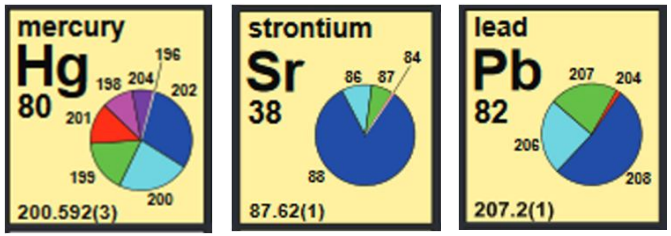


Isotopic signatures of Hg, Pb, Sr in the environment: unravelling biogeochemical pathways at ultra-traces levels and high precision

mass twin

MassTwin Workshop , Antwerpen, 18/04/2018

Olivier F.X. **DONARD**
Sylvain **BERAIL**
Ekaterina **EPOVA**
Emmanuel **TESSIER**
David **AMOUROUX**

Jan **KOSCHORRECK**
Ina **FETTIG**

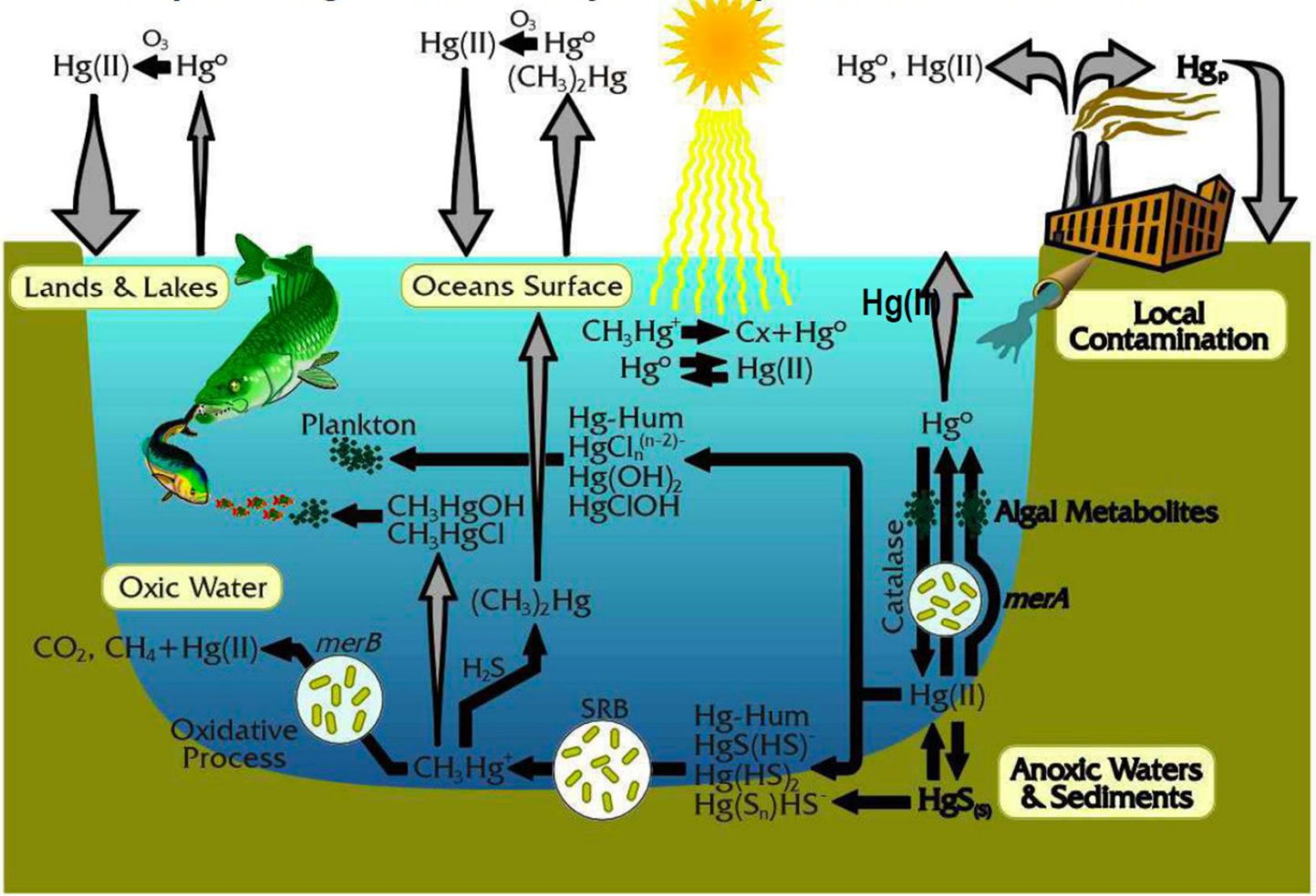
Fabienne **SEBY**
Veronique **VACCHINA**

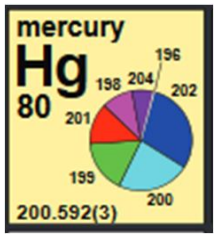
Heinz **RÜDEL**

Bernard **MEDINA**

Tea **ZULIANI**

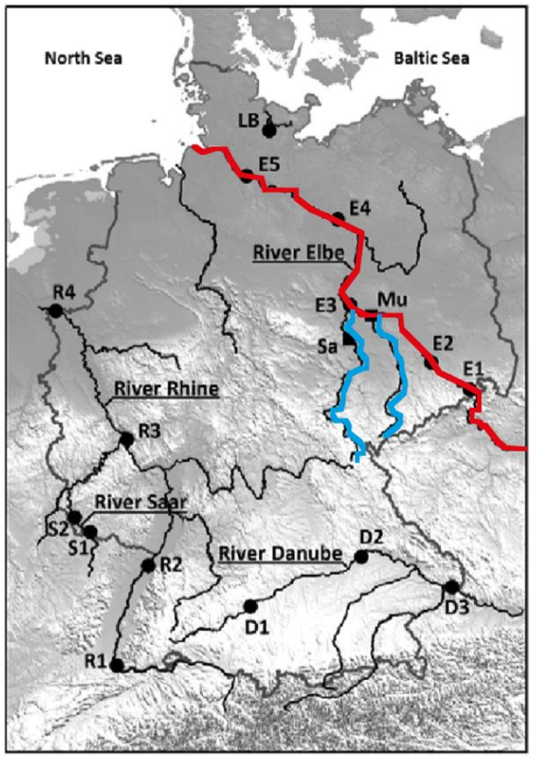
Complex biogeochemical cycle and potential bio-feedback ?

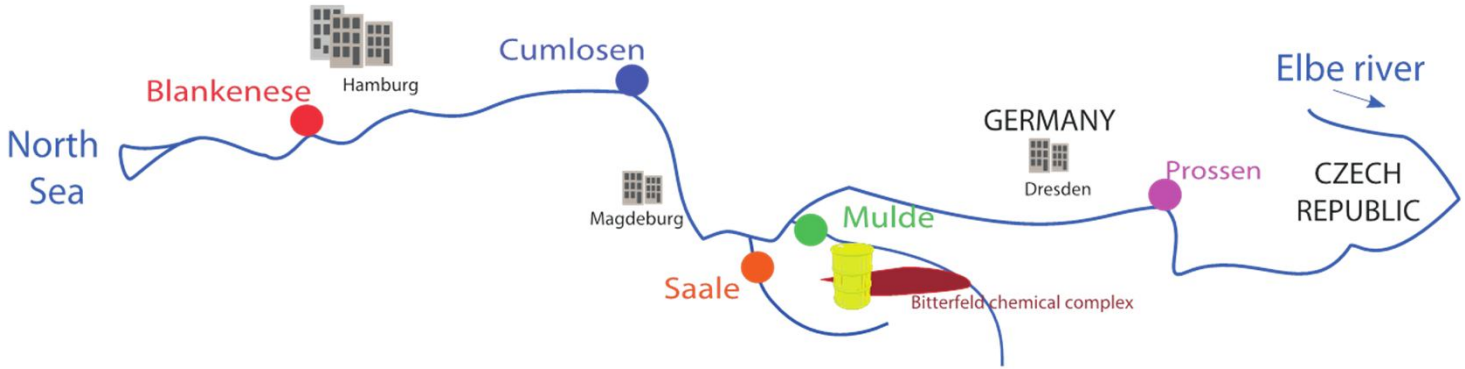




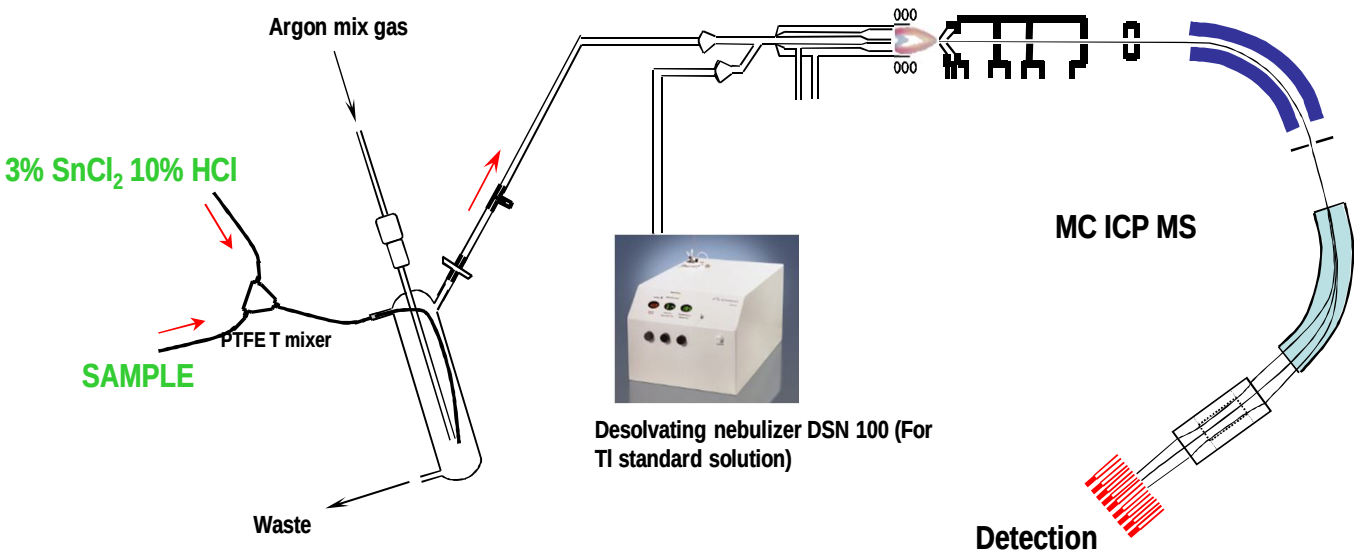
Based on Schaefer et al, 2002

Isotopes allow to open up new windows

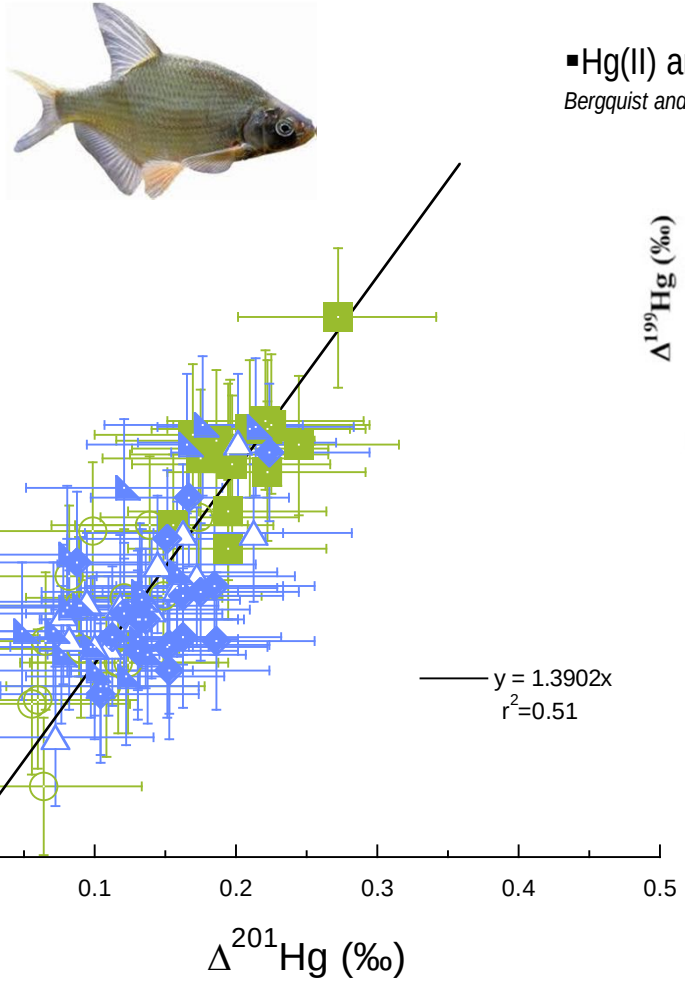

North Sea
Baltic Sea
LB
E5
E4
River Elbe
R4
E3
Mu
Sa
E2
E1
River Rhine
R3
River Saar
S2
S1
R2
River Danube
D2
D3
D1
R1


North Sea
Blankenese
Hamburg
Cumlosen
Elbe river
GERMANY
Dresden
Prossen
CZECH REPUBLIC
Magdeburg
Mulde
Saale
Bitterfeld chemical complex

CVG (Cold Vapor Generation) / MC-ICP-MS

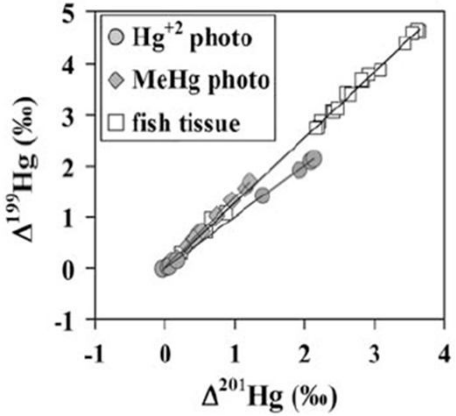


- CGV with SnCl2 : Matrix separation ➔ Increase sensitivity, decrease matrix effect.
- Able to measure precise Hg isotopic composition down to **[Hg]=1 µg.L^{-1}** in final solution.



▪Hg(II) and MeHg photoreduction in presence of DOM

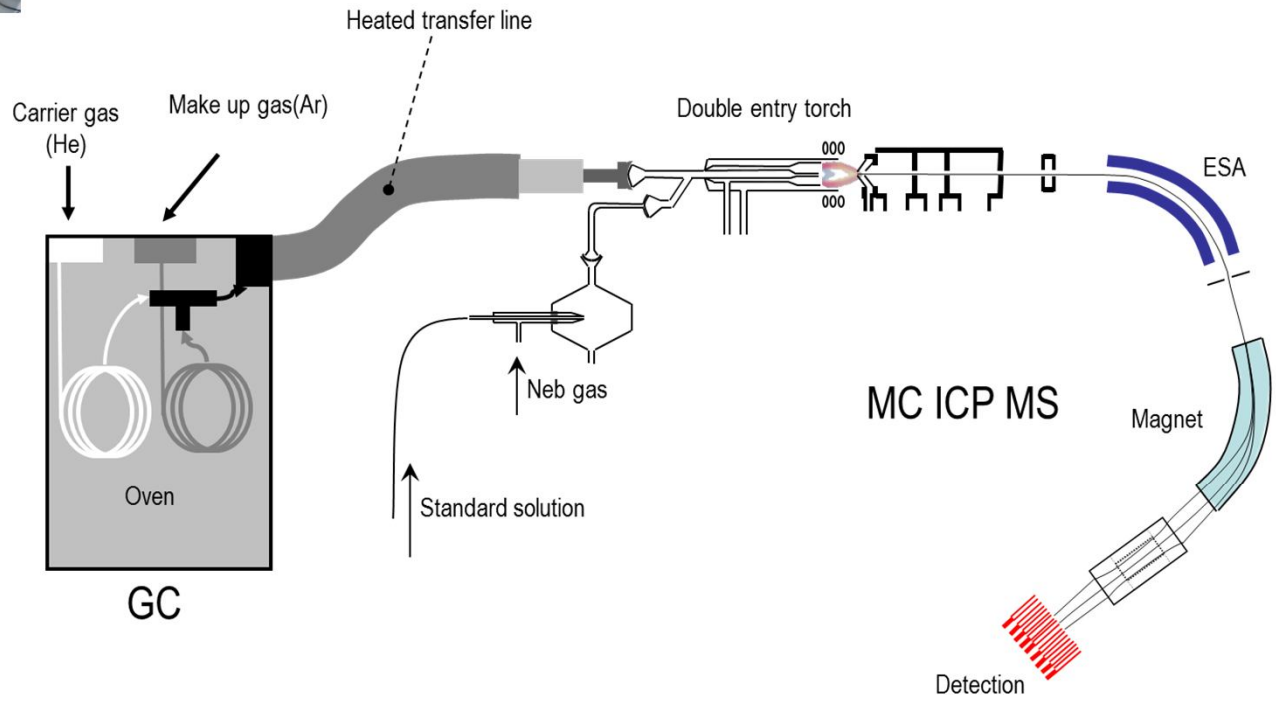
Bergquist and Blum, 2007 ***Slope : 1.3***



▪ Δ^{199}Hg and Δ^{201}Hg values close to 0.

Slope of 1.39 but r^2=0.51 (forced through 0)

incorporation of MeHg photo-demethylated into the water column (small extent).



- Same hyphenation strategy as GC / ICP-QMS
- WET PLASMA coupling
- Tl (NIST997) simultaneously analyzed for mass bias correction

Epov et al. , 2008

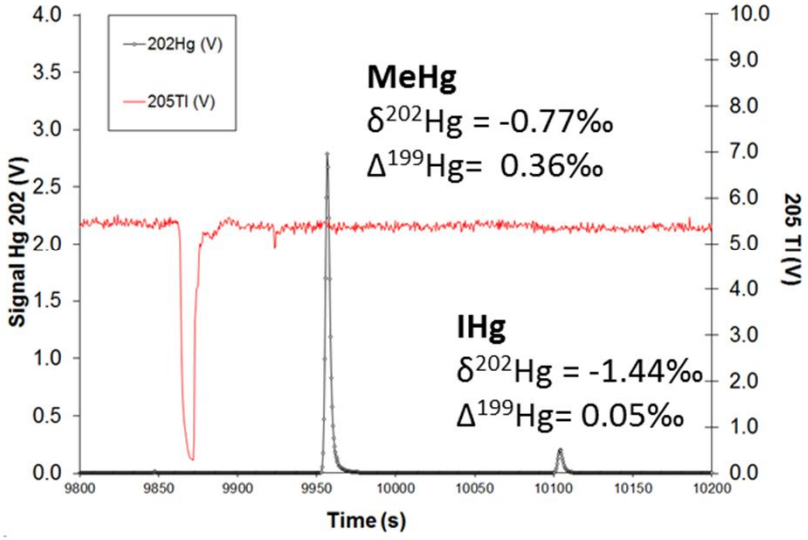
Compound Specific Isotopic Analysis

Bremen muscle
Speciation : [MeHg] = 94 % of total Hg
[IHg] = 6% of total Hg

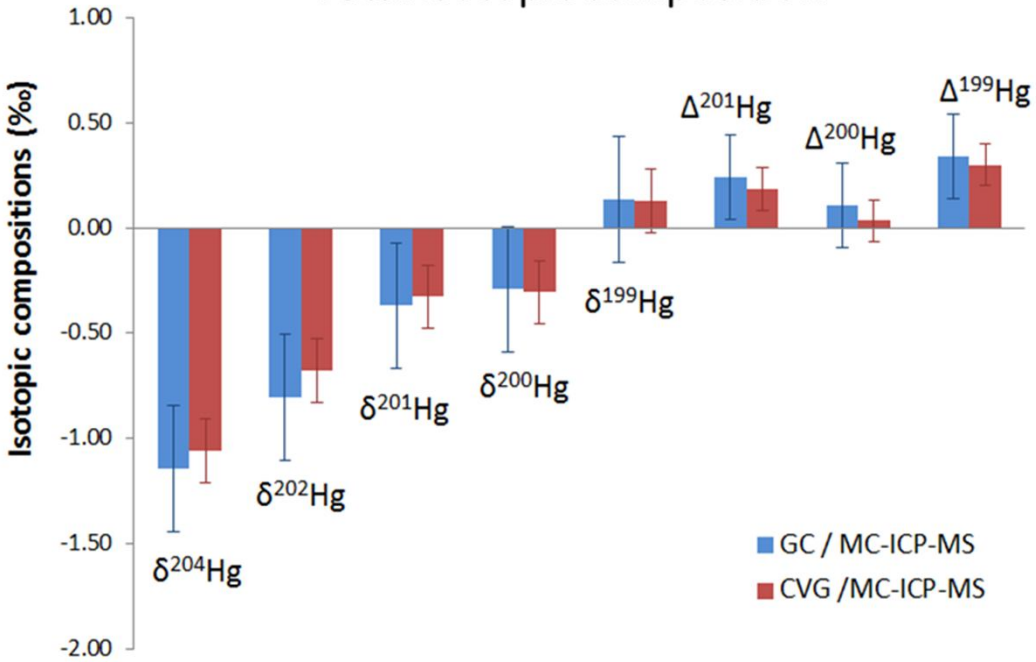
Umwelt Bundesamt

Fraunhofer IME

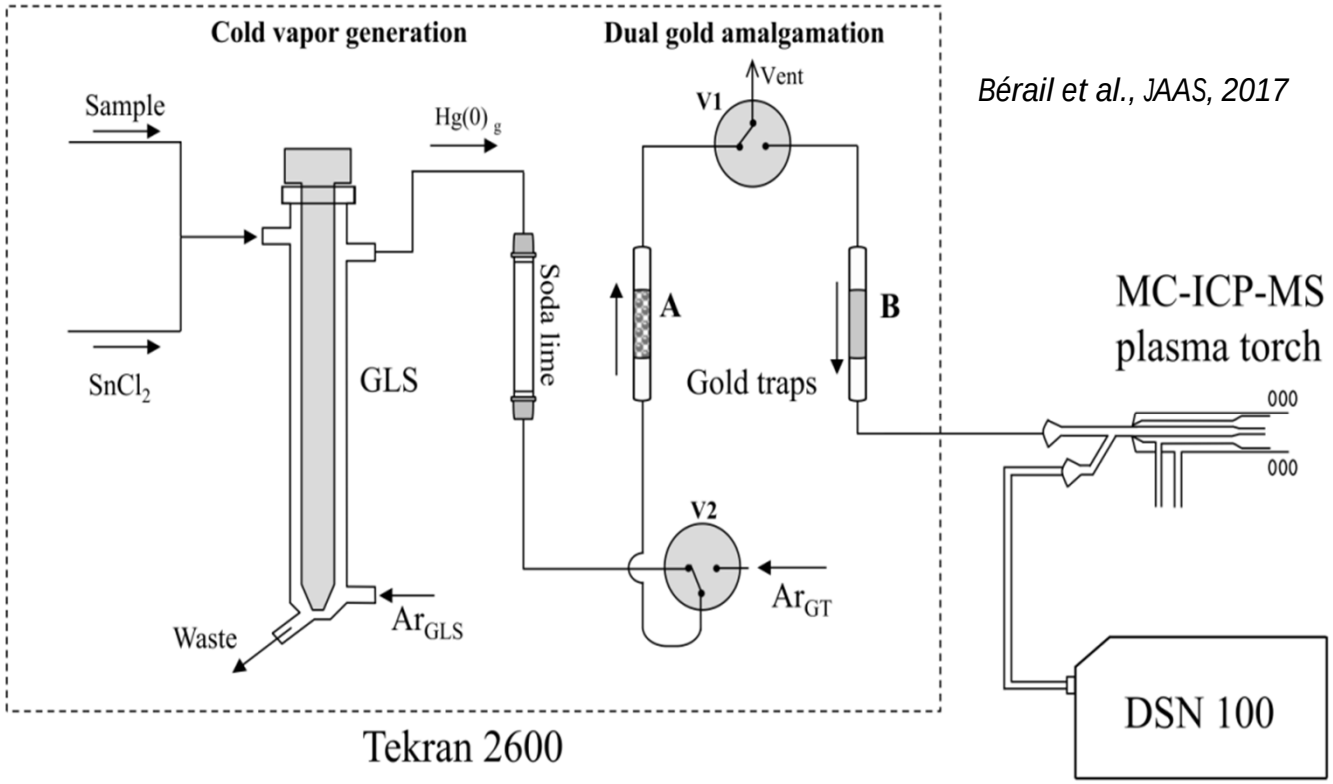
GC / MC-ICP-MS :



Total isotopic composition



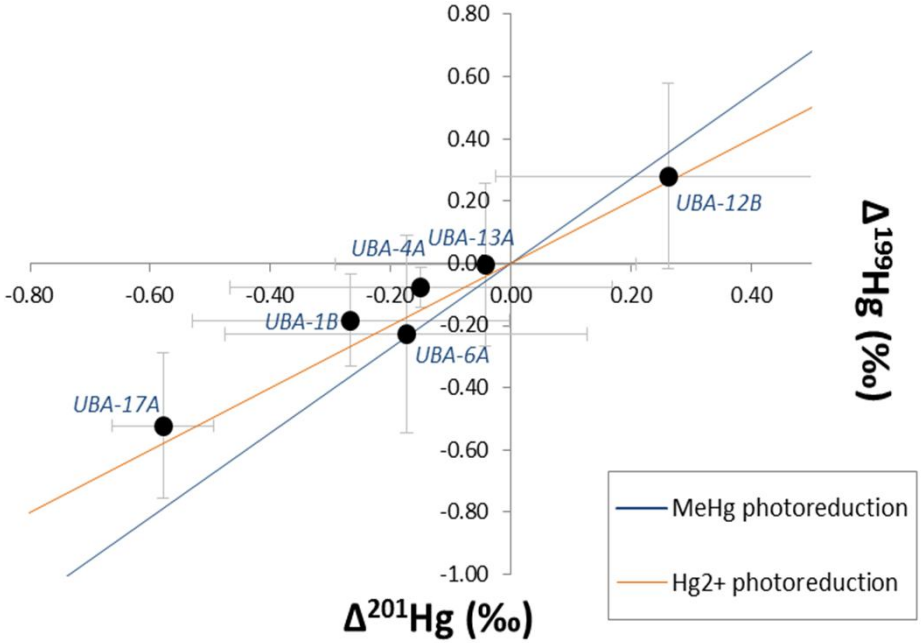
CVG -DGA



Bérail et al., JAAS, 2017

Sample	Date of sampling	[Hg] (ng/L)	Volume (ml)*	δ202Hg (‰)	Δ200Hg (‰)	Δ199Hg (‰)
UBA 1B	05/01/2016	3.8	912	-0.68	0.10	-0.18
UBA 4A	26/01/2016	3.5	851	-0.72	-0.05	-0.08
UBA 6A	09/02/2016	5.2	805	-0.61	0.04	-0.23
UBA 12B	22/03/2016	3.7	498	-0.35	0.12	0.28
UBA 13A	29/03/2016	4.7	633	-0.28	0.22	0.00
UBA 17A	26/04/2016	5.5	512	-0.47	0.17	-0.52

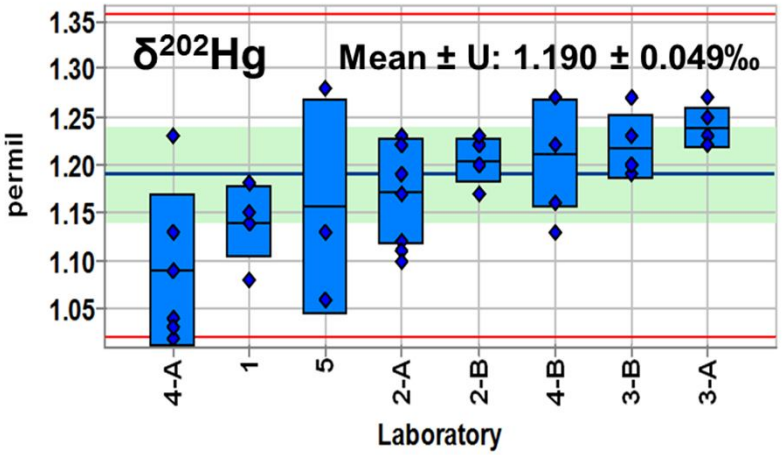
** collected on 1 we*

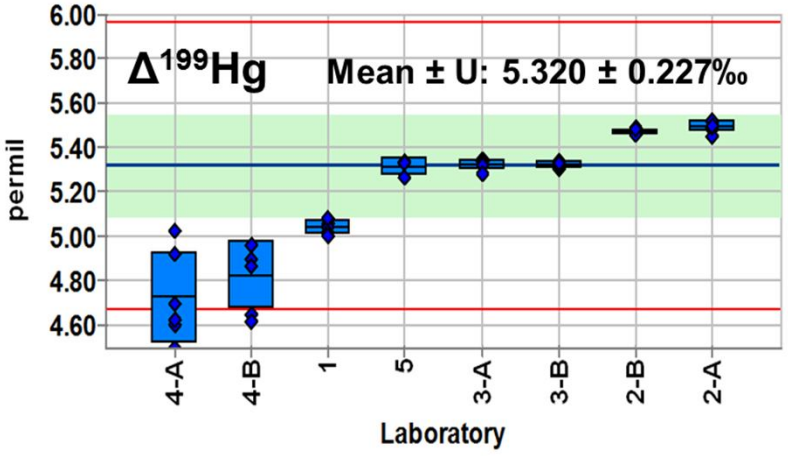


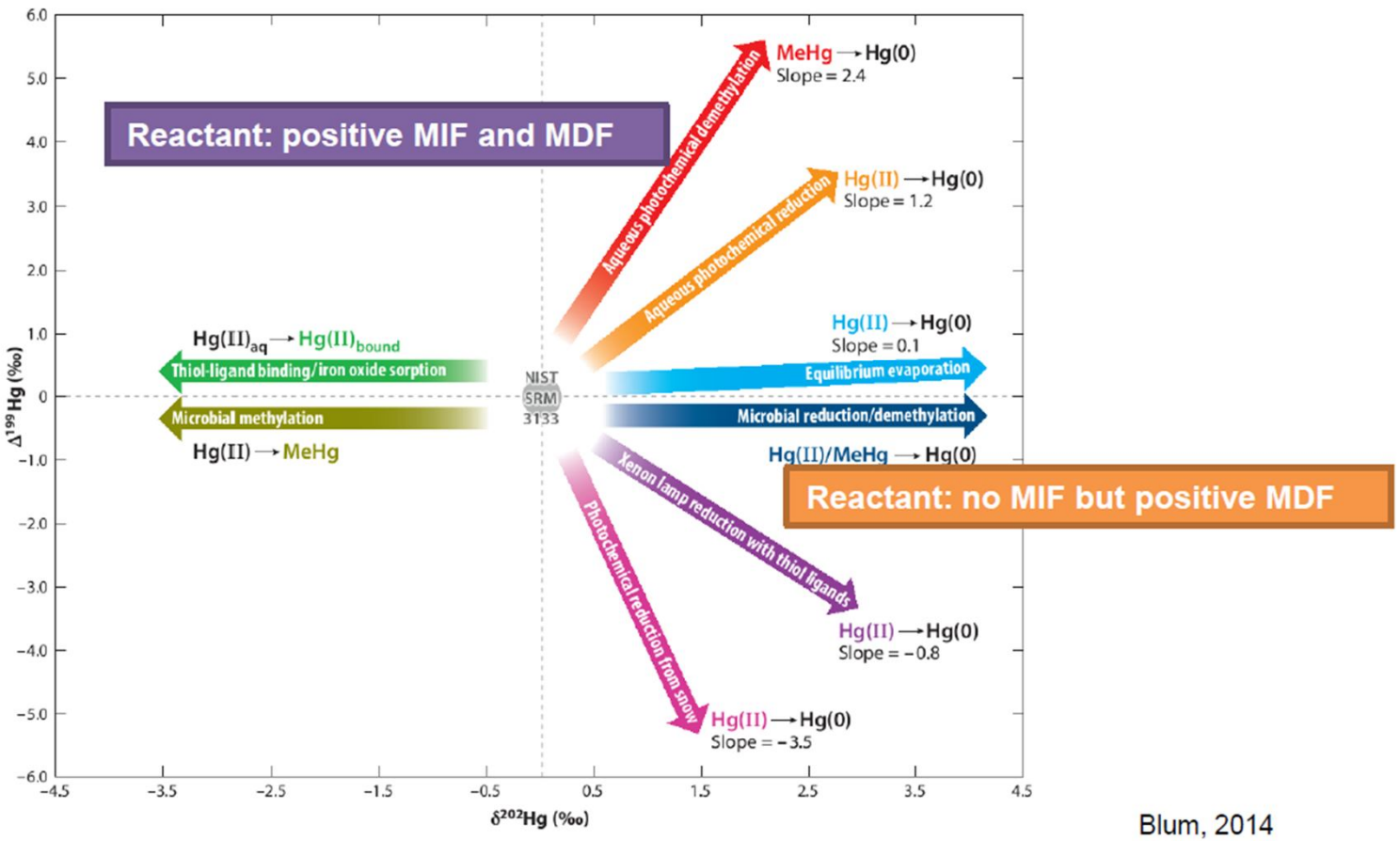
Significant ≠ MIF : different origin of Hg ?

NIST
National Institute of
Standards and Technology
U.S. Department of Commerce

- **Preliminary results from Inter-Lab Exercise**
  - Good overall inter-lab agreement
  - Higher intra- and inter-lab variability
  - Matrix presents more analytical challenge
- **Update to certificate imminent**







Blum, 2014

MDF

- Chemical processes
- Physical processes
- Biological processes

MIF

- Photo-reduction
- Photo-demethylation
- ~~Biological processes~~

Recent developments and trends in the application of strontium and its isotopes in biological related fields

Inês Coelho, Isabel Castanheira, João Moura Bordado, Olivier F.X. Donard, José Armando L. Silva

***Trends in Analytical Chemistry** 2017*

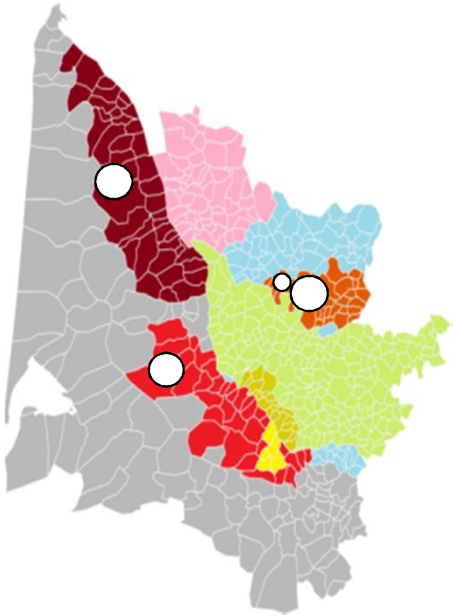
Echantillons de vins

Bordeaux achetés en Chine

14 vins:

Bordeaux à l'origine certifié

48 vins:



- 11 Pomerol (rouge)
- 4 Saint-Emilion (rouge)
- 16 Pessac-Léognan (rouge)
- 9 Pessac-Léognan (blanc)
- 8 Pauillac (dont 4 suspectes)

Rapports Isotopiques appliqués à la traçabilité des produit alimentaires

Éléments légers (bio-, traditionnels):

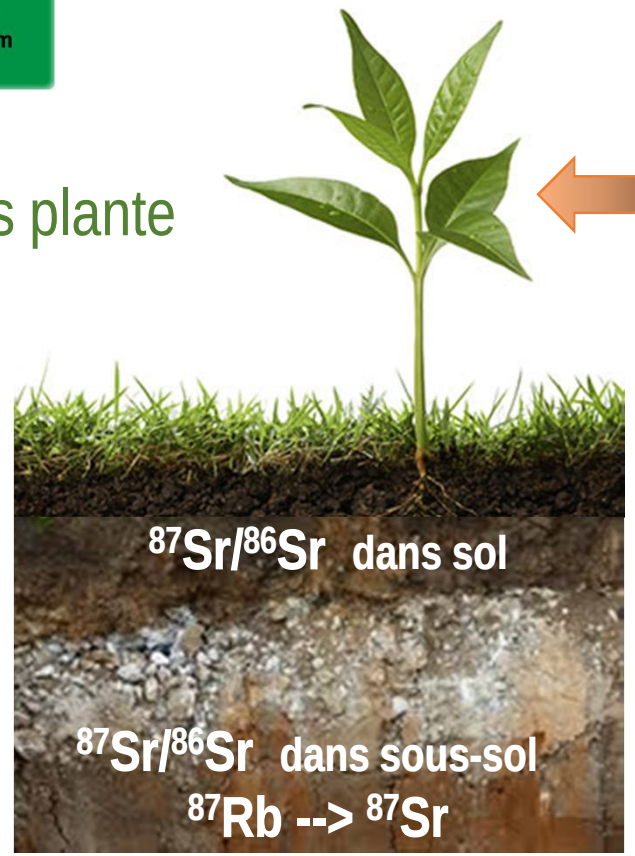
- 1 H Hydrogen [1.00784 - 1.00811] — *Eau*
- 8 O Oxygen 15.9994 — *Eau*
- 6 C Carbon 12.011 — *Climat, agriculture*
- 7 N Nitrogen 14.007 — *Climat, agriculture*
- 16 S Sulfur 32.066 — *Géologie Volcans*

Éléments lourdes (non-traditionels)

38 Sr Strontium 87.62

82 Pb Lead 207.2

$^{87}Sr/^{86}Sr$ dans plante



Anthropogénique

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

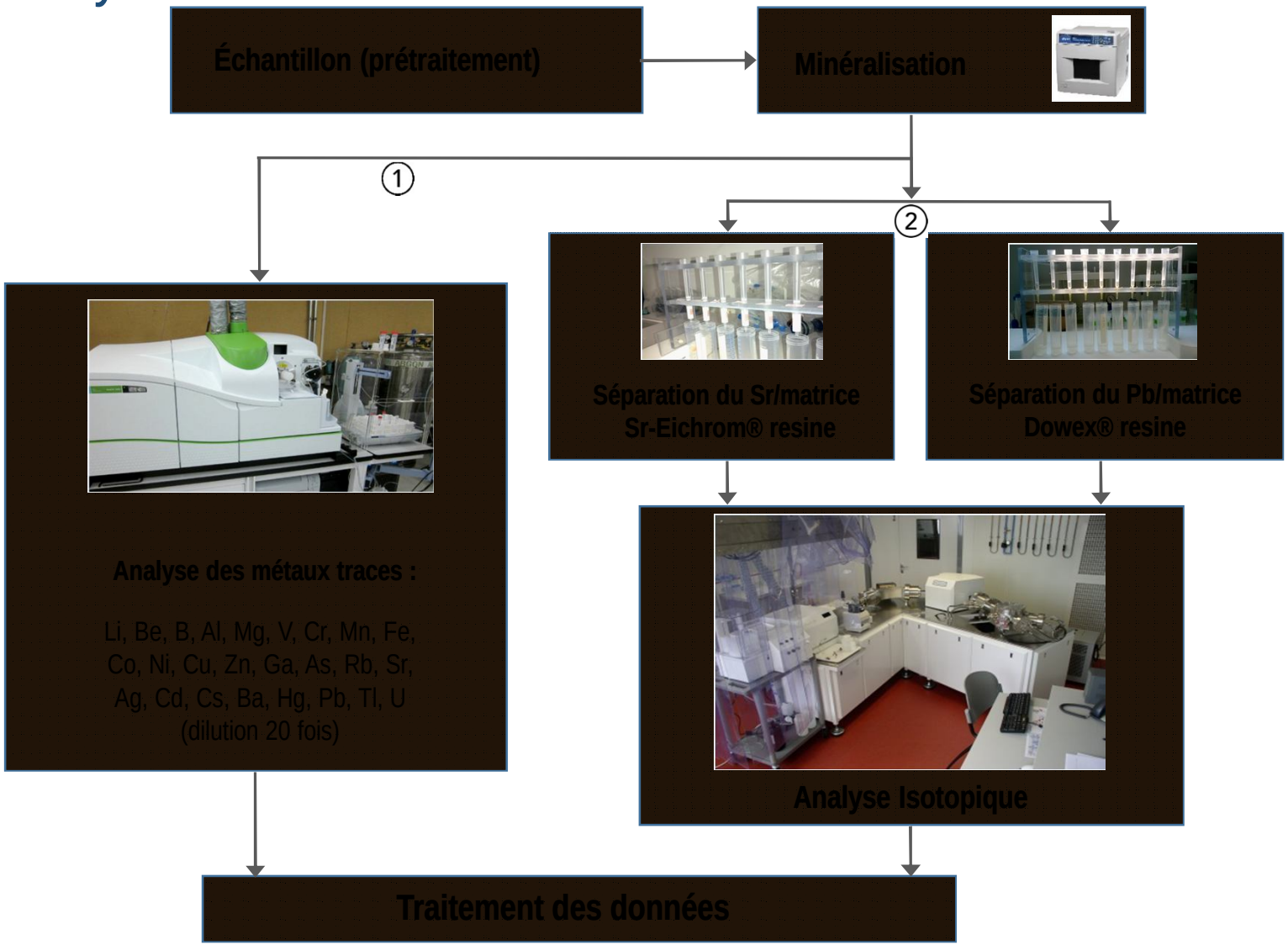
$^{207}Pb/^{206}Pb$

Geogénique

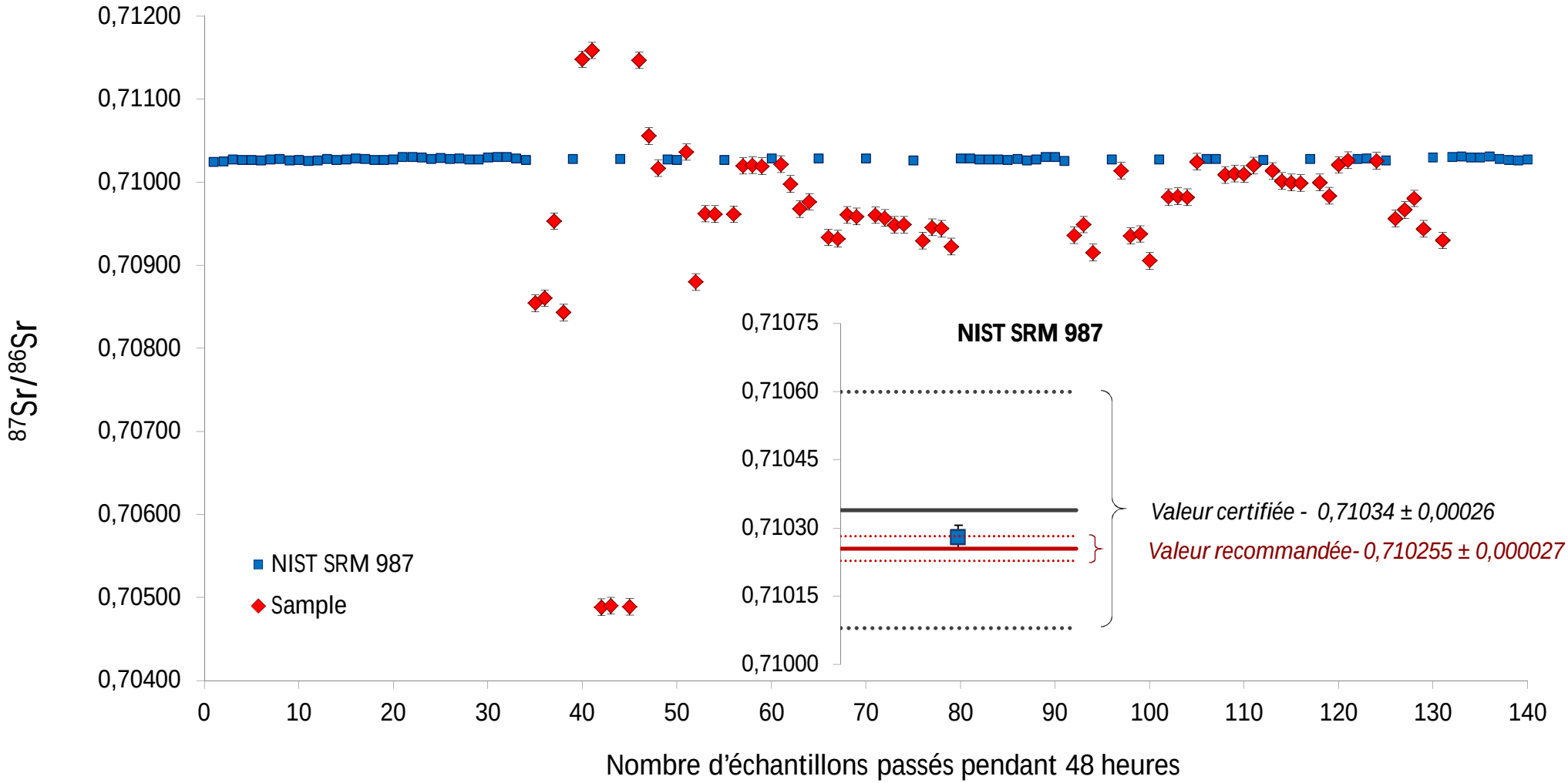
$^{208}Pb/^{204}Pb$

$^{206}Pb/^{204}Pb$

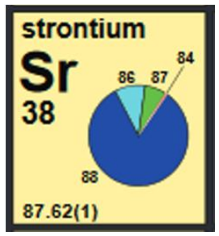
Circuits d'analyses



Accuracy and precision of the $^{87}Sr/^{86}Sr$



$^{87}Sr/^{86}Sr$ in Bordeaux Wines and other regions



Pomerol 0,7097 - 0,7102

Pauillac 0,7090 - 0,7098
Pessac-Léognan

Saint-Émilion 0,7083 - 0,7090

Slovénie 0,7087 - 0,7142

Californie 0,7052 - 0,7127

Chine 0,7052 - 0,7127

$^{87}Sr/^{86}Sr$

0,7130
0,7120
0,7110
0,7100
0,7090
0,7080
0,7070
0,7060
0,7050

Valeur typique maximale pour la région de Bordeaux

Valeur typique minimale pour la région de Bordeaux

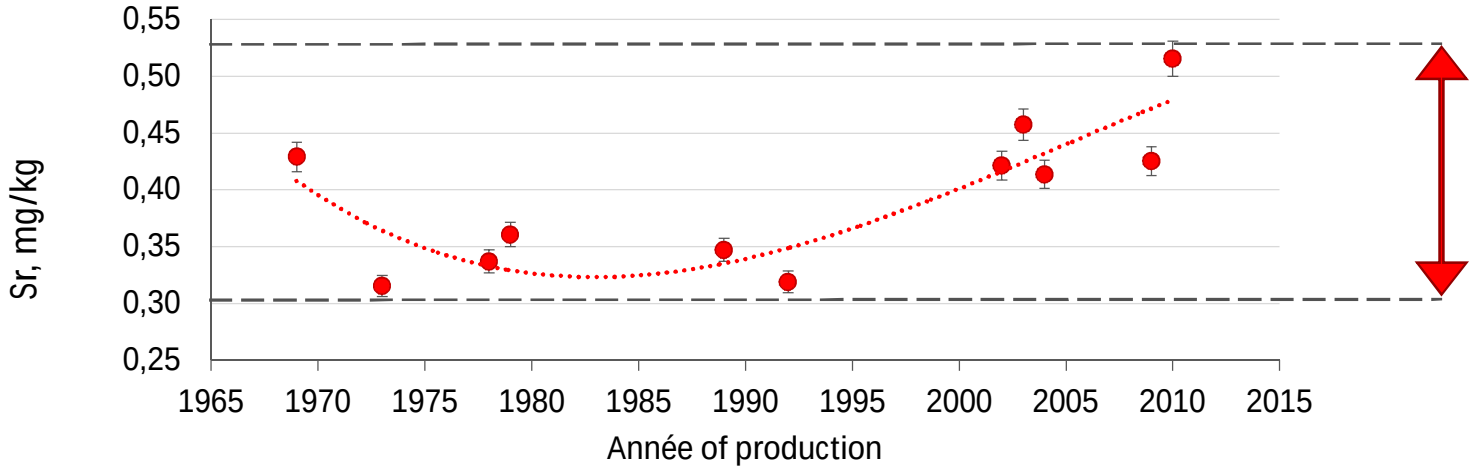
0 10 20 30 40 50 60 70 80

Numéro d'échantillon assigné

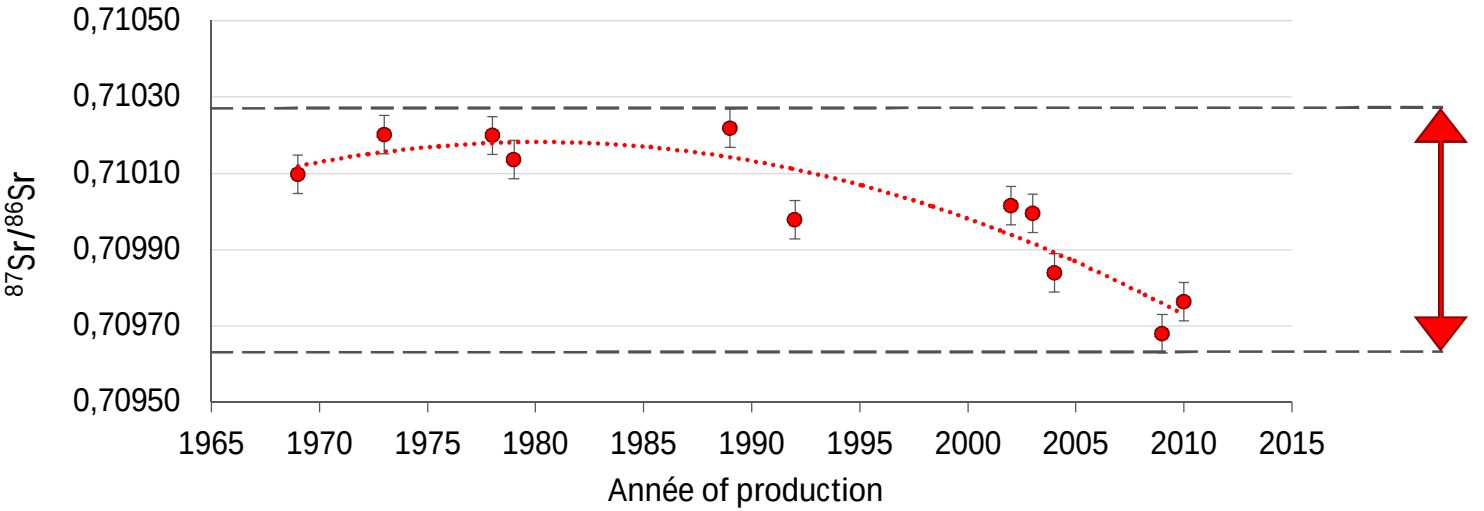
- Pomerol
- Saint Emilion
- Pessac-Léognan red
- Pessac-Léognan blanc
- Pauillac vrai
- Slovenie
- California (USA)
- China

Variations des concentrations en Sr and $^{87}Sr/^{86}Sr$ en fonction des années

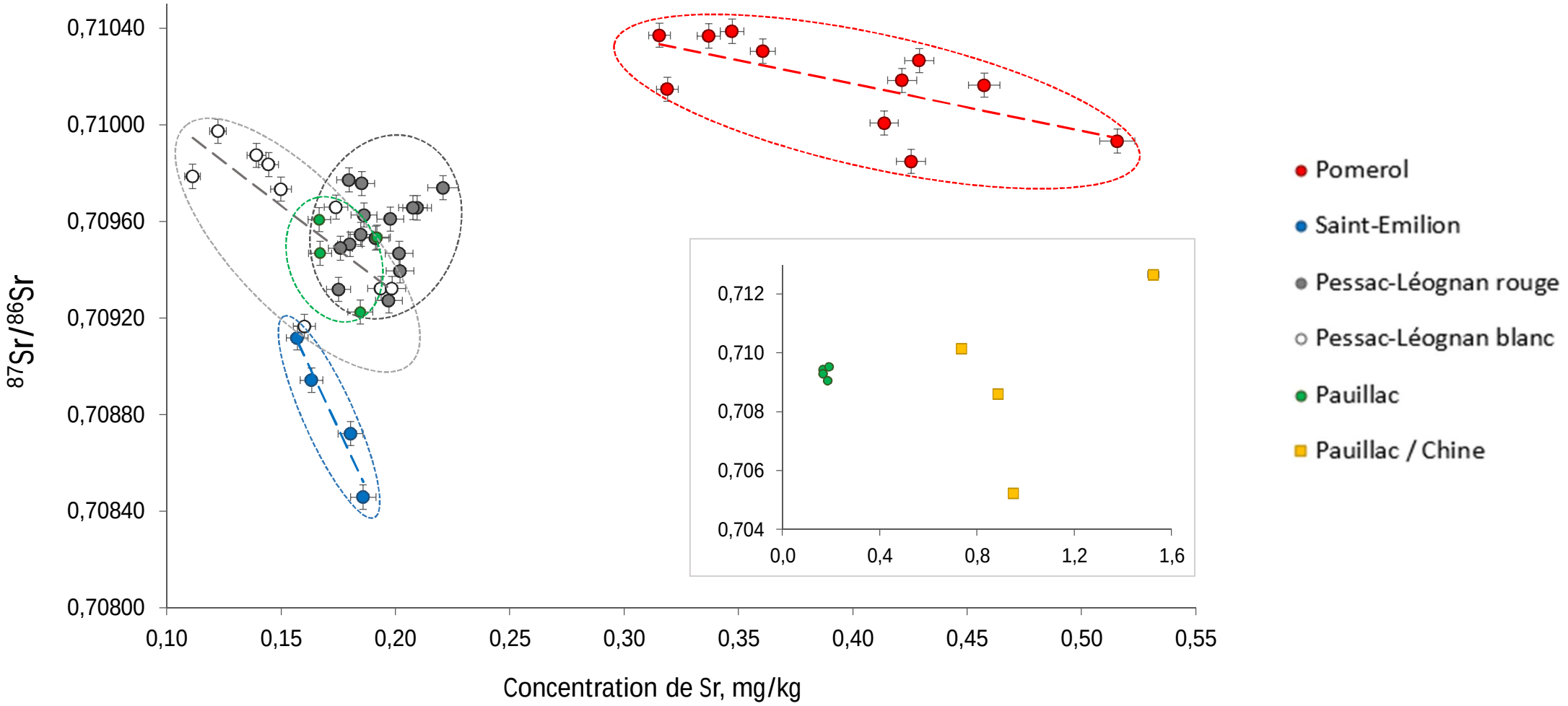
Sr, mg/L



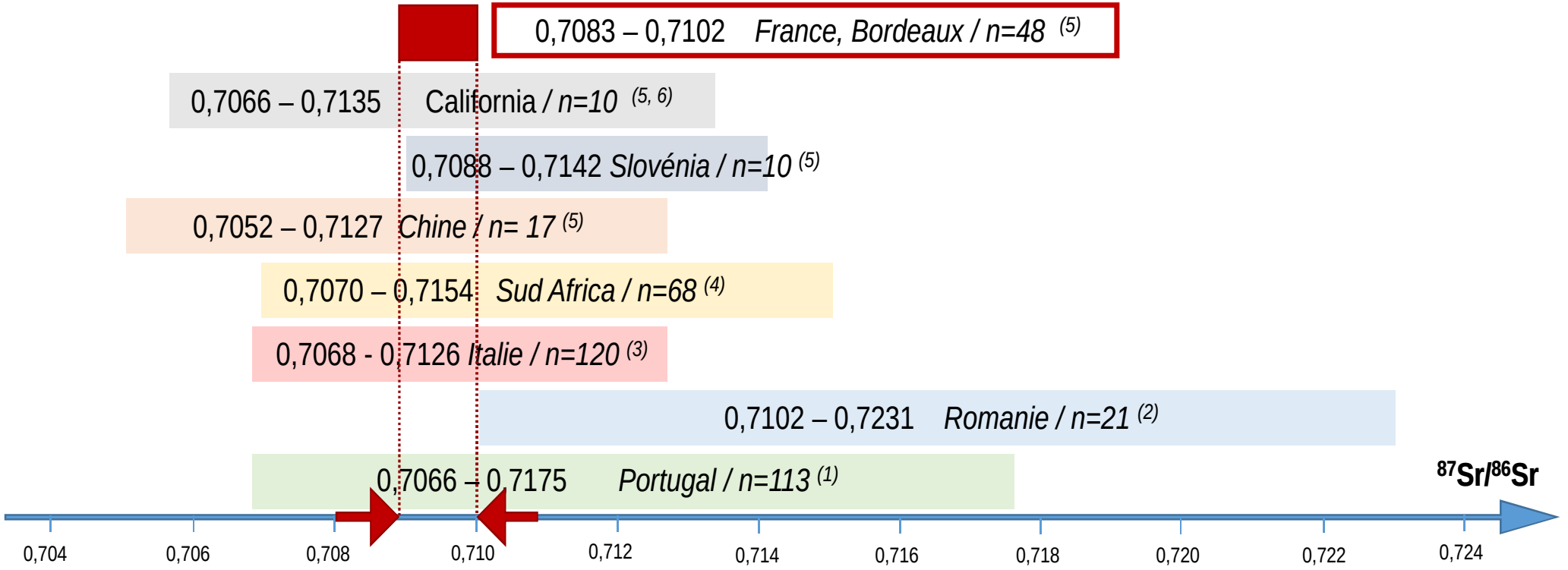
$^{87}Sr/^{86}Sr$



Rapports isotopiques du $^{87}Sr/^{86}Sr$ et concentration en Sr pour discrimination des vins de Bordeaux

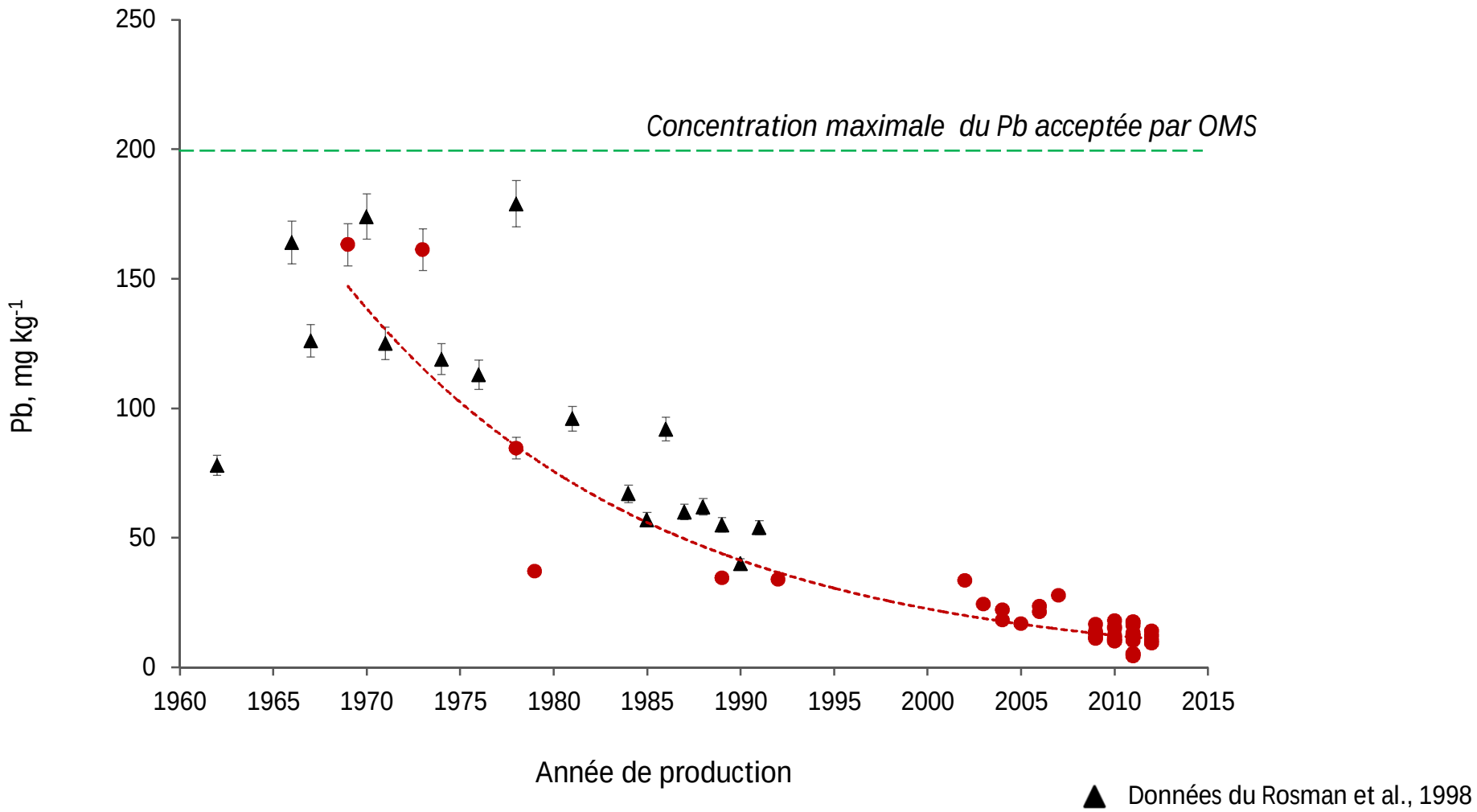


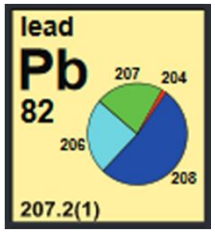
$^{87}Sr/^{86}Sr$ in wines from world wide basis



(1) Barbaste et al., (2002); Almeida et al., (2004); Vorster et al., (2010); Fernandes et al., (2015); Catarino et al., (2016)
(2) Brunner et al., (2010); Geană et al., (2016)
(3) Marchionni et al., (2013, 2016); Mercurio et al., (2014); Durante et al., (2013, 2015, 2016); Petrini et al. (2015); Tescione et al. (2015)
(4) Barbaste et al., (2002); Vorster et al., (2010)
(5) Our data, not yet published
(6) Barbaste et al., (2002)

Lead concentration in french wines over time





Food Additives and Contaminants, 2000, Vol. 17, No. 6, 435–445

Influence of atmospheric pollution on the lead content of wines

B. Médina†*, S. Augagneur†, M. Barbaste†,
F. E. Grousset‡ and P. Buat-Ménard‡
†Laboratoire Interrégional de la DGCCRF, 351 Cours de la Libération, 33405 Talence Cédex, France; ‡*Département de Géologie et Océanographie, URA CNRS 197, Université Bordeaux I, Avenue des Facultés, 33405 Talence Cedex, France*

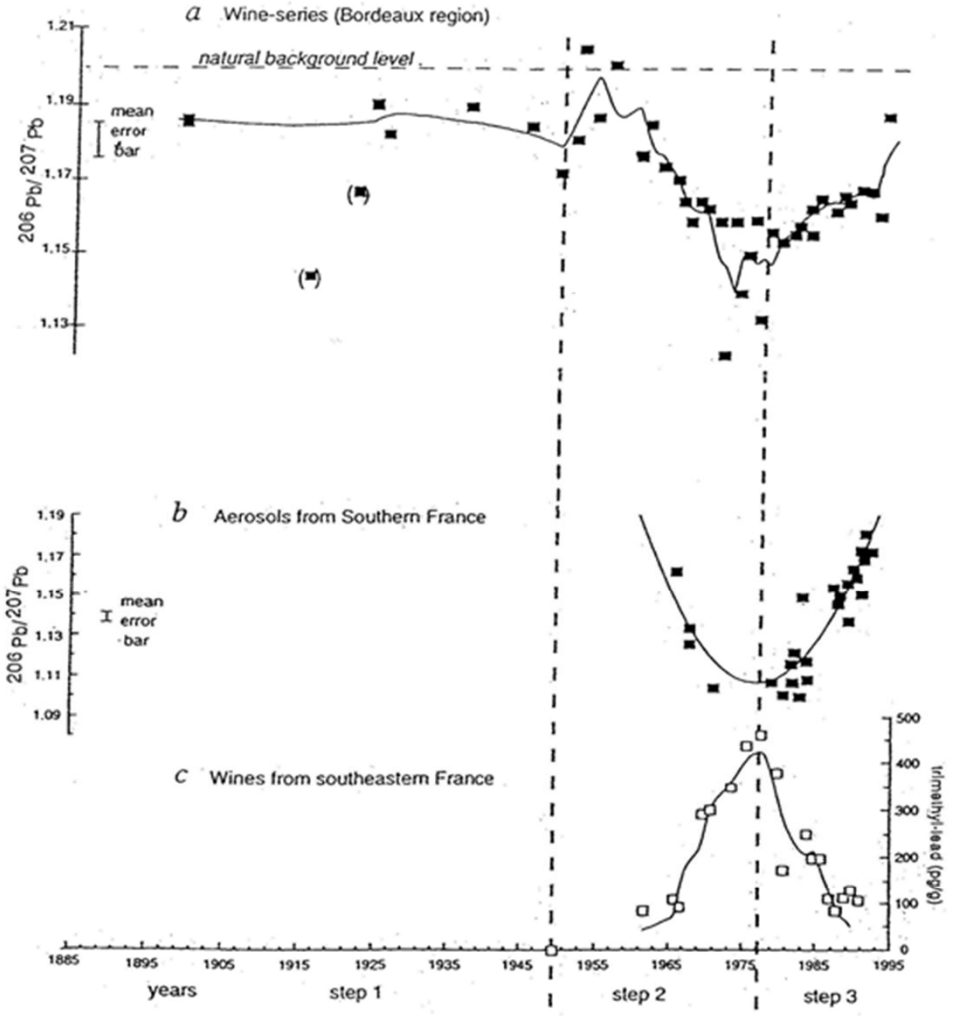
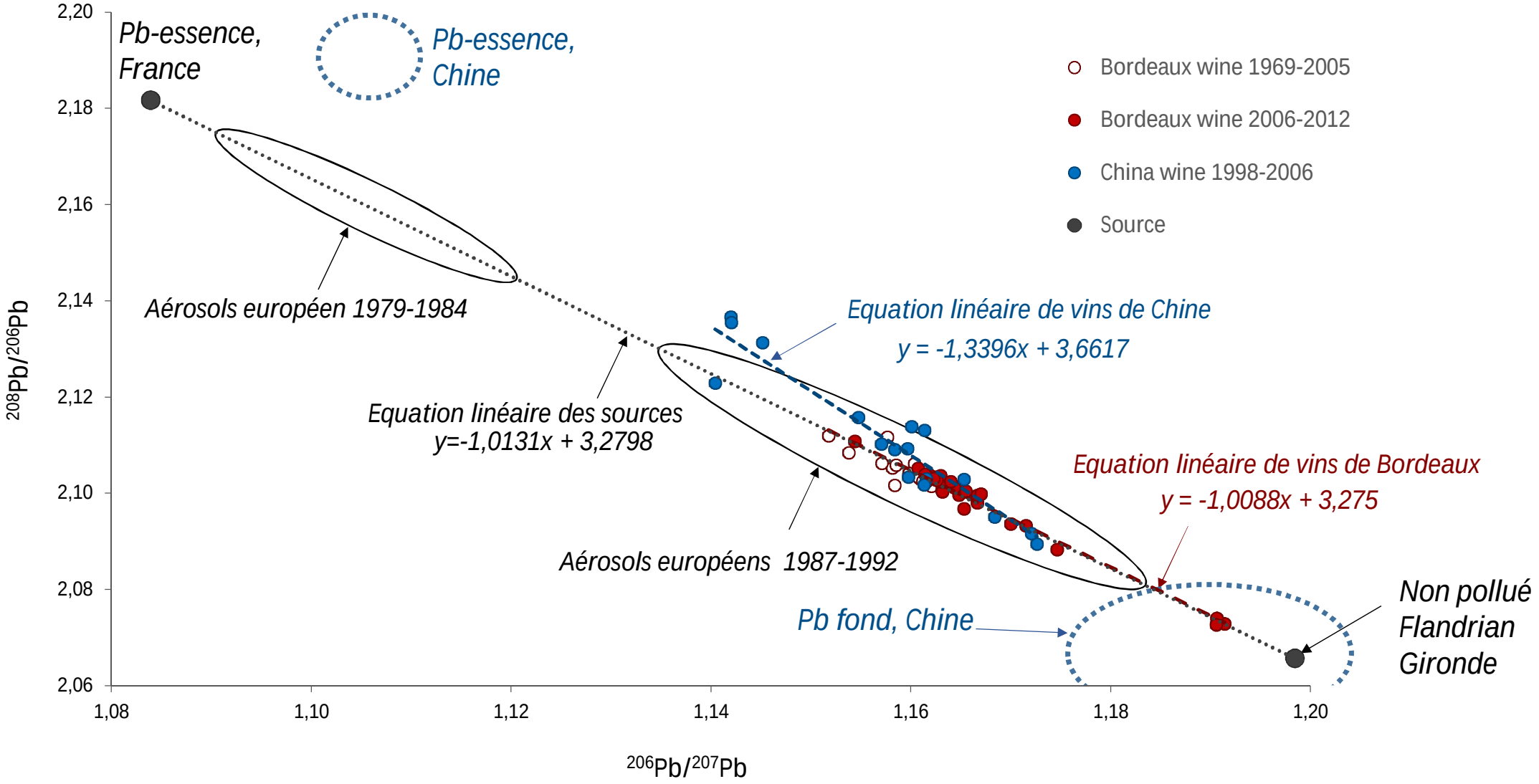
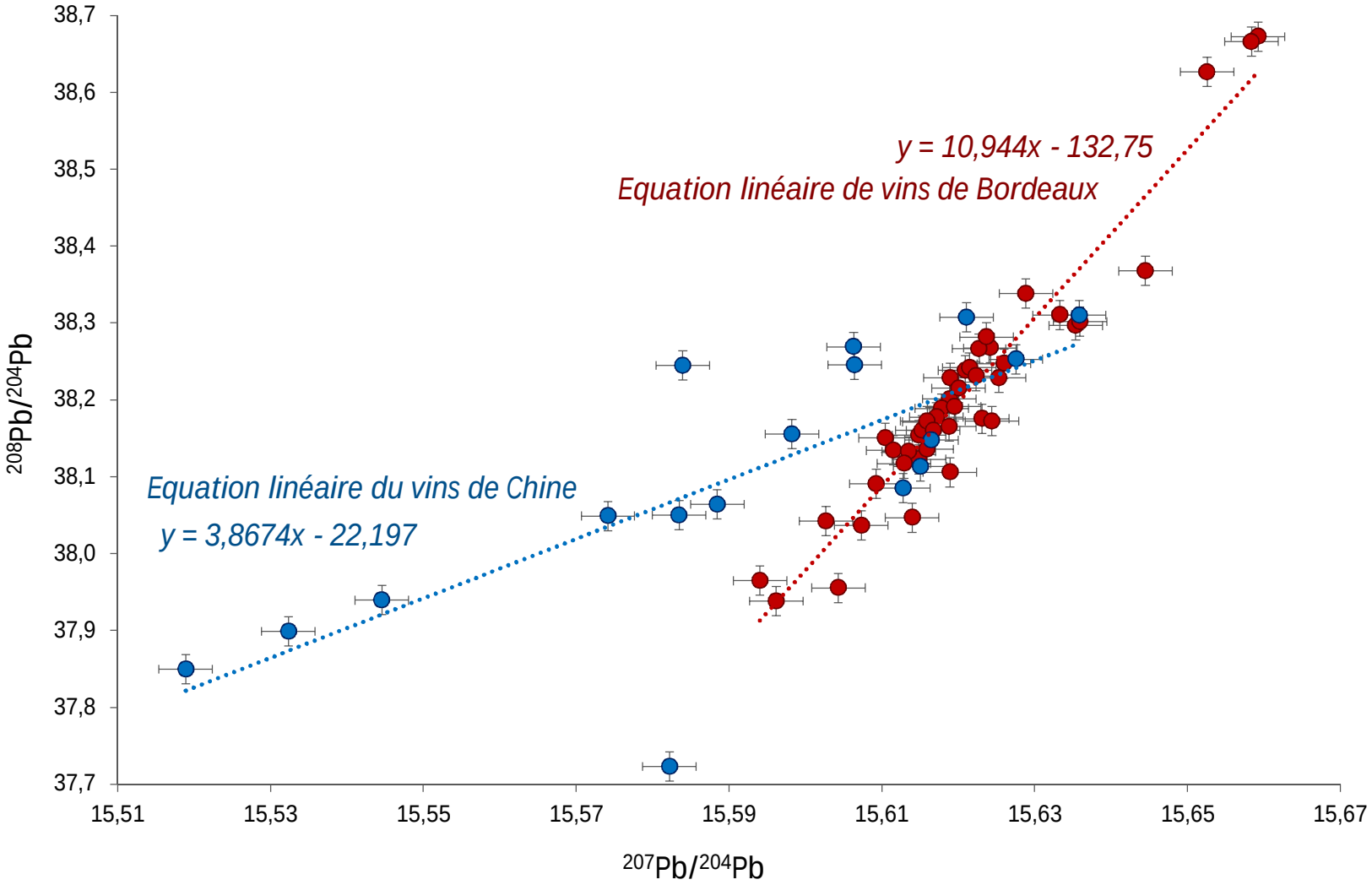


Figure 2. a: Chronological evolution of the lead isotopic composition ($^{206}Pb/^{207}Pb$ ratios) (closed squares) in French wines since 1898. b: Isotopic composition ($^{206}Pb/^{207}Pb$ ratios) of the lead associated with aerosols from southern France (Grousset et al. 1994). c: Trimethyl-lead concentration in wines from southeastern France (Lobinski et al. (1994). Solid line trends are three-point running averaged data (smoothed trends). In (a), the smoothed trend is drawn without considering the two, bracketed closed squares, which are not reliable samples (see text).

Rapport isotopique du Pb pour discrimination de vins de Bordeaux et de Chine



Rapport isotopique du Pb pour discrimination de vins provenant de Bordeaux et de Chine



Isotopic fractionation of Fe under controlled growth cultures conditions

HR MC-ICP-MS Nu1700 (Nu Instruments)

Installation : July 2017

Resolving power capabilities :
True High Res. (10% Valley): 5000
Pseudo High Res. (5-95% Edge): 20000

Detectors: 16 Faradays, 5 IC

First test : Fe
True HR (wet plasma , [Fe]=2.5 ppm)

		δ^{57}Fe (‰)	δ^{56}Fe (‰)
IRMM 524a "Self Bracketting"	**Average**	**0.002**	**0.001**
n=63	2SD	0.15	0.12
Tomatoe Leaves (NIST 1573a)	**Average**	**-0**	
Sample prep* replicates (n=3)	2SD	0.	

** : Hot block acid digestion + Ion exchange purification*

Targeted Systems for HR: Cu, Se, Si…

Composition isotopique légère pour les levures

Il y a un fractionnement isotopique pendant l'assimilation du Fer par les levures

Résultats en bon accord avec un fractionnement indépendant de la masse. Pas d'interférence isobarique pendant la mesure.