

Stable isotopes in hydrology and ecology

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Most important isotopes in biogeochemistry

1.01																	4.00																		
H																	He																		
6.94	3	9.01	4																	20.18	18														
Li		Be																	Ne																
22.99	11	24.30	12																	39.95	17														
Na		Mg																	Ar																
39.10	19	40.08	20	44.96	21	47.90	22	50.94	23	51.99	24	54.94	25	55.85	26	58.93	27	58.71	28	63.55	29	65.37	30	69.72	31	72.59	32	74.92	33	78.96	34	79.90	35	83.80	36
K		Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																	
85.47	37	87.62	38	88.91	39	91.22	40	92.91	41	95.94	42	98.91	43	101.07	44	102.91	45	106.40	46	107.87	47	112.40	48	114.82	49	118.69	50	121.75	51	127.60	52	126.90	53	131.30	54
Rb		Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																	
132.91	55	137.34	56		178.49	72	180.95	73	183.85	74	186.20	75	190.20	76	192.22	77	195.09	78	196.97	79	200.59	80	204.37	81	207.20	82	208.98	83	210*	84	210*	85	222*	86	
Cs		Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																	
223*	87	226.03	88		260*	104		105		106		107		108		109																			
Fr		Ra	Ac-Lw	Rf	Db	Sg	Bh	Hs	Mt																										

138.91	57	140.12	58	140.91	59	144.24	60	147*	61	150.35	62	151.96	63	157.25	64	158.93	65	162.50	66	164.93	67	167.26	68	168.93	69	173.04	70	174.97	71
La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
227*	89	232.04	90	231.04	91	238.03	92	237.05	93	239*	94	243*	95	247*	96	249*	97	251*	98	254*	99	257*	100	256*	101	254*	102	257*	103
Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lw	

H	¹ H	99.985%
	² H	0.015%
	³ H	(radioactive)

C	^{12}C	99.89%
	^{13}C	0.11%
	^{14}C	(radioactive)

N	^{14}N	99.634%
	^{15}N	0.366%

O	¹⁶ O	99.759%
	¹⁷ O	0.037%
	¹⁸ O	0.204%

S	³² S	95.00%
	³³ S	0.76%
	³⁴ S	4.22%
	³⁶ S	0.014%

Standards and δ notation

H	VSMOW Vienna Standard Mean Ocean Water	$^2\text{H} = 0.01558\%$
C	PDB Pee Dee Belemnite	$^{13}\text{C} = 1.12372\%$
N	air	$^{15}\text{N} = 0.3663\%$
O	VSMOW Vienna Standard Mean Ocean Water	$^{18}\text{O} = 0.20052\%$

attention: 2 definitions coexist, either on isotope ratio R or on isotope fraction F

$$\delta^{15}\text{N} = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \quad \text{where: } R = \frac{^{15}\text{N}}{^{14}\text{N}} \quad R_{\text{standard}} = 0.0036765$$

$$\delta^{15}\text{N} = \frac{F_{\text{sample}}}{F_{\text{standard}}} - 1 \quad \text{where: } F = \frac{^{15}\text{N}}{^{14}\text{N} + ^{15}\text{N}} \quad F_{\text{standard}} = 0.003663$$

δ usually expressed in ‰

Three main types of applications

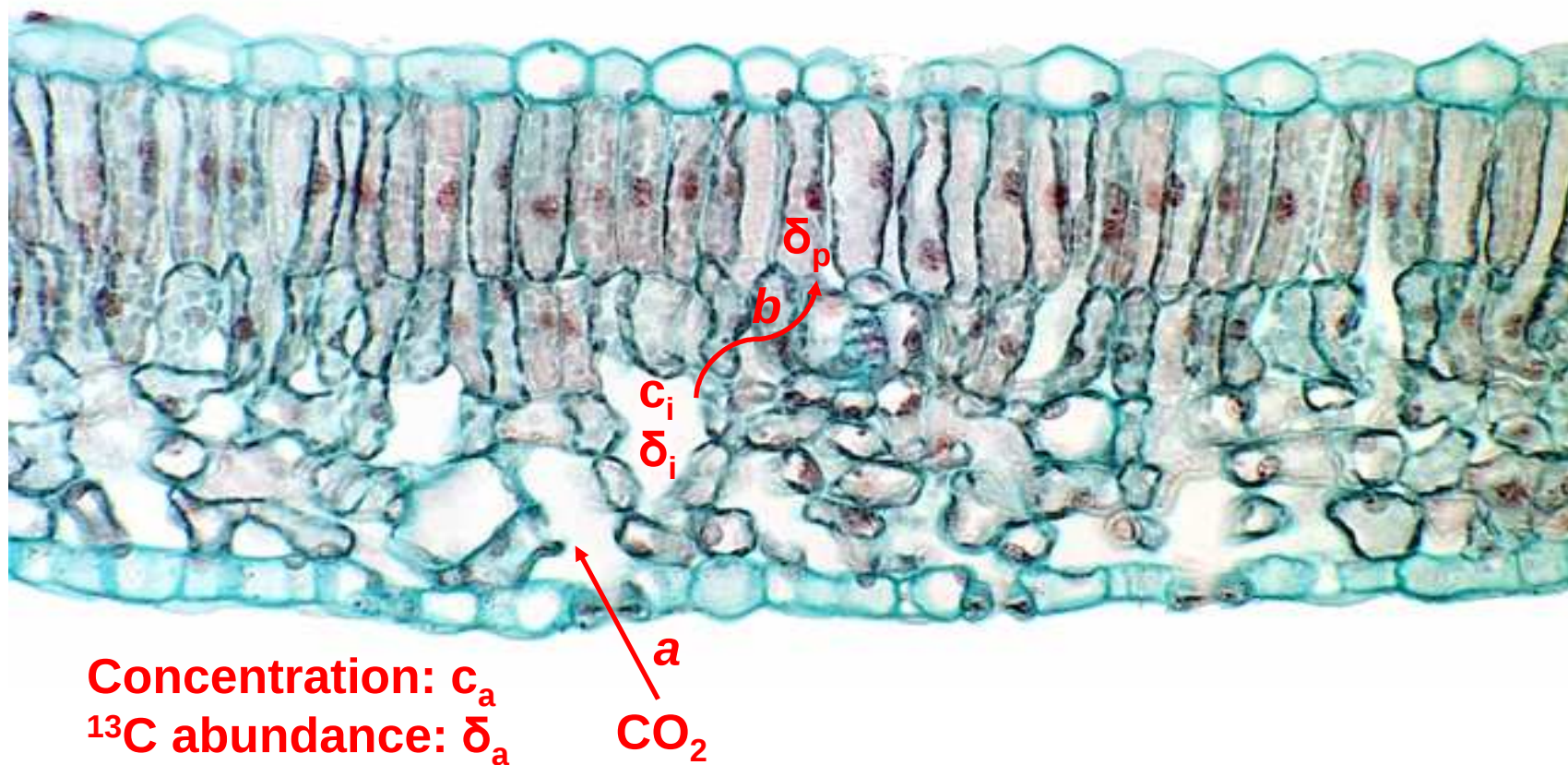
- **Process studies through natural isotope fractionation**

fractionation: differential behaviour between isotopes in (bio-)chemical or physical processes => abundance in product $\neq$ substrate
(only in open systems with branched reaction pathways)

- **Tracing of natural sources with contrasting abundances**

- **Experimental labelling and tracing**

Example 1: C fractionation during C3 photosynthesis



Photograph: Michael Clayton

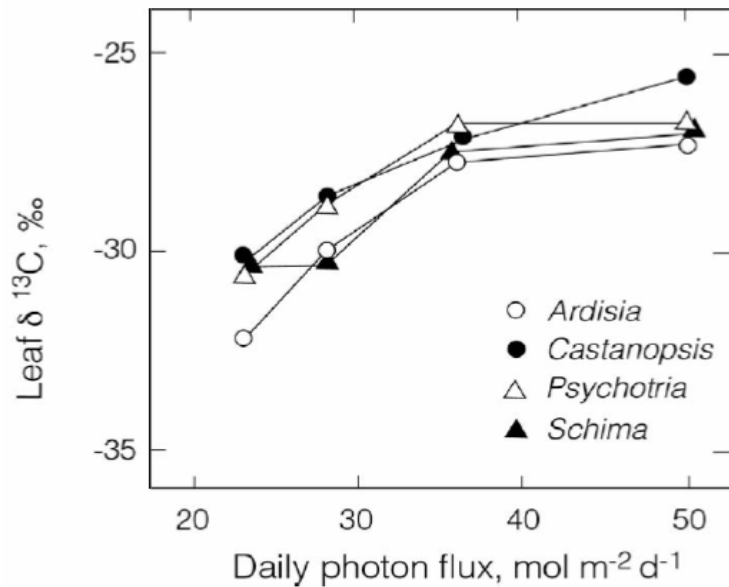
a: diffusion => physical fractionation $\approx 4.4\text{‰}$

b: Rubisco => enzymatic fractionation $\approx 27\text{‰}$

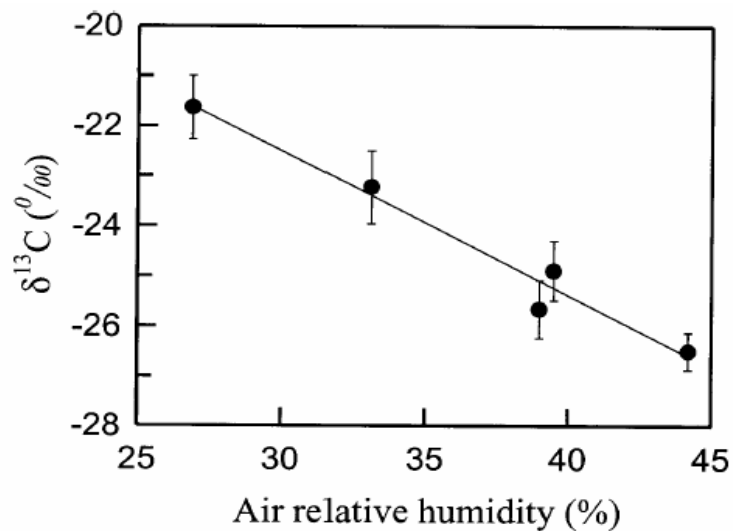
$$\Delta = \delta_a - \delta_p = a + (b-a) c_i / c_a$$

active photosynthesis + stomatal closure => $c_i \downarrow \Rightarrow \Delta \downarrow \Rightarrow \delta_p \uparrow$

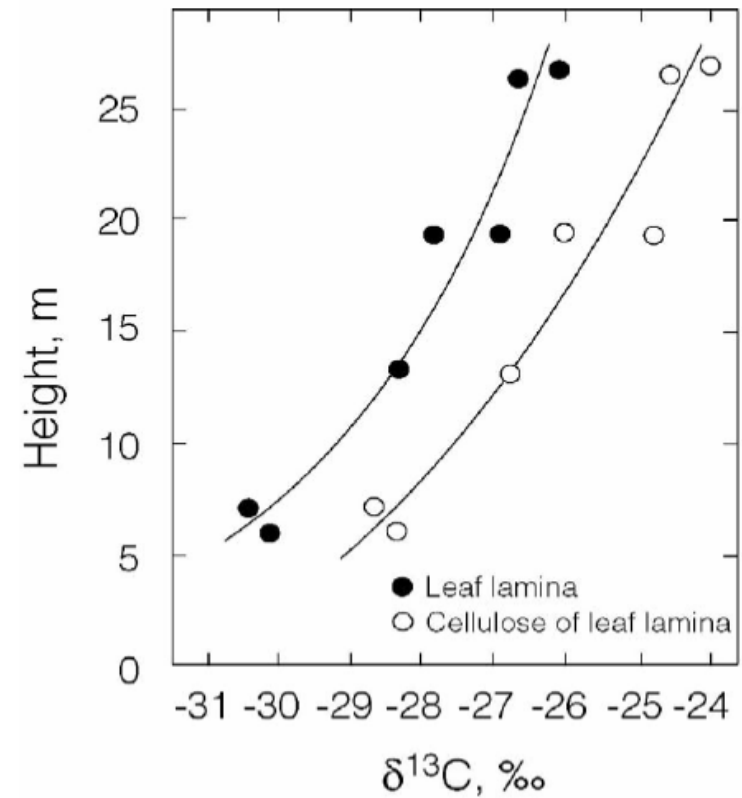
Example 1: C fractionation in C3 plants



Ehleringer *et al.*, 1986:
 ^{13}C in leaves vs. light intensity

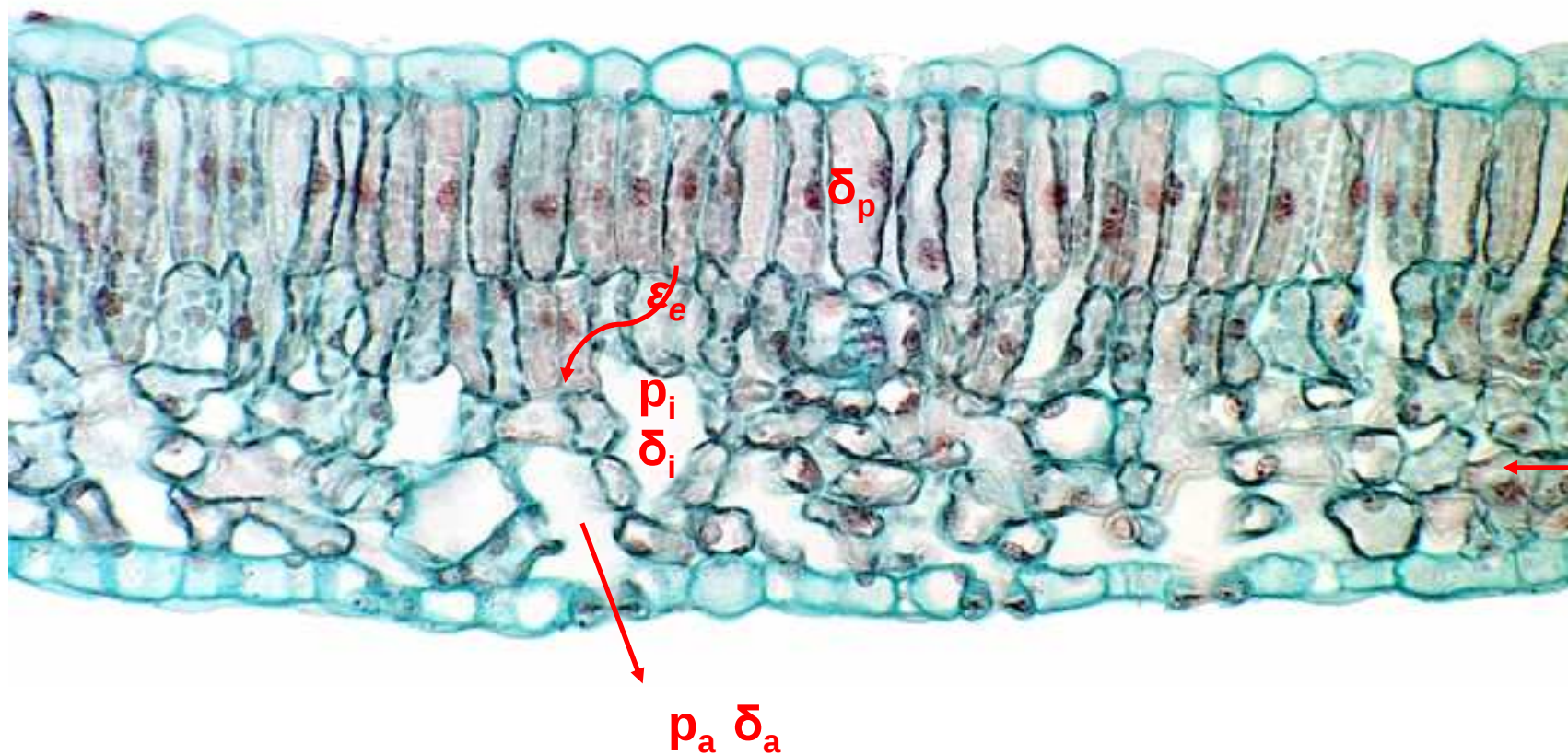


Ekblad & Högberg, 2001:
forest soil respiration vs. air humidity 1-4 days before



Leavitt & Long, 1982: ^{13}C in leaves vs. tree height

Example 2: O fractionation during transpiration



Photograph: Michael Clayton

δ_s
 H_2O

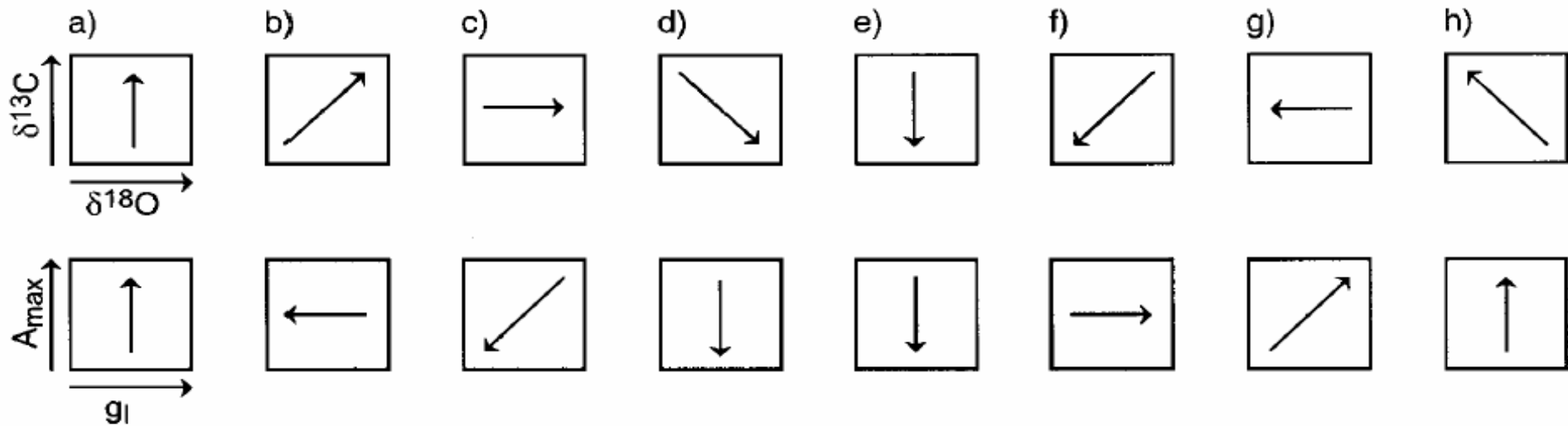
δ_s : abundance in xylem sap = in the soil (no fractionation)

ϵ_e : evaporation $\Rightarrow$ equilibrium fractionation

ϵ_k : diffusion to free atmosphere $\Rightarrow$ kinetic fractionation

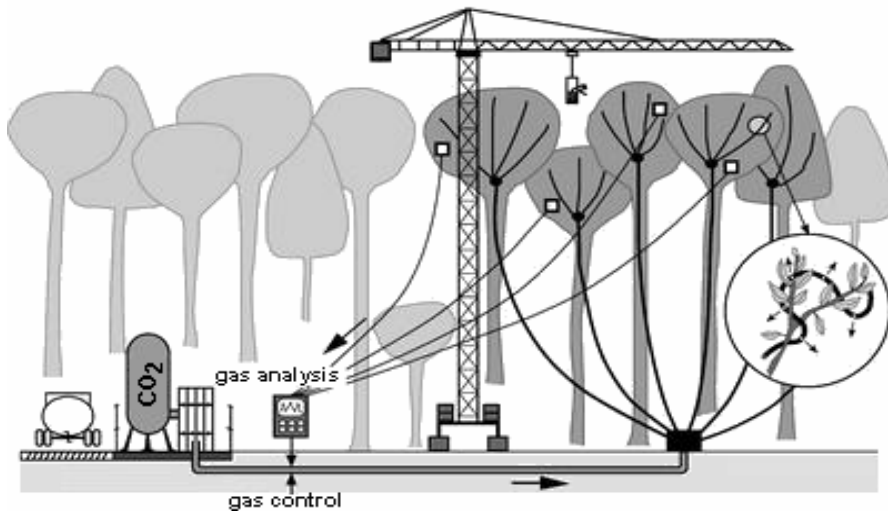
Examples 1+2: combining ^{13}C and ^{18}O

2 unknown variables: photosynthesis $A_{\max}$ and stomatal conductance g_l
=> 2 independent measures necessary: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in leaves



Scheidegger *et al.*, 2000

Tracing of sources with naturally contrasting abundances: the Swiss canopy crane experiment



CO₂ enrichment in tree crowns

CO₂ originates from fossil fuel and is naturally depleted in ¹³C

Tracing of sources with naturally contrasting abundances

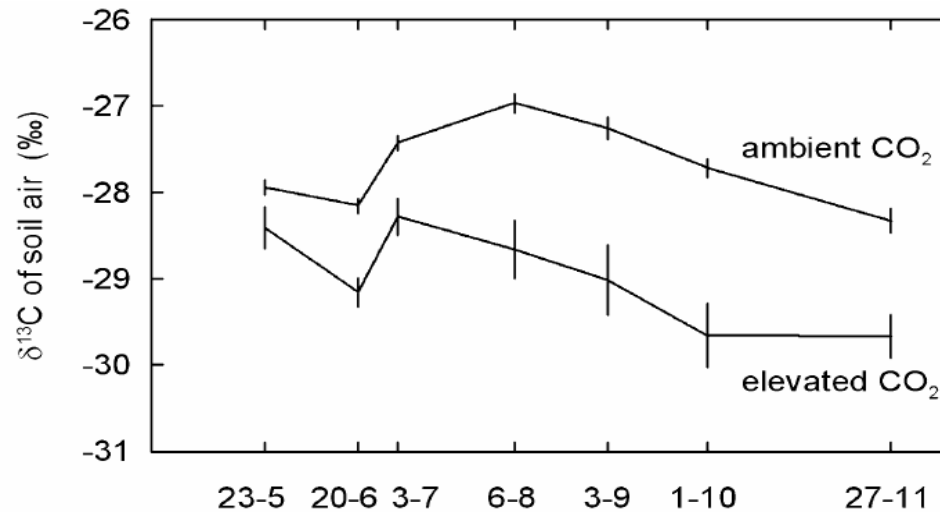
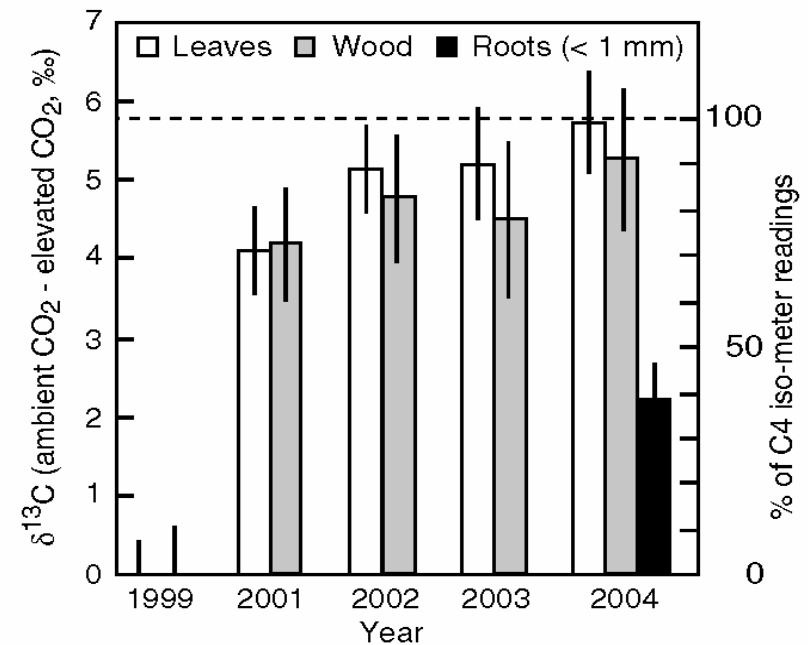
C goes from ^{13}C -depleted

CO_2 to...

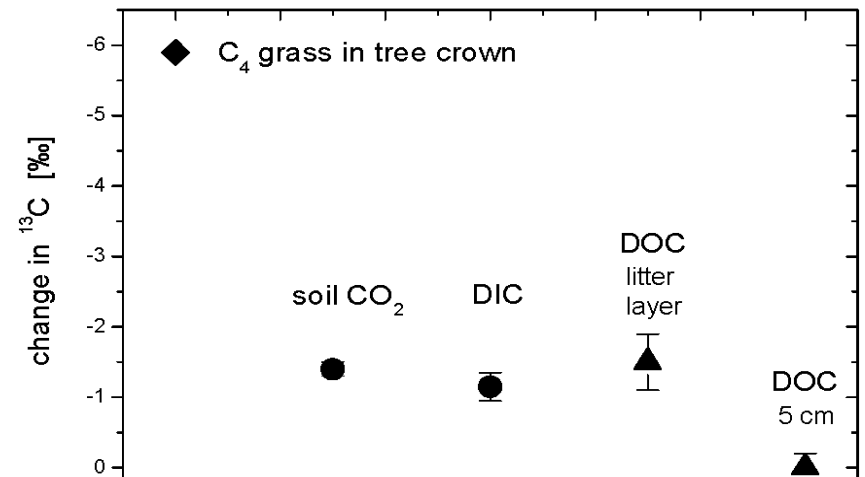
trees...

and soil

Körner
et al.,
2005



Steinmann *et al.*, 2004

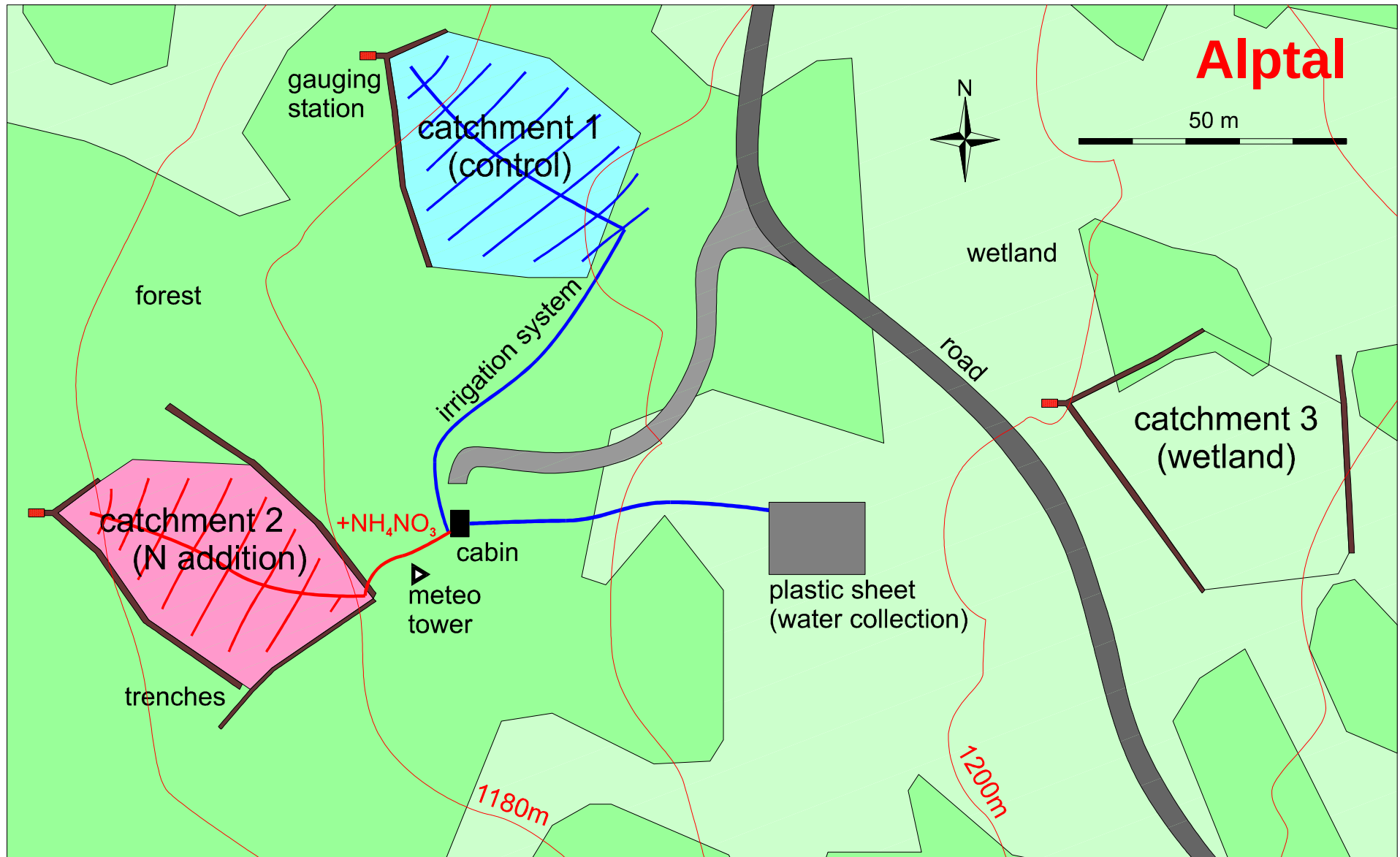




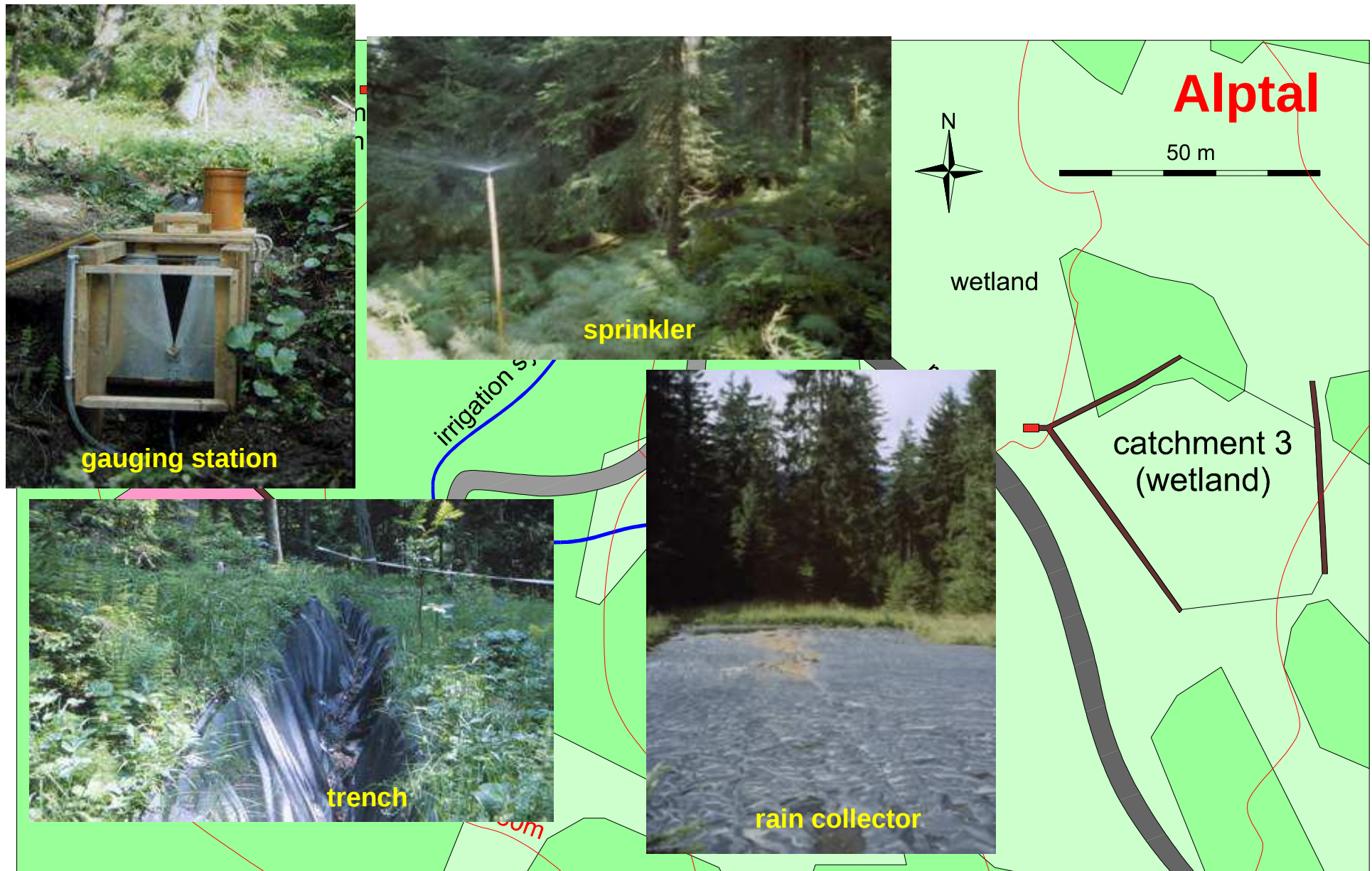
Isotopes are powerful tracers
... even if labelling water at
Pass Lunghin* will not allow to
detect the signal in the Danube
in Vienna

*where the basins of Black Sea
(Danube), North Sea (Rhine) and
Mediterranean (Po) come together

Experimental tracer application: NITREX experiments

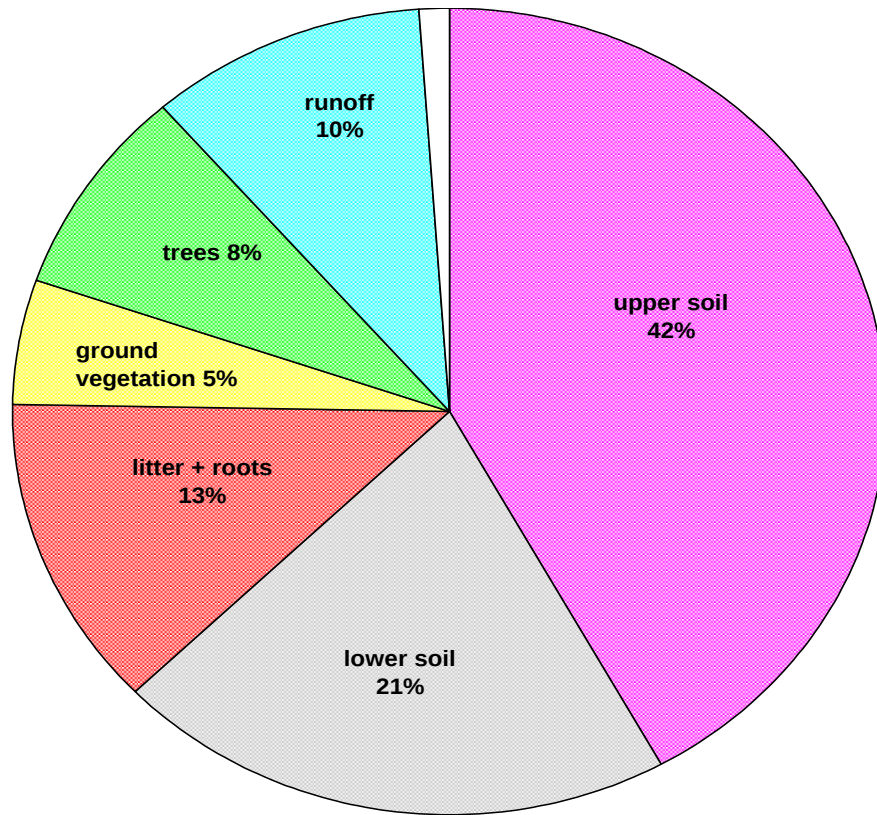


Experimental tracer application: NITREX experiments



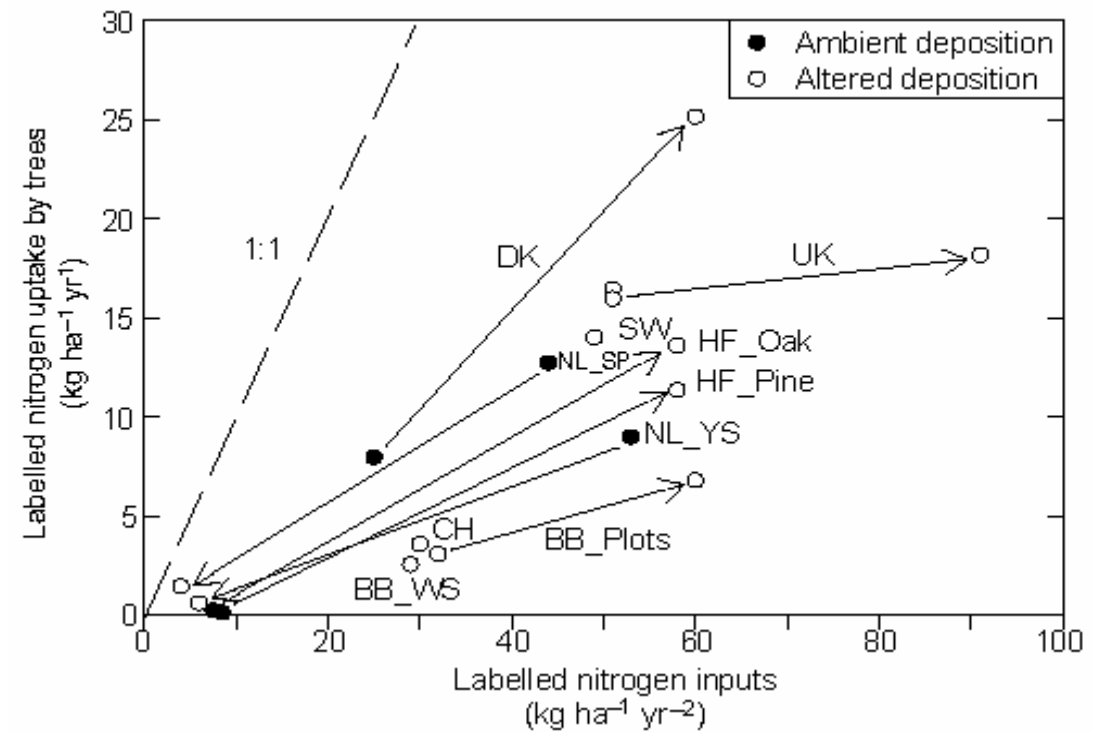
Experimental tracer application: NITREX experiments

Alptal: partitioning of ^{15}N after 1 year



Schleppi *et al.*, 1999

EU and US sites: uptake by trees



Nadelhoffer *et al.*, 1999

Isotope analysis 1: mass spectrometry

- Laboratory
- All kinds of samples: solid, liquid or gas; organic or mineral
- Costly (from 500 k€ on)
- Requires a qualified technician



Isotope analysis 2: laser absorption spectroscopy

- Also for field applications
- For liquid or gas samples, for relatively abundant elements
- E.g. $^{13}\text{CO}_2$, H_2^{18}O
- Relatively cheap (from 20 k€ on)

