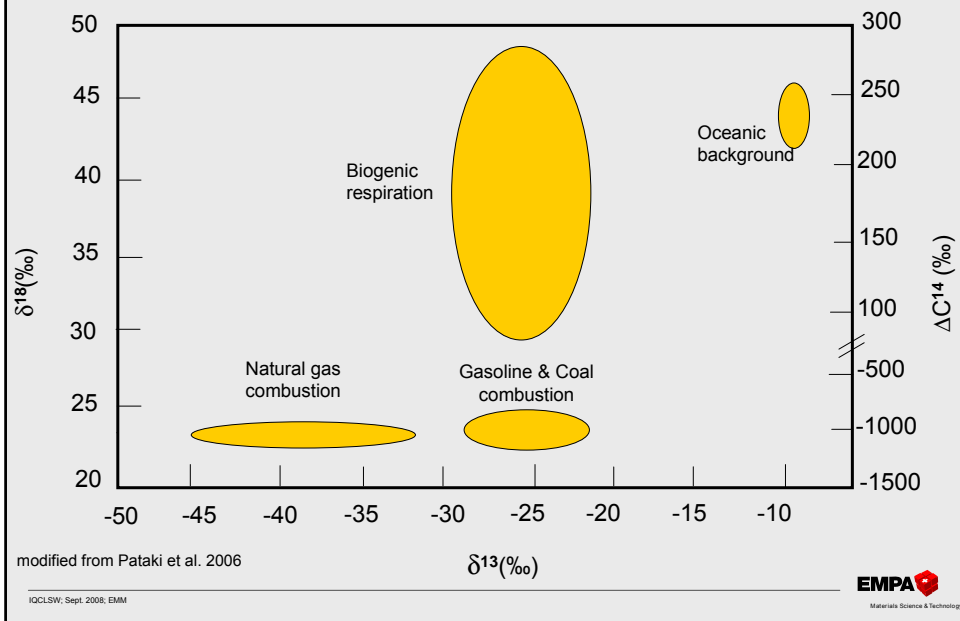
## Forest soil respiration



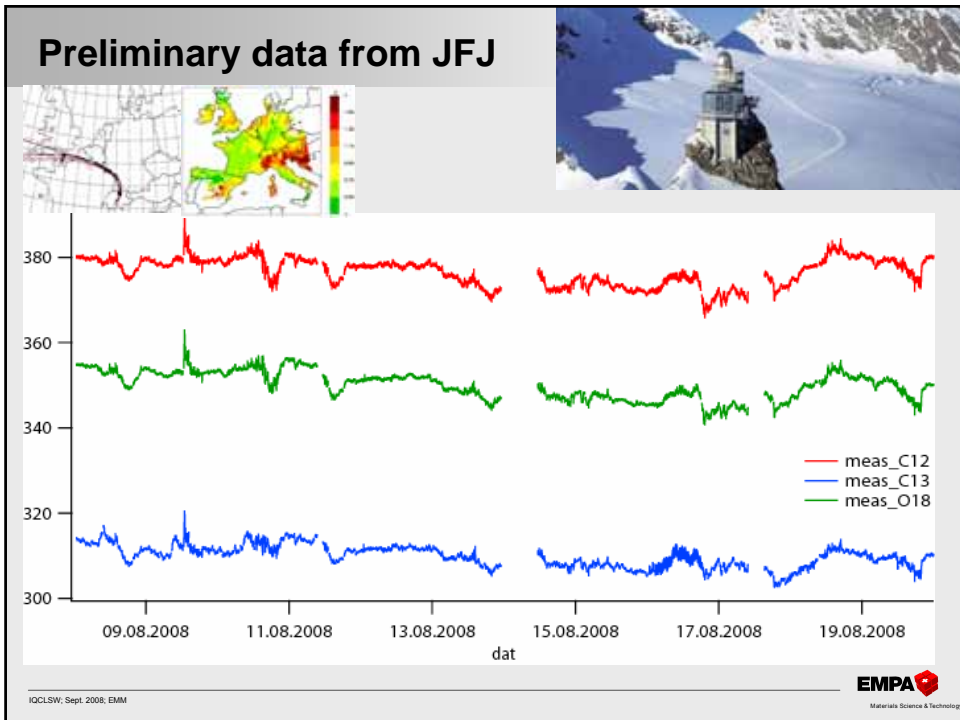
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## Source signatures



## Preliminary data from JFJ



# Acknowledgements

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