Histoires de métaux que l'on dit lourds :
Questions d'environnements

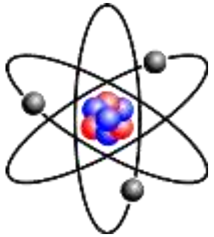
Olivier F.X. DONARD, CNRS, Université de Pau

L'histoire des **métaux lourds** n'a pas été écrite. Et pourtant, ils paraissent **étroitement liés à la civilisation.** L'**or**, l'**argent**, le **cuivre** ont permis de fabriquer les premières pièces de monnaie. Sans métaux lourds, il n'y aurait pas eu de distribution d'eau potable à Rome par les canalisations en plomb. Ni peintures, car les peintures anciennes ont résisté au temps grâce aux métaux incorporés aux pigments (le « jaune de Naples », à base de plomb, le « vermillon de mercure »...), ni vitraux dans les cathédrales, ni miroirs, étamés d'un amalgame d'étain et de mercure... **L'homme a utilisé les métaux lourds et continue à les utiliser. Parfois avec excès, souvent avec inconscience.** Ou pire, en toute conscience. **Si les métaux lourds ont fait la civilisation, ils peuvent aussi la défaire.** Car les métaux lourds sont aussi des toxiques puissants.

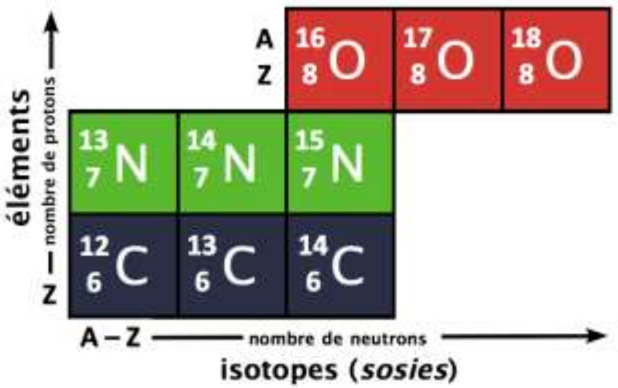
SÉNAT
UN SITE AU SERVICE DES CITOYENS

Un **élément chimique** est l'ensemble des atomes caractérisés par un nombre défini de protons dans leur noyau. Ce nombre, noté Z, est le numéro atomique de l'élément chimique. En effet, les propriétés chimiques des atomes sont déterminées par leur structure électronique, laquelle dépend directement du nombre de protons de leur noyau, de sorte que tous les atomes ayant le même numéro atomique partagent les mêmes propriétés chimiques. En revanche, les atomes d'un même élément chimique peuvent avoir un nombre variable de neutrons dans leur noyau, ce qu'on appelle des isotopes.

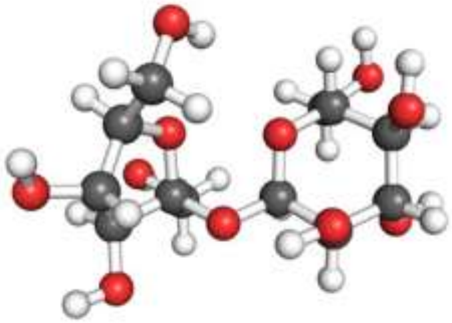
Un atome est un minuscule morceau de matière, une sorte de « brique » qui la constitue. Un atome contient un noyau (ensemble de protons et de neutrons), et autour de ce noyau, il y a des électrons.

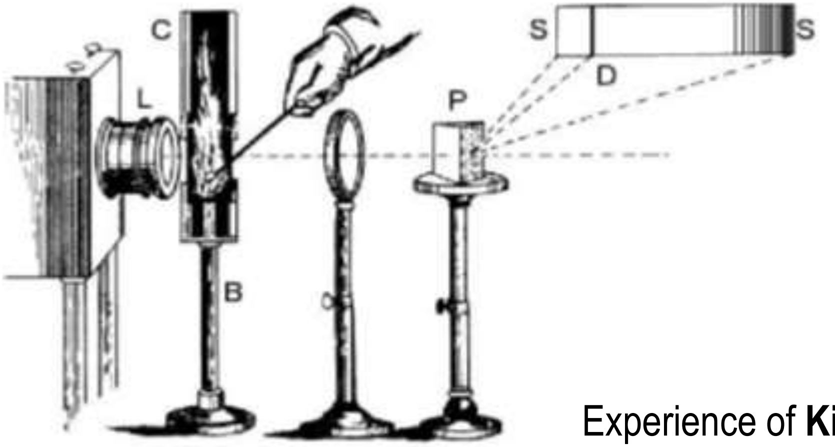


On appelle **isotopes** (d'un certain élément chimique) les nucléides partageant le même nombre de protons (caractéristique de cet élément), mais ayant un nombre de neutrons différent. Autrement dit, si l'on considère deux nucléides dont les nombres de protons sont Z et Z', et les nombres de neutrons N et N', ces nucléides sont dits isotopes si $Z = Z'$ et $N \neq N'$.

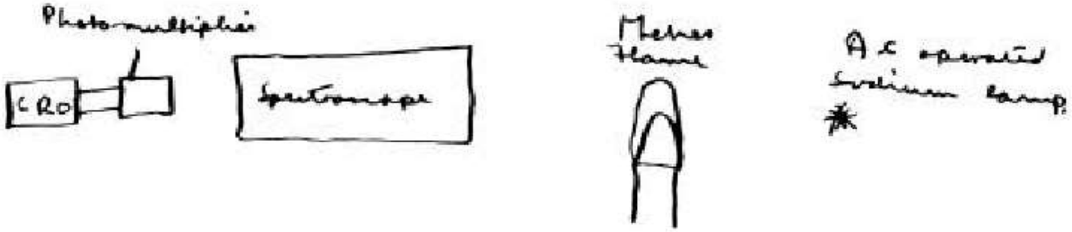


Qu'est-ce qu'une molécule ? Une molécule est constituée de deux atomes ou plus tenus ensemble par des liaisons chimiques. Ces atomes peuvent être de même sorte ou différents.





Experience of **Kirchoff** et **Busen** in 1859



February 1952 « Internal report » ***Sir A. Walsh***

« Assuming that the sample is vaporised by the usual methods, e.g. flame, arc, or spark, then the emission spectrum is « removed » by means of the chopper principle. Thus the emission spectrum produces no output signal and only the atomic spectrum is recorded. »


OR
CUIVRE
FER
ARGENT
PLATINE
LES MÉTAUX

TABLEAU PÉRIODIQUE DES ÉLÉMENTS

http://www.periodni.com/fr/

GROUPE / PÉRIODE

MASSE ATOMIQUE RELATIVE (1)
GROUPE IUPAC — GROUPE CAS: 13 IIIA
NOMBRE ATOMIQUE: 5 — 10.811
SYMBOLE: B
NOM DE L'ÉLÉMENT: BORE

Métaux — Métalloïdes — Non-métaux
Métaux alcalins — Chalcogènes
Métaux alcalino-terreux — Halogènes
Métaux de transition — Gaz nobles
Lanthanides
Actinides

ETAT PHYSIQUE (25 °C; 101 kPa)
Ne - gaz — Fe - solide
Hg - liquide — Tc - synthétique

PÉRIODE	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGÈNE																	2 4.0026 He HÉLIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BÉRYLLIUM											5 10.811 B BORE	6 12.011 C CARBONE	7 14.007 N AZOTE	8 15.999 O OXYGÈNE	9 18.998 F FLUOR	10 20.180 Ne NÉON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNÉSIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICIUM	15 30.974 P PHOSPHORE	16 32.065 S SOUFRE	17 35.453 Cl CHLORE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANE	23 50.942 V VANADIUM	24 51.996 Cr CHROME	25 54.938 Mn MANGANÈSE	26 55.845 Fe FER	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu CUIVRE	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SÉLÉNIUM	35 79.904 Br BROME	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.96 Mo MOLYBDÈNE	43 (98) Tc TECHNÉTIUM	44 101.07 Ru RUTHÉNIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag ARGENT	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn ETAIN	51 121.76 Sb ANTIMOINE	52 127.60 Te TELLURE	53 126.90 I IODE	54 131.29 Xe XÉNON
6	55 132.91 Cs CÉSIUM	56 137.33 Ba BARYUM	57-71 La-Lu Lanthanides	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALE	74 183.84 W TUNGSTÈNE	75 186.21 Re RHÉNIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINE	79 196.97 Au OR	80 200.59 Hg MERCURE	81 204.38 Tl THALLIUM	82 207.2 Pb PLOMB	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinides	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (...) Uut UNUNTRIUM	114 (287) Fl FLEROVIUM	115 (...) Uup UNUNPENTIUM	116 (291) Lv LIVERMORIUM	117 (...) Uus UNUNSEPTIUM	118 (...) Uuo UNUNOCTIUM

LANTHANIDES

57 138.91 La LANTHANE	58 140.12 Ce CÉRIUM	59 140.91 Pr PRASÉODYME	60 144.24 Nd NÉODYME	61 (145) Pm PROMÉTHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTÉTIUM

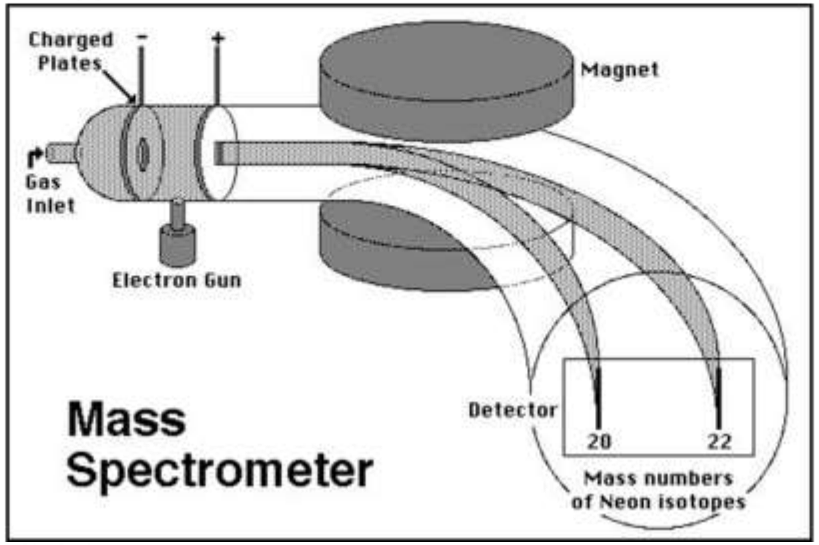
ACTINIDES

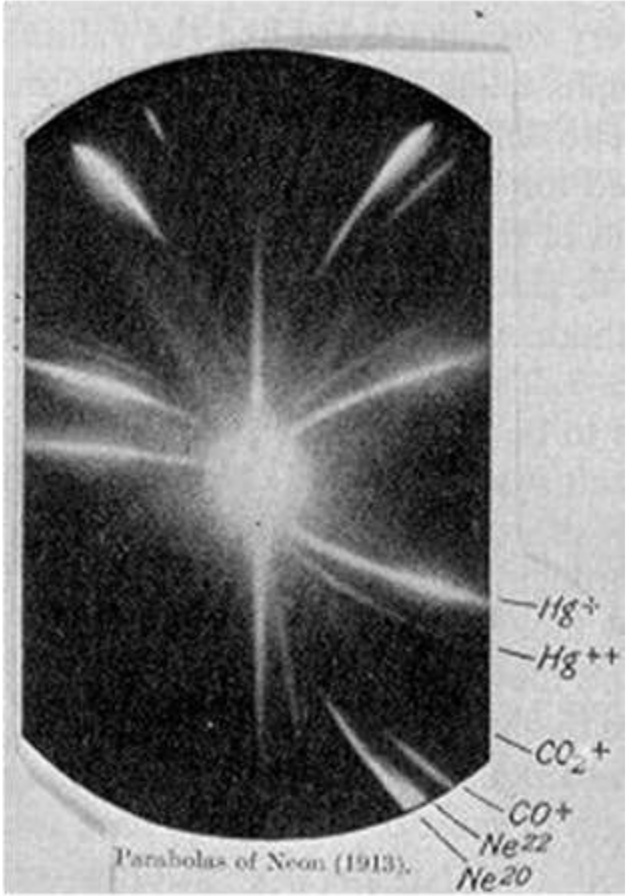
89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMÉRICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKÉLIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELÉVIUM	102 (259) No NOBÉLIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., **81**, No. 11, 2131-2156 (2009)
La masse atomique relative est donnée avec cinq chiffres significatifs. Pour les éléments qui n'ont pas de nucléides stables, la valeur entre parenthèses indique le nombre de masse de l'isotope de l'élément ayant la durée de vie la plus grande. Toutefois, pour les trois éléments (Th, Pa et U) qui ont une composition isotopique terrestre connue, une masse atomique est indiquée.

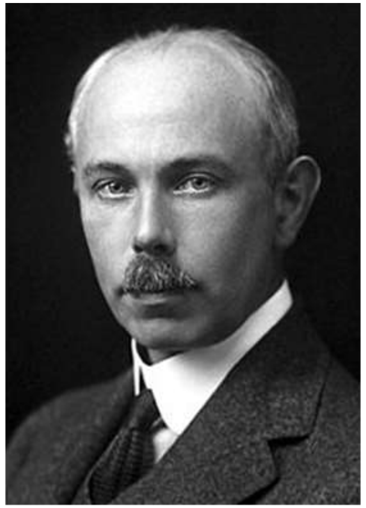
JJ Thomson, 1856 – 1940
Cambridge University
Nobel price of Physic in 1906

In 1897 :





Parabolas of Neon (1913).



FW Aston 1877-1945
Cambridge University
Nobel price of Chemistry in 1922

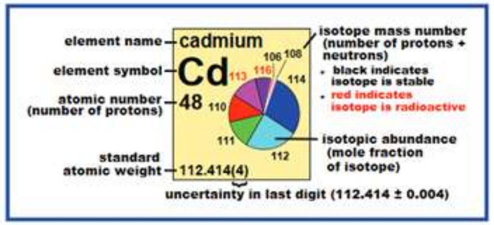
Discovered most of stable isotopes

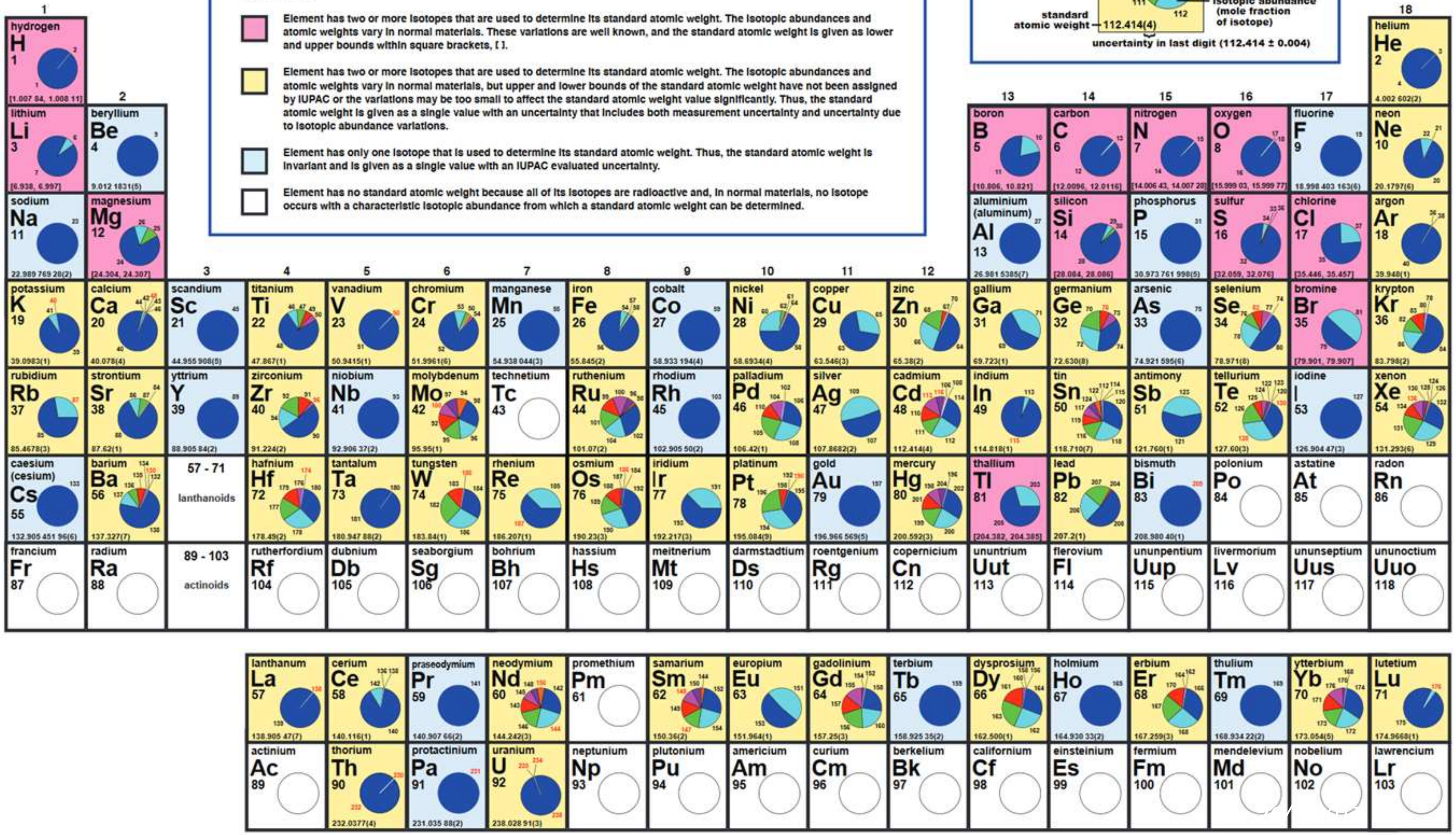
IUPAC Periodic Table of the Isotopes

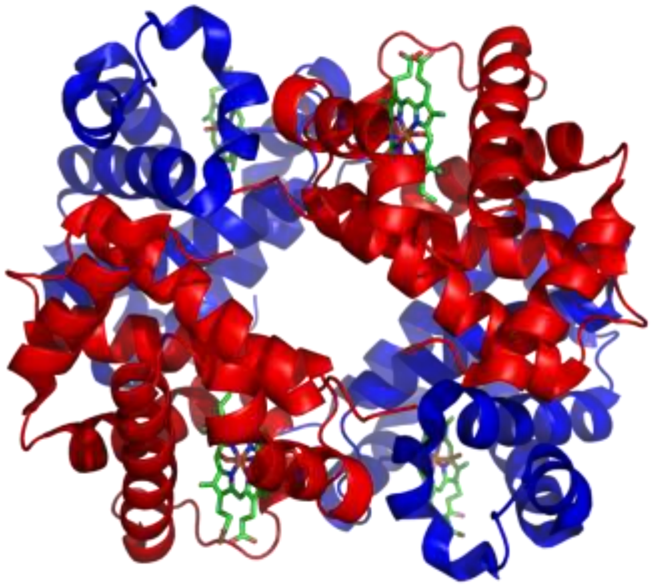
Element Background Color Key

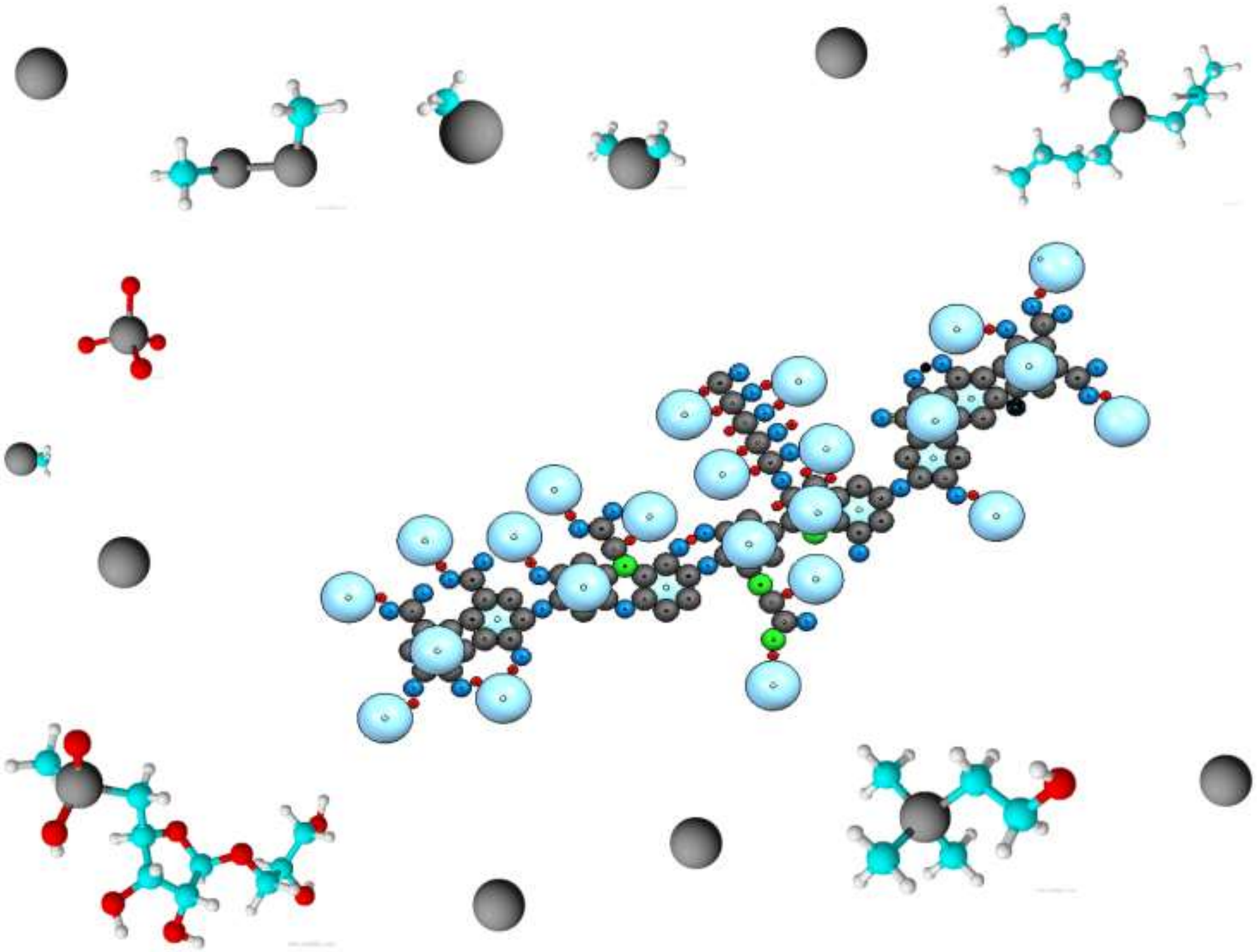
Standard atomic weights are the best estimates by IUPAC of atomic weights that are found in normal materials, which are terrestrial materials that are reasonably possible sources for elements and their compounds in commerce, industry, or science. These are determined using all stable isotopes and selected radioactive isotopes (having relatively long half-lives and characteristic terrestrial isotopic compositions). Isotopes are considered stable (non-radioactive) if evidence for radioactive decay has not been detected experimentally.

- (pink) Element has two or more isotopes that are used to determine its standard atomic weight. The isotopic abundances and atomic weights vary in normal materials. These variations are well known, and the standard atomic weight is given as lower and upper bounds within square brackets, [ ].
- (yellow) Element has two or more isotopes that are used to determine its standard atomic weight. The isotopic abundances and atomic weights vary in normal materials, but upper and lower bounds of the standard atomic weight have not been assigned by IUPAC or the variations may be too small to affect the standard atomic weight value significantly. Thus, the standard atomic weight is given as a single value with an uncertainty that includes both measurement uncertainty and uncertainty due to isotopic abundance variations.
- (light blue) Element has only one isotope that is used to determine its standard atomic weight. Thus, the standard atomic weight is invariant and is given as a single value with an IUPAC evaluated uncertainty.
- (white) Element has no standard atomic weight because all of its isotopes are radioactive and, in normal materials, no isotope occurs with a characteristic isotopic abundance from which a standard atomic weight can be determined.

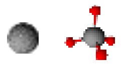




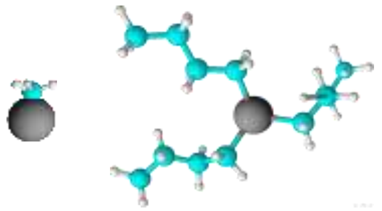




Formes chimiques des éléments

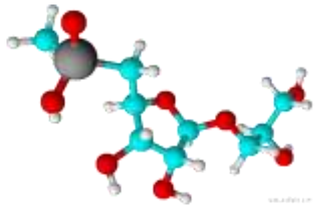


Inorganique

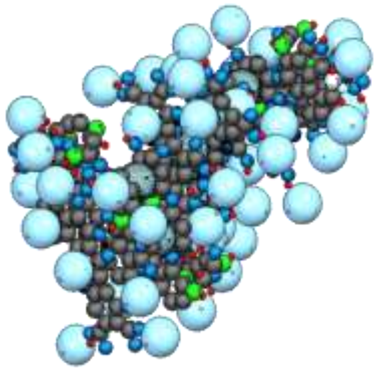


Organométalliques

Naturel versus Anthropique



Biomolécules



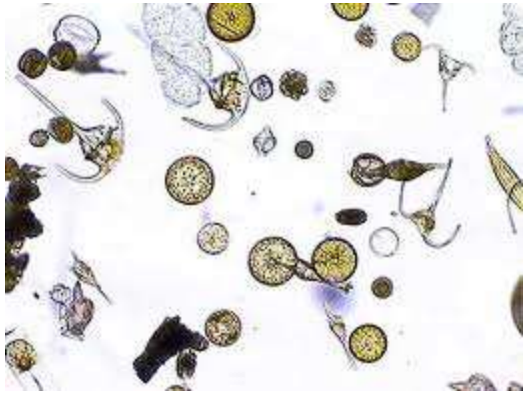
Complexes avec les substances humiques

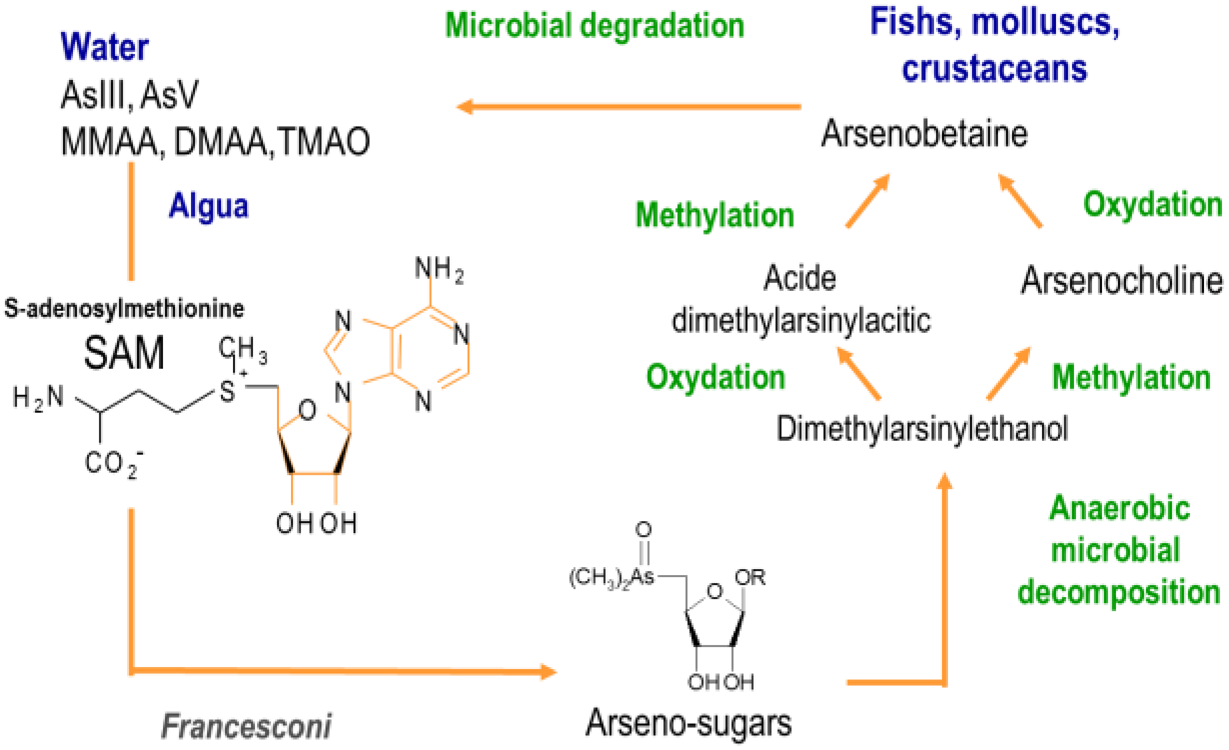
FORMES REDOX	COMPOSÉS ORGANOMÉTALLIQUES	BIOMOLÉCULES
As(III)/As(V)	Méthyl-Hg	Acides Aminés Se
Sb(III)/Sb(V)	Butyl et Phényl-Sn	Sucres arséniés
Cr(III)/Cr(VI)		Métalloprotéines

D'où viennent les métaux?

33
As
Arsenic
74.92160

Transformation de l'Arsenic dans l'environnement





As *Les formes chimiques de l'arsenic*

Espèces A

Arsénocholine
Arsénobétaïne

Non toxiques

DL_{50}rat > 10000 mg/kg

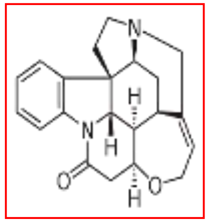
Espèces B

Acide monométhylarsonique (MMA)
Acide diméthylarsinique (DMA)

Non toxiques

DL_{50}rat : 700-2600 mg/kg

Composés de référence

Aspirine	**Strychnine**
	

DL_{50}rat (mg/kg)

Aspirine	Strychnine
1000-1600	2-16

Espèces C

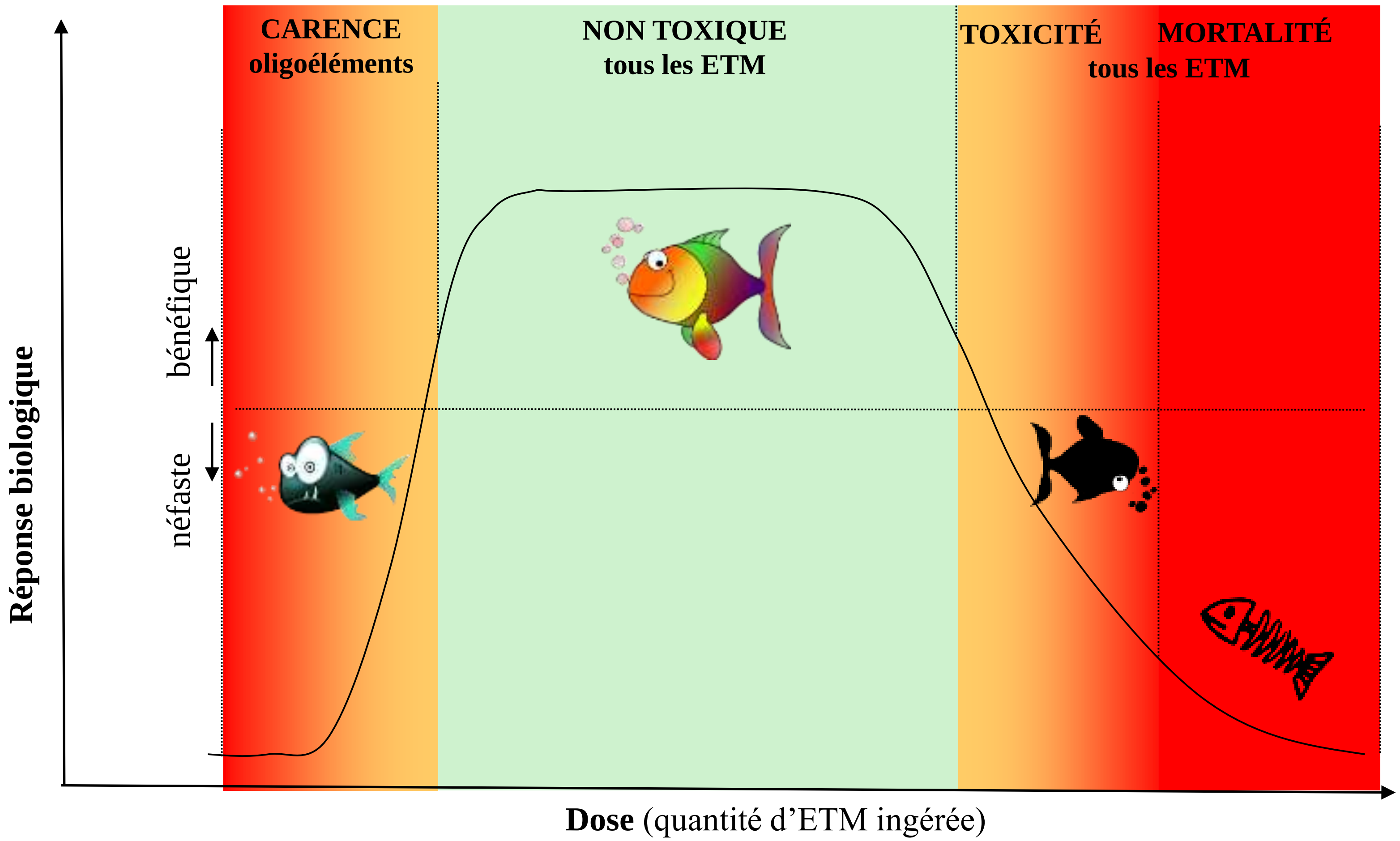
Arsénite (As(III))
Arséniate (As(V))
Arsine (AsH_3)

Très toxiques

DL_{50}rat : 3-20 mg/kg

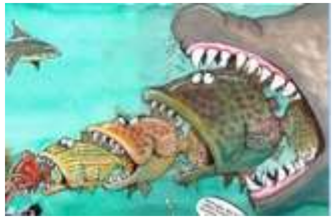
Evaluation du risque **Mesure de [As_{total}] très insuffisante**

Effet de la dose sur la dangerosité des ETM

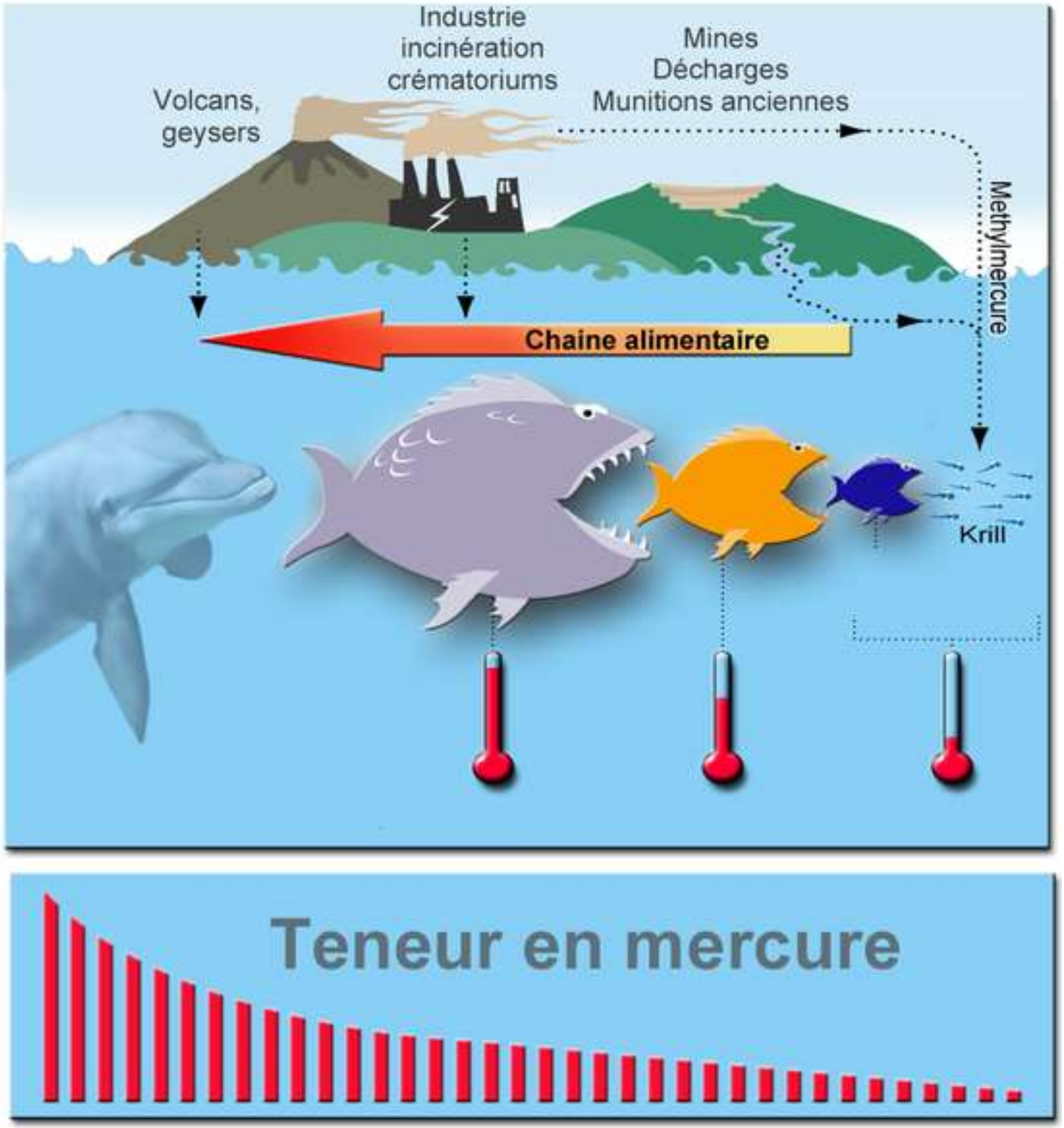


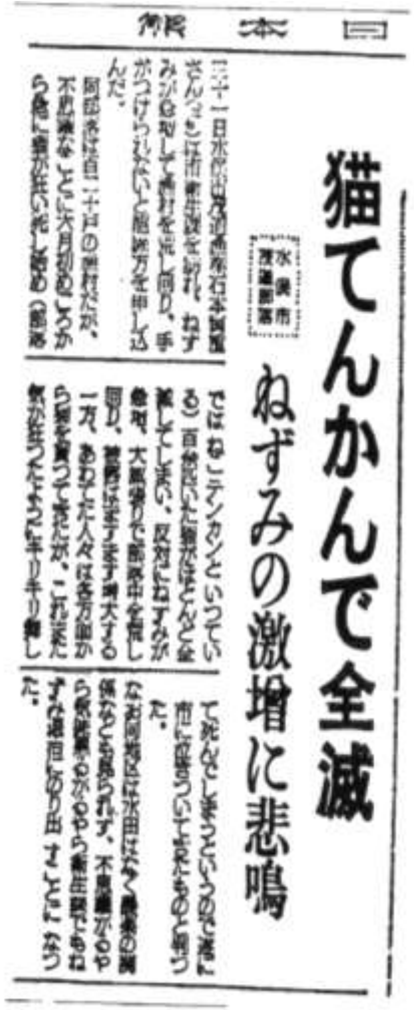
Métaux essentiels: Cu, Se, Fe

Métaux toxiques: Cd, Hg, Pb



Bioamplification



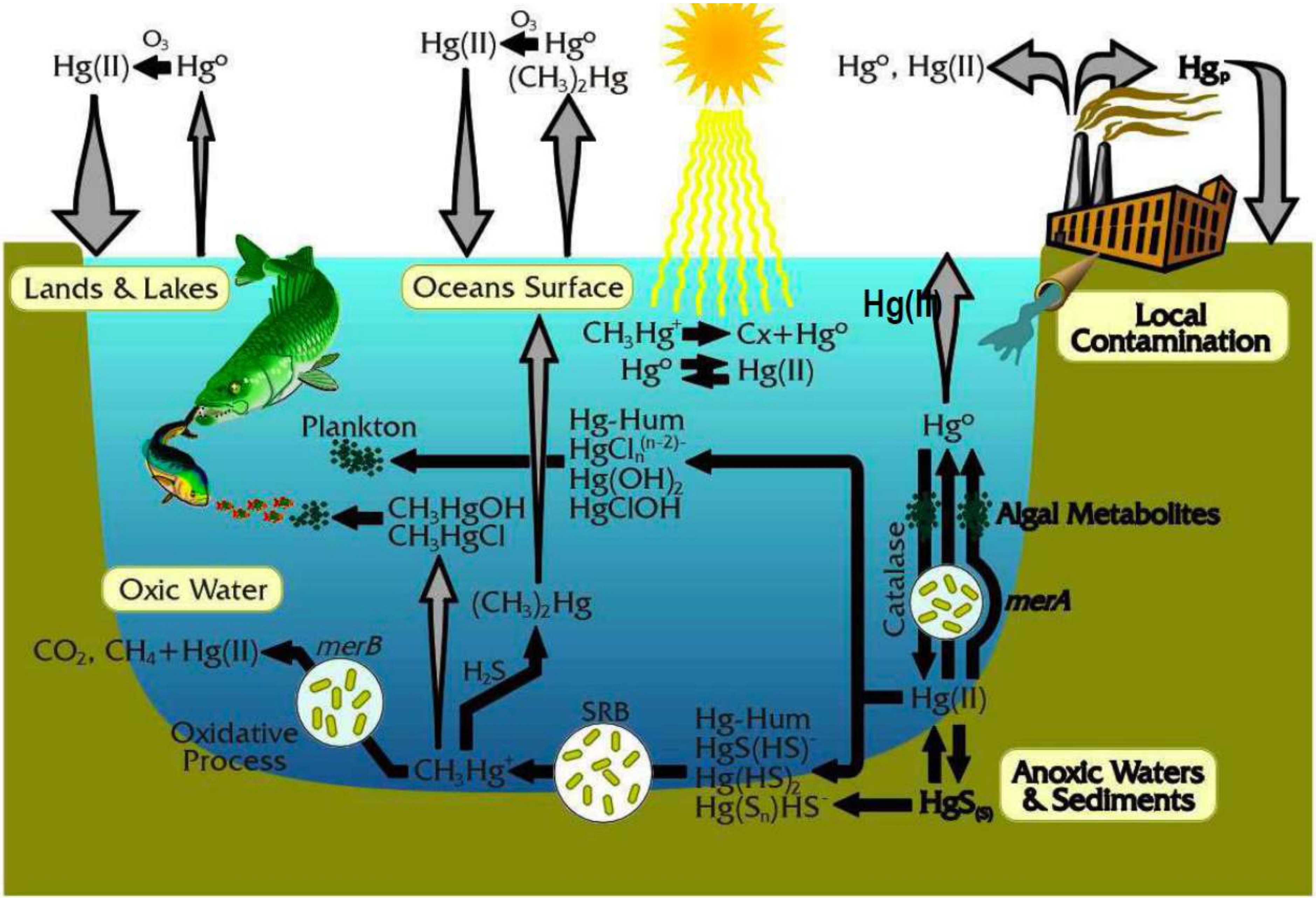


猫てんかんで全滅

ねずみの激増に悲鳴

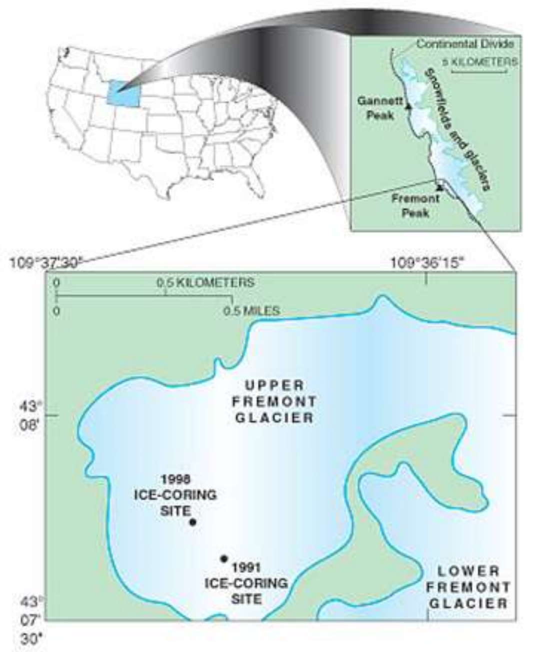
水俣市
茂道部落

Photo d’ Eugene Smith

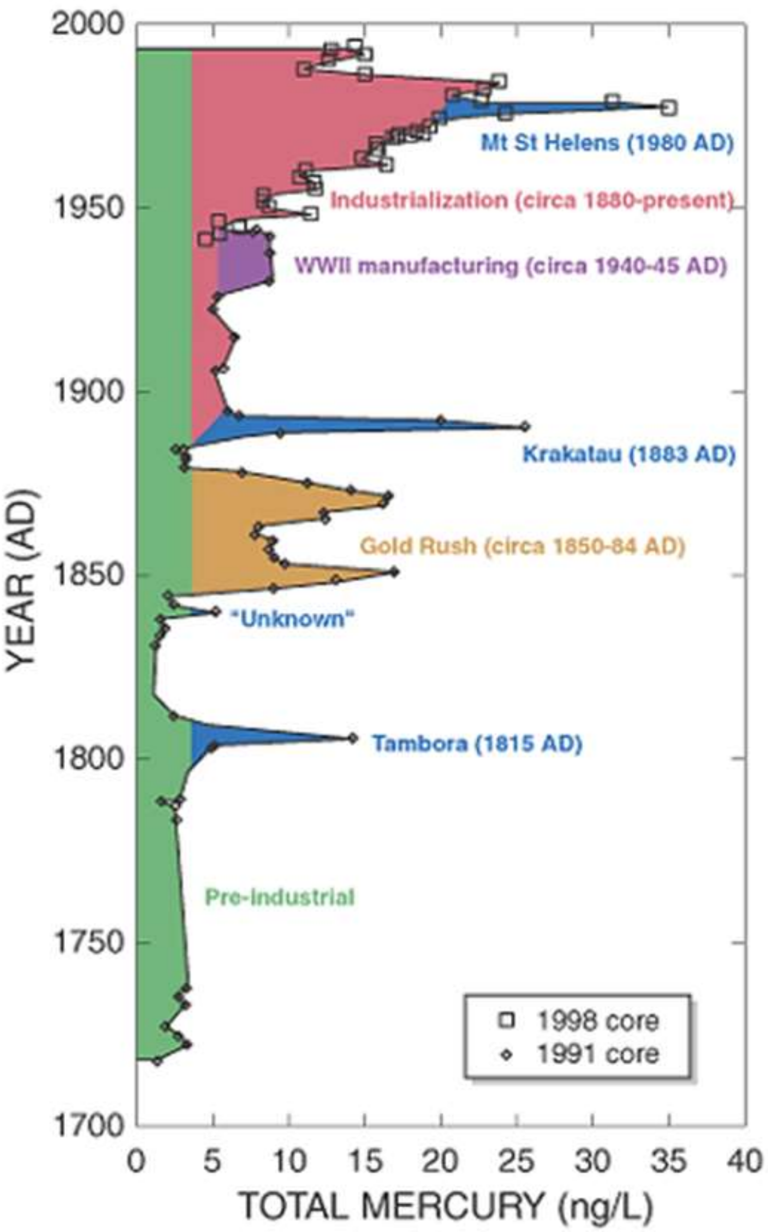


Based on Schaefer et al, 2002

USGS
2002



Continental Divide
5 KILOMETERS
Gannett Peak
Snowfields and glaciers
Fremont Peak
109°37'30"
109°36'15"
0.5 KILOMETERS
0.5 MILES
43° 08'
43° 07' 30"
UPPER FREMONT GLACIER
1998 ICE-CORING SITE
1991 ICE-CORING SITE
LOWER FREMONT GLACIER



YEAR (AD)
2000
1950
1900
1850
1800
1750
1700
0
5
10
15
20
25
30
35
40
TOTAL MERCURY (ng/L)
Mt St Helens (1980 AD)
Industrialization (circa 1880-present)
WWII manufacturing (circa 1940-45 AD)
Krakatau (1883 AD)
Gold Rush (circa 1850-84 AD)
"Unknown"
Tambora (1815 AD)
Pre-industrial
1998 core
1991 core


KOTC

Sn

Tin speciation and toxicity

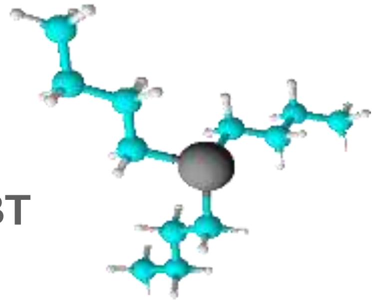
2 ng/L

ou

2 ppt

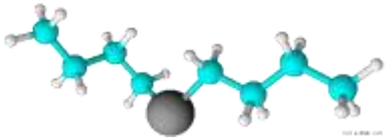
Bloque la reproduction

TBT

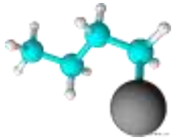


Toxicity

DBT

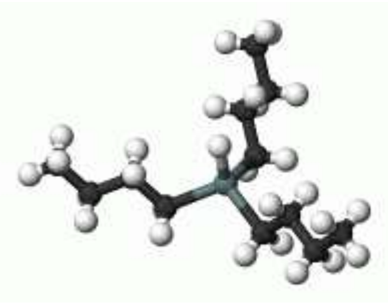


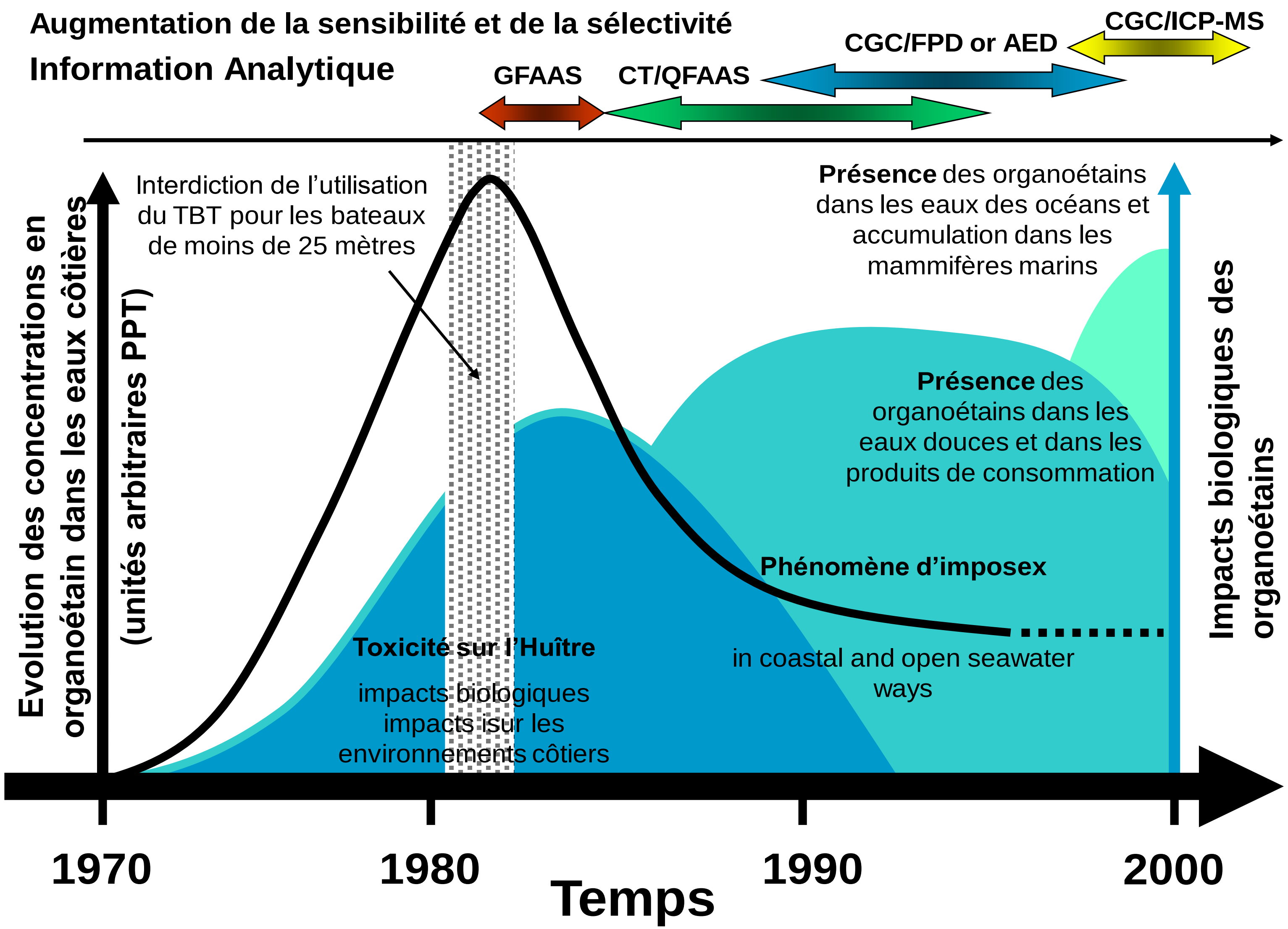
MBT



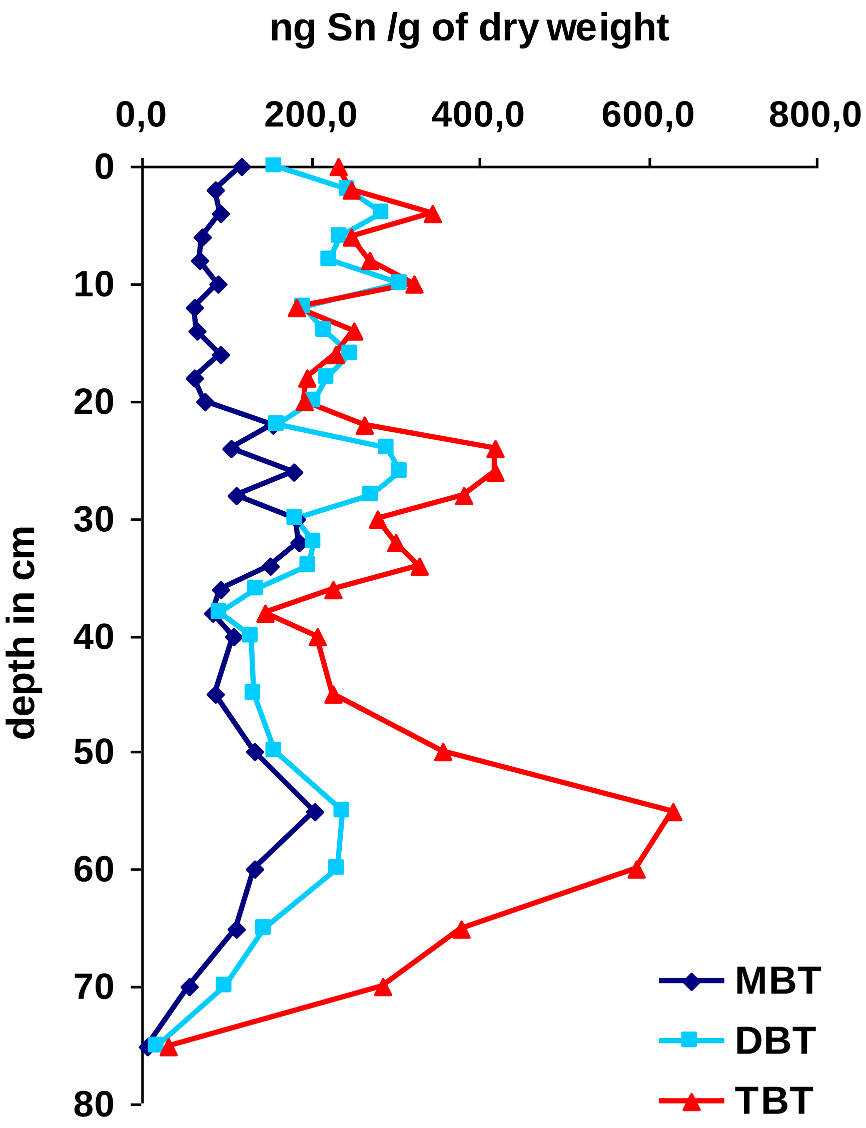
Sn Inorg.

Progrès de l'instrumentation et information obtenue





Le Tributylétain, toujours une question d'actualité

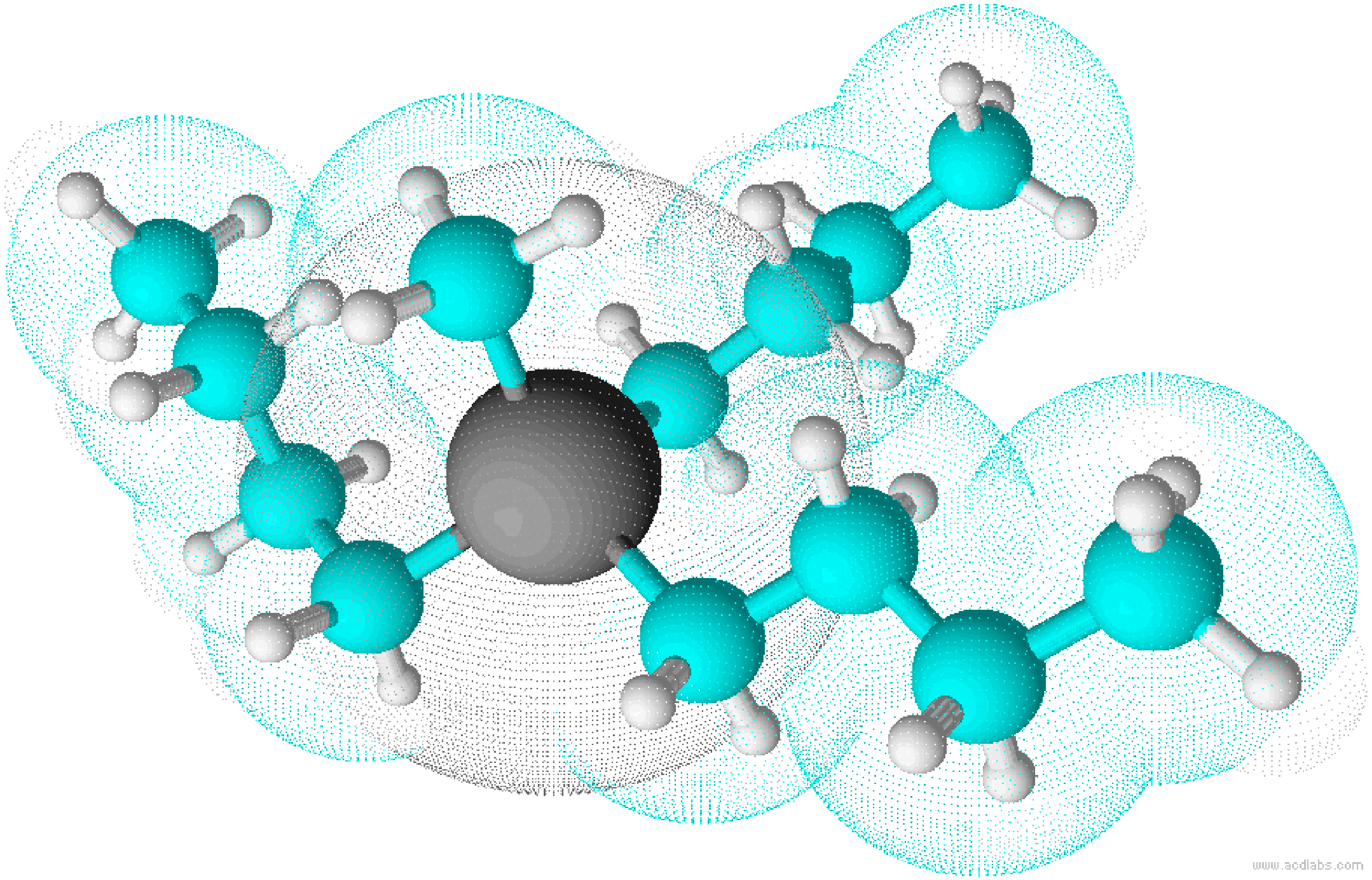


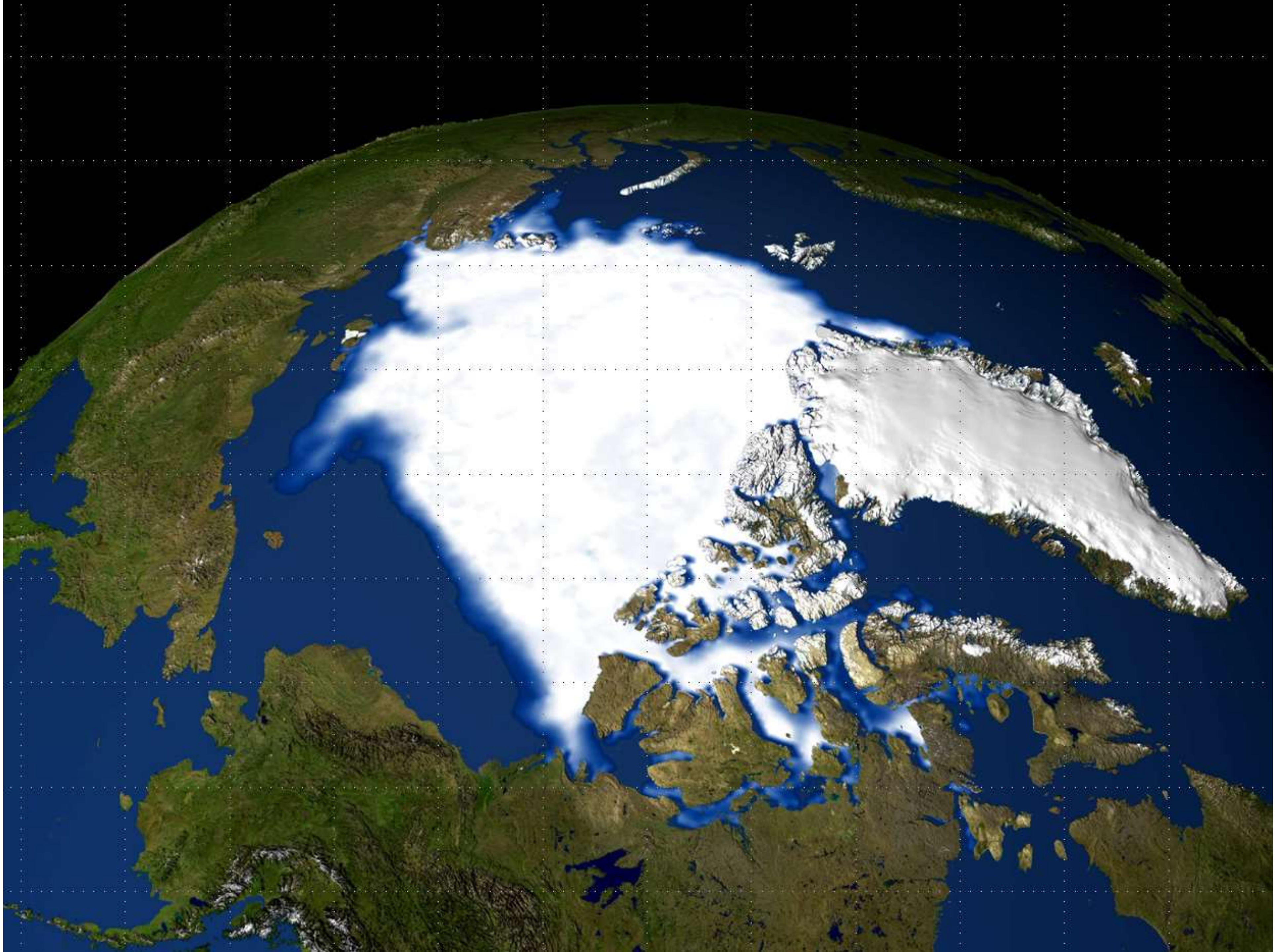
Années 80

Années 70

Methyl -TriButylTin

Compound	log Kow pred
Bu3SnCl	4,70
MeBu3Sn	7,90





Banking for the Alaska Marine Mammal Tissue Archival Project (AMMTAP)



Sources:
- strandings
- subsistence takes

Scope: Alaska

Matrices:
- liver
- kidney
- fat or blubber

Butyltin speciation procedure (SID)

Sample Spiking

^{119}Sn BuSn mix
^{119}Sn TBT
^{119}Sn DBT
^{119}Sn MBT

3 mL TMAH

Sample 1g

MW extraction

Derivatization

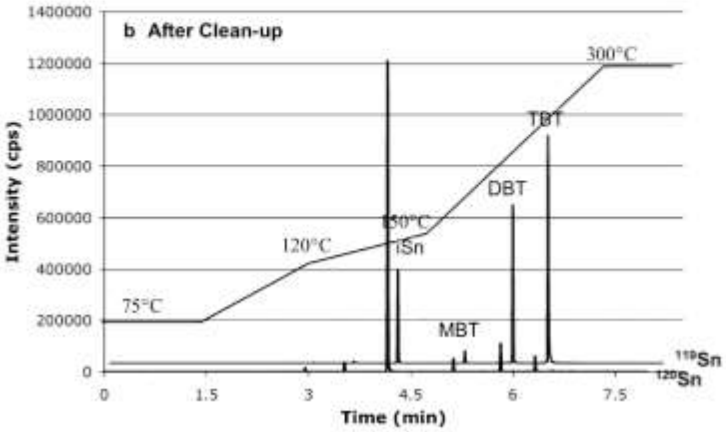
Adjust to pH 5.0

0.8 mL Hexane

0.1 mL $NaBEt_4$ (20% w/w)

Clean-up

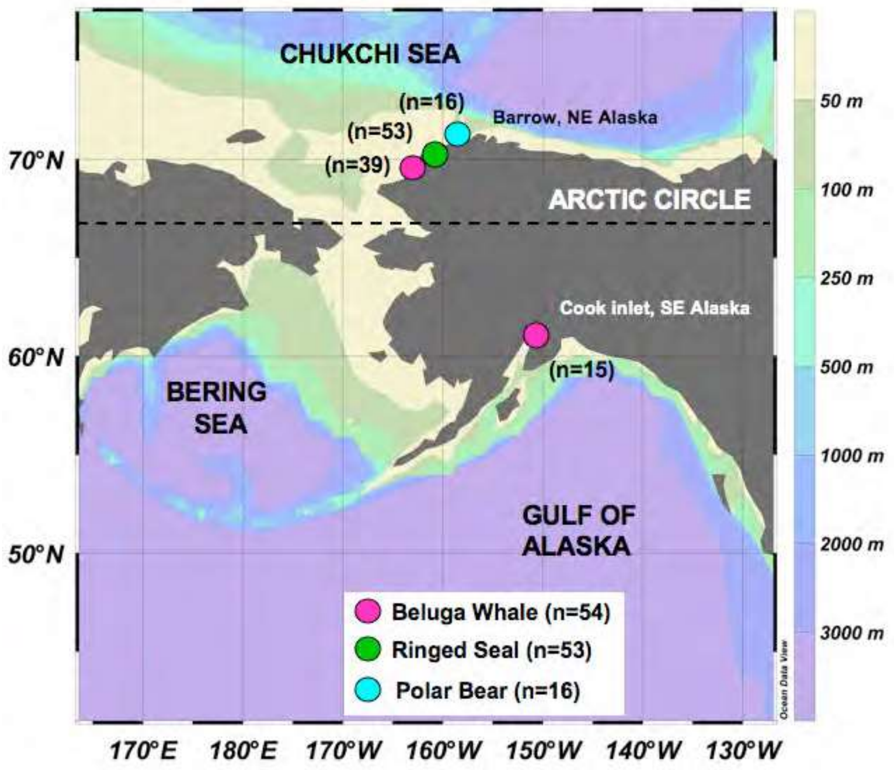
GC/ICP-MS Analysis



Detection Limits
MBT 0.006 ng/g Sn
DBT 0.001 ng/g Sn
TBT 0.008 ng/g Sn

(Point et al., 2007)

Temporal Trends



	Sex	Size (cm)	Age (y)
Polar Bear	9F, 7M	168-241	2-29
Beluga Whale	20F, 34M	238-663	5-55
Ringed Seal	22F, 31M	71-131	1-17

Polar Bear

Ursus maritimus

(1996-2002, 6y)

Beluga Whale

Delphinapterus leuca

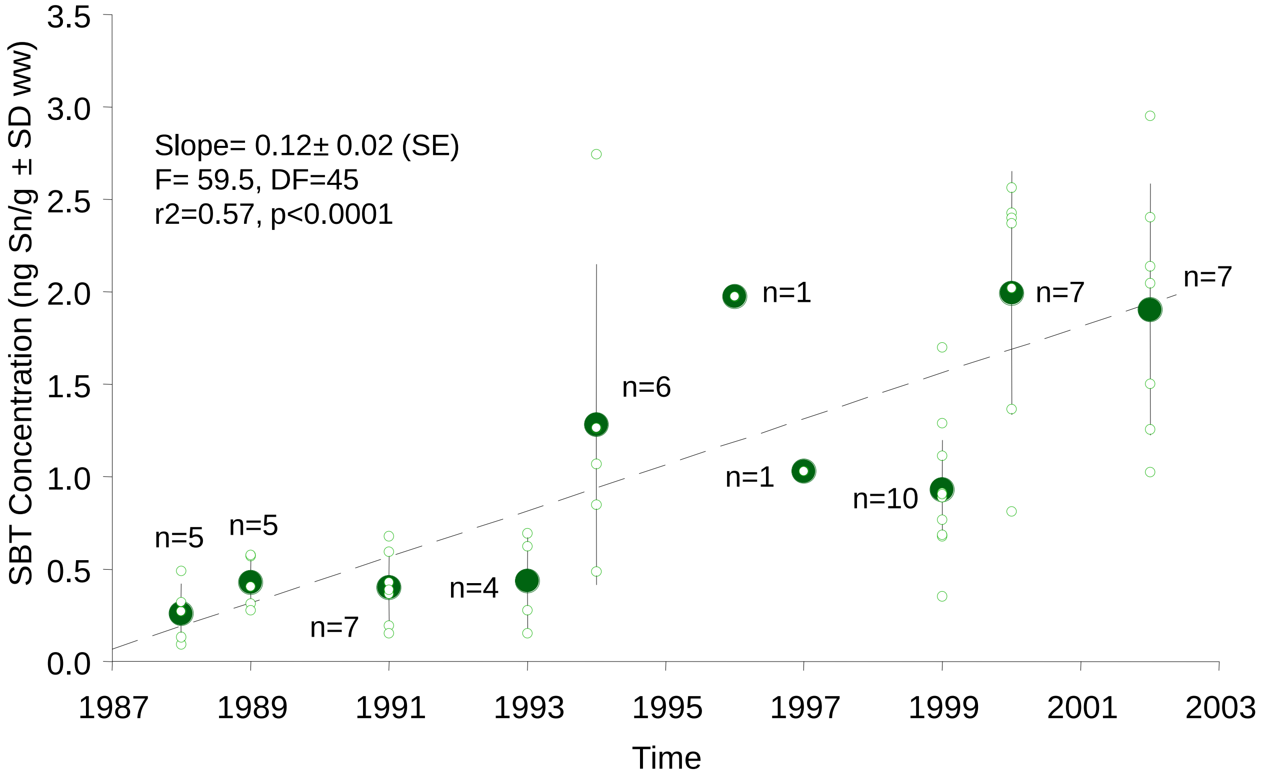
(1989-2000, 11y)

Ringed Seal

Phoca hispida

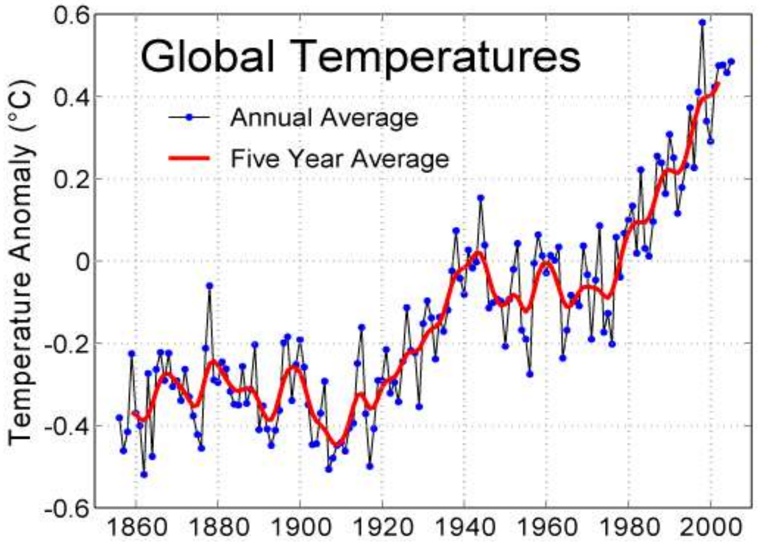
(1988-2002, 14y)

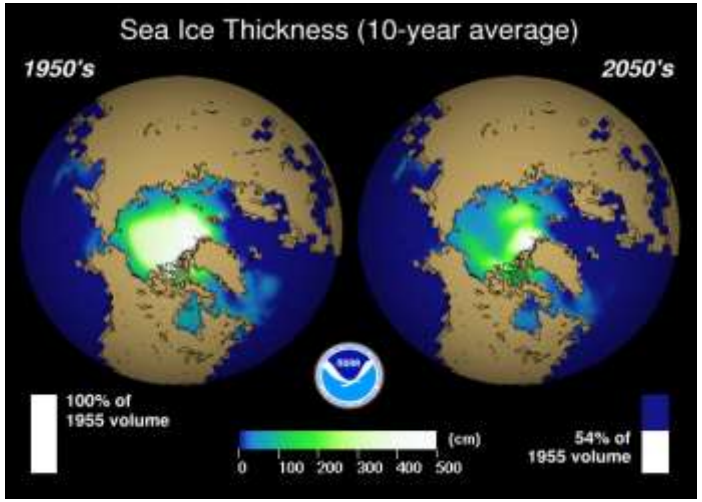
Temporal Trends - Ringed Seal



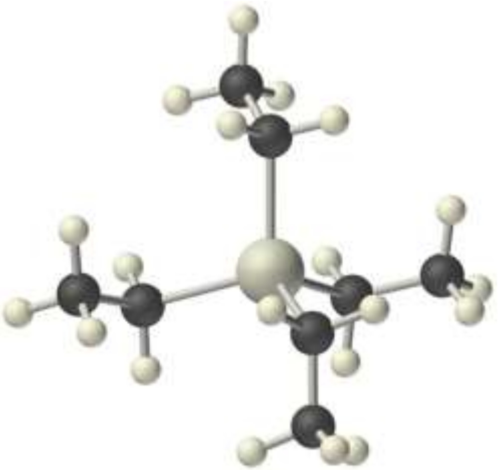
- N.W Alaska
- Doubling time: 3.5 y.

Réchauffement climatique

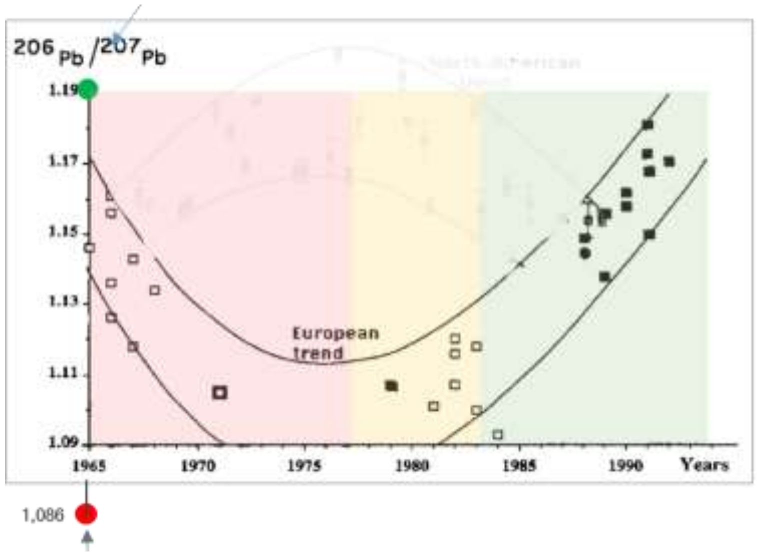




Principales routes navigables traversant le pole nord



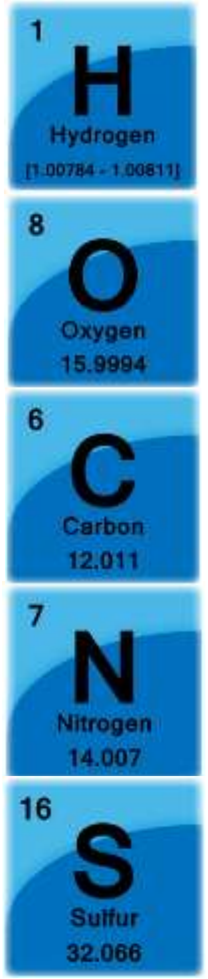
Tetraethyllead



Transient Pb isotopic signatures in the Western European atmosphere Grousset, F.E., Quetel, C.R., Thomas, B., Buat-Menard, P., Donard, O.F.X., Bucher, A. EST 1994

Stable Isotopes Ratios for food origin traceability

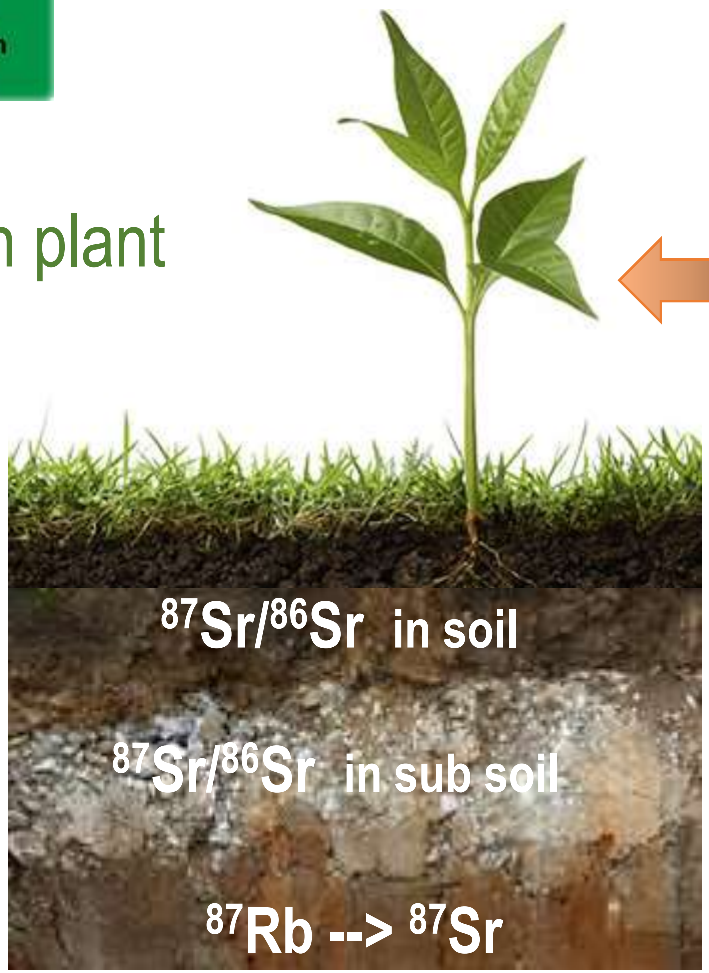
Light Elements (Bio-, Traditional):

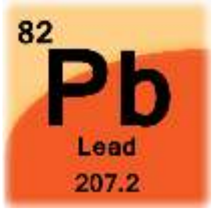


- H, O: *Water*
- C, N: *Climate , agriculture*
- S: *Geology Volcanos*

Heavy Elements (Non-traditional)

^{87}Sr/^{86}Sr in plant





Anthropogenic

^{208}Pb/^{206}Pb

^{207}Pb/^{206}Pb

^{208}Pb/^{204}Pb

^{206}Pb/^{204}Pb

Workflow

Food Samples (pre-treatement) → **Mineralization**

① →

PerkinElmer NexION 300D with ICP

Trace metals analysis :

Li, Be, B, Al, Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, Cs, Ba, Hg, Pb, Tl, U (in 20 times dilution)

② →

Sr separation using Sr-Eichrom® resin

Pb separation using Pb-selective resin

Isotope Analysis

Data processing

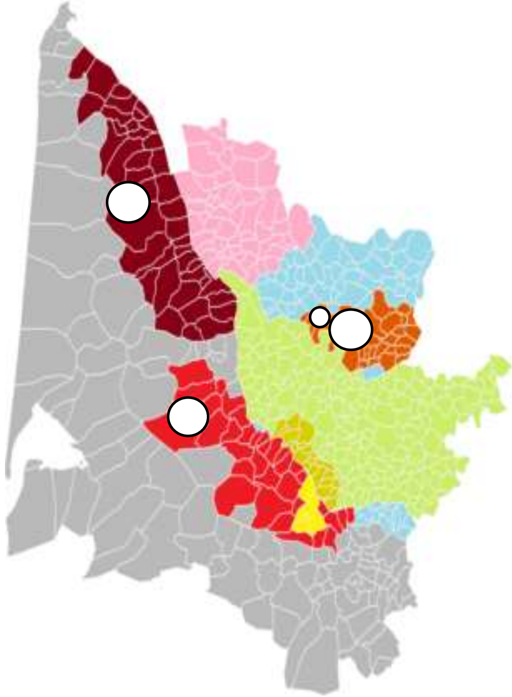
Wine samples:

Bordeaux from China's Market

14 wines:

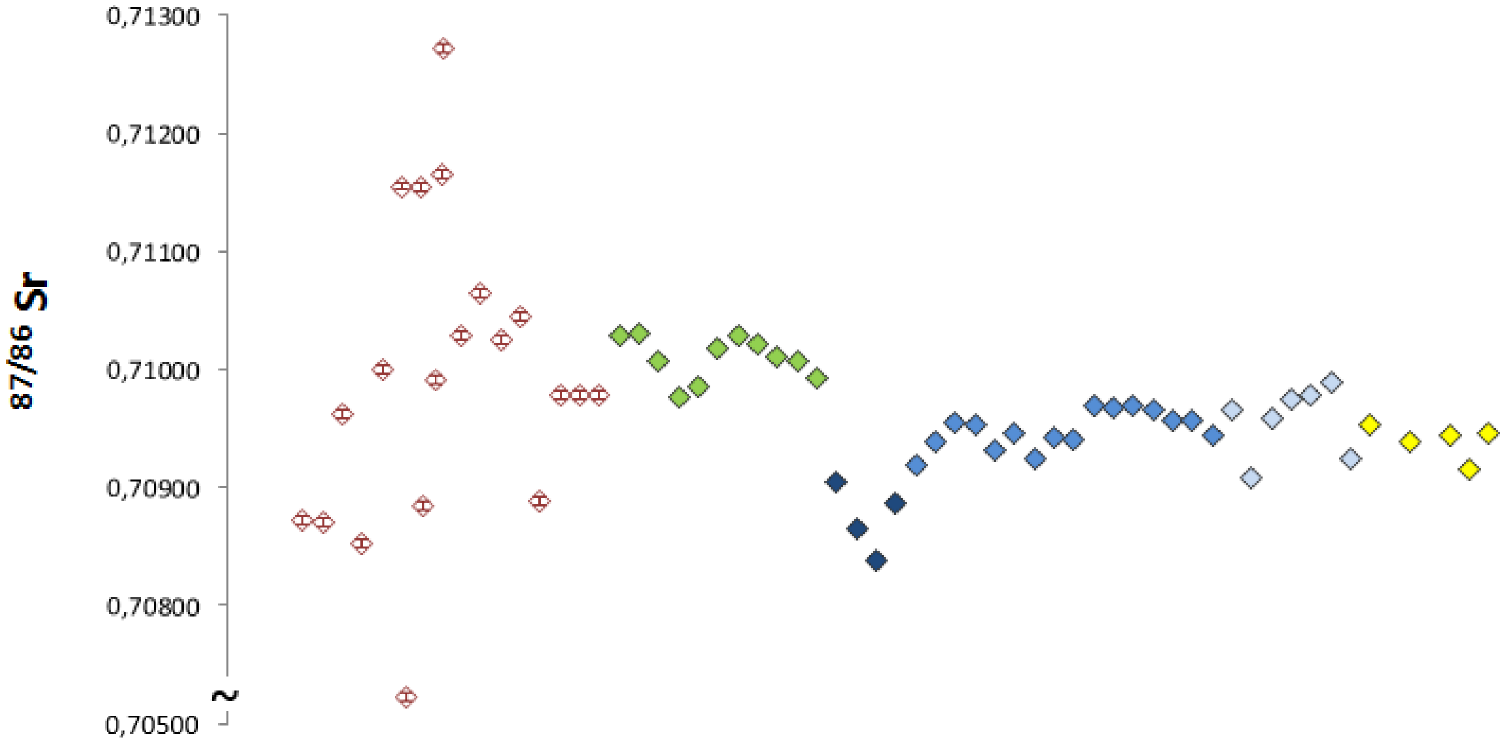
Authentic Bordeaux

48 wines:

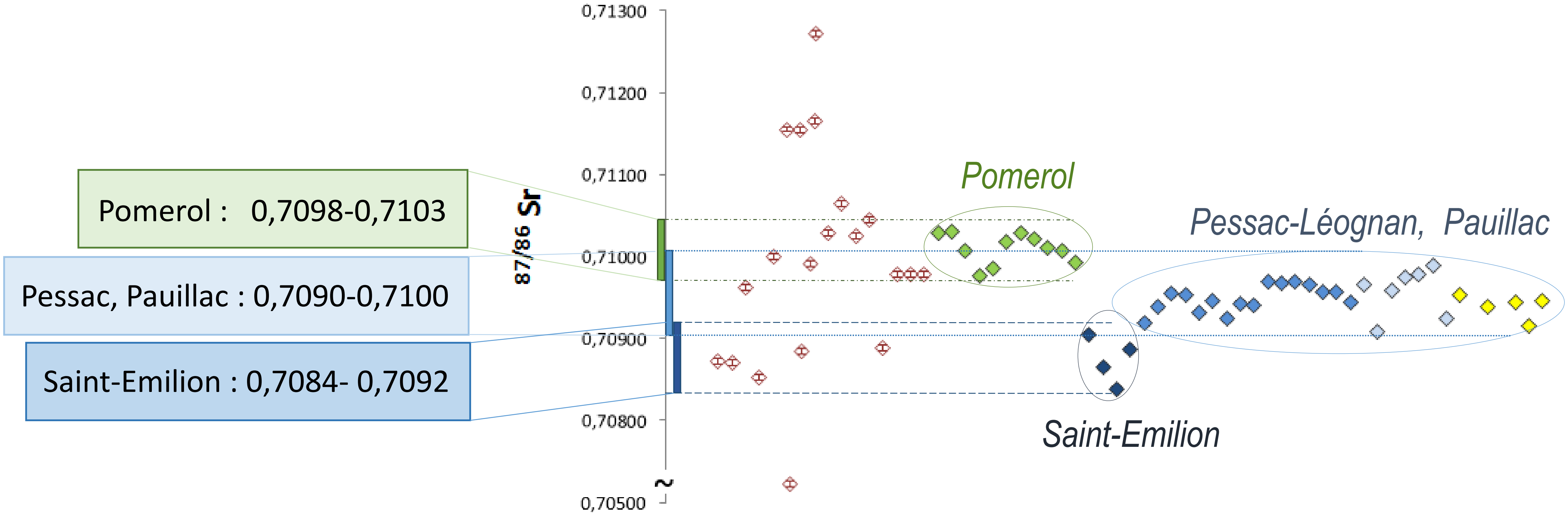


- 11 Pomerol (red)
- 4 Saint-Emilion (red)
- 16 Pessac-Léognan (red)
- 9 Pessac-Léognan (white)
- 8 Pauillac (with 4 suspects)

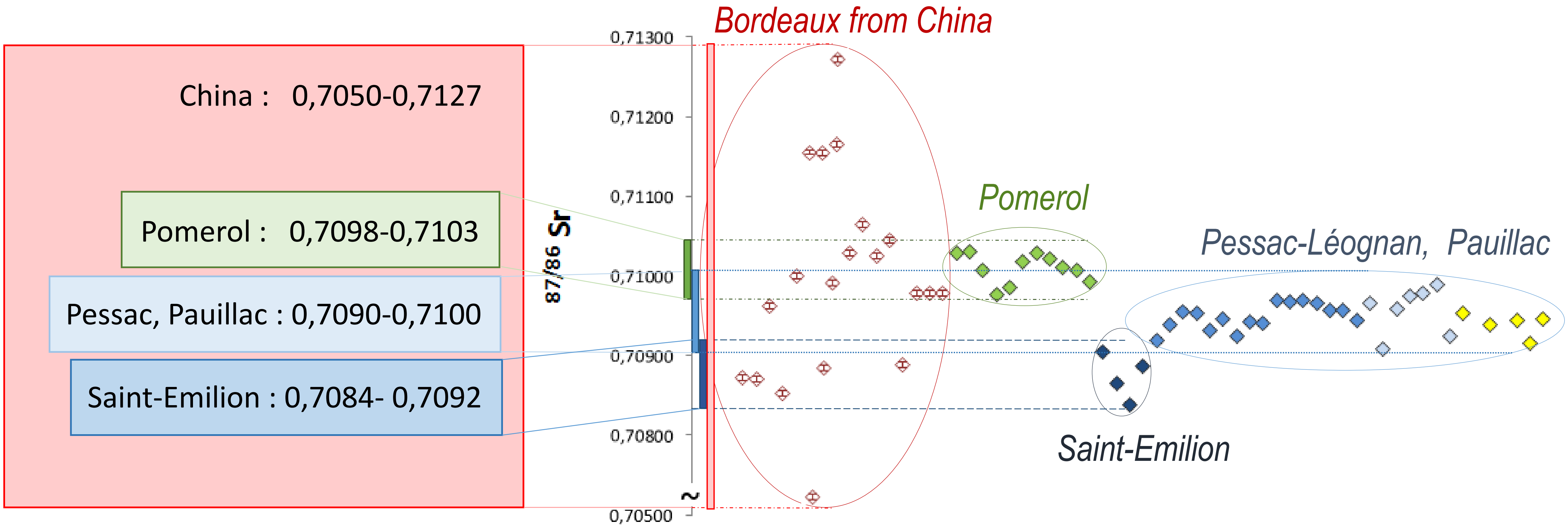
$^{87}Sr/^{86}Sr$: Geographical origin of Bordeaux Wines



$^{87}Sr/^{86}Sr$: Geographical origin of Bordeaux Wines



$^{87}Sr/^{86}Sr$: Geographical origin of Bordeaux Wines

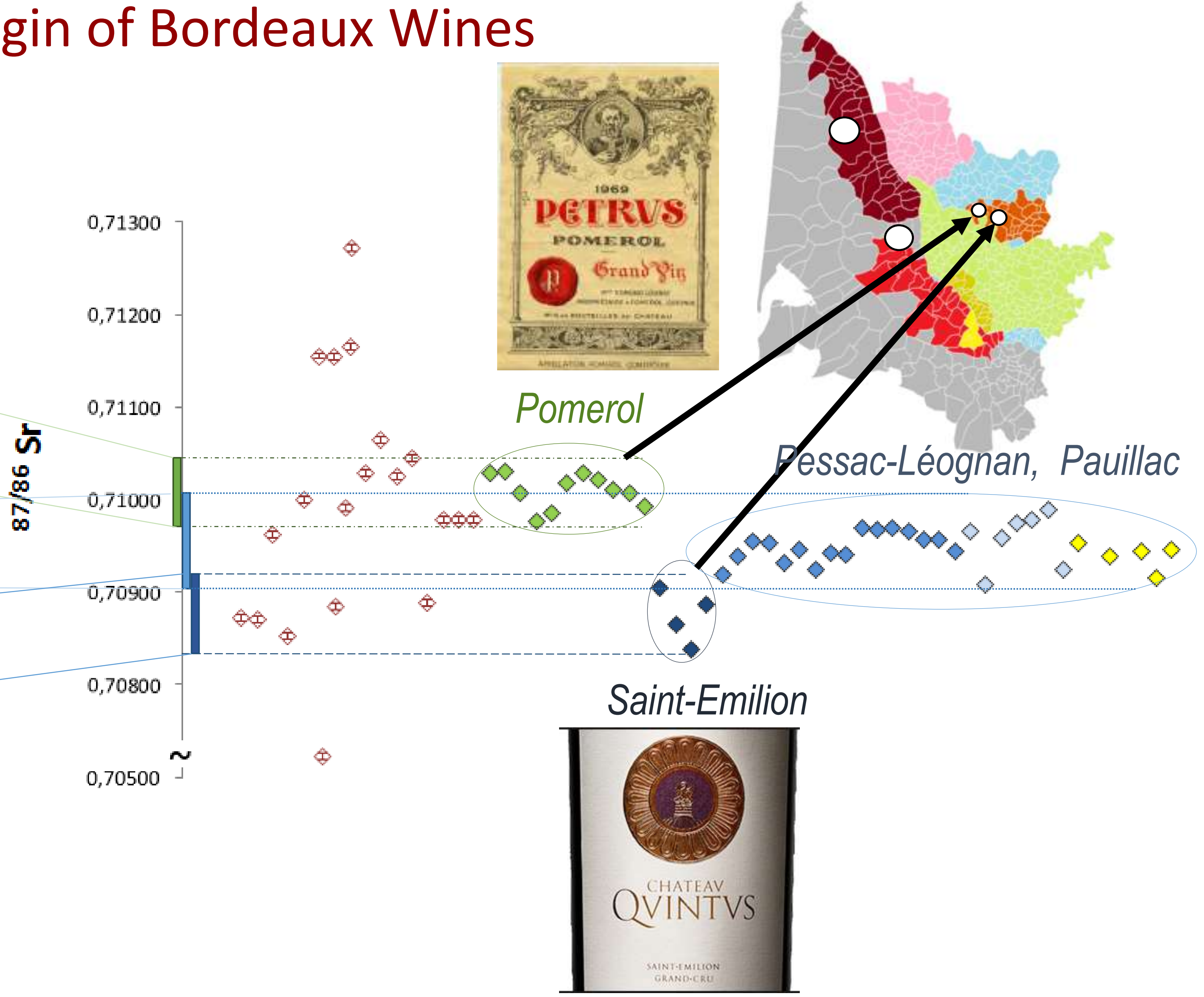


$^{87}Sr/^{86}Sr$: Geographical origin of Bordeaux Wines

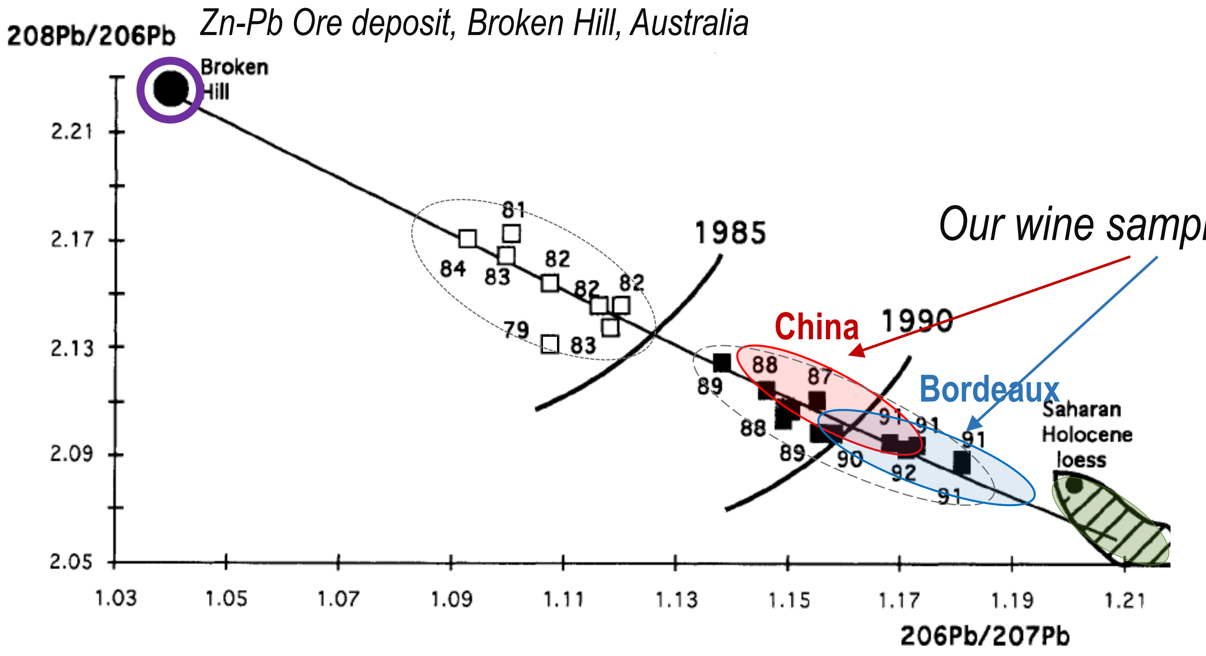
Pomerol : 0,7098-0,7103

Pessac, Pauillac : 0,7090-0,7100

Saint-Emilion : 0,7084- 0,7092



Tracer l'origine du Pb à l'aide de ces isotopes



Grousset F.E et al., 1994 Transient Pb Isotopic Signatures in the Western European Atmosphere

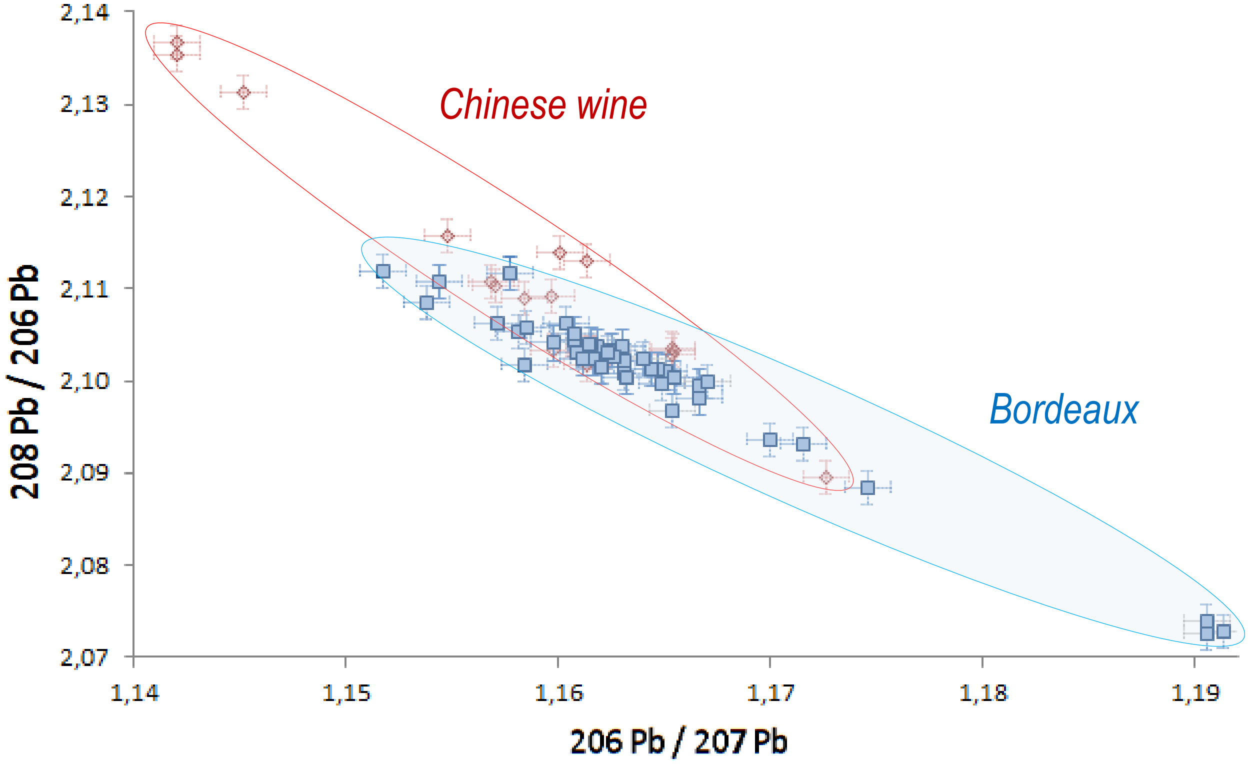
Phased out leaded gasoline:
Europe: early 1980-s
Chine: 2000

Different source of Pb in atmosphere

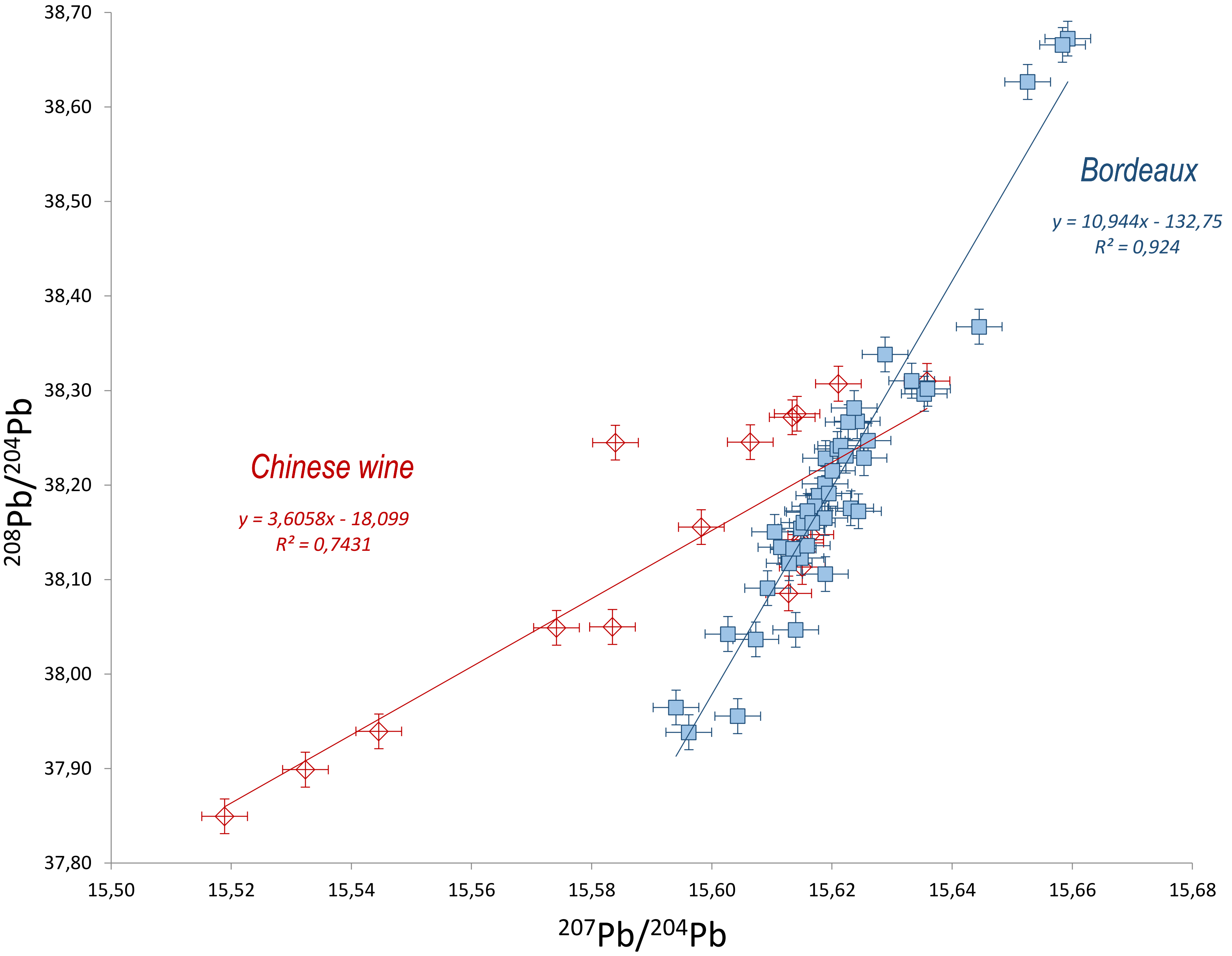
↓

Different distribution

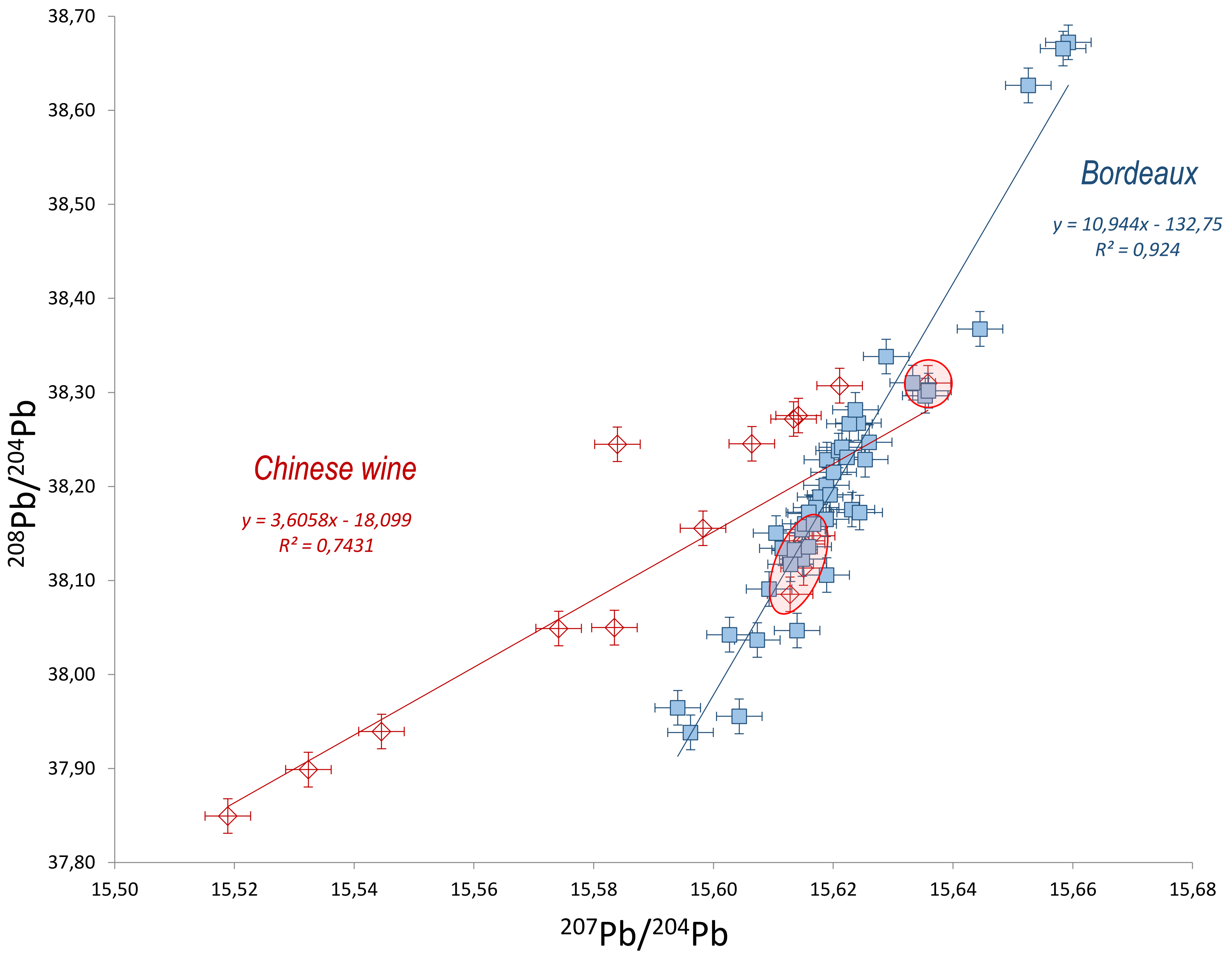
$^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$



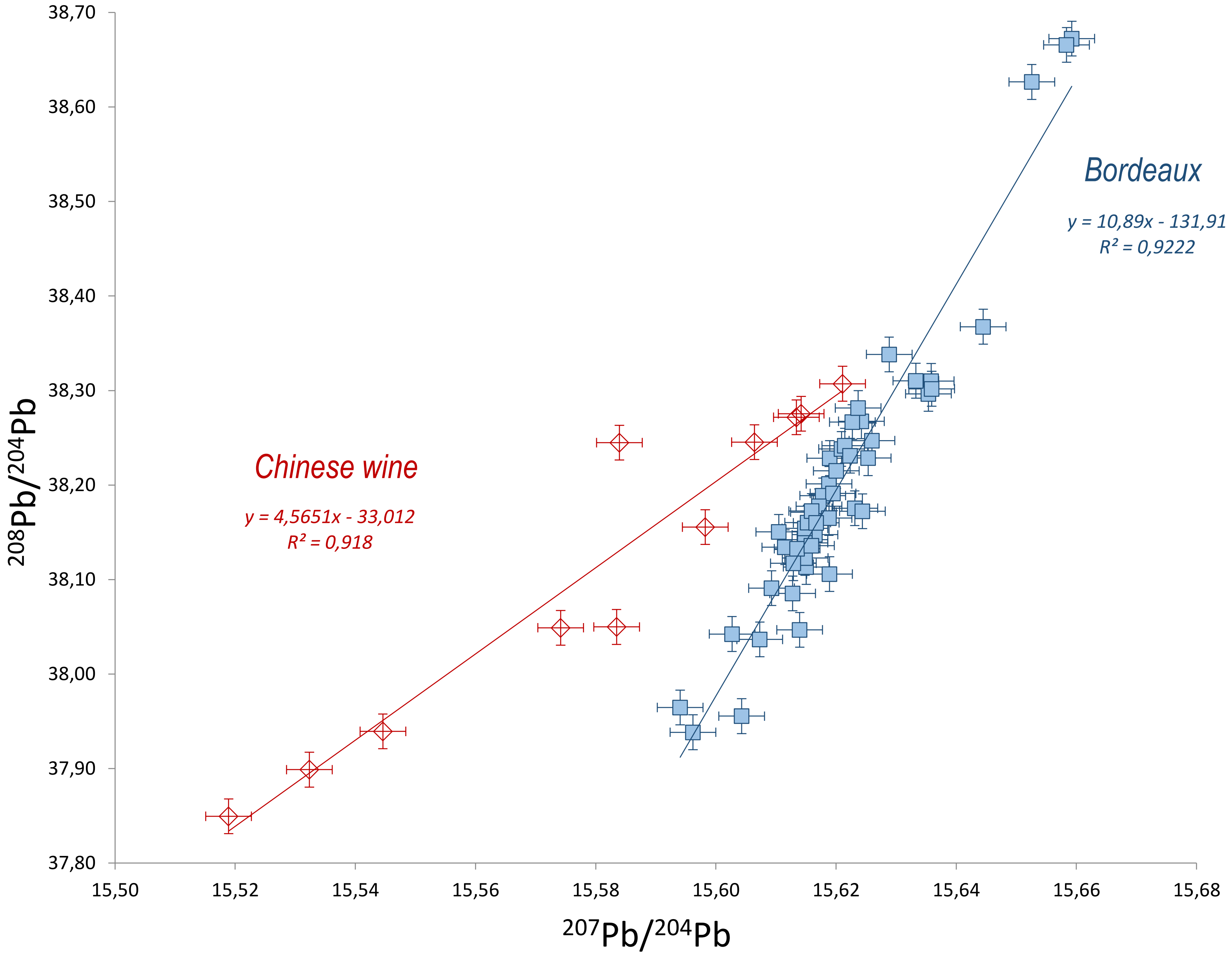
$^{208}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$: Geographical origin of Bordeaux Wines



$^{208}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$: Geographical origin of Bordeaux Wines



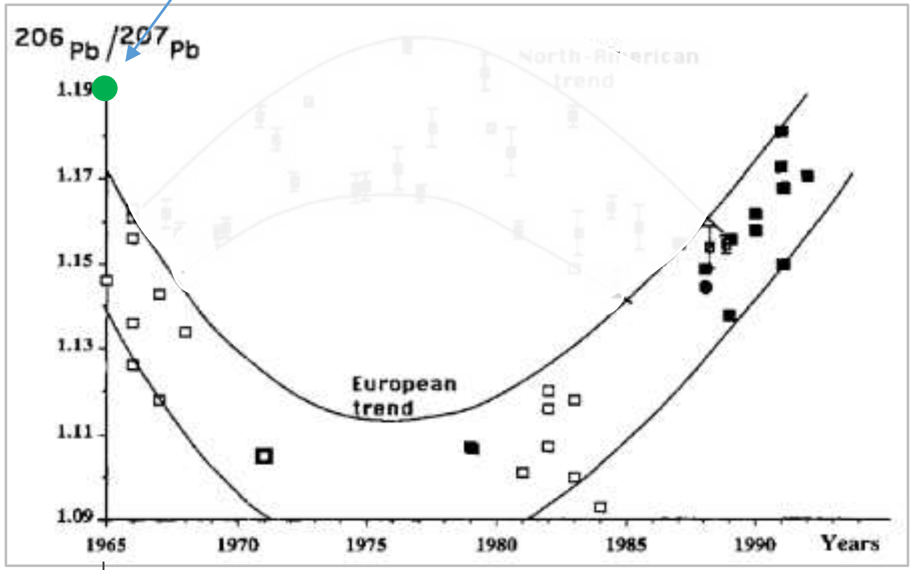
$^{208}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$: Geographical origin of Bordeaux Wines



$^{206}Pb/^{207}Pb$: Bordeaux wine vintage record

$^{206}Pb/^{207}Pb$ = 1,197 Geogenic value

(Elbaz-Poulichet 1984)

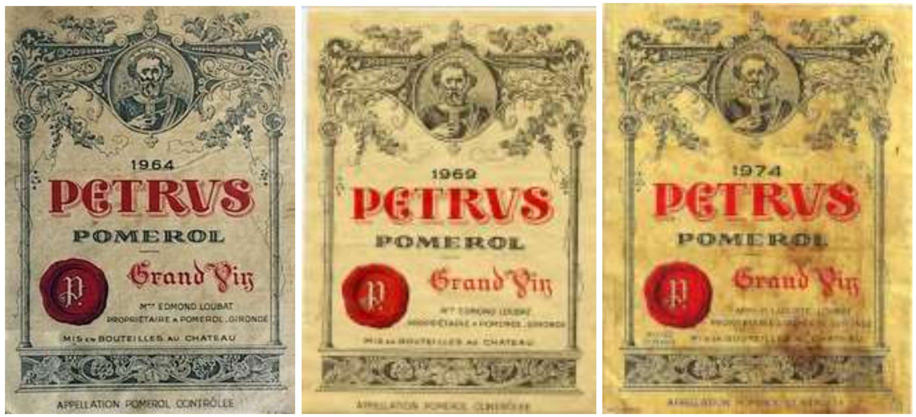


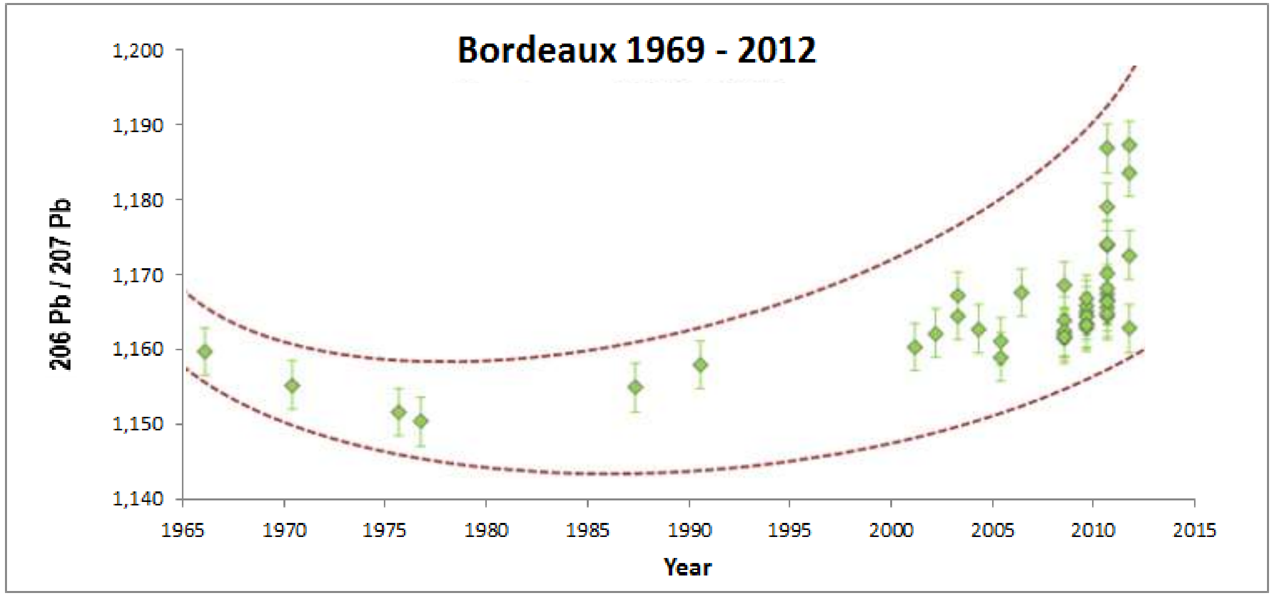
1,086

Grousset F.E et al., Environ. Sci. Technol., 1994

$^{206}Pb/^{207}Pb$ = 1,086 French gasoline

(Monna et al. 1997)



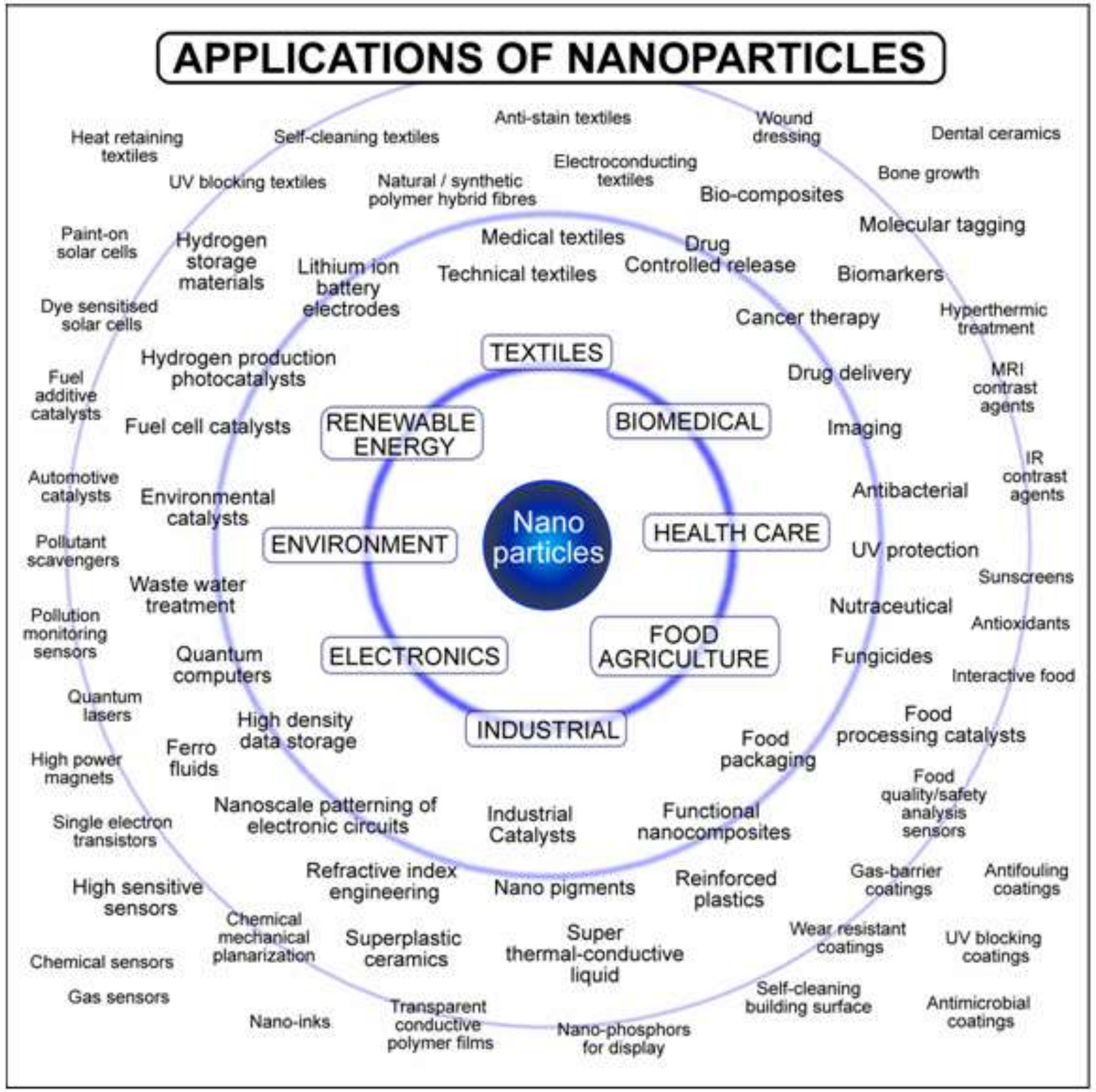


Les nanoparticules dans notre quotidien

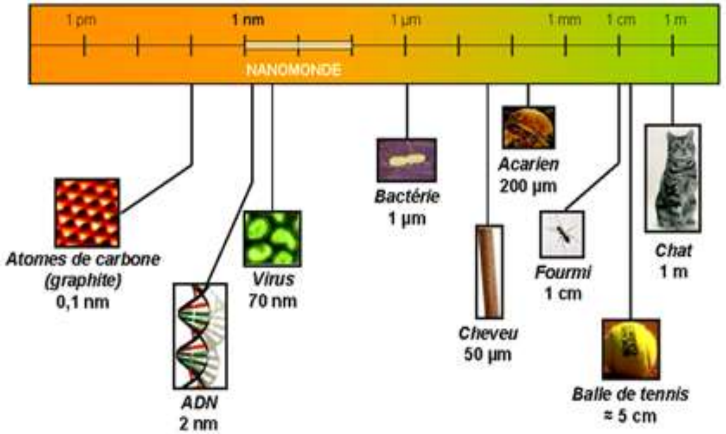
http://www.nanotechproject.org/cpi/

INVENTORY OF NANOTECHNOLOGY-BASED CONSUMER PRODUCTS

> 1600 products

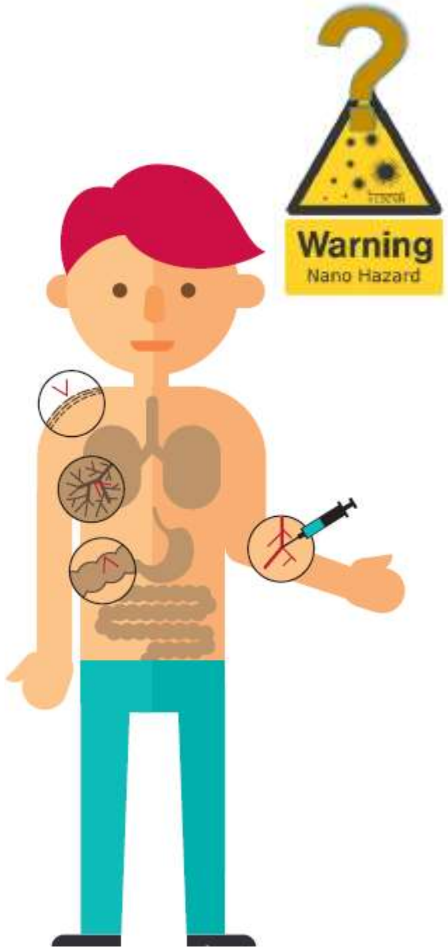


Définition des NPs:



1 nanomètre (nm) = 10^{-9} m = 0, 000 000 001 m

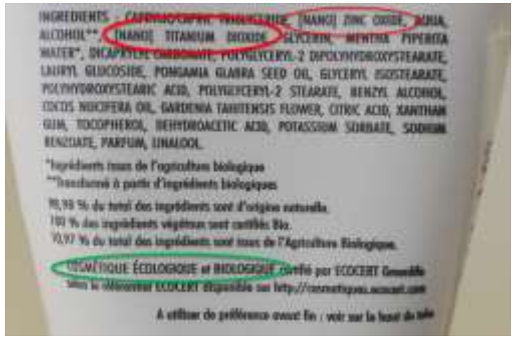
Nanomatériaux: exposition des consommateurs et législation



Directive (EC) 1363/2013

Définition des nanomatériaux: tout matériau **fabriqué intentionnellement** et se caractérisant par une ou plusieurs dimensions externes ou une structure interne, sur une échelle de **1 à 100 nm**

Identification claire dans la liste des ingrédients de l'étiquette: **[nano]**



Cosmétiques

Directive (EC) N° 1223/2009

✔ **NP de TiO_2 et ZnO**

Aliments

Directives (EC) N° 1169/2011 & N°1363/2013

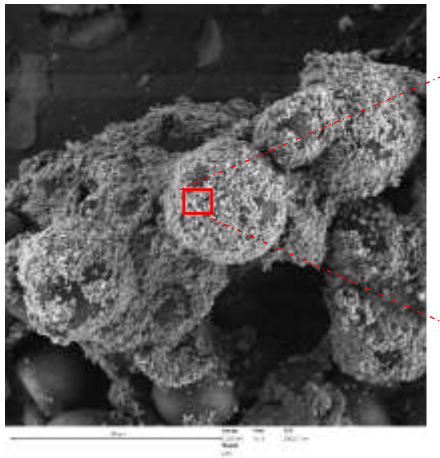
✔ **Carbonate de calcium (E170) nano-forme**
Carbone végétal (E153) nano-forme

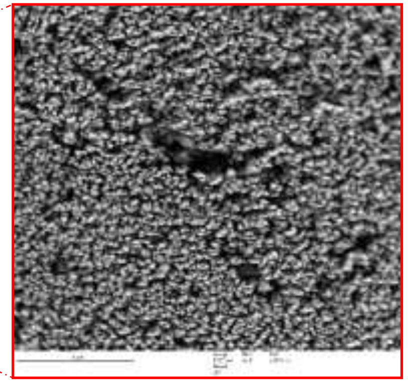
Autres NP: en cours d'évaluation

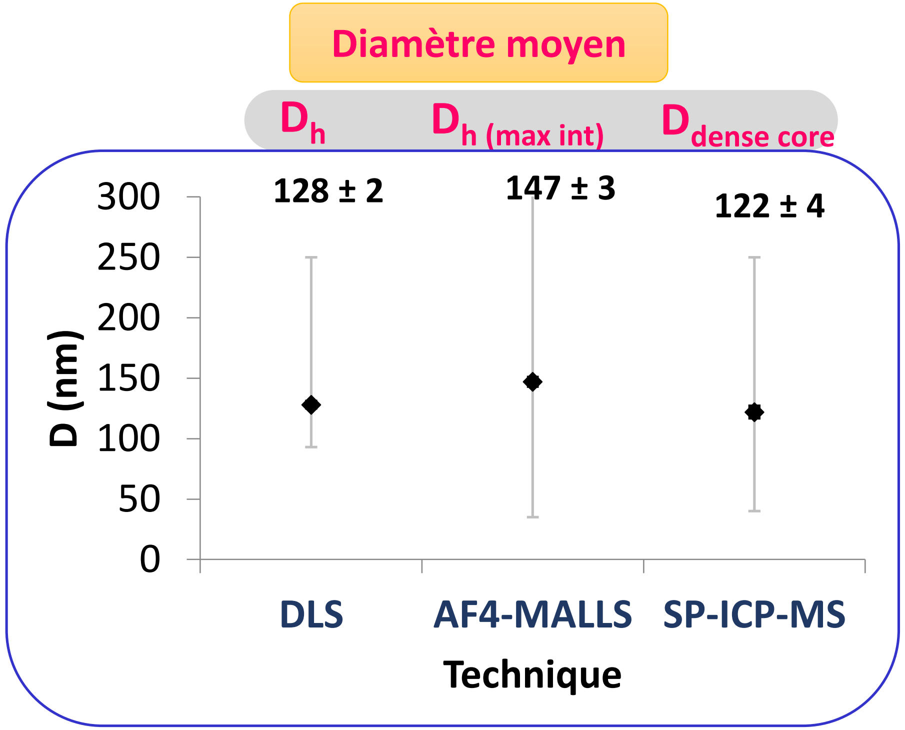
Besoin urgent de méthodes d'analyse → **Aucun protocole normalisé**

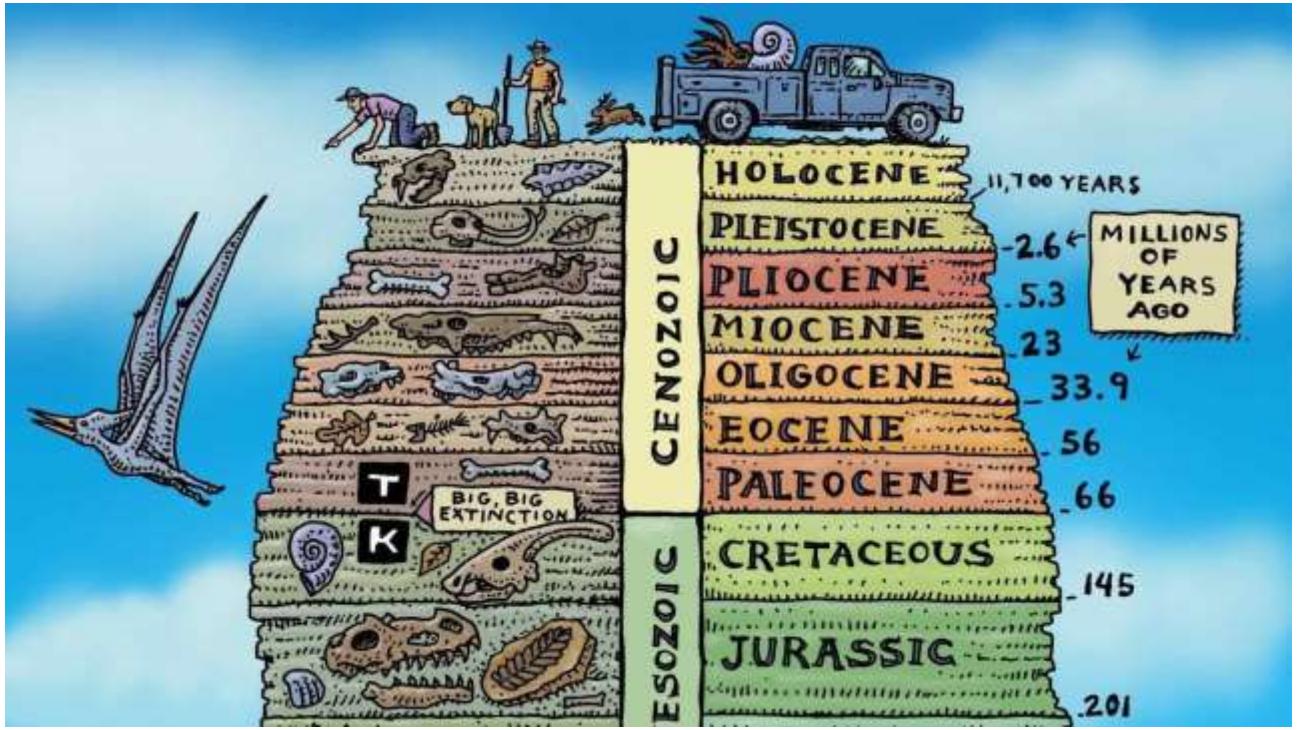
Nanoparticules de TiO_2 dans des bonbons au chocolat

Extraction à l'eau → DLS, A4F-MALLS-ICP-MS, SP-ICP-MS → NP de TiO_2








HOLOCENE
11,700 YEARS
PLEISTOCENE
2.6
MILLIONS OF YEARS AGO
PLIOCENE
5.3
MIOCENE
23
OLIGOCENE
33.9
EOCENE
56
PALEOCENE
66
CENOZOIC
T
K
BIG, BIG EXTINCTION
CRETACEOUS
145
JURASSIC
201
ESOZOIC


Bilicki
RESEARCH CONCLUDES:
WE ARE DESTROYING EARTH.
COULD YOU KINDLY REPHRASE THAT IN EQUIVOCAL, INACCURATE, VAGUE, SELF-SERVING AND ROUNDABOUT TERMS THAT WE CAN ALL UNDERSTAND?
GOVERNMENT