



Théories Isotopiques



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MISTRAMO, 27-30 mars 2017; Sèvres, France

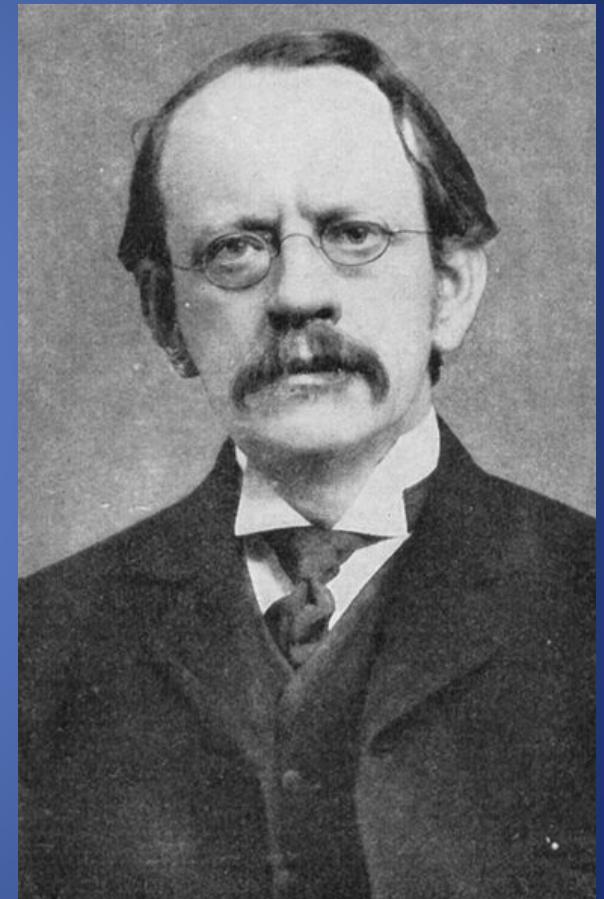
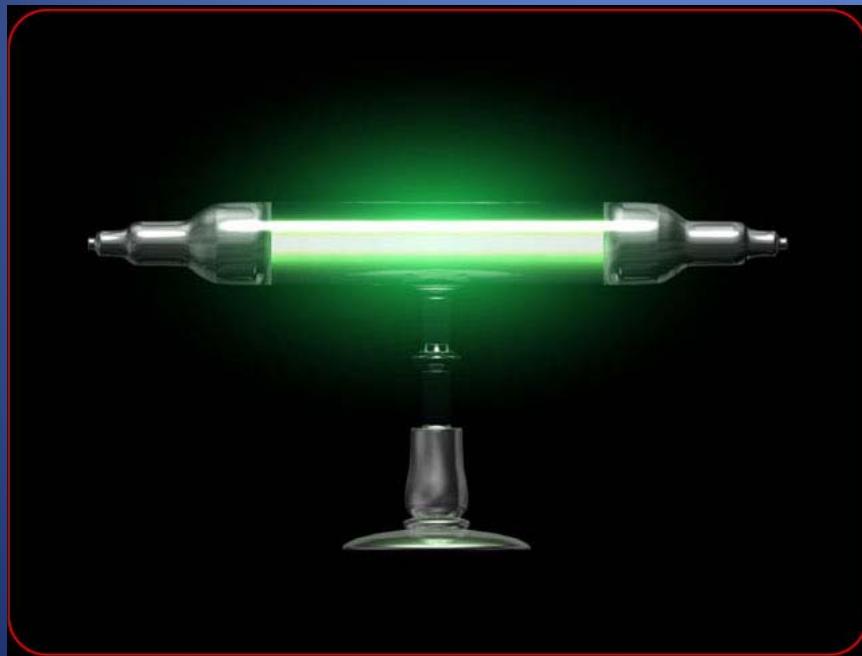


Théories Isotopiques

- Historique
- De nos jour
- Théorie et distribution
- Calculs et exemple

Sir Joseph John Thompson (1856-1940)

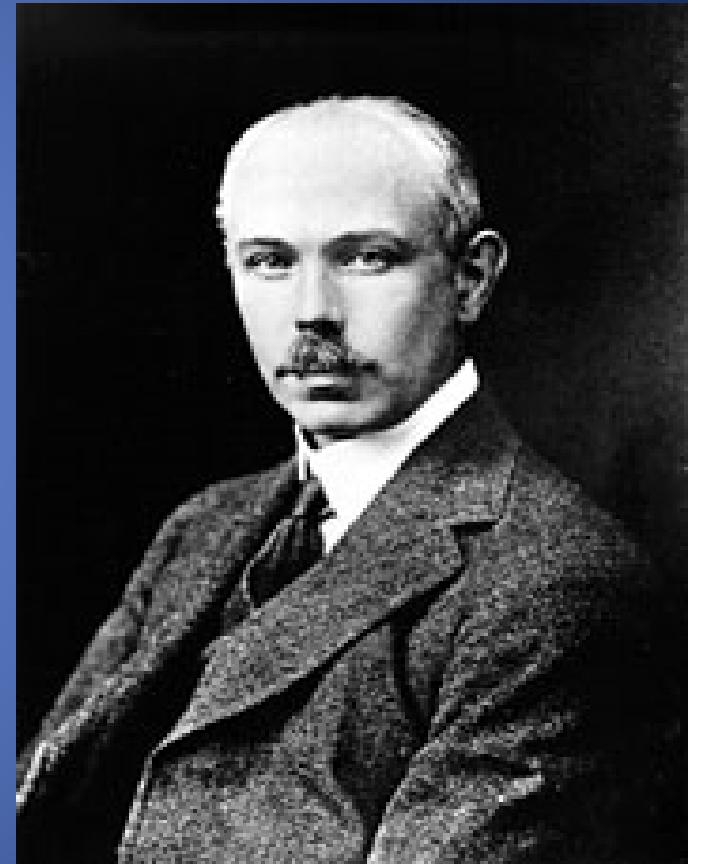
- Physicien Britannique
- Lauréat du prix Nobel pour la découverte des "corpuscles" (électrons)



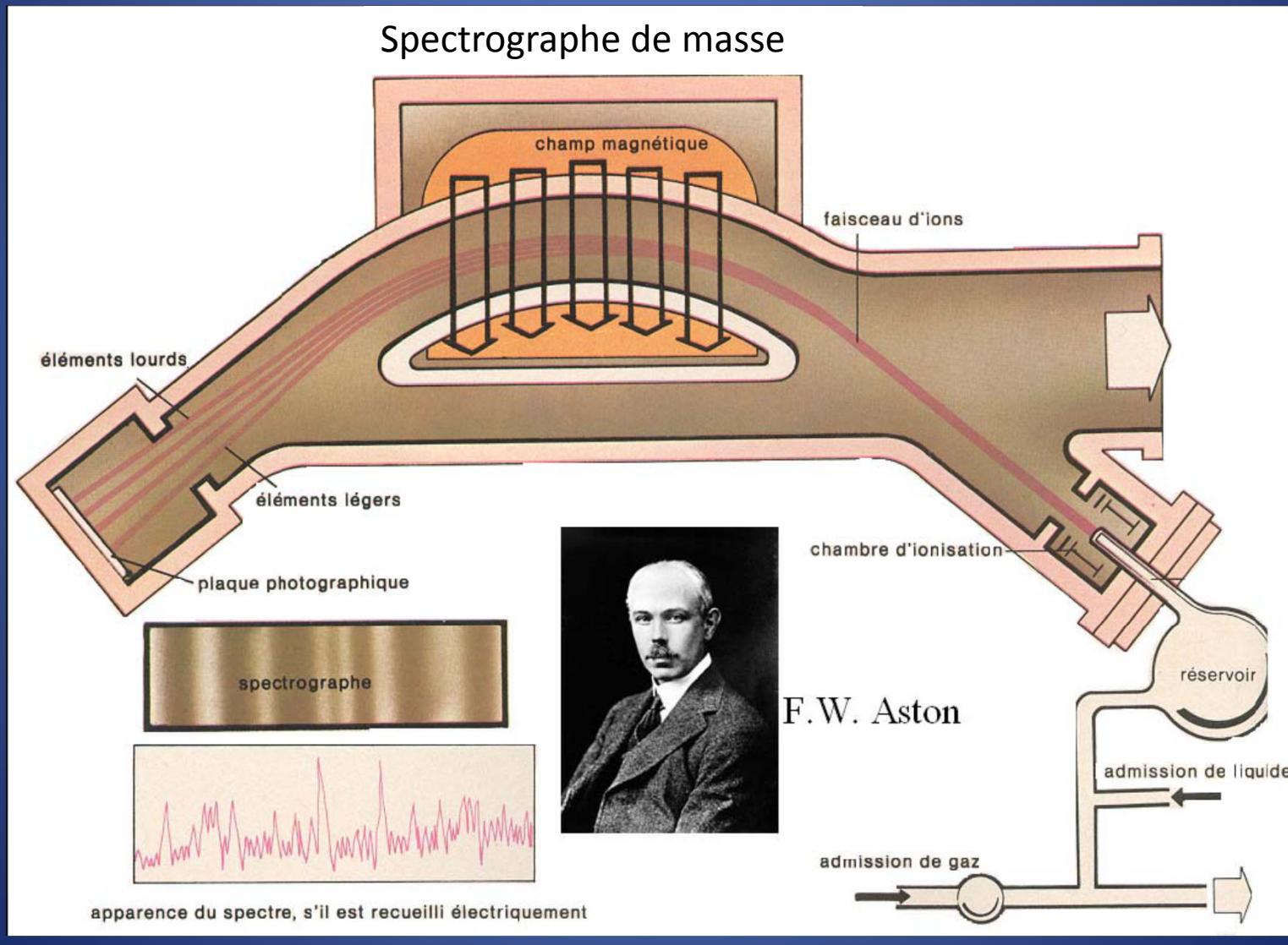
Francis William Aston

(1877-1945)

- En 1909, Aston travaille avec Sir J.J. Thomson comme assistant sur l'études des rayons positifs
- Invente le spectrographe de masse (SM), appareil pour mesurer les rayons positif
- Avec 3 générations de SM, Aston découvre 212 des « isotopes » naturels.
- Reçoit le prix Nobel, en 1922, pour ses premières travaux.



Francis William Aston (1877-1945)



Frederick Soddy

(1877-1956)

- Il est le géniteur du mot « Isotope »
Iso: ancien grec voulant dire égale
Topos: place ou local
- Lauréat du prix Nobel de chimie en 1921 pour ses enquêtes sur la désintégration radioactive, en particulier, pour sa théorie des isotopes



Whoo hoo!
Les isotopes règnent!

Harold Clayton Urey (1893-1981)

- Les mesures très précises d'Aston sur O₂ et l'H₂ révèlent certaines divergences.
- Un isotope d'hydrogène a deux fois la masse de l' hydrogène ordinaire
- Ferdinand Brickwedde distille 5L d'H₂ liquide finissant avec 1ml au labo cryo de la NBS. Urey fait la même chose avec de l'eau et montre l'enrichissement.
- Le deutérium est découvert ; avec une concentration de 1 atome sur 6400.



Harold Clayton Urey (1893-1981)

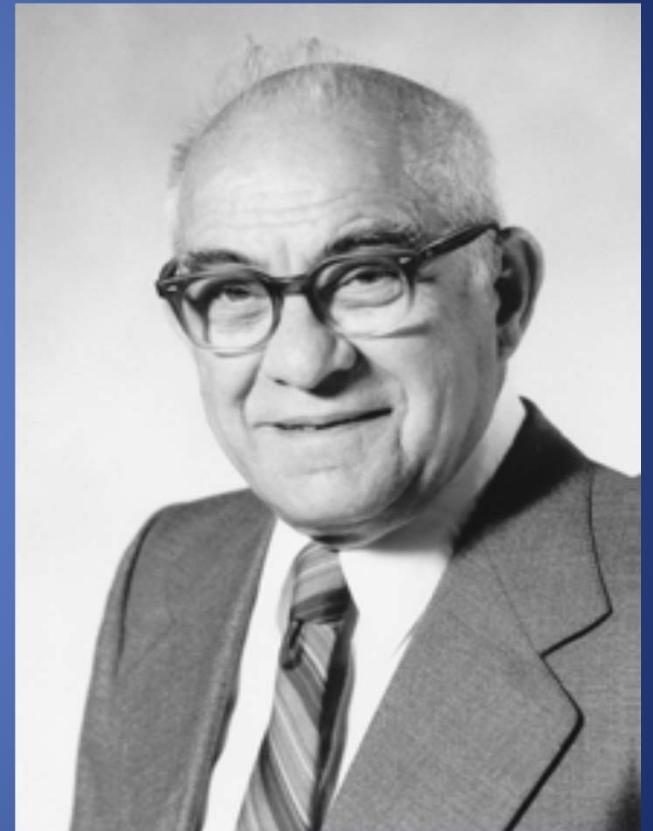
- Par conséquence, la découverte du deutérium vient avant la découverte du neutron en 1932
- Gilbert Newton Lewis a préparé les premiers échantillons d'eau lourde pure en 1933
- Après la découverte du neutron, Urey remporte le prix Nobel de chimie en 1934 pour la découverte du deutérium.
- En 1947, publie l'article bien connu:
« The Thermodynamic Properties of Isotopic Substances »



Alfred O.C. Nier

(1911-1994)

- Développe un SM à double focalisation et double-intro ainsi qu'avec deux collecteurs.
- Permet la mesure directe des rapports isotopiques.
- Une des premières études regardait l'échange isotopique « eau –carbonate » dirigée par Urey.
- Urey conçois la possibilité d'effectuer des calculs de **paléo-température** des Océans.
- Outil utilisé presque exclusivement par les sciences de la terre pendant les années 50 et 60.



Margaret Bender (1916-2008)

- En 1968 et 1971, le premier fractionnement biogénique est expliquées par Margaret Bender en ce qui concerne les voies photosynthétiques nouvellement compris:

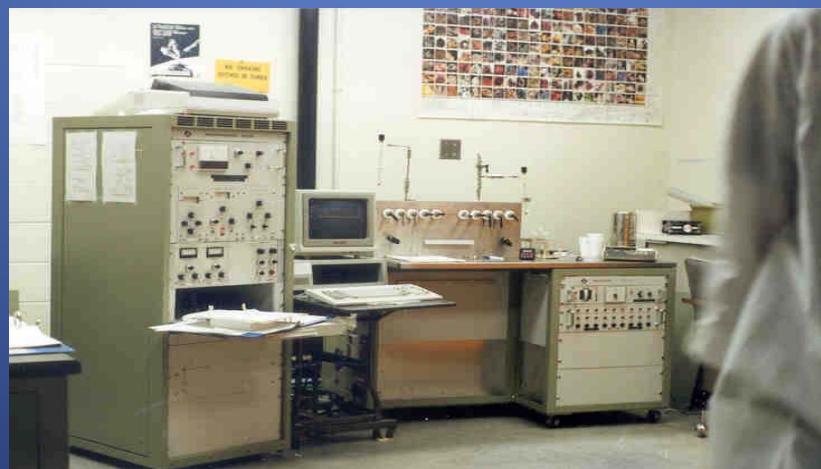
- C3 : cycle de Calvin
- C4 : Hatch & Slack



- Plus tard, due à des anomalies de ^{13}C , explique la voie photosynthétique appellé:
 - Métabolisme Acide Crassulacéene (MAC) en 1973.

De nos jour

- Les autres domaines de recherche furent lents à faire usage des outils de recherche des isotopes stables; en raison de la nature laborieuse de la préparation des échantillons et la quantité de matériaux nécessaire.



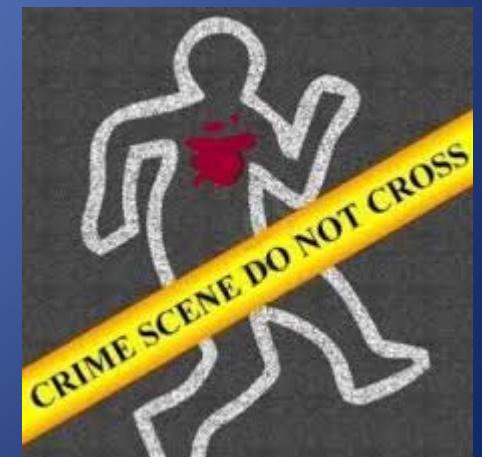
De nos jour

- Le flux continu à changé tout cela.
- Les échantillons sont plus petits avec beaucoup plus d'automatisation . Les premiers échantillons nécessitaient des milligrammes tandis que les nouvelles technologies atteignent le nanogramme.



De nos jour

- Les champs d'utilisation comprennent la géologie, biologie, médecine, chimie, alimentation, ainsi que la fraude et la criminalistique.



Théorie: Effet cinétique

a = $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ = masse 44

b = $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ = masse 45

E.C.



$$\frac{1}{2} m_a v_a^2 = \frac{1}{2} m_b v_b^2$$

$$\frac{1}{2} (44 v_a^2) = \frac{1}{2} (45 v_b^2)$$

$$\frac{v_a}{v_b} = \sqrt{\frac{45}{44}} = 1.0113$$

Cela signifie que, indépendamment de la température, les rapports de vitesses entre ces deux espèces isotopiques, lourds et légers, est de 1.0113; ou que la vitesse moyenne de la masse 44 est de 1,1 % (ou 11‰) supérieure à la masse 45.

Théorie: Énergie de liaison

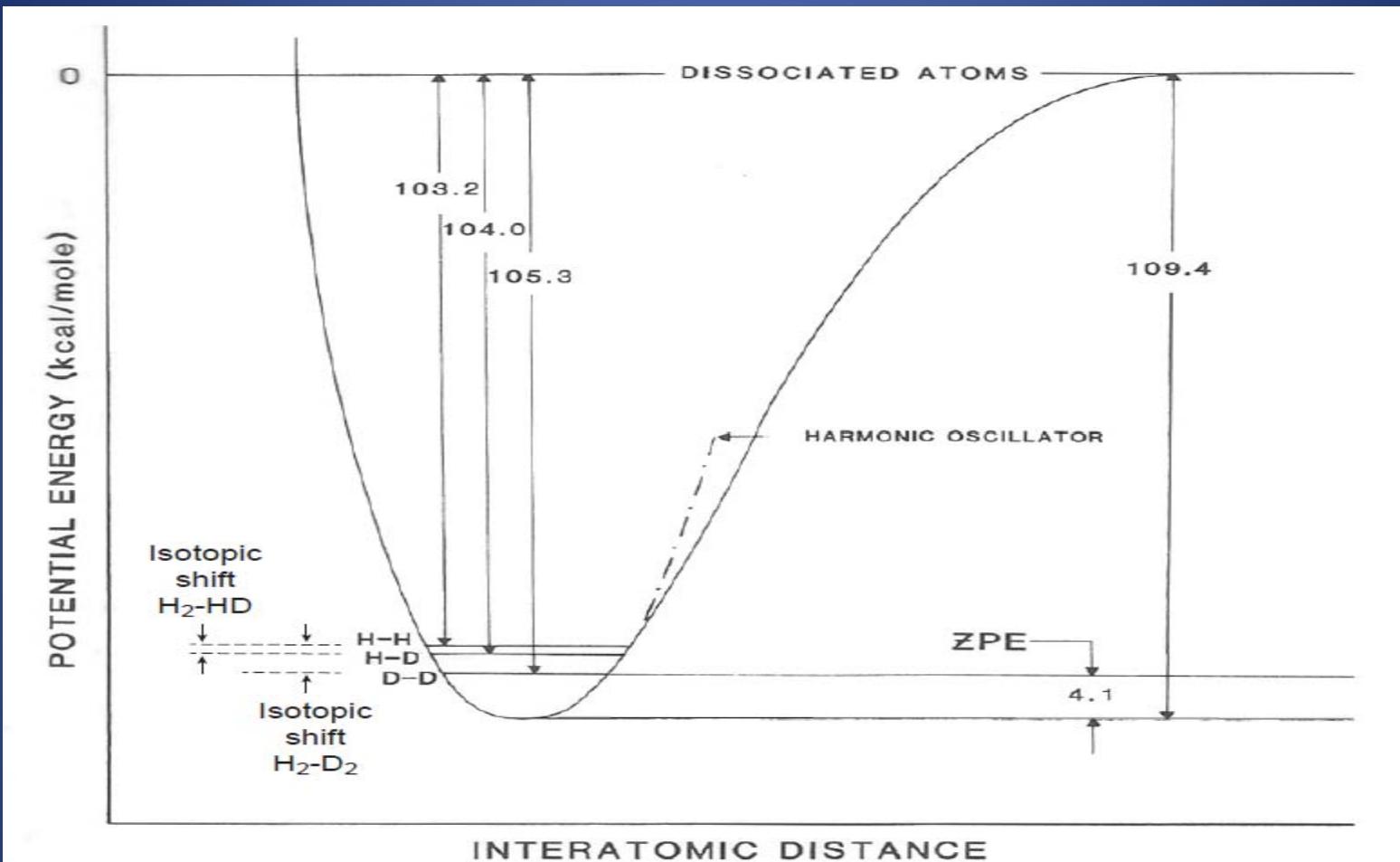
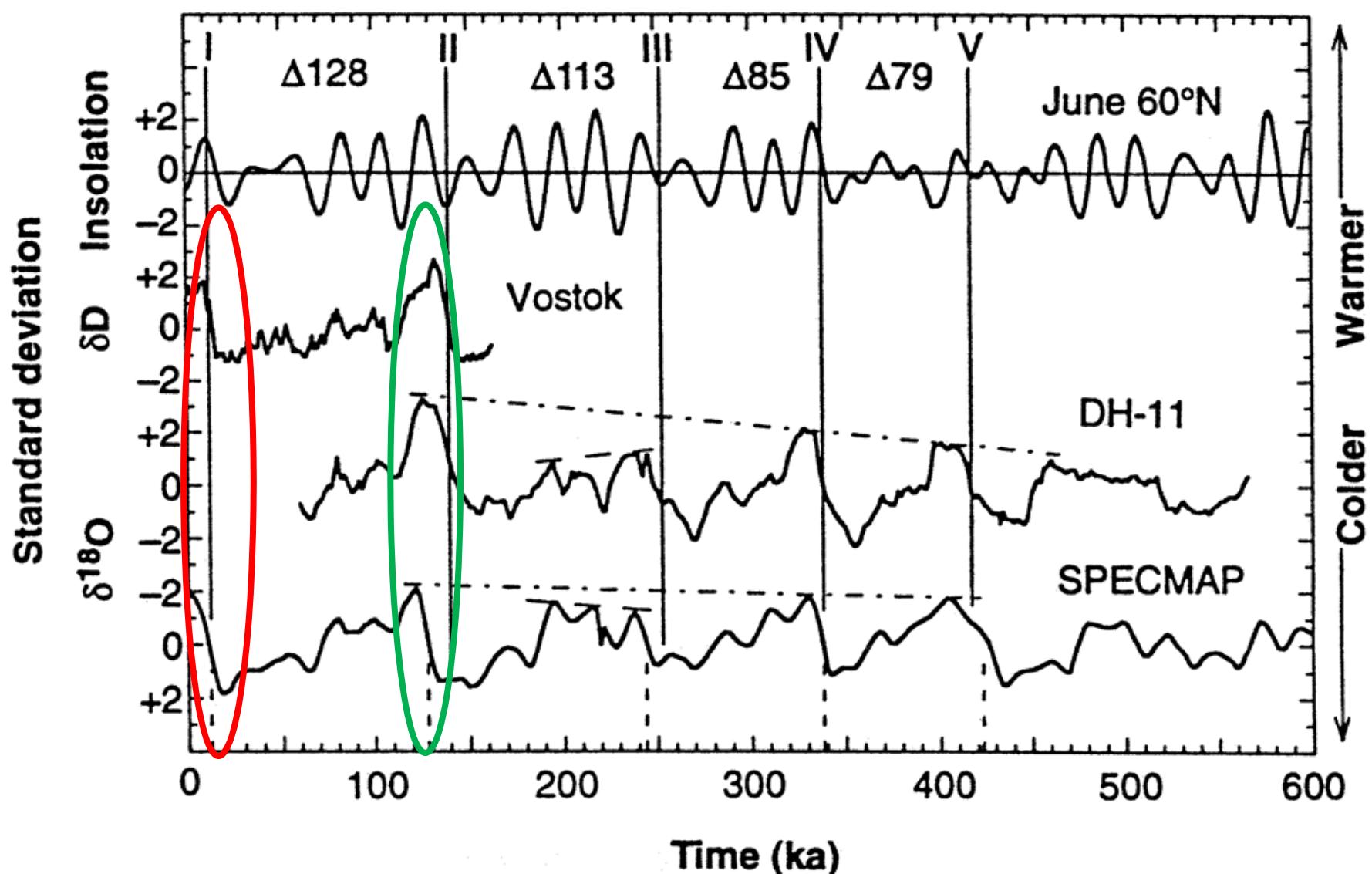


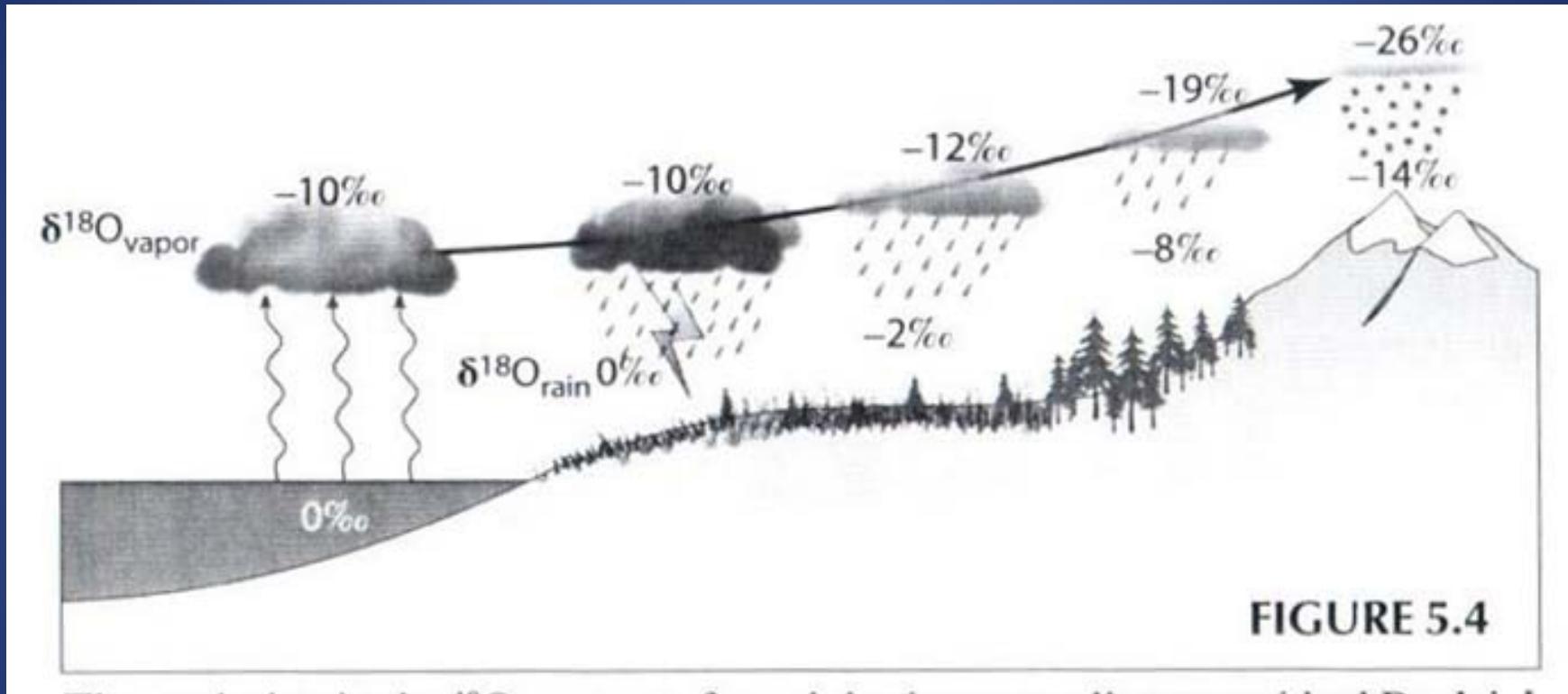
Figure 1. Schematic potential energy diagram for the hydrogen molecule with scale at bottom of the curve exaggerated to show relation between $n = 0$ vibrational energy levels of the three isotopic forms of the molecule. The fundamental vibrational frequencies are: H₂, 4405 cm⁻¹; HD, 3817 cm⁻¹; D₂, 3119 cm⁻¹. With increasing temperature, vibrations of all molecules become increasingly anharmonic and the spacings between energy levels (not shown) become smaller and smaller until dissociation occurs. All isotopic forms of hydrogen have the same spectroscopic dissociation energy (109.4 kcal/mole) but chemical dissociation energies and zero point energies (ZPE) that differ by up to 2 kcal/mole. Note that molecules containing the heavy isotope are more stable (have higher dissociation energies) than molecules with the light isotope. Isotopic fractionations between molecules are explained by differences in their ZPE.

Théorie: Énergie de liaison



Théorie: Énergie de liaison

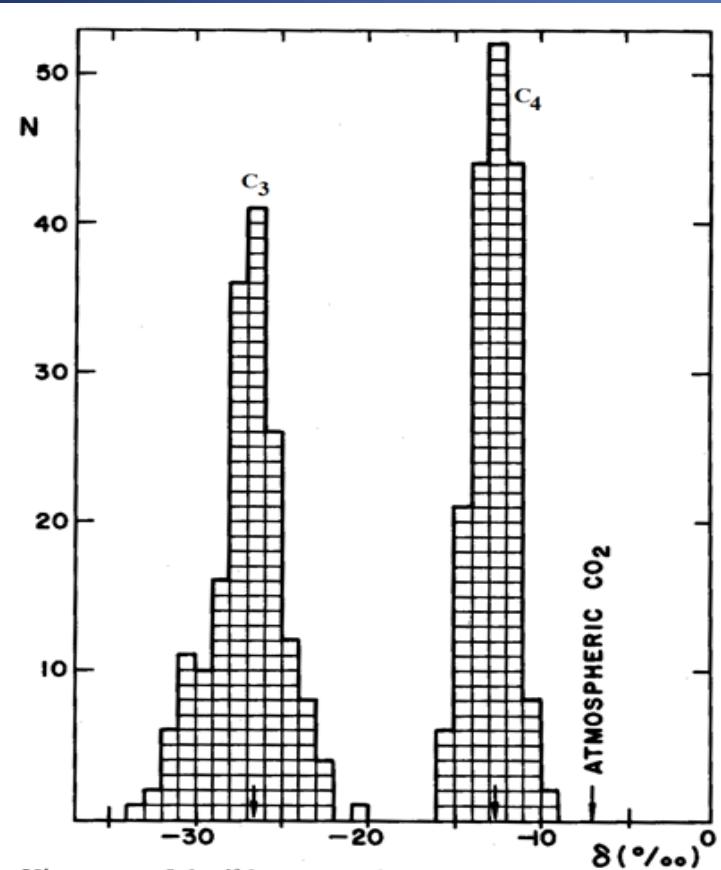
Distillation de Rayleigh



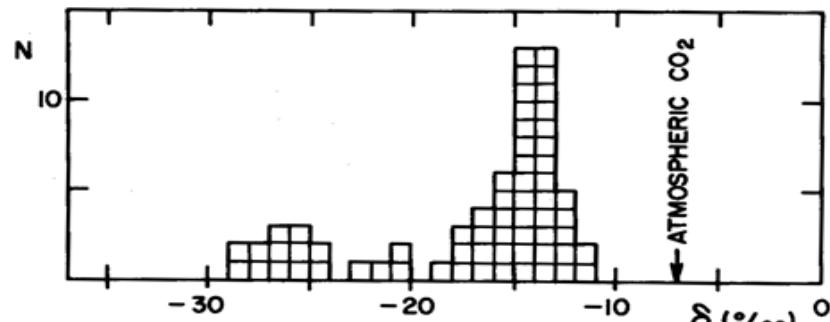
The evolution in the ^{18}O content of precipitation according to an ideal Rayleigh distillation during rainout. Deuterium follows a similar depletion trend.

Théorie: Fractionnement biogénique

- Effets thermodynamiques : Liaisons C-O sont plus forts que C-H.
- Effets cinétiques : Taux de réaction rapide (ex: réaction enzymatique).
- Diffusion: À travers les membranes cellulaires, donne un effet cinétique apparent.



Histogram of the ^{13}C content of 351 species of the *Poaceae* family from Vogel (1980). The separation is unique: all the C₄ species have δ -values more positive than $-16\text{\textperthousand}$, (modal value $-12.6\text{\textperthousand}$), while only C₃ species have δ -values between -22 and $-34\text{\textperthousand}$ (modal value $-26.7\text{\textperthousand}$).



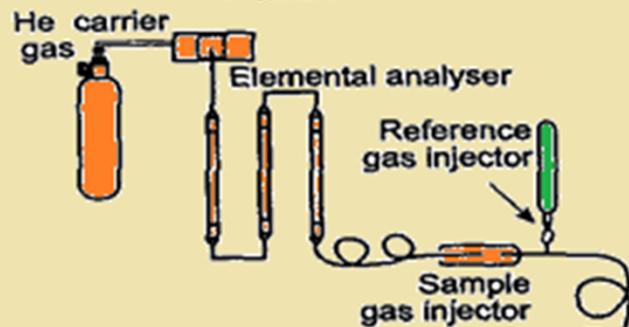
Histogram of the ^{13}C content of 63 species of the genus *Aloe* from Vogel (1980). Those species with a strong tendency to utilize the crassulacean acid metabolism (CAM) have δ -values more positive than $-16\text{\textperthousand}$, while the group with δ -values less negative than $-22\text{\textperthousand}$ only utilize CAM under water stress.

Figure 10, ^{13}C distribution according to photosynthetic pathway; C₃, C₄ and CAM (Ehleringer, 1993, Chap.4, Vogel J.C.)

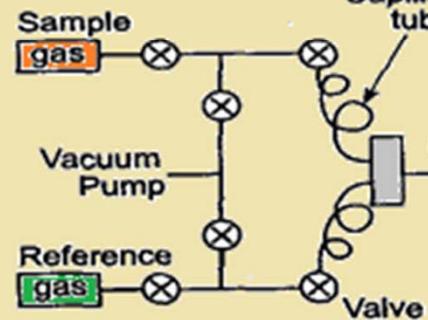
Élément	Isotope	Poid atom.	Abondance Relative (%)	Élémentaire Différence Masse Relative	Moléculaire Différence Masse Relative	Étendue terrestre		Précision technique	
						δ‰	ppm	%	ppm
Hydrogène Deutérium (D)	${}^1_1\text{H}^1$ ${}^2_1\text{H}^1$	1.0078 2.0141	99.984 0.0156	D / H 100%	${}^1\text{HD} / {}^1\text{H}^1\text{H}$ (3 / 2) 50.0%	840	130	1	0.16
Bore	${}^{10}_5\text{B}^5$ ${}^{11}_5\text{B}^6$	10.0129 11.0093	19.7 80.3	${}^{11}\text{B} / {}^{10}\text{B}$ 10%	-----	90	363926	1	4043
Carbone	${}^{12}_6\text{C}^6$ ${}^{13}_6\text{C}^7$	12.0000 13.0034	98.892 1.108	${}^{13}\text{C} / {}^{12}\text{C}$ 8.3%	${}^{13}\text{C}^{16}\text{O}^{16}\text{O} / {}^{12}\text{C}^{16}\text{O}^{16}\text{O}$ (45 / 44) 2.3%	140	1565	0.05	0.56
Azote	${}^{14}_7\text{N}^7$ ${}^{15}_7\text{N}^8$	14.0031 15.0001	99.635 0.365	${}^{15}\text{N} / {}^{14}\text{N}$ 7.1%	${}^{15}\text{N}^{14}\text{N} / {}^{14}\text{N}^{14}\text{N}$ (29 / 28) 3.6%	200	735	0.1	0.37
Oxygène	${}^{16}_8\text{O}^8$ ${}^{17}_8\text{O}^9$ ${}^{18}_8\text{O}^{10}$	15.9949 16.9991 17.9992	99.759 0.037 0.204	${}^{18}\text{O} / {}^{16}\text{O}$ 12.5%	${}^{12}\text{C}^{16}\text{O}^{18}\text{O} / {}^{12}\text{C}^{16}\text{O}^{16}\text{O}$ (46 / 44) 4.5%	160	321	0.1	0.20
Silice	${}^{28}_{14}\text{Si}^{14}$ ${}^{29}_{14}\text{Si}^{15}$ ${}^{30}_{14}\text{Si}^{16}$	27.9769 28.9765 29.9738	92.21 4.7 3.09	${}^{30}\text{Si} / {}^{28}\text{Si}$ 7.1%	${}^{30}\text{Si}^{19}\text{F}_4 / {}^{28}\text{Si}^{19}\text{F}_4$ (106/104) 1.9%	8	268	0.1	34
Soufre	${}^{32}_{16}\text{S}^{16}$ ${}^{33}_{16}\text{S}^{17}$ ${}^{34}_{16}\text{S}^{18}$ ${}^{36}_{16}\text{S}^{20}$	31.9721 32.9714 33.9679 35.9671	95.02 0.76 4.22 0.014	${}^{34}\text{S} / {}^{32}\text{S}$ 6.3%	${}^{34}\text{S}^{16}\text{O}^{16}\text{O} / {}^{32}\text{S}^{16}\text{O}^{16}\text{O}$ (66 / 64) 3.1%	200	8833	0.2	9.16
Chlore	${}^{35}_{17}\text{Cl}^{18}$ ${}^{37}_{17}\text{Cl}^{20}$	34.9689 36.9659	75.77 24.23	${}^{37}\text{Cl} / {}^{35}\text{Cl}$ 5.7%	${}^{12}\text{CH}_3^{37}\text{Cl} / {}^{12}\text{CH}_3^{35}\text{Cl}$ (52/50) 4.0%	12	3836	0.1	32.00

Système de Préparation

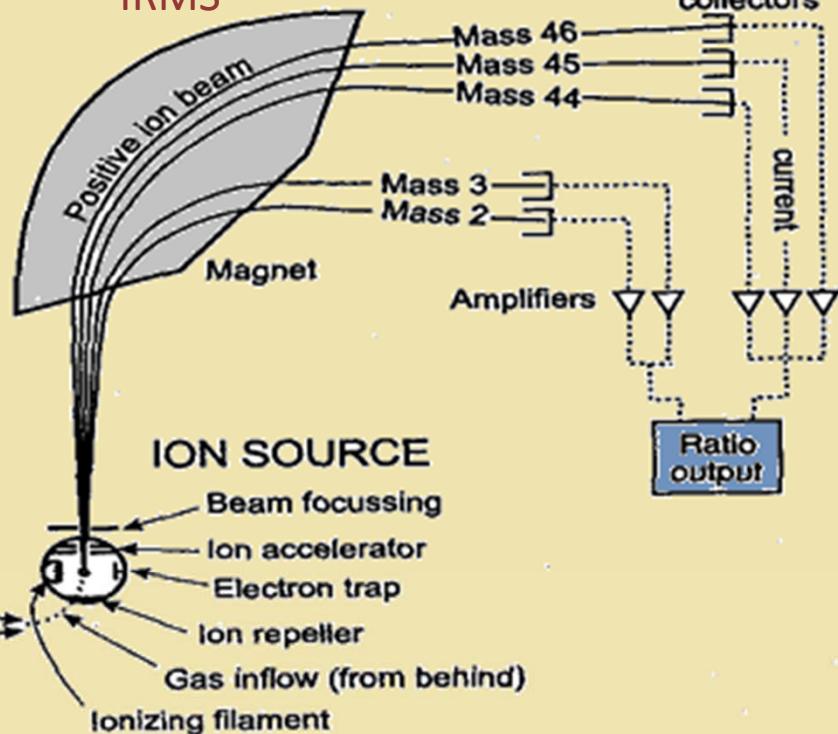
CONTINUOUS FLOW INLET



DUAL INLET



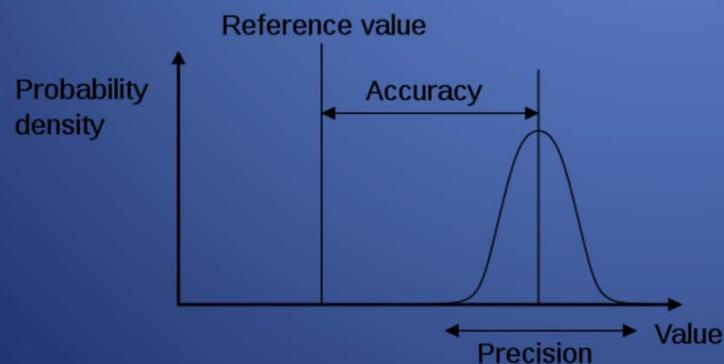
IRMS



ION SOURCE



Mod from Clark & Fritz, 1997

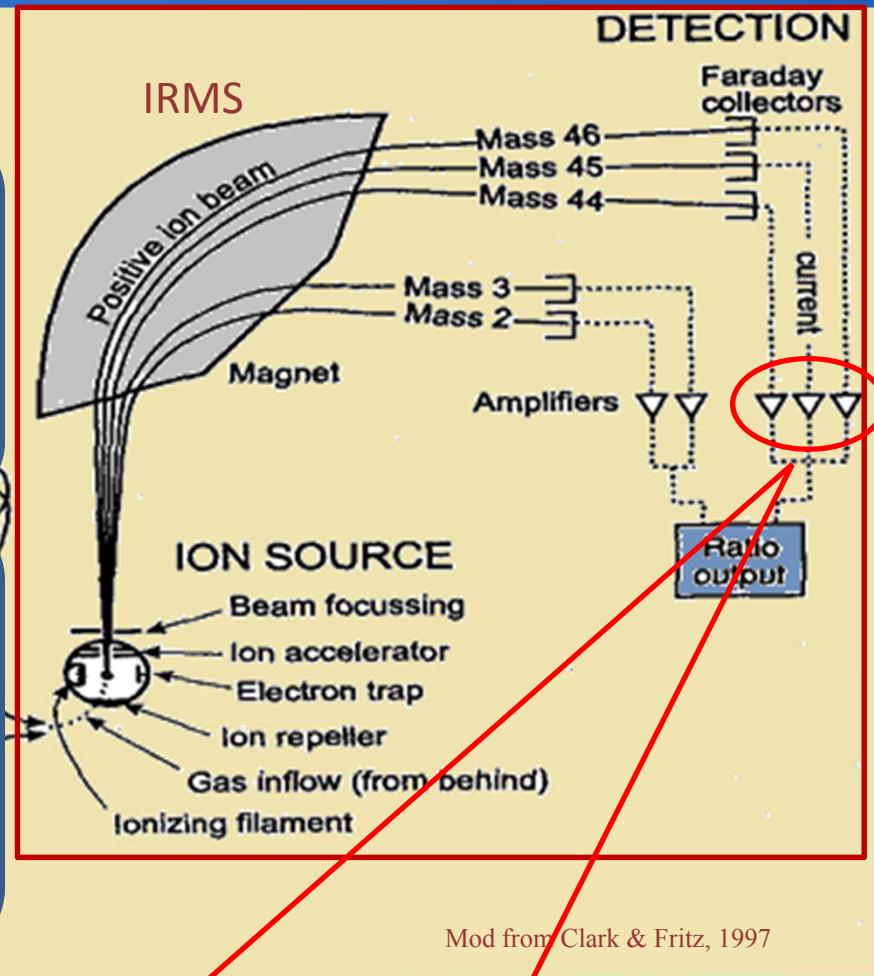
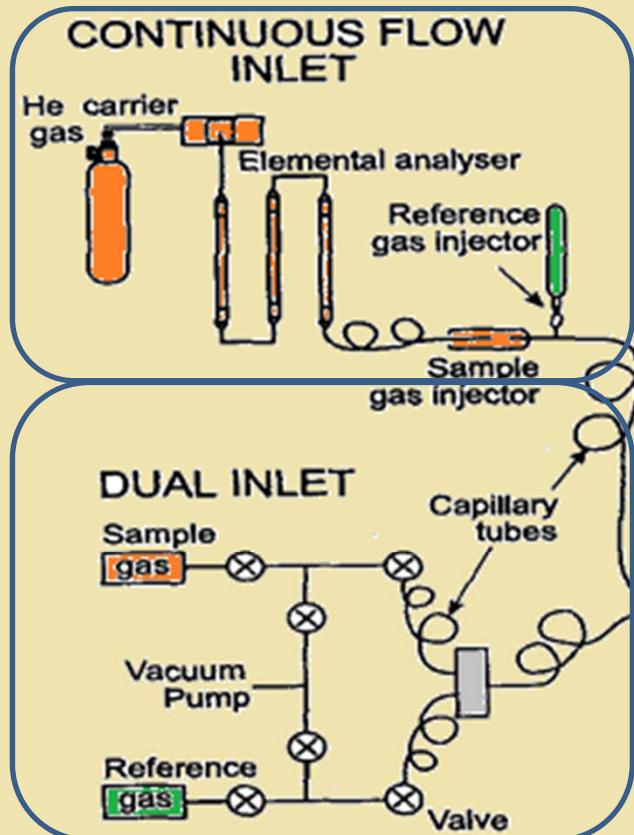


High accuracy
Low precision



High precision
Low accuracy

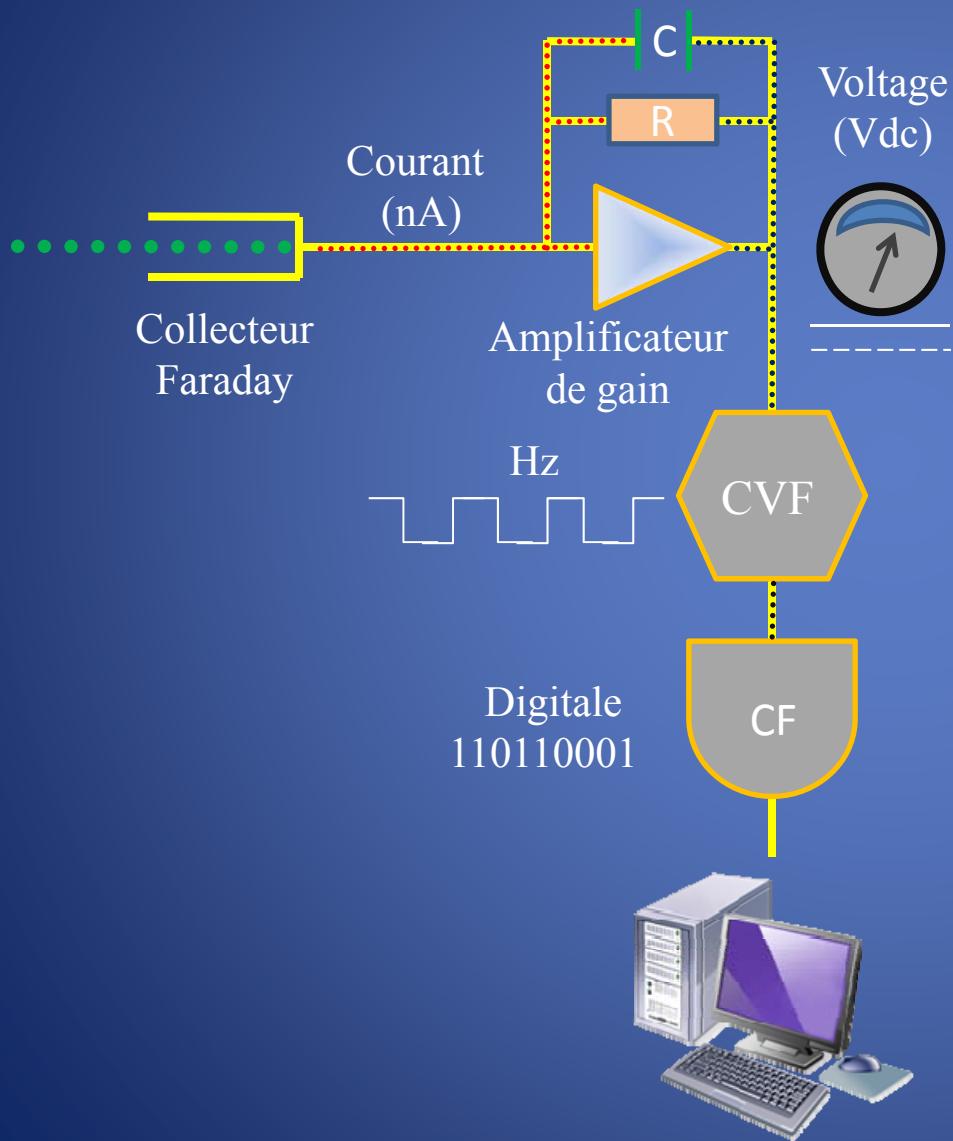
Système de Préparation



Mesure des rapports (R): $\frac{\text{masse } 45}{\text{masse } 44}$ & $\frac{\text{masse } 46}{\text{masse } 44}$

Compagnies différentes

Différentes représentations des signaux



$$V = RI$$

Où

V = Volts

R = Résistance (Ω)

I = Courant (A)

Pour

Courant au collecteur = 10^{-9} Ampère
Résistance de Gain = 10^9 Ohm

Alors

$V = 1.000000$ Volt

Représentation sur l'ordinateur :

Thermo

1000 mV

Europa, Sercon, Micromass, Isoprime Ltd

1.00^{E-9} A

La notation Delta

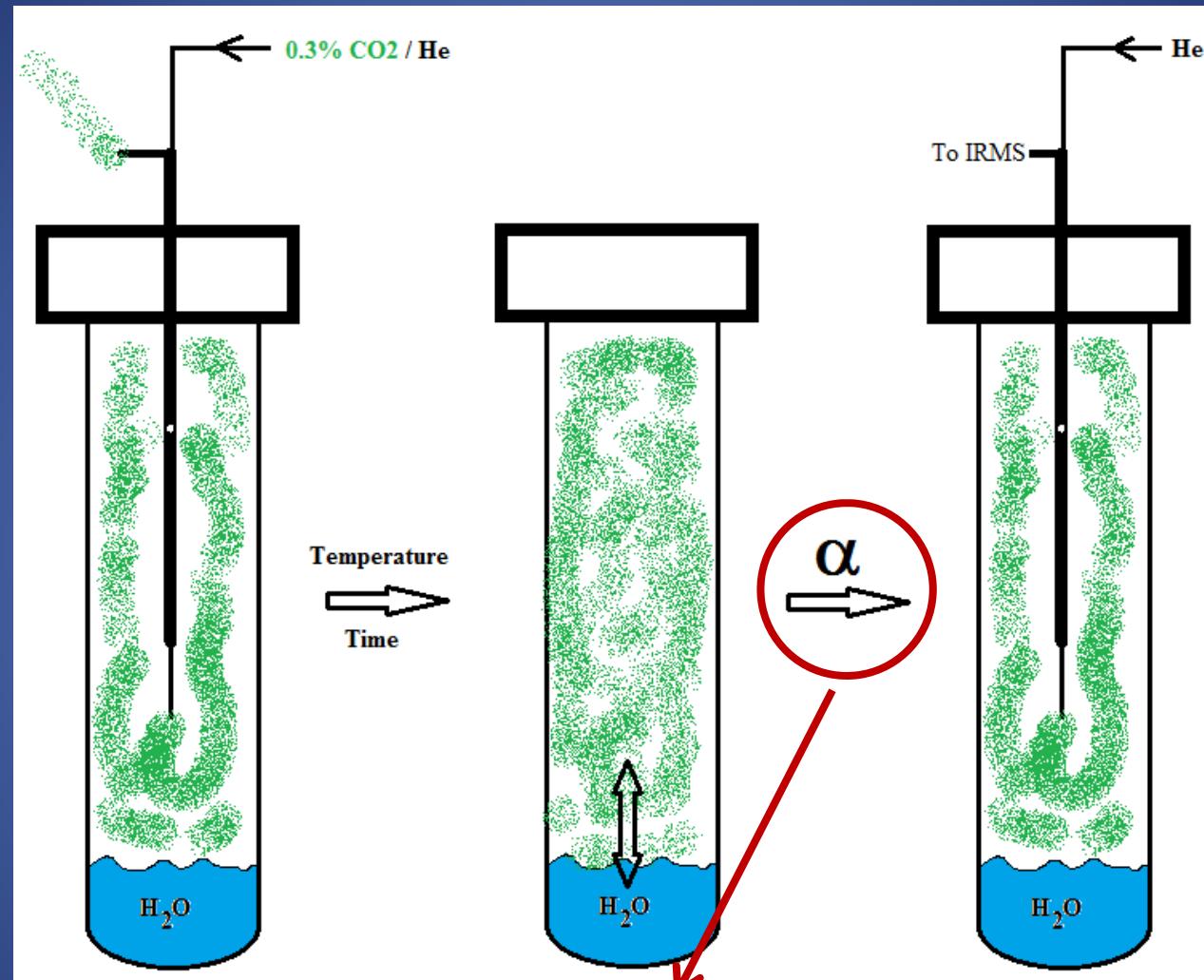
$$R = \frac{\text{Isotope lourd}}{\text{Isotope commun}}$$

$$R = \frac{{}^{13}\text{C}}{{}^{12}\text{C}} = 0.011\text{xxx}$$

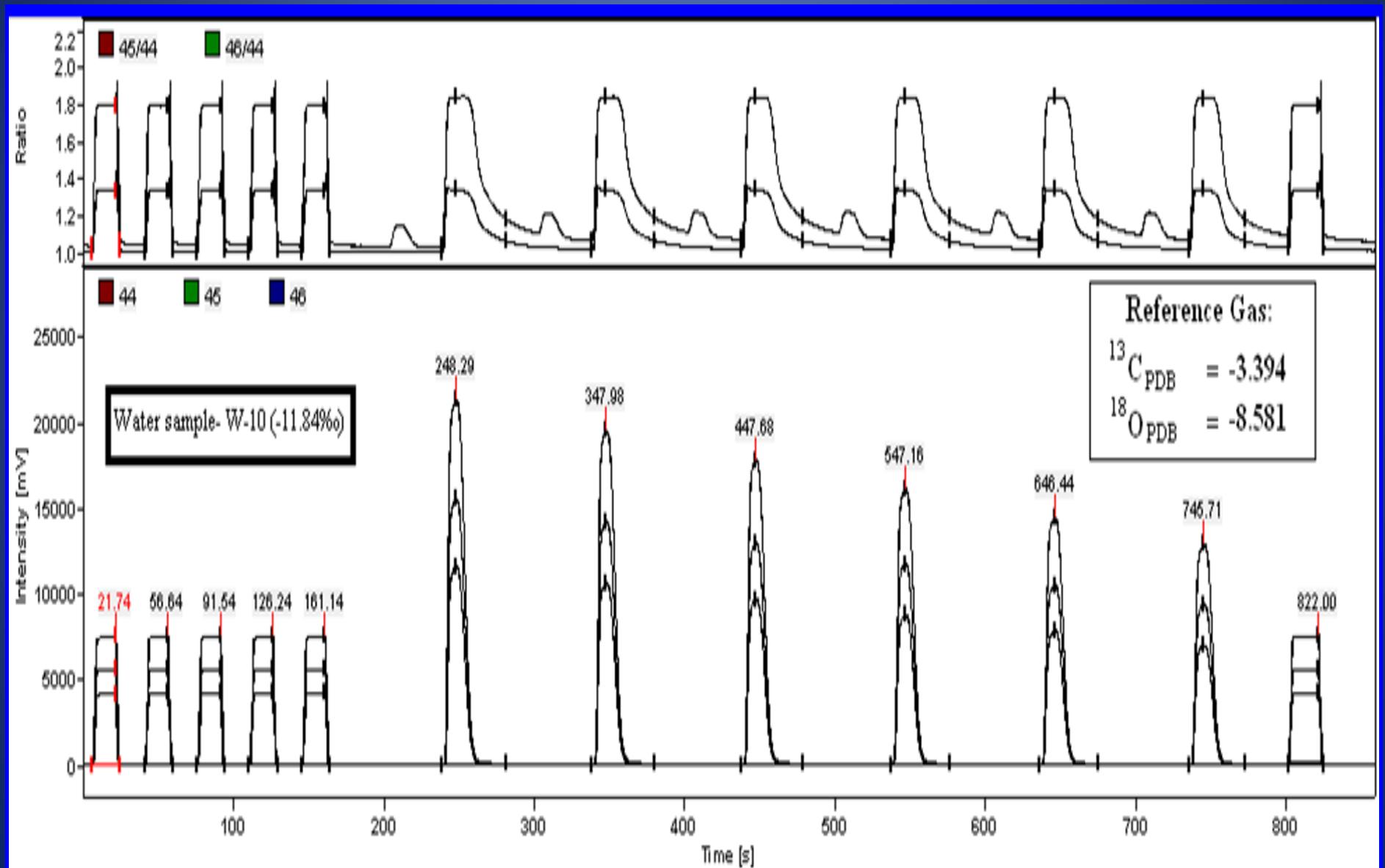
$$R = \frac{{}^{18}\text{O}}{{}^{16}\text{O}} = 0.002\text{xxx}$$

$$\delta \frac{R_{\text{Éch}}}{R_{\text{Réf}}} = \left[\frac{R_{\text{Éch}} - R_{\text{Réf}}}{R_{\text{Réf}}} \right] 10^3 = \left[\frac{\frac{R_{\text{Éch}}}{R_{\text{Réf}}} - 1}{R_{\text{Réf}}} \right] 10^3$$

Equilibration CO₂-Eau



Equilibration CO₂-Eau



Analyse d'un échantillon d'eau

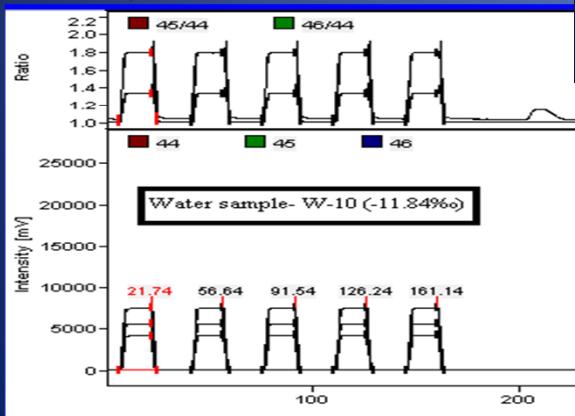
Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf (A)
0	248	133683.4	57929.458	5.79
0	348	120824.1	52357.105	5.23
0	448	109774.8	47569.087	4.76
0	547	99742.3	43221.655	4.32
0	646	90277.2	39120.119	3.91
0	746	81540.5	35334.209	3.53

R 45 via
mVs ou As

R 46 via
mVs ou As

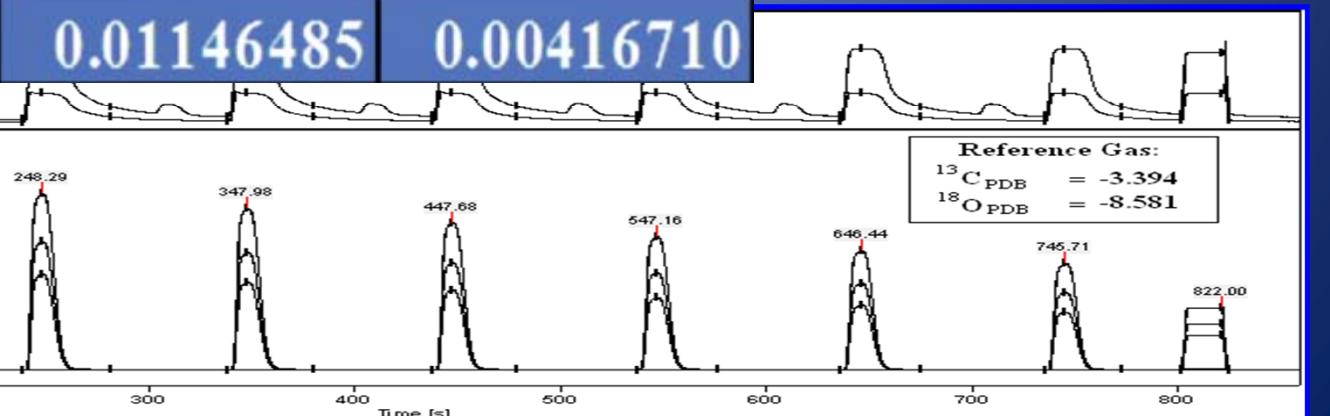
1	22	60280.1	26121.390	2.6
1	57	60397.5	26172.229	2.6
1	92	60382.5	26165.764	2.6
1	126	60292.4	26126.695	2.6
1	161	60368.9	26159.844	2.6
1	822	80753.1	34992.999	3.4

AVG=



rf 46 As)	R 45 via mVs on As	R 46 via mVs on As
414E-09	0.01146430	0.00416683
482E-09	0.01146428	0.00416687
82E-09	0.01146506	0.00416707
01E-09	0.01146501	0.00416719
30E-09	0.01146500	0.00416728
73E-09	0.01146542	0.00416737
AVG =	0.01146485	0.00416710
82E-09	0.01191943	0.00414100
84E-09	0.01191978	0.00414135
84E-09	0.01192005	0.00414138
82E-09	0.01192042	0.00414160
83E-09	0.01192038	0.00414135
49E-09	0.01192055	0.00414180
AVG =	0.01192010	0.00414141

Résistance Amplifi.	Valeur (Ω)	Facteur de gain rel. à $10^8\Omega$
Gain 44	2.31E+08	2.31
Gain 45	2.73E+10	272.73
Gain 46	1.00E+11	1000.00



Calcule des rapports

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Area 46 (mVs)	Surf 46 (As)	R 45 via mVs ou As	R 46 via mVs ou As
0	248	133683.4	57929.458	5.793E-07	181123.8	664.121	6.641E-09	241382.2	241.382	2.414E-09	0.01146430	0.00416683
0	348	120824.1	52357.105	5.236E-07	163700.9	600.237	6.002E-09	218165.2	218.165	2.182E-09	0.01146428	0.00416687
0	448	109774.8	47569.087	4.757E-07	148740.7	545.382	5.454E-09	198223.7	198.224	1.982E-09	0.01146506	0.00416707
0	547	99742.3	43221.655	4.322E-07	135146.4	495.537	4.955E-09	180112.9	180.113	1.801E-09	0.01146501	0.00416719
0	646	90277.2	39120.119	3.912E-07	122321.5	448.512	4.485E-09	163024.5	163.024	1.630E-09	0.01146500	0.00416728
0	746	81540.5	35334.209	3.533E-07	110487.7	405.122	4.051E-09	147250.7	147.251	1.473E-09	0.01146542	0.00416737
										MOY =	0.01146485	0.00416710
1	22	60280.1	26121.390	2.612E-07	84914.2	311.352	3.114E-09	108168.7	108.169	1.082E-09	0.01191943	0.00414100
1	57	60397.5	26172.229	2.617E-07	85082.0	311.967	3.120E-09	108388.4	108.388	1.084E-09	0.01191978	0.00414135
1	92	60382.5	26165.764	2.617E-07	85062.9	311.897	3.119E-09	108362.4	108.362	1.084E-09	0.01192005	0.00414138
1	126	60292.4	26126.695	2.613E-07	84938.5	311.441	3.114E-09	108206.3	108.206	1.082E-09	0.01192042	0.00414160
1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038	0.00414135
1	822	80753.1	34992.999	3.499E-07	113764.3	417.136	4.171E-09	144934.0	144.934	1.449E-09	0.01192055	0.00414180
										MOY =	0.01192010	0.00414141

ÉCH

RÉF

$$R45_{\text{éch}} = \frac{\text{Surf}45}{\text{Surf}44} = \frac{405.122}{35334.209} = \underline{4.051^{\text{E}-09}} = 0.1146485 \text{ (ÉCH)}$$

$$R46_{\text{éch}} = \frac{\text{Surf}46}{\text{Surf}44} = \frac{147.251}{35334.209} = \underline{1.473^{\text{E}-09}} = 0.00416737 \text{ (ÉCH)}$$

Calcule du DELTA (δ)

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Surf 46 (mVs)	R 45 via mVs ou As	R 46 via mVs ou As
0	248	133683.4	57929.458	5.793E-07	181123.8	664.121	6.641E-09	241382.2	241.382	2.414E-09	0.01146430
0	348	120824.1	52357.105	5.236E-07	163700.9	600.237	6.002E-09	218165.2	218.165	2.182E-09	0.01146428
0	448	109774.8	47569.087	4.757E-07	148740.7	545.382	5.454E-09	198223.7	198.224	1.982E-09	0.01146506
0	547	99742.3	43221.655	4.322E-07	135146.4	495.537	4.955E-09	180112.9	180.113	1.801E-09	0.01146501
0	646	90277.2	39120.119	3.912E-07	122321.5	448.512	4.485E-09	163024.5	163.024	1.630E-09	0.01146500
0	746	81540.5	35334.209	3.533E-07	110487.7	405.122	4.051E-09	147250.7	147.251	1.473E-09	0.01146542
											MOY = 0.01146485 0.00416710
1	22	60280.1	26121.390	2.612E-07	84914.2	311.352	3.114E-09	108168.7	108.169	1.082E-09	0.01191943
1	57	60397.5	26172.229	2.617E-07	85082.0	311.967	3.120E-09	108388.4	108.388	1.084E-09	0.01191978
1	92	60382.5	26165.764	2.617E-07	85062.9	311.897	3.119E-09	108362.4	108.362	1.084E-09	0.01192005
1	126	60292.4	26126.695	2.613E-07	84938.5	311.441	3.114E-09	108206.3	108.206	1.082E-09	0.01192042
1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038
1	822	80753.1	34992.999	3.499E-07	113764.3	417.136	4.171E-09	144934.0	144.934	1.449E-09	0.01192055
											MOY = 0.01192010 0.00414141

ÉCH

RÉF

$$\delta_{45} = \frac{R_{45\text{ Éch}}}{R_{45\text{ Réf}}} = \frac{0.01146485}{0.01192010} = -38.19\%$$

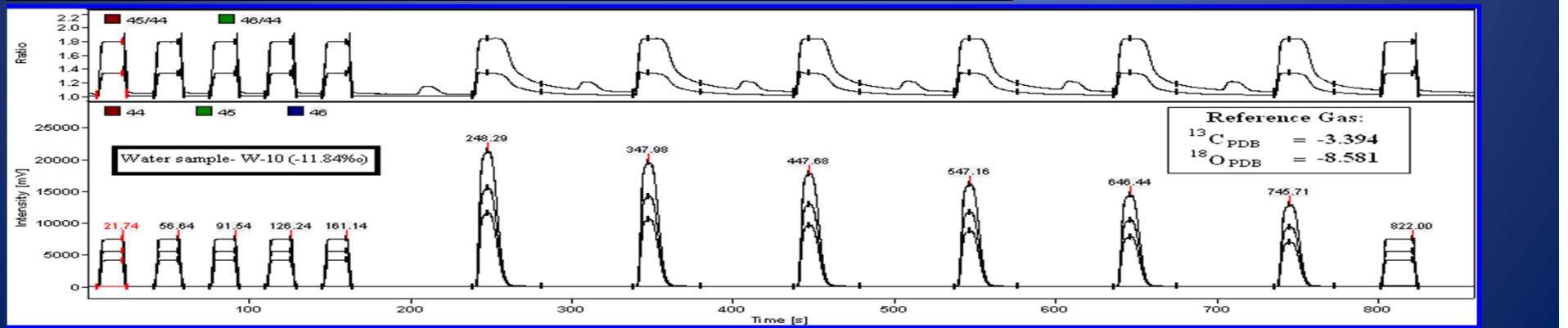
$$\delta_{46} = \frac{R_{46\text{ Éch}}}{R_{46\text{ Réf}}} = \frac{0.00416710}{0.00414141} = 6.20\%$$

$$\delta \frac{S_{am}}{R_{Ref}} = \left[\frac{R_{Sam}}{R_{Ref}} - 1 \right] 10^3$$

Analyse d'un échantillon d'eau

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Surf 46 (mVs)	Surf 46 (As)	R 45 via mVs or As	R 46 via mVs or As
0	248	133683.4	57929.458	5.793E-07	181123.8	664.121	6.641E-09	241382.2	241.382	2.414E-09	0.01146430	0.00416683
0	348	120824.1	52357.105	5.236E-07	163700.9	600.237	6.002E-09	218165.2	218.165	2.182E-09	0.01146428	0.00416687
0	448	109774.8	47569.087	4.757E-07	148740.7	545.382	5.454E-09	198223.7	198.224	1.982E-09	0.01146506	0.00416707
0	547	99742.3	43221.655	4.322E-07	135146.4	495.537	4.955E-09	180112.9	180.113	1.801E-09	0.01146501	0.00416719
0	646	90277.2	39120.119	3.912E-07	122321.5	448.512	4.485E-09	163024.5	163.024	1.630E-09	0.01146500	0.00416728
0	746	81540.5	35334.209	3.533E-07	110487.7	405.122	4.051E-09	147250.7	147.251	1.473E-09	0.01146542	0.00416737
												AVG= 0.01146485 0.00416710
1	22	60280.1	26121.390	2.612E-07	84914.2	311.352	3.114E-09	108168.7	108.169	1.082E-09	0.01191943	0.00414100
1	57	60397.5	26172.229	2.617E-07	85082.0	311.967	3.120E-09	108388.4	108.388	1.084E-09	0.01191978	0.00414135
1	92	60382.5	26165.764	2.617E-07	85062.9	311.897	3.119E-09	108362.4	108.362	1.084E-09	0.01192005	0.00414138
1	126	60292.4	26126.695	2.613E-07	84938.5	311.441	3.114E-09	108206.3	108.206	1.082E-09	0.01192042	0.00414160
1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038	0.00414135
1	822	80753.1	34992.999	3.499E-07	113764.3	417.136	4.171E-09	144934.0	144.934	1.449E-09	0.01192055	0.00414180
												AVG= 0.01192010 0.00414141

δ 45	δ 46	δ ⁴⁵ _{PDB}	δ ⁴⁶ _{PDB}	Craig	Craig	δ ¹⁸ O ^{wt} PDB	δ ¹⁸ O ^{wt} SMOW	Résistance Ampli.	Valeur (Ω)	Facteur de gain rel. à $10^8\Omega$
				$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$			Gain 44	2.31E+08	2.31
								Gain 45	2.73E+10	272.73
								Gain 46	1.00E+11	1000.00
AVG = -38.19	6.20							Ref Name	$\delta^{45}_{\text{PDB}} (\%)$	$\delta^{46}_{\text{PDB}} (\%)$
								Luxfer 1	-3.451	-8.580
Normalisé										



Standard international

V-SMOW (Standard Mean Ocean Water)

V-PDB (Pee Dee Belemnite)

V-CDT (Canyon Diablo Troilite)

AIR (Atmospheric N₂)

SMOC (Standard Mean Ocean Chloride)

Atome	Standard	Rapport	Calc. R _{st} Données Coplen, 2002
² H (D)	SMOW	D/H	0.00015576
¹³ C	PDB	¹³ C/ ¹² C	0.01117960
¹⁸ O	SMOW	¹⁸ O/ ¹⁶ O	0.00200517
¹⁵ N	AIR	¹⁵ N/ ¹⁴ N	0.00367647
³⁴ S	CDT	³⁴ S/ ³² S	0.04416255
³⁷ Cl	SMOC	³⁷ Cl/ ³⁵ Cl	0.31962681

Relatif au STD INTERNATIONAL

$$\delta_1 = \delta \frac{\text{sam}}{\text{ref}}$$

where δ_1 is measured in the lab

$$\delta_2 = \delta \frac{\text{ref}}{\text{std}}$$

where δ_2 is known

$$\delta_3 = \delta \frac{\text{sam}}{\text{std}}$$

where δ_3 is the unknown

$$(1) \delta_1 = \left[\frac{R_s}{R_R} - 1 \right] 10^3 \quad (2) \delta_2 = \left[\frac{R_R}{R_I} - 1 \right] 10^3 \quad (3) \delta_3 = \left[\frac{R_s}{R_I} - 1 \right] 10^3$$

And R_s the sample isotopic ratio (e.g. $^{13}\text{C} / {^{12}\text{C}}$)

R_R is the reference isotopic ratio

R_I is the international standard isotopic ratio

By rearranging (1) and (2) we get:

$$R_s = R_R \left(\frac{\delta_1 + 10^3}{10^3} \right) \text{ and } R_I = R_R \left(\frac{10^3}{\delta_2 + 10^3} \right)$$

Where by substituting R_s and R_I in (3):

$$\delta_3 = \left(\frac{R_R \left(\frac{\delta_1 + 10^3}{10^3} \right)}{R_R \left(\frac{10^3}{\delta_2 + 10^3} \right)} - 1 \right) 10^3 \text{ and simplifying: } \delta_3 = (\delta_1 + 10^3) \frac{\delta_2 + 10^3}{10^3} - 10^3$$

Relatif au STD INTERNATIONAL

$$\delta_1 = \delta \frac{\text{Éch}}{\text{Réf}}$$

Où δ_1 est mesuré au labo

$$\delta_2 = \delta \frac{\text{Réf}}{\text{STD}}$$

Où δ_2 est connue

$$\delta_3 = \delta \frac{\text{Éch}}{\text{STD}}$$

Où δ_3 est inconnue

$$\delta_3 = \delta_1 + \delta_2 + \frac{\delta_1 \delta_2}{10^3}$$

CORRECTIONS ^{17}O pour le CO_2

m/z	Ions
44	$^{12}\text{C}^{16}\text{O}^{16}\text{O}$
45	$^{13}\text{C}^{16}\text{O}^{16}\text{O}$, $^{12}\text{C}^{16}\text{O}^{17}\text{O}$
46	$^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $^{13}\text{C}^{17}\text{O}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}^{17}\text{O}$

a) Correction Craig

$$\begin{array}{l} \delta^{13} = 1.0676 \delta^{45} - 0.0338 \delta^{18} \\ \hline \delta^{18} = 1.0010 \delta^{46} - 0.0021 \delta^{13} \end{array}$$

Ces formules ne peuvent être appliqués tels quels que si l'échantillon à l'étude a été mesuré par rapport à PDB

b) Santrock, Studley & Hayes (SSH)

$$^{17}\text{R} = ^{18}\text{R}^a * K$$

Analyse d'un échantillon d'eau

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Surf 46 (mVs)	Surf 46 (As)	R 45 via mVs or As	R 46 via mVs or As	
0	248	133683.4	57929.458	5.793E-07	181123.8	664.121	6.641E-09	241382.2	241.382	2.414E-09	0.01146430	0.00416683	
0	348	120824.1	52357.105	5.236E-07	163700.9	600.237	6.002E-09	218165.2	218.165	2.182E-09	0.01146428	0.00416687	
0	448	109774.8	47569.087	4.757E-07	148740.7	545.382	5.454E-09	198223.7	198.224	1.982E-09	0.01146506	0.00416707	
0	547	99742.3	43221.655	4.322E-07	135146.4	495.537	4.955E-09	180112.9	180.113	1.801E-09	0.01146501	0.00416719	
0	646	90277.2	39120.119	3.912E-07	122321.5	448.512	4.485E-09	163024.5	163.024	1.630E-09	0.01146500	0.00416728	
0	746	81540.5	35334.209	3.533E-07	110487.7	405.122	4.051E-09	147250.7	147.251	1.473E-09	0.01146542	0.00416737	
											AVG =	0.01146485	0.00416710
1	22	60280.1	26121.390	2.612E-07	84914.2	311.352	3.114E-09	108168.7	108.169	1.082E-09	0.01191943	0.00414100	
1	57	60397.5	26172.229	2.617E-07	85082.0	311.967	3.120E-09	108388.4	108.388	1.084E-09	0.01191978	0.00414135	
1	92	60382.5	26165.764	2.617E-07	85062.9	311.897	3.119E-09	108362.4	108.362	1.084E-09	0.01192005	0.00414138	
1	126	60292.4	26126.695	2.613E-07	84938.5	311.441	3.114E-09	108206.3	108.206	1.082E-09	0.01192042	0.00414160	
1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038	0.00414135	
1	822	80753.1	34992.999	3.499E-07	113764.3	417.136	4.171E-09	144934.0	144.934	1.449E-09	0.01192055	0.00414180	
											AVG =	0.01192010	0.00414141

	δ 45	δ 46	δ 45 _{PDB}	δ 46 _{PDB}	Craig $\delta^{13}\text{C}_{\text{PDB}}$	Craig $\delta^{18}\text{O}_{\text{CO}_2}$ $\delta^{18}\text{O}_{\text{PDB}}$	$\delta^{18}\text{O}^{\text{wt}}$ PDB	$\delta^{18}\text{O}^{\text{wt}}$ SMOW
AVG =	-38.19	6.20	-41.51	-2.43				

Résistance Ampli.	Valeur (Ω)	Facteur de gain rel. à $10^8\Omega$
Gain 44	2.31E+08	2.31
Gain 45	2.73E+10	272.73
Gain 46	1.00E+11	1000.00
<hr/>		
Nom Réf	δ^{45}_{PDB} (%)	δ^{46}_{PDB} (%)
Luxfer 1	-3.451	-8.580

$$\delta_3 = \delta_1 + \delta_2 + \frac{\delta_1 \delta_2}{10^3}$$

Analyse d'un échantillon d'eau

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Surf 46 (mVs)	Surf 46 (As)	R 45 via mVs or As	R 46 via mVs or As	
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1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038	0.00414135	
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											AVG =	0.01192010	0.00414141

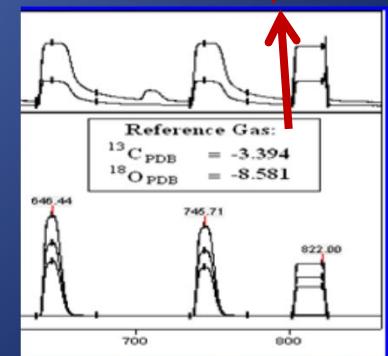
δ_{45}	δ_{46}	$\delta_{45\text{PDB}}$	$\delta_{46\text{PDB}}$	Craig	Craig	$\delta^{18}\text{O}^{\text{wt}}$	$\delta^{18}\text{O}^{\text{wt}}$
				$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$	PDB	SMOW
Normalised							
AVG =	-38.19	6.20	-41.51	-2.43	-44.24	-2.34	

$$\delta^{13} = 1.0676 \delta^{45} - 0.0338 \delta^{18}$$

$$\delta^{18} = 1.0010 \delta^{46} - 0.0021 \delta^{13}$$

Résistance Amplifi.	Valeur (Ω)	Facteur de gain rel. à $10^8\Omega$
Gain 44	2.31E+08	2.31
Gain 45	2.73E+10	272.73
Gain 46	1.00E+11	1000.00

Nom Réf	δ^{45}_{PDB} (‰)	δ^{46}_{PDB} (‰)
Luxfer 1	-3.451	-8.580



Le facteur de fractionnement isotopique (α)

Pour exprimer le fractionnement isotopique entre deux phases ou substances, nous utilisons souvent la notation « ϵ » ; qui est défini pour représenter ,sous forme de delta, le facteur de fractionnement isotopique:

$$\epsilon = 10^3 \ln \alpha \approx (\alpha - 1) 10^3$$

Par exemple, le fractionnement de l'oxygène-18 entre le CO₂ et H₂O est de 1,0412 à 25,0 °C. On dit souvent qu'à 25,0 °C, le fractionnement entre le dioxyde de carbone et l'eau est de 41,2 pour mil, ou que le CO₂ est enrichie en ¹⁸O de 41,2 pour mil par rapport à l'eau. Il est généralement écrit comme:

$$\alpha_{CO_2 - H_2O} = 1.0412$$

$$K = \alpha = \frac{\left(\frac{^{18}O}{^{16}O} \right)_{CO_2}}{\left(\frac{^{18}O}{^{16}O} \right)_{H_2O}}$$

Le facteur de fractionnement isotopique (α)

$$\alpha_{a-b} = \frac{R_a}{R_b}$$

Where $R_a = \frac{I_{Heavy}}{I_{Common}}$ such as $\frac{^{13}C}{^{12}C}$

And since the natural abundance is generally $I_H \ll I_C$ then $\alpha_{a-b} = \frac{I_{H(a)}}{I_{H(b)}}$

In δ notation we know that: $\alpha_{a-b} = \frac{R_a}{R_b}$ and $\delta_a = (\frac{R_a}{R_{std}} - 1)10^3$, $\delta_b = (\frac{R_b}{R_{std}} - 1)10^3$

Thus by rearranging

$$R_a = R_{std} \left(\frac{\delta_a}{10^3} + 1 \right), R_b = R_{std} \left(\frac{\delta_b}{10^3} + 1 \right)$$

By substitution

$$\alpha_{a-b} = \frac{R_{std} \left(\frac{\delta_a}{10^3} + 1 \right)}{R_{std} \left(\frac{\delta_b}{10^3} + 1 \right)}$$

where $\alpha_{a-b} \left(\frac{\delta_b}{10^3} + 1 \right) = \left(\frac{\delta_a}{10^3} + 1 \right)$

Further simplifying

$$\alpha_{a-b} \left(\frac{\delta_b + 10^3}{10^3} \right) = \frac{\delta_a + 10^3}{10^3} \quad \text{and} \quad \alpha_{a-b} (\delta_b + 10^3) = \delta_a + 10^3$$

$$\alpha_{a-b} = \frac{\delta_a + 10^3}{\delta_b + 10^3}$$

Laboratoire des isotopes stables – G.G. Hatch - Stable Isotope Laboratory
 Facteurs de fractionnement pour le CO_2 libéré par la réaction H_3PO_4 - Carbonate / Fractionation factors for CO_2 liberated by H_3PO_4 - Carbonate reactions
 juin 2006 / June 2006

1) CARBONE / CARBON (Aucune correction nécessaire / No correction needed)

$$\delta^{13}C_{VPDB}^{\text{Min.}} = \delta^{13}C_{VPDB}^{CO_2}$$

2) OXYGÈNE / OXYGEN (Note in all equations: $T = {}^\circ\text{K}$)

Calcite 25°C $\alpha = 1.01025$ $\varepsilon = 10^3 \ln \alpha = 10.20$ $\delta^{18}O_{VPDB}^{\text{cal}} = 0.9899 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 1460$ où / where $10^3 \ln \alpha = 5.608 \forall 0.151 * 10^5 \left(\frac{1}{T^2} \right) + 3.89 \forall 0.08$ (S. Das Sharma, D.J. Patil, and K. Gopalan, 2002) (I. Friedman and J.R. O'Neil, 1977) (T. Sharma and R.N. Clayton, 1965)	Dolomite 50°C $\alpha = 1.01017$ $\varepsilon = 10^3 \ln \alpha = 10.12$ $\delta^{18}O_{VPDB}^{\text{dol}} = 0.9899 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 1700$ où / where $10^3 \ln \alpha = 5.858 \forall 0.189 * 10^5 \left(\frac{1}{T^2} \right) + 4.51 \forall 0.06$ (S. Das Sharma, D.J. Patil, and K. Gopalan, 2002) (J. Rosenbaum and S.M.F. Sheppard, 1986)
Ankerite 50°C $\alpha = 1.010603$ $\varepsilon = 10^3 \ln \alpha = 10.55$ $\delta^{18}O_{VPDB}^{\text{ank}} = 0.9895 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 4915$ où / where $10^3 \ln \alpha = 6.68 * 10^5 \left(\frac{1}{T^2} \right) + 4.15$ (J. Rosenbaum and S.M.F. Sheppard, 1986)	Siderite 50°C $\alpha = 1.010454$ $\varepsilon = 10^3 \ln \alpha = 10.40$ $\delta^{18}O_{VPDB}^{\text{sid}} = 0.9897 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 3462$ où / where $10^3 \ln \alpha = 6.84 * 10^5 \left(\frac{1}{T^2} \right) + 3.85$ (J. Rosenbaum and S.M.F. Sheppard, 1986)
Magnesite 50°C $\alpha = 1.010833$ $\varepsilon = 10^3 \ln \alpha = 11.53$ $\delta^{18}O_{VPDB}^{\text{mag}} = 0.9893 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 8330$ où / where $10^3 \ln \alpha = 6.845 \forall 0.475 * 10^5 \left(\frac{1}{T^2} \right) + 4.22 \forall 0.08$ (S. Das Sharma, D.J. Patil, and K. Gopalan, 2002) (E.C. Perry and E.C. Tan, 1972)	Rhodochrosite 25°C $\alpha = 1.0101203$ $\varepsilon = 10^3 \ln \alpha = 10.07$ $\delta^{18}O_{VPDB}^{\text{rhod}} = 0.9900 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 0189$ (I. Friedman and J.R. O'Neil, 1977)
Witherite 25°C $\alpha = 1.0109697$ $\varepsilon = 10^3 \ln \alpha = 10.91$ $\delta^{18}O_{VPDB}^{\text{with}} = 0.9891 \quad \delta^{18}O_{VPDB}^{CO_2} - 10 . 8507$ (I. Friedman and J.R. O'Neil, 1977)	Eau / Water 25°C $\alpha = 1.04120$ $\varepsilon = 10^3 \ln \alpha = 40.37$ $\delta^{18}O_{VPDB}^{\text{wat}} = 0.9604 \delta^{18}O_{VPDB}^{CO_2} - 39.5697$ (I. Friedman and J.R. O'Neil, 1977)
Calcite 50°C $\alpha = 1.009303$ $\varepsilon = 10^3 \ln \alpha = 9.26$ $\delta^{18}O_{VPDB}^{\text{cal}} = 0.9908 \quad \delta^{18}O_{VPDB}^{CO_2} - 9 . 3030$ où / where $10^3 \ln \alpha = 5.608 \forall 0.151 * 10^5 \left(\frac{1}{T^2} \right) + 3.89 \forall 0.08$ (S. Das Sharma, D.J. Patil, and K. Gopalan, 2002) (P.K. Swart, S.J. Burge and J.L. Loder, 1991)	Strontianite 25 °C $\alpha = 1.010485$ $\varepsilon = 10^3 \ln \alpha = 10.43$ $\delta^{18}O_{VPDB}^{\text{cal}} = 0.9899 \quad \delta^{18}O_{VPDB}^{CO_2} - 8 . 9190$ (I. Friedman and J.R. O'Neil, 1977)

CONVERSIONS

PDB-SMOW	$\delta^{18}O_{VSMOW} = 1 . 03092 \quad \delta^{18}O_{VPDB} + 30 . 92$
SMOW-PDB	$\delta^{18}O_{VPDB} = 0 . 97001 \quad \delta^{18}O_{VSMOW} - 29 . 99$

Analyse d'un échantillon d'eau

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Surf 46 (mVs)	Surf 46 (As)	R 45 via mVs or As	R 46 via mVs or As	
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											AVG =	0.01146485	0.00416710
1	22	60280.1	26121.390	2.612E-07	84914.2	311.352	3.114E-09	108168.7	108.169	1.082E-09	0.01191943	0.00414100	
1	57	60397.5	26172.229	2.617E-07	85082.0	311.967	3.120E-09	108388.4	108.388	1.084E-09	0.01191978	0.00414135	
1	92	60382.5	26165.764	2.617E-07	85062.9	311.897	3.119E-09	108362.4	108.362	1.084E-09	0.01192005	0.00414138	
1	126	60292.4	26126.695	2.613E-07	84938.5	311.441	3.114E-09	108206.3	108.206	1.082E-09	0.01192042	0.00414160	
1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038	0.00414135	
1	822	80753.1	34992.999	3.499E-07	113764.3	417.136	4.171E-09	144934.0	144.934	1.449E-09	0.01192055	0.00414180	
											AVG =	0.01192010	0.00414141

}

δ_{45}	δ_{46}	δ_{45}^{PDB}	δ_{46}^{PDB}	Craig	Craig	$\delta^{18}\text{O}_{\text{PDB}}^{\text{wt}}$	$\delta^{18}\text{O}_{\text{SMOW}}^{\text{wt}}$	Résistance Amplifi.	Valeur (Ω)	Facteur de gain rel. à $10^8\Omega$
								Gain 44	2.31E+08	2.31
								Gain 45	2.73E+10	272.73
								Gain 46	1.00E+11	1000.00
								Nom Réf	$\delta^{45}_{\text{PDB}} (\%)$	$\delta^{46}_{\text{PDB}} (\%)$
								Luxfer 1	-3.451	-8.580
AVG =	-38.19	6.20	-41.51	-2.43	-44.24	-2.34	-41.82	-12.19	Normalisé	

Eau / Water 25°C

$$\alpha = 1.04120 \cdot$$

$$\epsilon = 10^3 \ln \alpha = 40.37 \text{ ‰}$$

$$\delta^{18}\text{O}_{\text{VPDB}}^{\text{wat}} = 0.9604 \delta^{18}\text{O}_{\text{VPDB}}^{\text{CO}_2} - 39.5697 \text{ ‰}$$

(I. Friedman and J.R. O'Neil, 1977) □

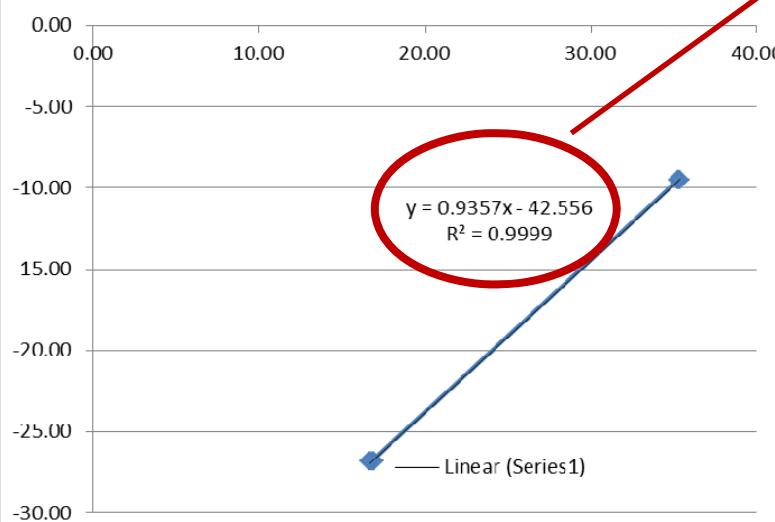
$$\alpha_{a-b} = \frac{\delta_a + 10^3}{\delta_b + 10^3}$$



$$\text{PDB-SMOW} \quad \delta^{18}\text{O}_{\text{VSMOW}} = 1.03092 \delta^{18}\text{O}_{\text{VPDB}} + 30.92$$



Analysis	Identifier 1	Identifier 2	Ampl 44	Rt	d 13C/12C	Known 13C PDB	Corrected Del 13C PDB	What if reference gas value was fixed (-42.56)?	Difference between normalised data and a fixed ref gas	Comments
B-3524	Alcohol	Conditioning	4805	162.1	32.24	-12.30	-12.39	-11.59	-0.80	
B-3525	Alcohol	Conditioning	4894	162.1	32.30	-12.30	-12.33	-11.53	-0.80	
B-3526	Alcohol	Conditioning	4820	162.0	32.21	-12.30	-12.42	-11.62	-0.80	
B-3527	Alcohol	Conditioning	4849	162.1	32.32	-12.30	-12.32	-11.52	-0.80	
B-3532	Alcohol	sample-1	4909	162.2	32.22	-12.30	-12.40	-11.60	-0.80	Used as check
B-3541	Sherry	sample-10	2787	162.3	19.13		-24.66	-24.19	-0.48	
B-3542	Sherry	sample-11	2840	162.3	19.16		-24.63	-24.15	-0.48	
B-3543	Sherry	sample-12	2861	162.2	19.36		-24.44	-23.96	-0.48	
B-3544	entre cote	sample-13	1479	162.4	19.80		-24.03	-23.54	-0.49	
B-3545	entre cote	sample-14	1466	162.3	19.99		-23.85	-23.36	-0.50	
B-3546	entre cote	sample-15	1460	162.4	19.83		-24.01	-23.51	-0.49	
B-3547	Australian	sample-16	1755	162.3	16.30		-27.30	-26.90	-0.40	
B-3548	Australian	sample-17	1772	162.4	16.57		-27.05	-26.64	-0.41	
B-3549	Australian	sample-18	1778	162.4	16.40		-27.21	-26.81	-0.41	



-12.30	-12.34	-11.54	-0.80	Used as check
	-14.50	-13.75	-0.74	
	-18.81	-18.19	-0.63	
	-18.63	-18.00	-0.63	
	-18.82	-18.19	-0.63	
	-19.09	-18.47	-0.62	
	-19.22	-18.60	-0.61	
	-19.03	-18.41	-0.62	
-12.30	-12.16	-11.35	-0.81	Used as check
	-19.30	-18.68	-0.62	
	-19.51	-18.90	-0.61	
	-20.08	-19.48	-0.60	
	-26.48	-26.05	-0.43	
	-26.38	-25.95	-0.43	
	-26.24	-25.80	-0.43	

B-3528	Finlandia	standard	4937	162.0	16.90	-26.81	-26.74	-26.32	-0.42	Standards used in exercise
B-3529	Finlandia	standard	4928	162.3	16.96	-26.81	-26.69	-26.27	-0.42	Standards used in exercise
B-3530	Finlandia	standard	4963	162.1	16.70	-26.81	-26.93	-26.51	-0.42	Standards used in exercise
B-3531	Finlandia	standard	5027	162.2	16.75	-26.81	-26.88	-26.46	-0.42	Standards used in exercise
B-3559	Indigo	standard	4874	162.2	35.26	-9.51	-9.57	-8.69	-0.87	Standards used in exercise
B-3560	Indigo	standard	4889	162.2	35.39	-9.51	-9.44	-8.57	-0.88	Standards used in exercise
B-3561	Indigo	standard	4867	162.1	35.26	-9.51	-9.56	-8.69	-0.87	Standards used in exercise
B-3562	Indigo	standard	4891	162.2	35.36	-9.51	-9.47	-8.592	-0.88	Standards used in exercise

Analyse d'un échantillon d'eau

Réf	Rt	rSurf 44 (mVs)	Surf 44 (mVs)	Surf 44 (As)	rSurf 45 (mVs)	Surf 45 (mVs)	Surf 45 (As)	rSurf 46 (mVs)	Surf 46 (mVs)	Surf 46 (As)	R 45 via mVs or As	R 46 via mVs or As	
0	248	133683.4	57929.458	5.793E-07	181123.8	664.121	6.641E-09	241382.2	241.382	2.414E-09	0.01146430	0.00416683	
0	348	120824.1	52357.105	5.236E-07	163700.9	600.237	6.002E-09	218165.2	218.165	2.182E-09	0.01146428	0.00416687	
0	448	109774.8	47569.087	4.757E-07	148740.7	545.382	5.454E-09	198223.7	198.224	1.982E-09	0.01146506	0.00416707	
0	547	99742.3	43221.655	4.322E-07	135146.4	495.537	4.955E-09	180112.9	180.113	1.801E-09	0.01146501	0.00416719	
0	646	90277.2	39120.119	3.912E-07	122321.5	448.512	4.485E-09	163024.5	163.024	1.630E-09	0.01146500	0.00416728	
0	746	81540.5	35334.209	3.533E-07	110487.7	405.122	4.051E-09	147250.7	147.251	1.473E-09	0.01146542	0.00416737	
											AVG =	0.01146485	0.00416710
1	22	60280.1	26121.390	2.612E-07	84914.2	311.352	3.114E-09	108168.7	108.169	1.082E-09	0.01191943	0.00414100	
1	57	60397.5	26172.229	2.617E-07	85082.0	311.967	3.120E-09	108388.4	108.388	1.084E-09	0.01191978	0.00414135	
1	92	60382.5	26165.764	2.617E-07	85062.9	311.897	3.119E-09	108362.4	108.362	1.084E-09	0.01192005	0.00414138	
1	126	60292.4	26126.695	2.613E-07	84938.5	311.441	3.114E-09	108206.3	108.206	1.082E-09	0.01192042	0.00414160	
1	161	60368.9	26159.844	2.616E-07	85046.0	311.835	3.118E-09	108337.1	108.337	1.083E-09	0.01192038	0.00414135	
1	822	80753.1	34992.999	3.499E-07	113764.3	417.136	4.171E-09	144934.0	144.934	1.449E-09	0.01192055	0.00414180	
											AVG =	0.01192010	0.00414141

Différence:

Normalisé vs Calc direct = 0.38%

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