# Measuring isotopes accurately for a safer, healthier and sustainable world

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IAEA Environment Laboratories

IAEA

International Atomic Energy Agency

# Acknowledgment

Thanks to my colleagues at IAEA, especially to:

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Steven Judge

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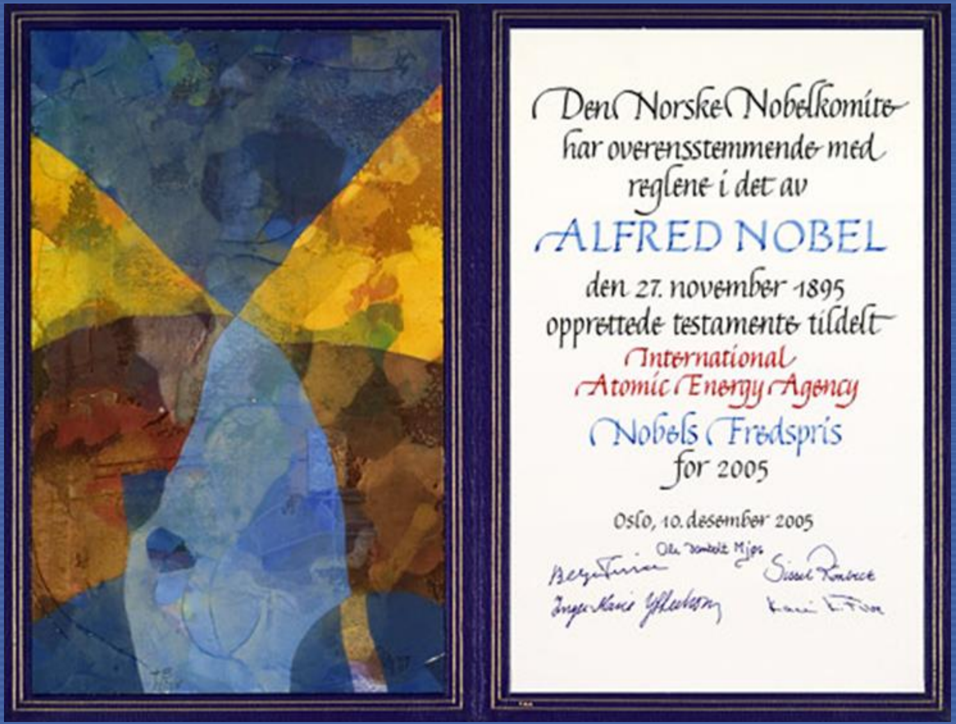
# International Atomic Energy Agency

## Technical Agency associated to the UN System

## Atoms for Peace and Development

"The Agency shall seek to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world."

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# Overview

Long term cooperation with BIPM:

1. Dosimetry and MRA
2. MoU between IAEA and BIPM
3. Trace Element Analysis and Nuclear Data
4. Stable Isotope Ratios and Radionuclides

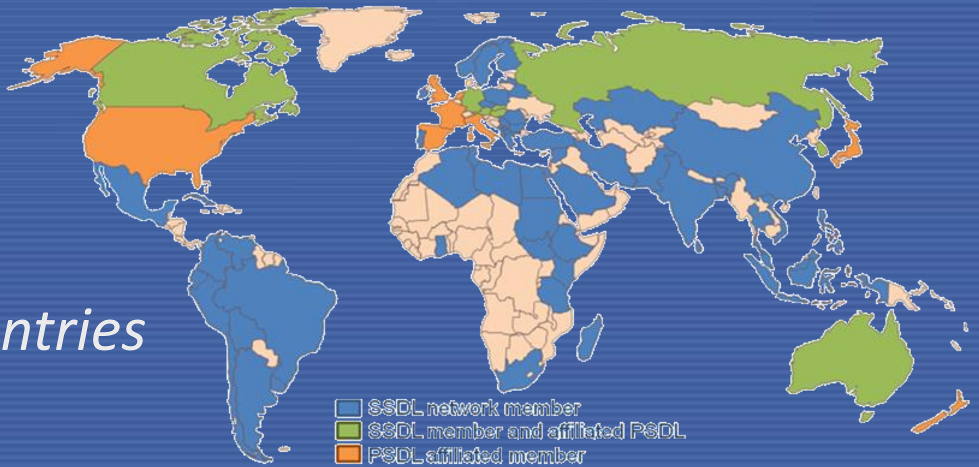
# 1. Dosimetry and the Mutual Recognition Agreement

Secondary Standard Dosimetry Laboratories:

Provision of calibration for dosimetry equipment. Dosimeters are used to determine dose level for patients, staff or the public – importance that measurement results are consistent with SI system (radiation measurements)

- Formal agreement to establish a **Network of SSDLs** signed by IAEA & WHO (1976)
- Since 1987, activities of the network are assessed by an independent SSDL Scientific Committee (includes **BIPM**)
- MRA signed in 1999
- Currently 26 CMCs

*86 SSDLs in 71 countries*

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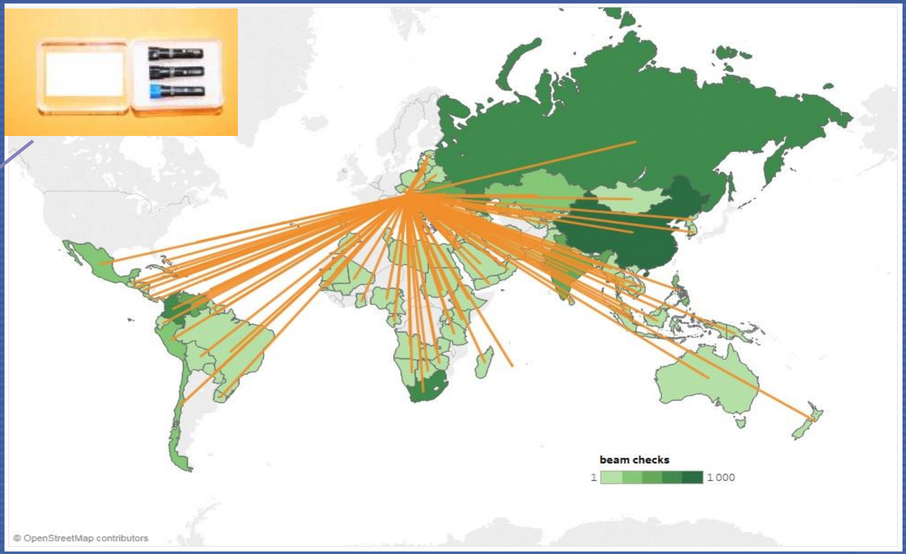
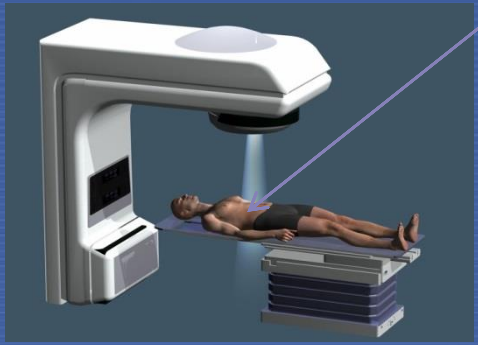
# IAEA/WHO dose audits for radiotherapy centres

**How is the audit carried out?**

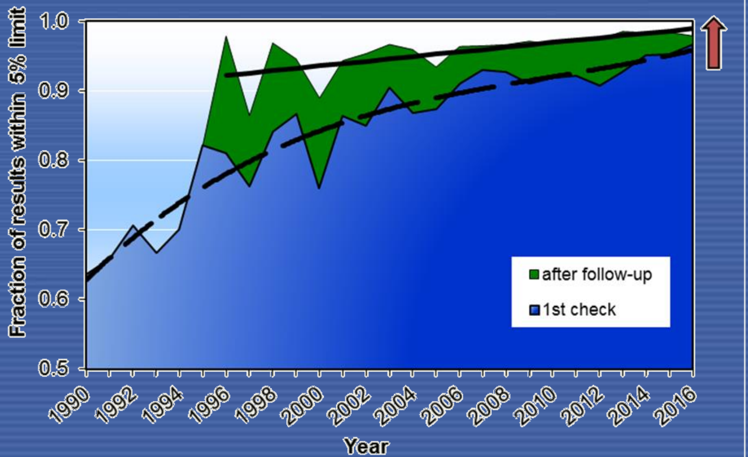
Small dosimeters are sent to radiotherapy centres for irradiation to verify the beam output used for patients' treatments.



**Dose audit services 1969–2018:**

- 49 years of the IAEA/WHO postal dose audits
- >13000 beam checks
- ~2300 radiotherapy centres in 136 Member States
- **BIPM has provided reference irradiations for the IAEA/WHO dose audits for >20 years**

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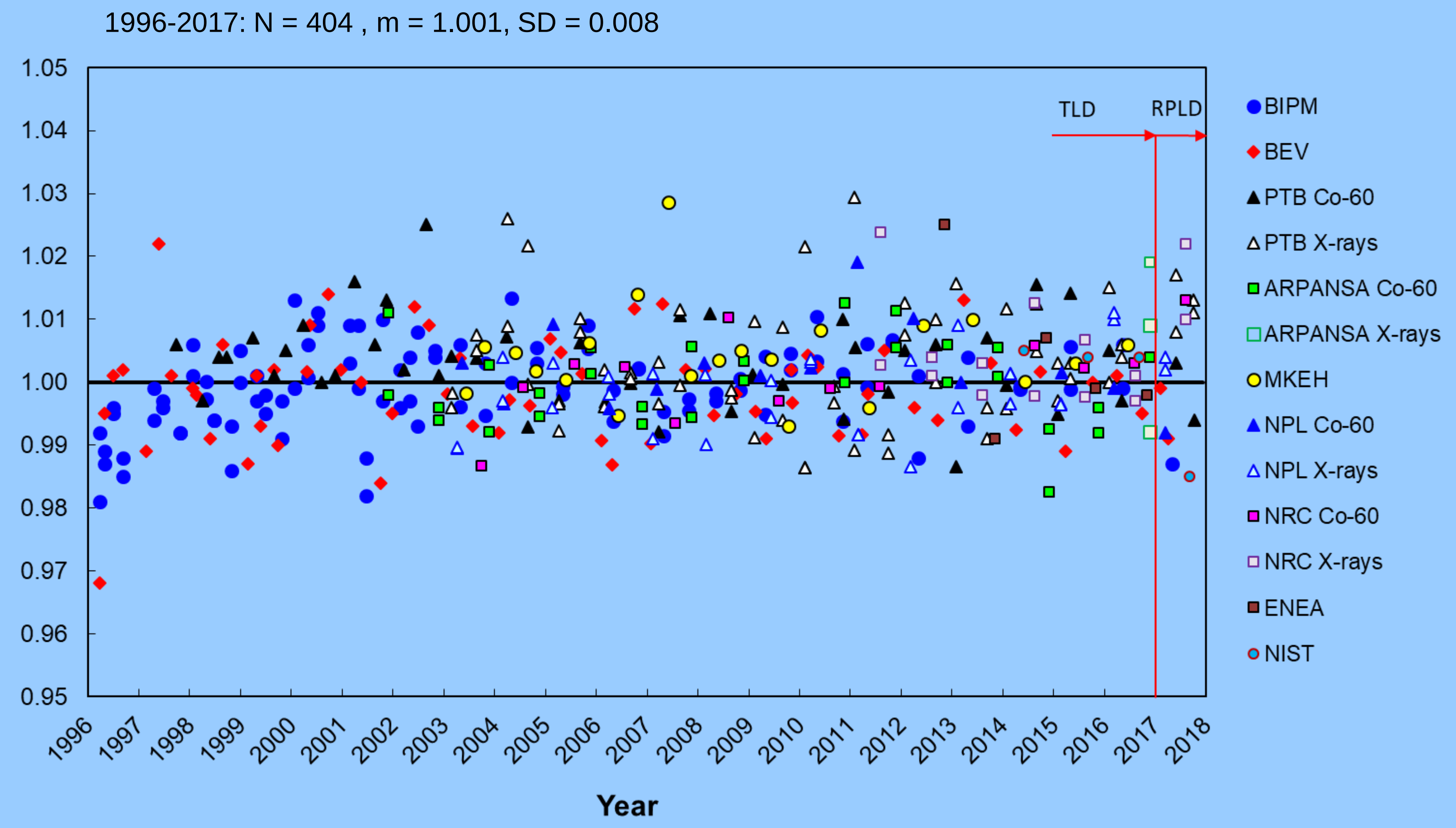
# Reference irradiations for dose audits

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# 2. Memorandum of Understanding

MOU formally signed in 2012, defines the main areas of cooperation:

- Mutual exchange of data and information in the area of metrology of ionizing radiation and chemical measurements
- IAEA representation in CCRI (full member 2011)
- IAEA participation - as a signatory - in activities related to CIPM MRA
- BIPM participation in the SSDL Scientific Committee
- BIPM support to the IAEA/WHO dosimetry audits and IAEA calibration services through reference irradiations and calibration of IAEA reference standards
- **Collaboration for measurement standards and reference materials**
- Publication and dissemination of nuclear data
- Participation in scientific events (e.g. IAEA conferences), education and training, etc.

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MEMORANDUM OF UNDERSTANDING

between

THE INTERNATIONAL BUREAU OF WEIGHTS AND MEASURES

(hereinafter referred to as the 'BIPM')

and

THE INTERNATIONAL ATOMIC ENERGY AGENCY

(hereinafter referred to as the 'IAEA')

Vienna, 2012-06-25

| For the BIPM | For the IAEA |
|---|---|
| Michael Kuehne<br>Director | Daud Mohamad<br>Deputy Director General |

*The IAEA Dosimetry Laboratory Cs-137 irradiator will be made available to BIPM staff for calibration purposes as of 2019*

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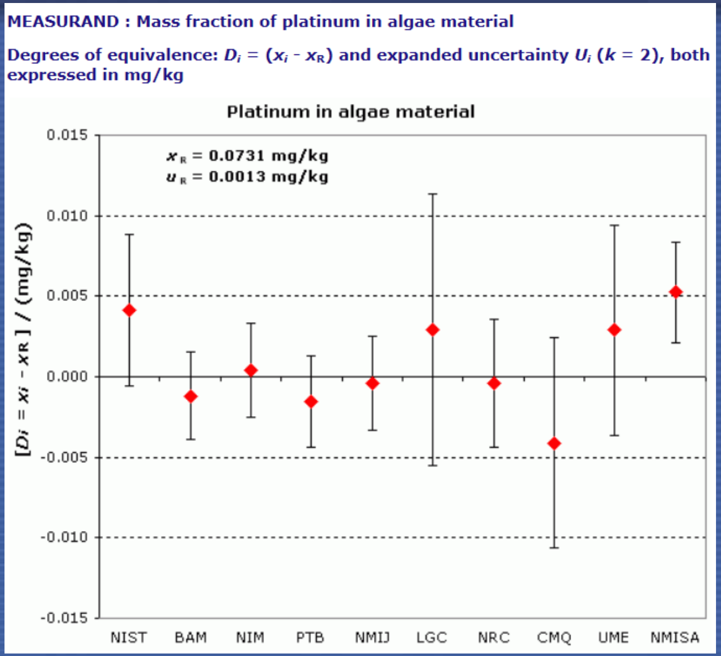
# 3. Trace Element Analysis & Nuclear Data

- CCQM Key Comparison K75 (and Pilot Study P118) “Determination of toxic metals in algae” – Platinum and Nickel , 2010 Shakhashiro et al.



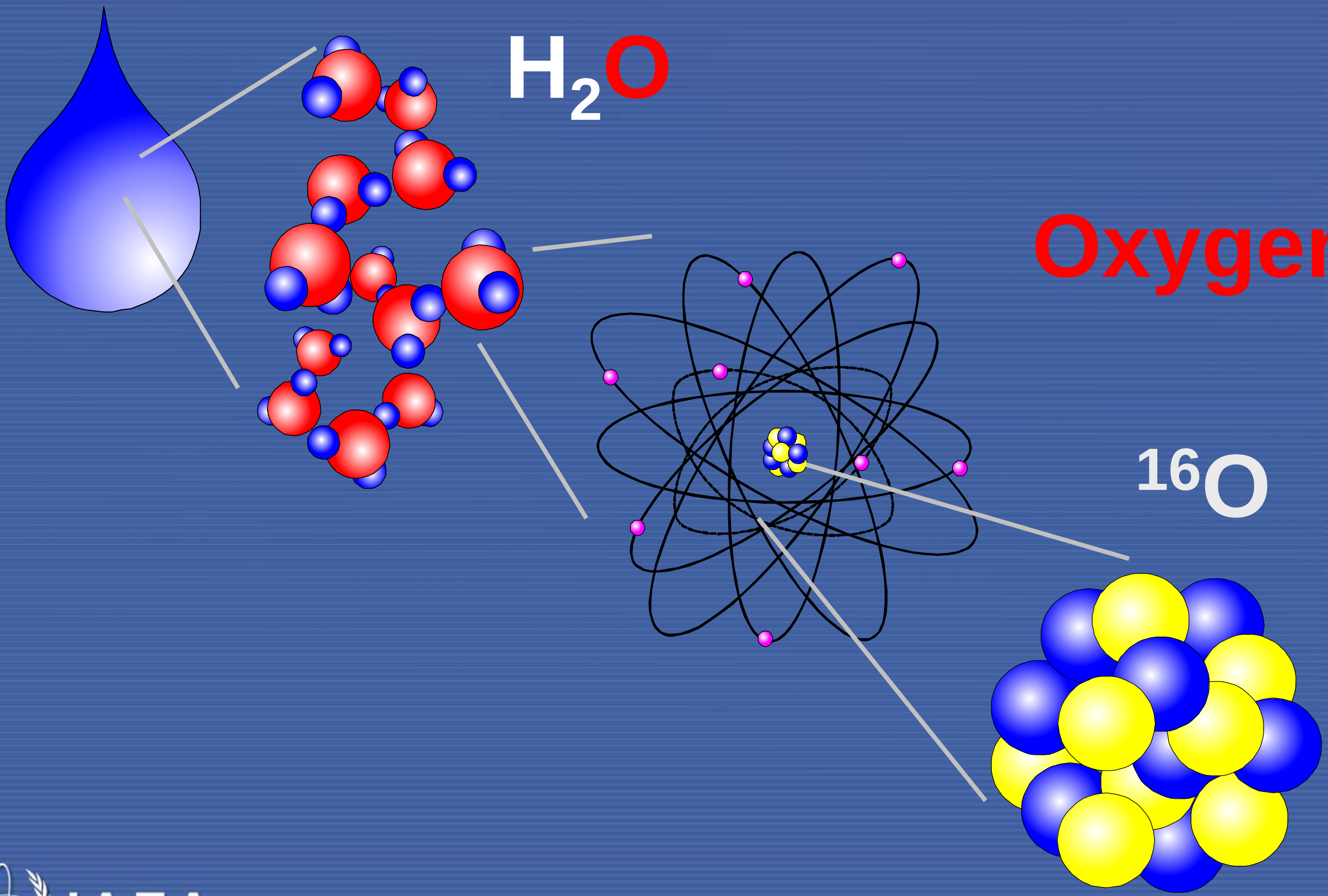

- Nuclear data – decay data evaluations with BIPM
- Attendance at CCRI – Neutron standard cross sections

# 4. Stable Isotope Ratios, and Radionuclides

- 100 Reference Materia




# Stable Isotopes: - e.g. oxygen in water

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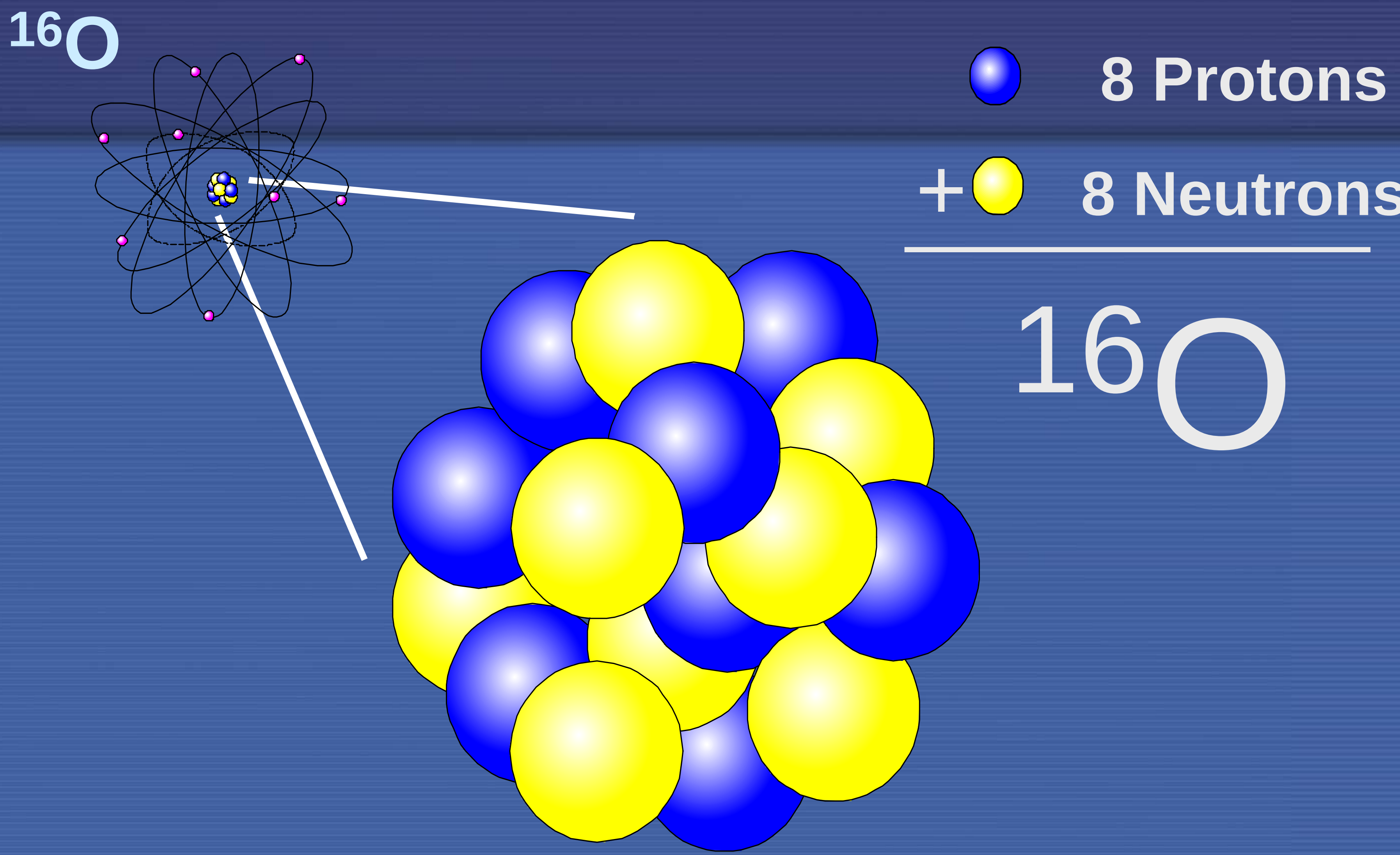


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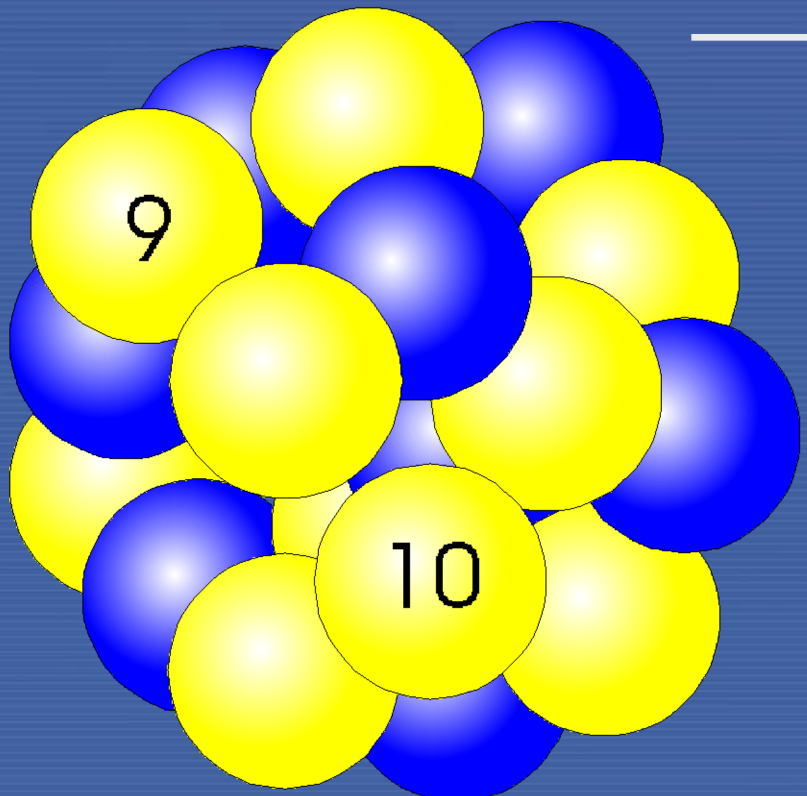
# $^{18}O$

8 Protons

+ 10 Neutrons

$^{18}O$

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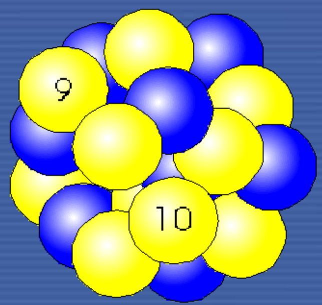
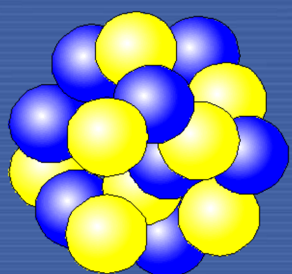
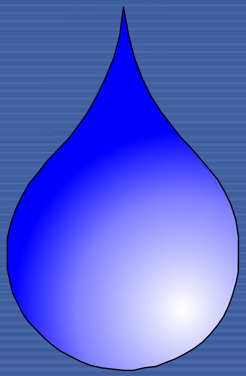
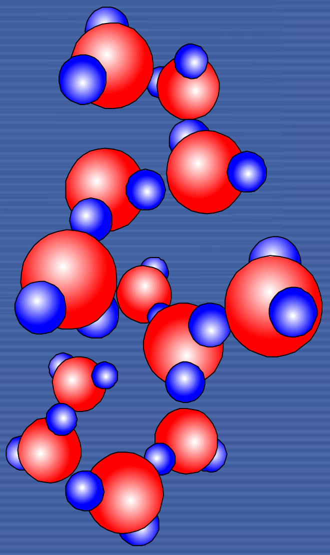
# Ratio of $^{18}O$ to $^{16}O$



$$\frac{^{18}O}{^{16}O} \sim \frac{1}{500}$$





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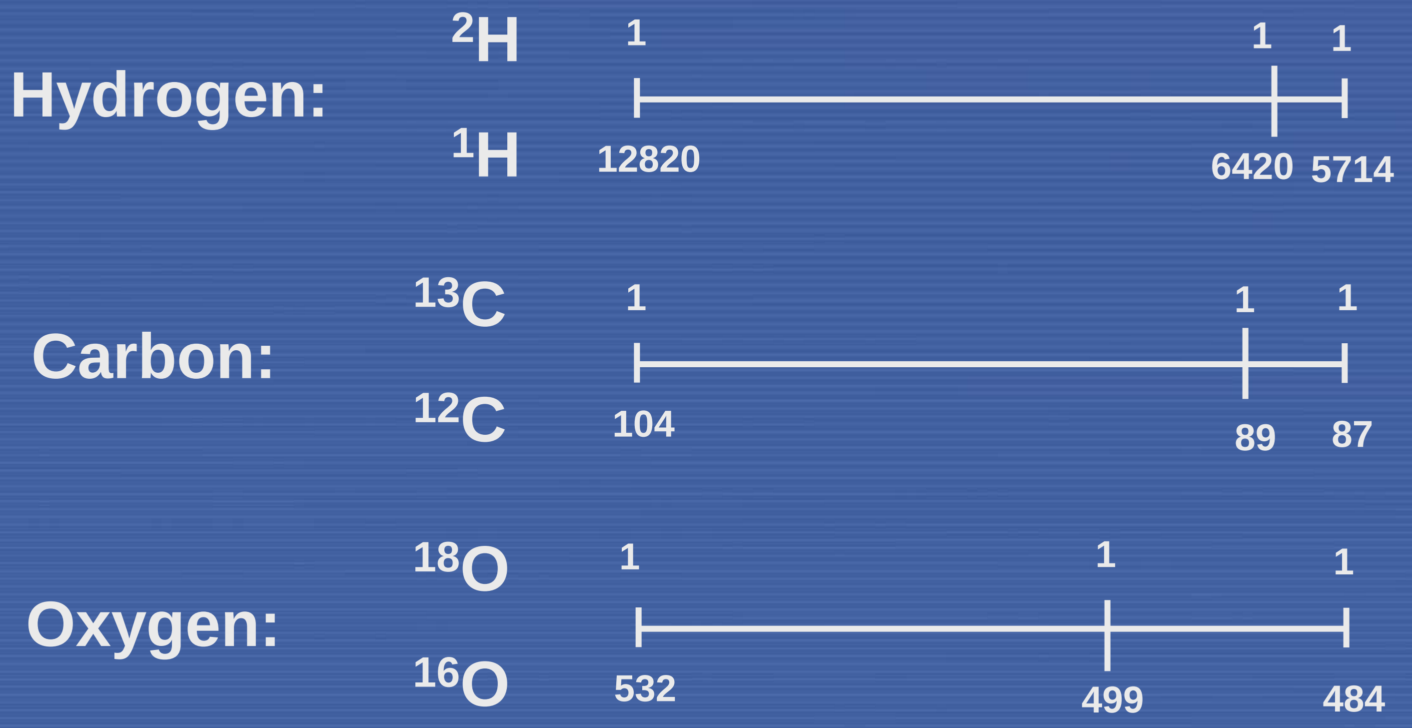
**Oxygen: $(^{18}O/^{16}O) = (2005.2 \pm 0.45) \cdot 10^{-6}$**

**Hydrogen: $(^{2}H/^{1}H) = (155.76 \pm 0.05) \cdot 10^{-6}$**

# Range of Stable Isotopes in Nature




from Coplen et al. 2002

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# Why to measure Stable Isotopes in Nature

Chemical analysis: ☑

Stable isotopes ? ☐

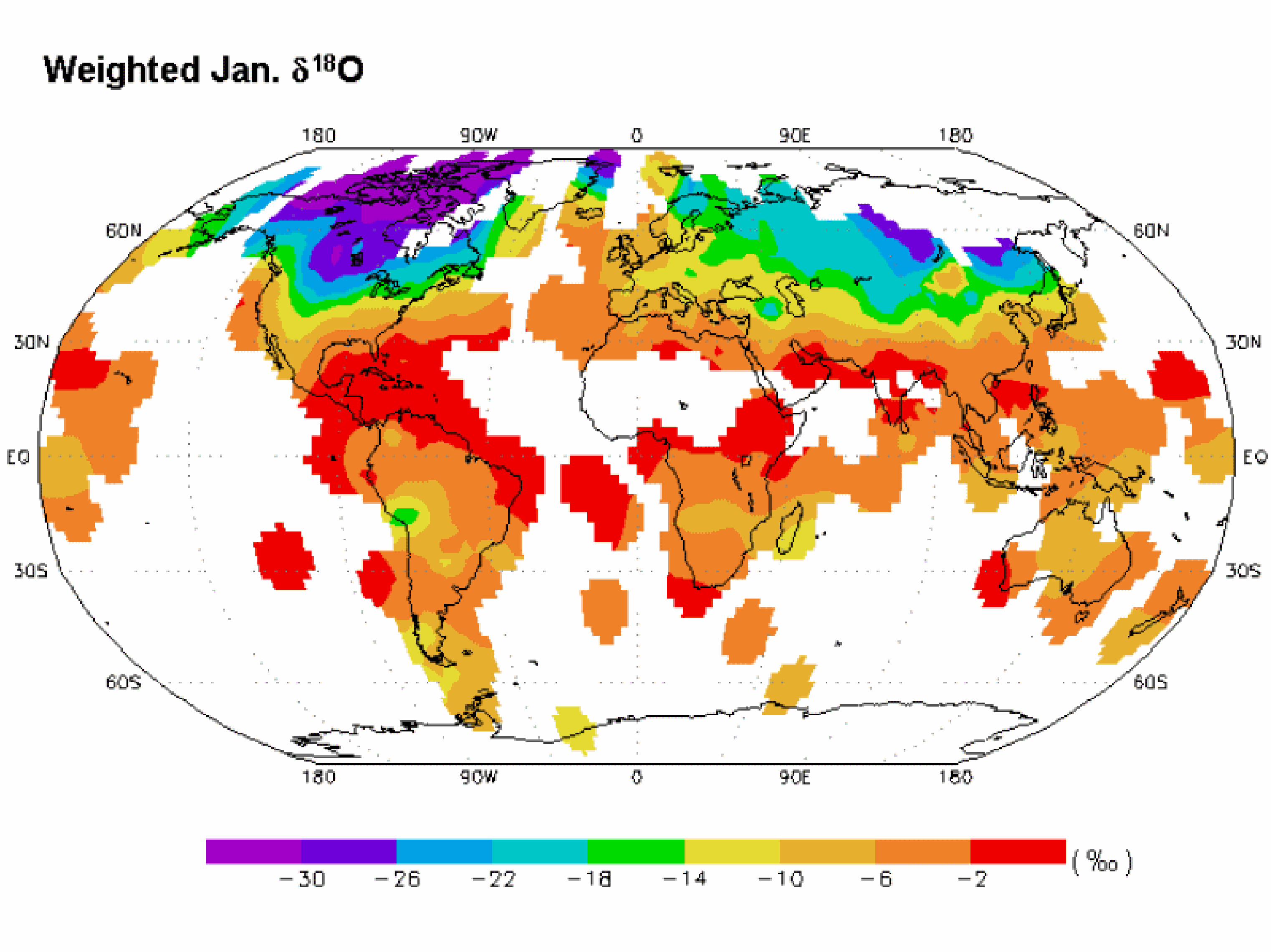
# Why to measure Stable Isotopes in Nature

Chemical analysis: ✓

Stable isotopes ?

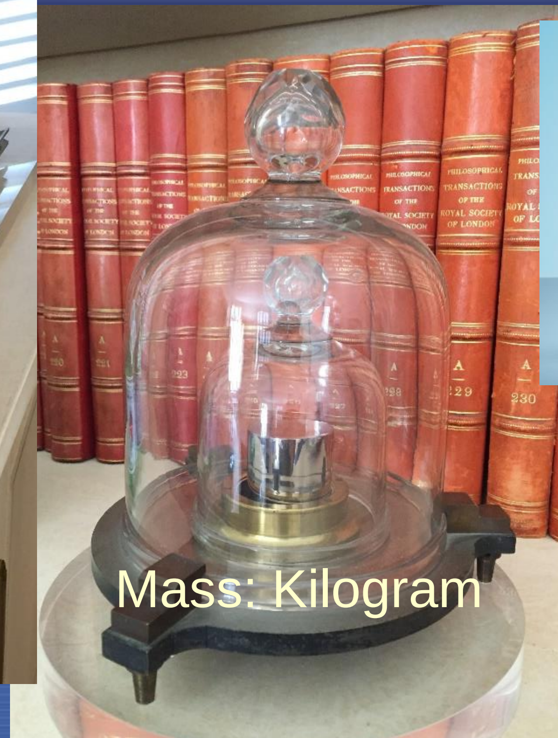
# "Stable Isotopes are the Colors for the Elements"

# Global Network Isotopes in Precipitation



# “Standards” required for any lab operation

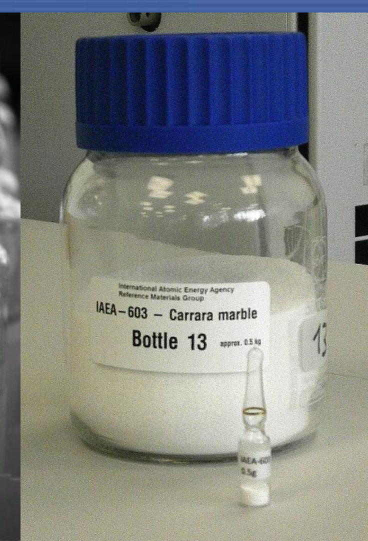
Length: Meter



Mass: Kilogram

Kilogram – new definition, still requiring measurements

Isotopes: Reference materials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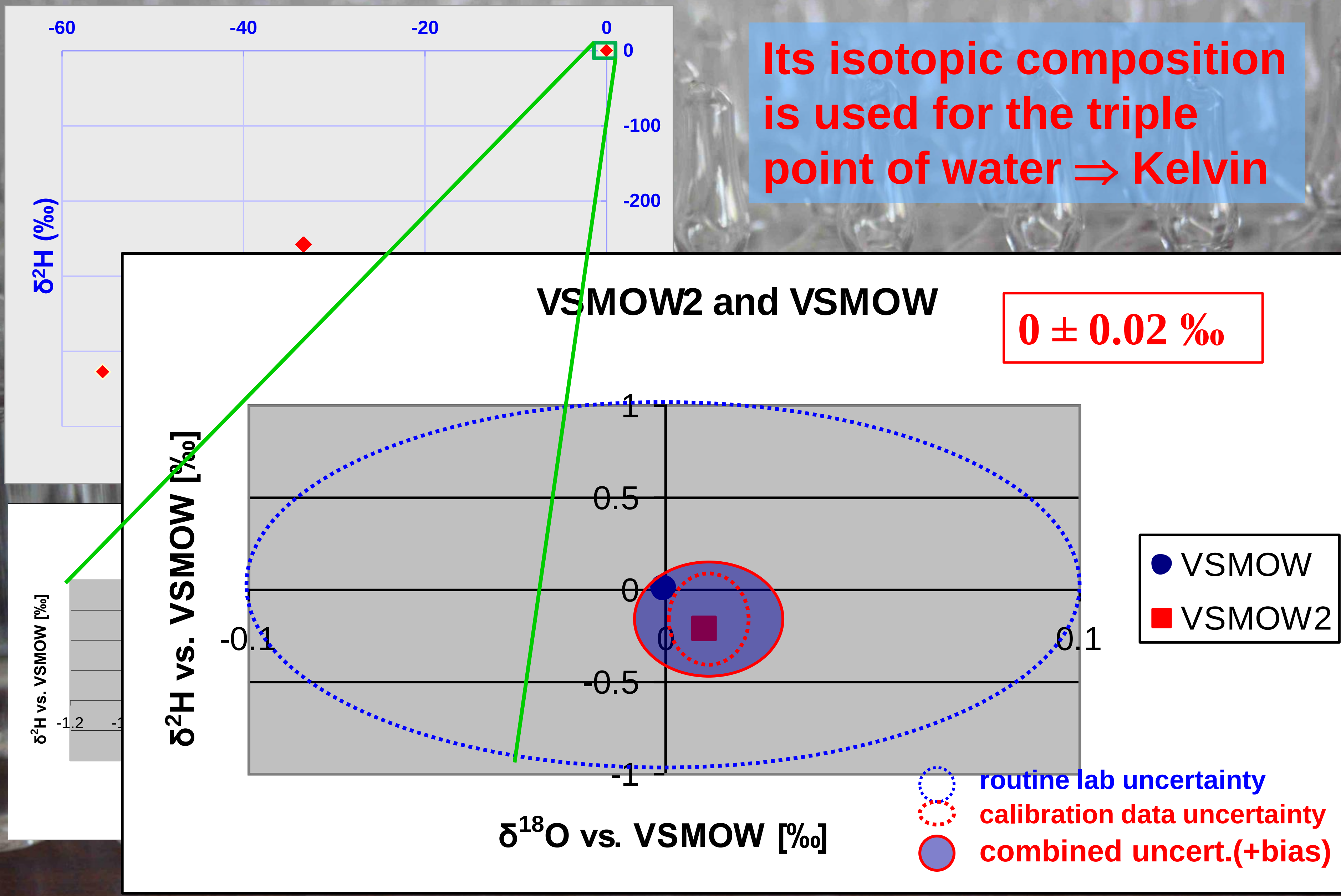
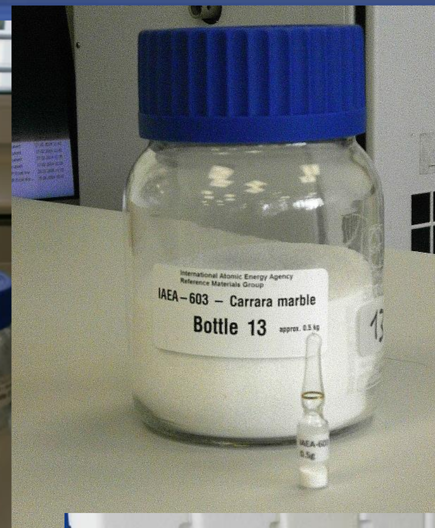
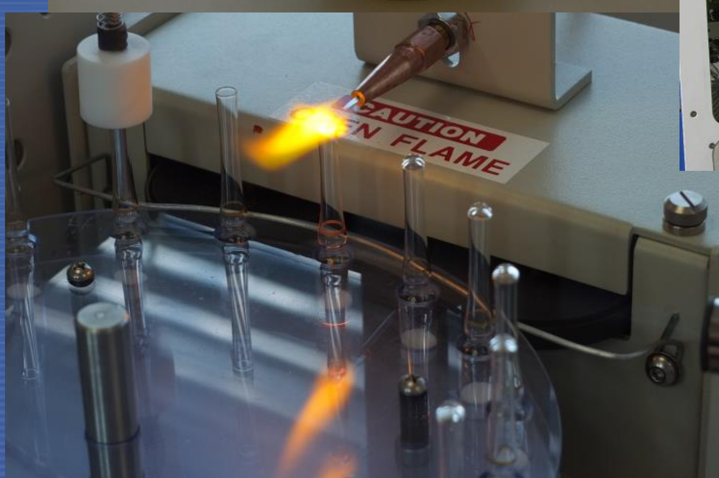
# VSMOW2 –Vienna Standard Mean Ocean Water 2

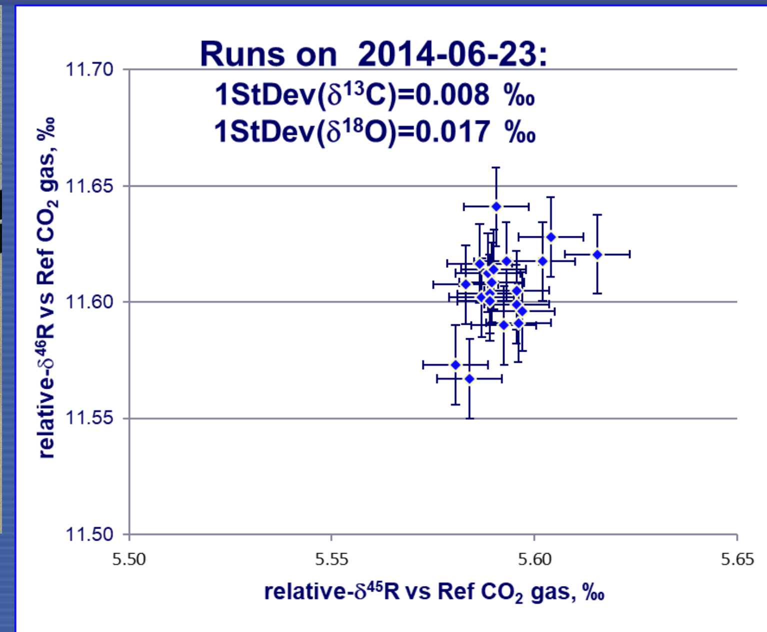
**Its isotopic composition is used for the triple point of water ⇒ Kelvin**



# IAEA-603 Marble - Carbon isotope standard




**Combined standard uncert. u($\delta^{13}$C)= ±0.01‰ (homog. & calibration versus NBS19)**

**⇒ nearly ideal material for $\delta^{13}$C VPDB scale realization**

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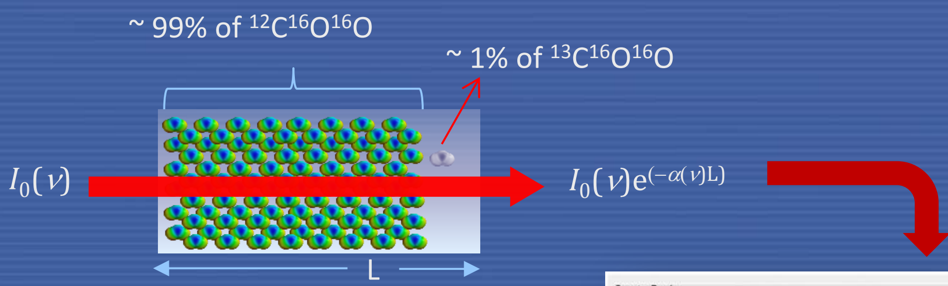
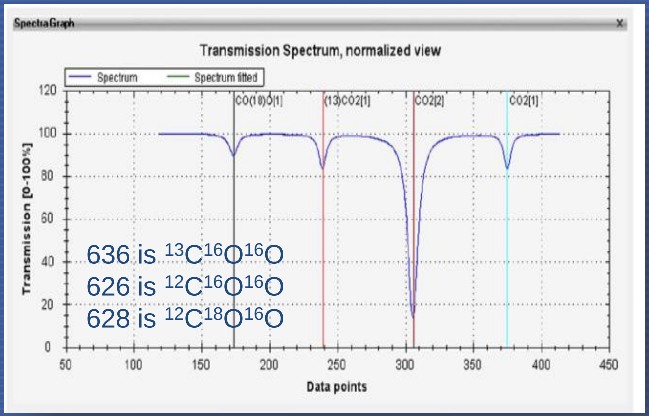
# New Instruments requiring novel standards for $CO_2$ Isotope Analysis


Commercially available 'Optical' instruments




$$R^{13} = \frac{x_{636}}{x_{626}}$$

$$R^{18} = \frac{x_{628}}{x_{626}}$$




- Measure infrared absorption of individual isotopologues
- Measure directly at concentration range of interest
- Absorption can be modelled
- Flow rates 0.1 to1 L/min

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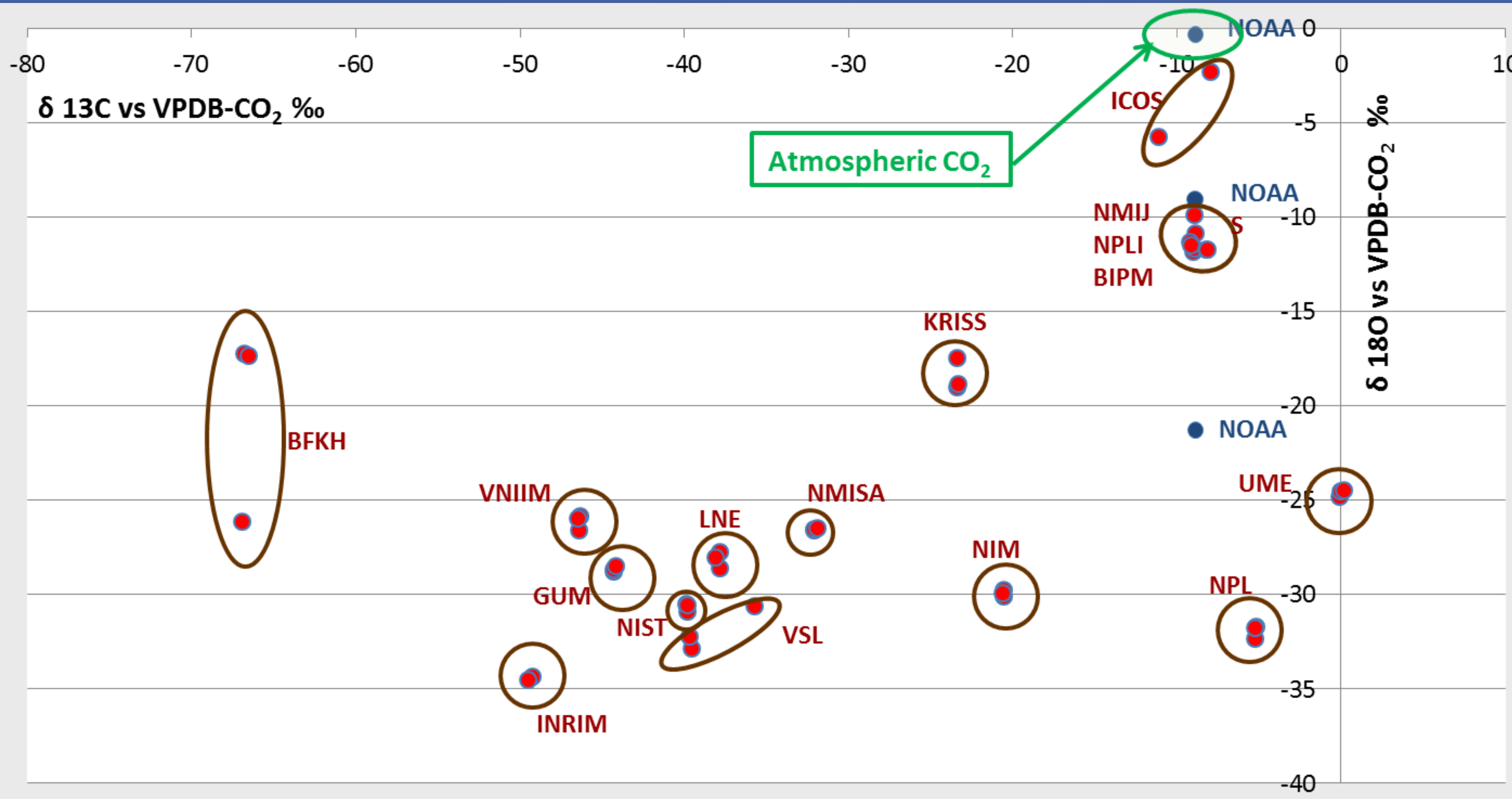
(Slide courtesy BIPM)

# Spread in isotope ratios of $CO_2$ Standards in CCQM-K120, coordinated by BIPM






(Slide courtesy BIPM)

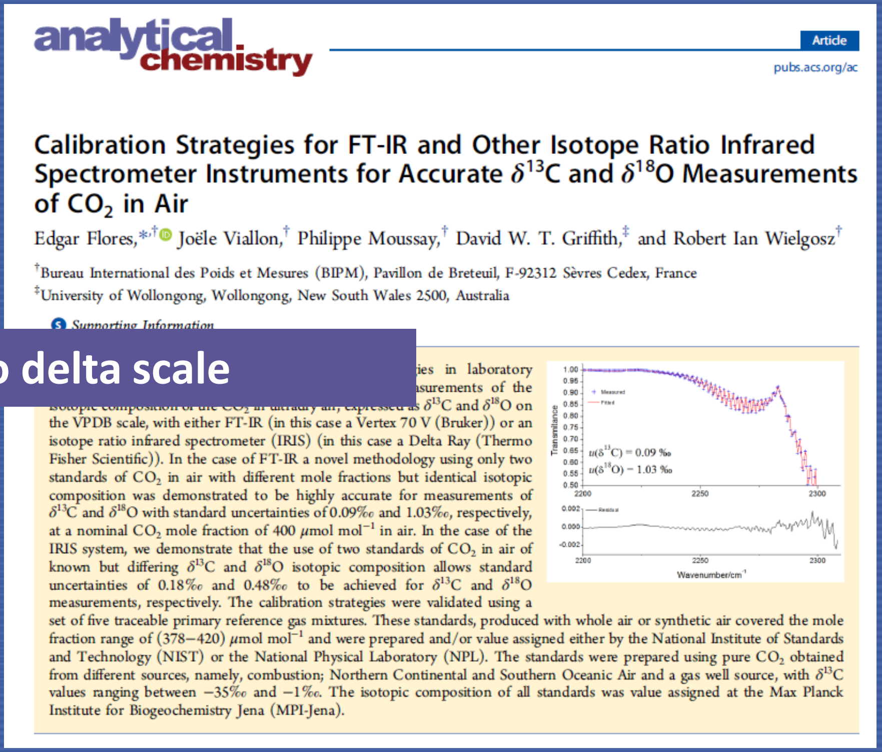
# Calibration Strategies for Optical Instrument Isotope Ratio Measurements developed by BIPM

## 1. Calibration in ‘delta scale space’ and correction for mole fraction effects

$\delta^{13}C_1$ $\delta^{13}C_2$ $x\,(CO_{2,\,A})$ $x\,(CO_{2,\,B})$

## 2. Calibration of mole fractions and conversion to delta scale

$x\,(626_{,\,A})$ $x\,(636_{,\,A})$ $x\,(626_{,\,B})$ $x\,(636_{,\,B})$



analytical chemistry

Article

pubs.acs.org/ac

**Calibration Strategies for FT-IR and Other Isotope Ratio Infrared Spectrometer Instruments for Accurate $\delta^{13}$C and $\delta^{18}$O Measurements of $CO_2$ in Air**

Edgar Flores,*[†] Joële Viallon,[†] Philippe Moussay,[†] David W. T. Griffith,[‡] and Robert Ian Wielgosz[†]

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[‡]University of Wollongong, Wollongong, New South Wales 2500, Australia

Supporting Information

...ies in laboratory ...asurements of the ... $\delta^{13}$C and $\delta^{18}$O on the VPDB scale, with either FT-IR (in this case a Vertex 70 V (Bruker)) or an isotope ratio infrared spectrometer (IRIS) (in this case a Delta Ray (Thermo Fisher Scientific)). In the case of FT-IR a novel methodology using only two standards of $CO_2$ in air with different mole fractions but identical isotopic composition was demonstrated to be highly accurate for measurements of $\delta^{13}$C and $\delta^{18}$O with standard uncertainties of 0.09‰ and 1.03‰, respectively, at a nominal $CO_2$ mole fraction of 400 μmol mol$^{-1}$ in air. In the case of the IRIS system, we demonstrate that the use of two standards of $CO_2$ in air of known but differing $\delta^{13}$C and $\delta^{18}$O isotopic composition allows standard uncertainties of 0.18‰ and 0.48‰ to be achieved for $\delta^{13}$C and $\delta^{18}$O measurements, respectively. The calibration strategies were validated using a set of five traceable primary reference gas mixtures. These standards, produced with whole air or synthetic air covered the mole fraction range of (378−420) μmol mol$^{-1}$ and were prepared and/or value assigned either by the National Institute of Standards and Technology (NIST) or the National Physical Laboratory (NPL). The standards were prepared using pure $CO_2$ obtained from different sources, namely, combustion; Northern Continental and Southern Oceanic Air and a gas well source, with $\delta^{13}$C values ranging between −35‰ and −1‰. The isotopic composition of all standards was value assigned at the Max Planck Institute for Biogeochemistry Jena (MPI-Jena).



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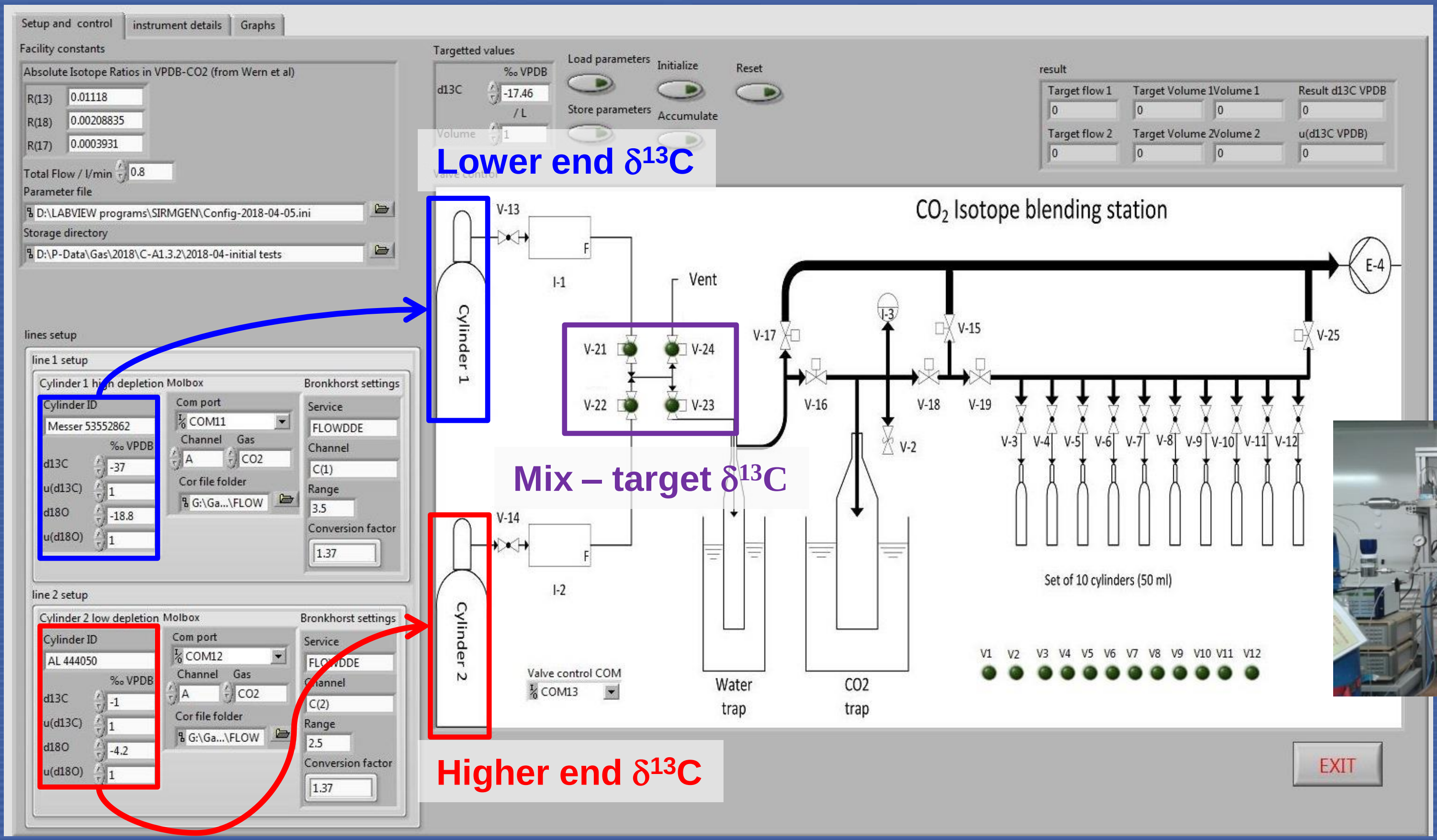
(Slide courtesy BIPM)

# BIPM Stable Isotope Reference Mixture Generator Facility




Filling aliquots with known pure $CO_2$

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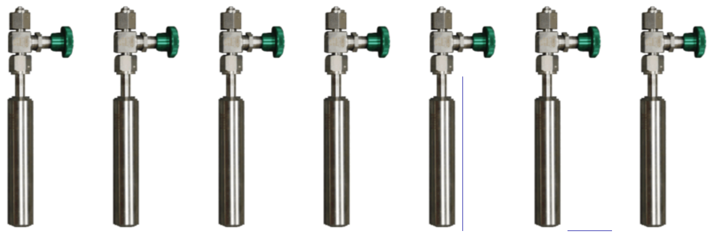
www.bipm.org

(Slide courtesy BIPM)

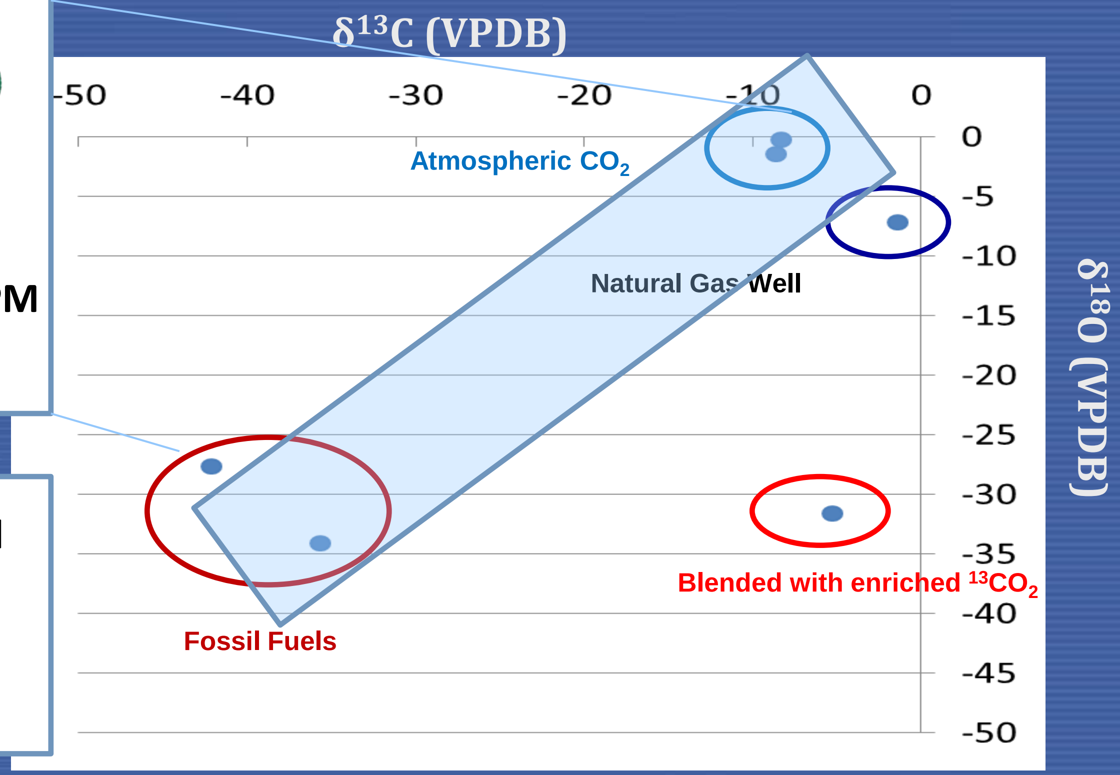
# $CO_2$ isotope ratio comparison (2020) (BIPM and IAEA Coordinators)

**Comparison samples produced at BIPM**

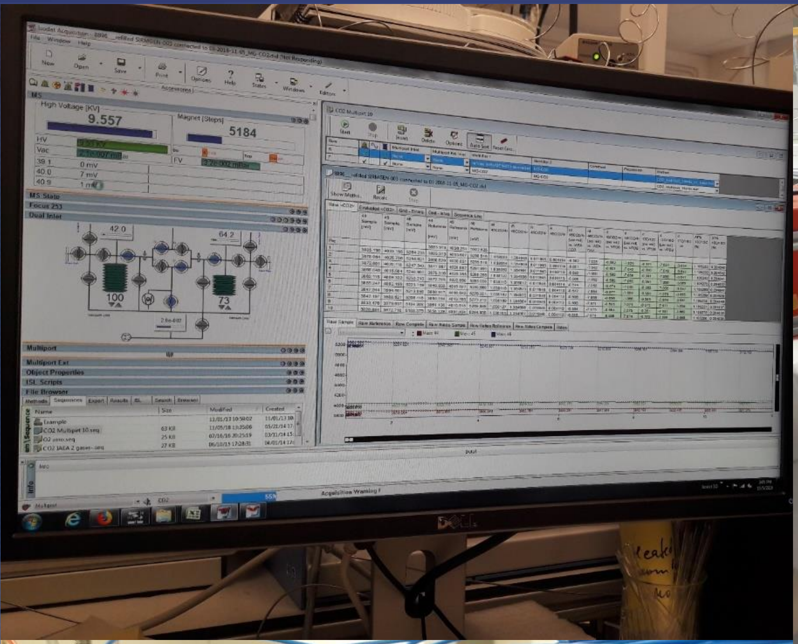


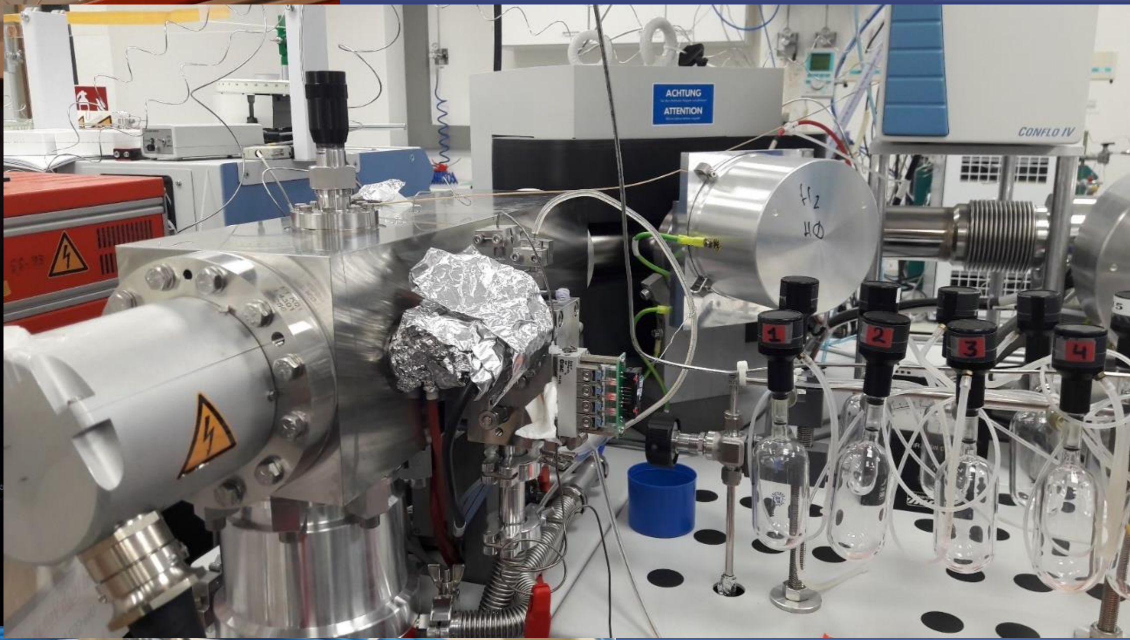
**Stability and homogeneity measured at BIPM**
**((1σ) $\delta^{13}C$ = 0.04 ‰  (1σ) $\delta^{18}O$ = 0.1 ‰ )**

**Reference Value assigned at IAEA**
**((1σ) $\delta^{13}C$ = 0.01 ‰**
**(1σ) $\delta^{18}O$ = 0.02‰**

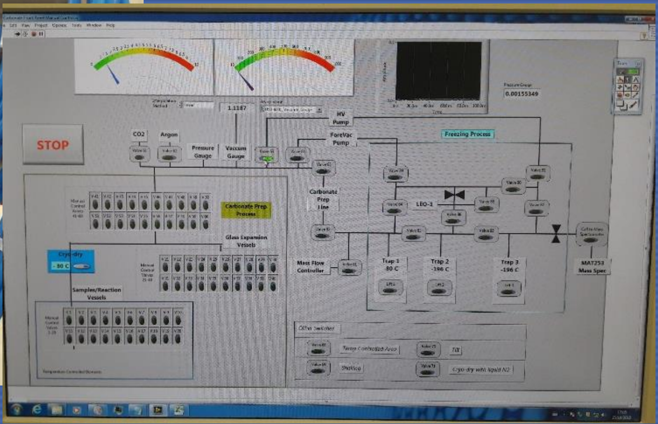


# IAEA Carbonate - $CO_2$ isotope analysis system





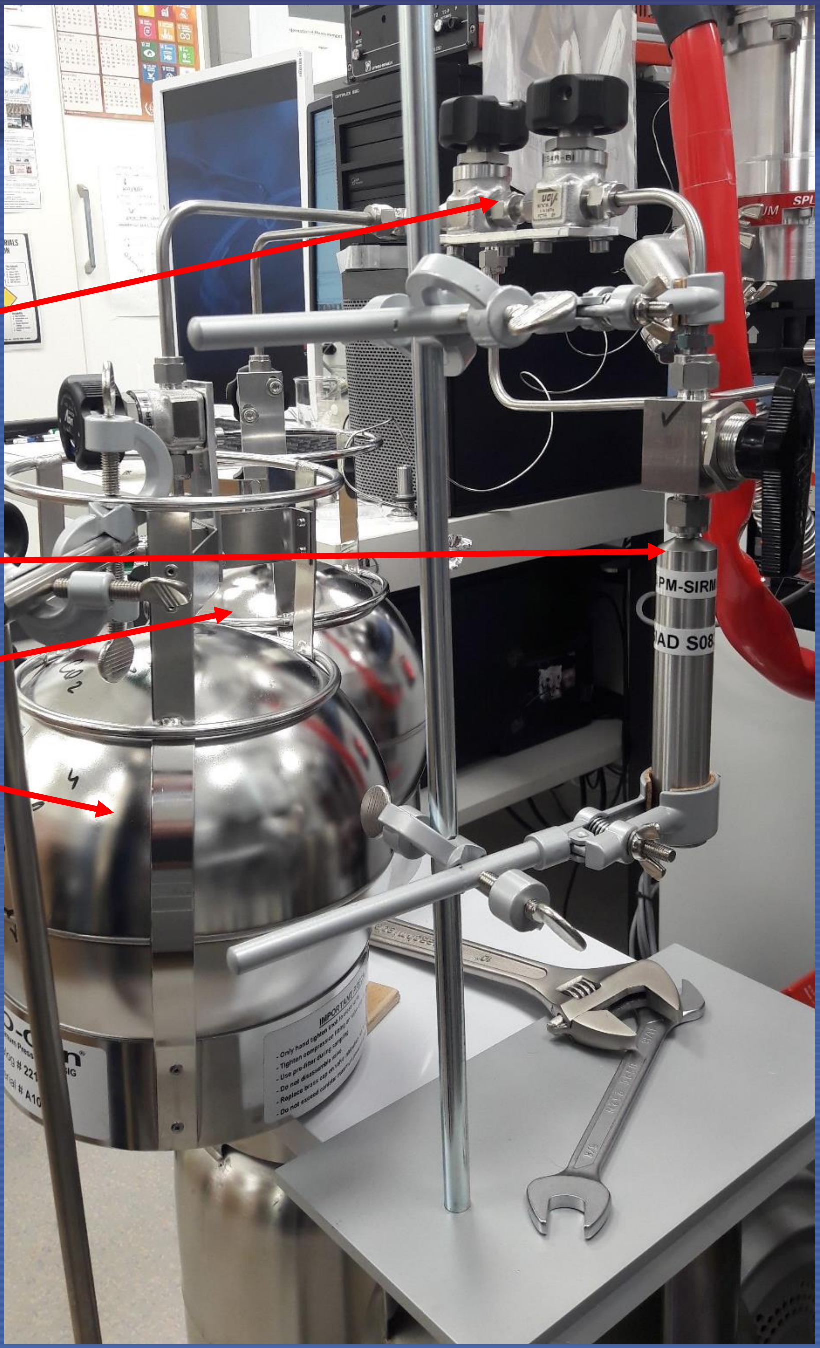


# Aliquoting $CO_2$ from BIPM vessels

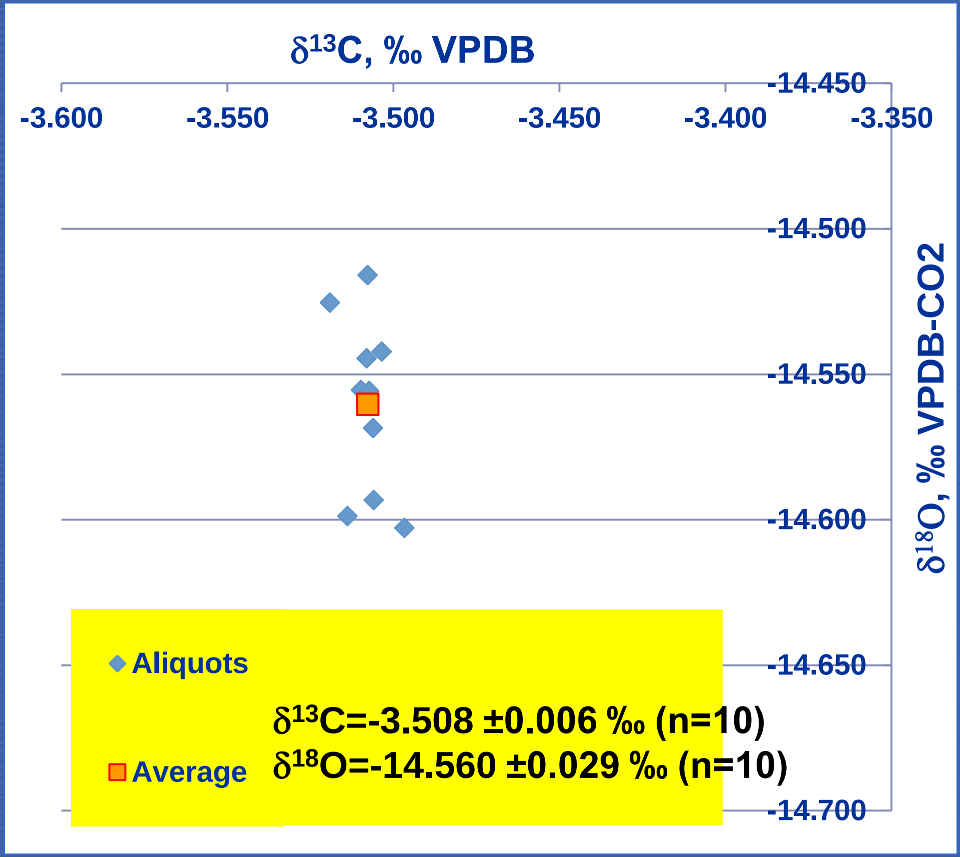
Dosing valves

BIPM vessels (~2 bar)

CO2 reference gases at IAEA-lab



# Tests at IAEA on BIPM mixed $CO_2$-vessels (last week) – Successful Performance check

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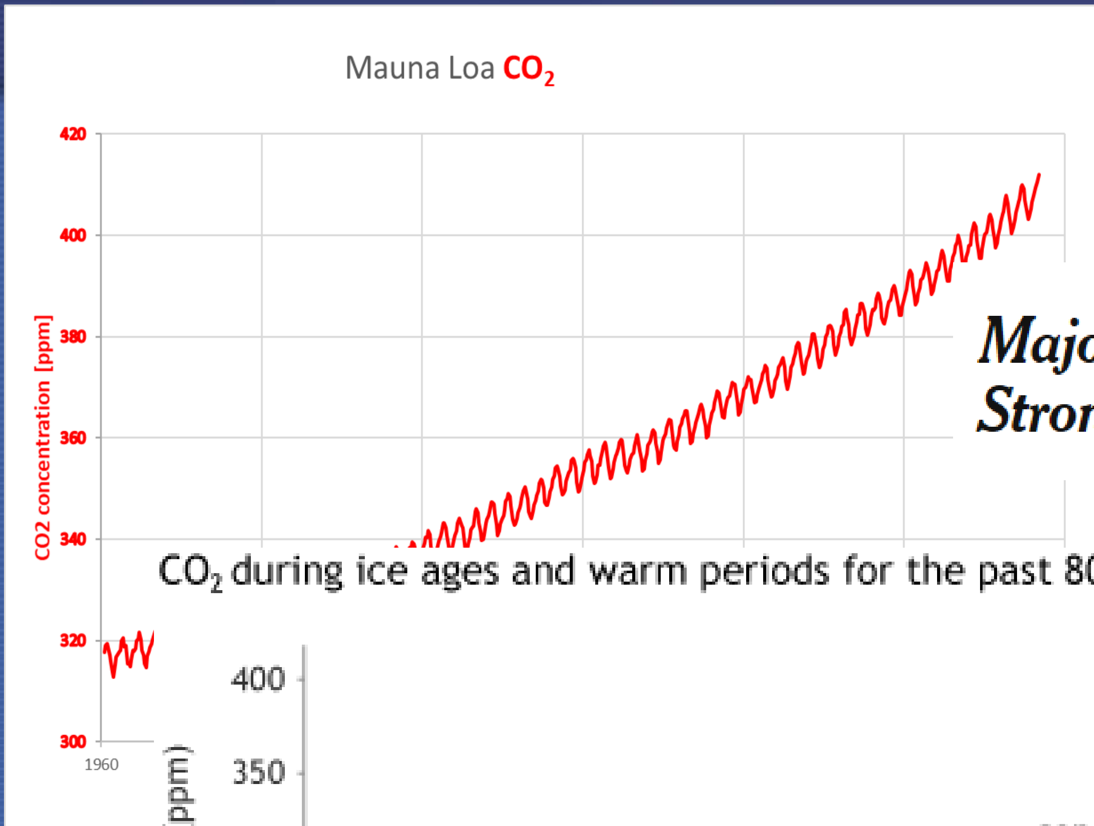
# $CO_2$ concentration in the atmosphere

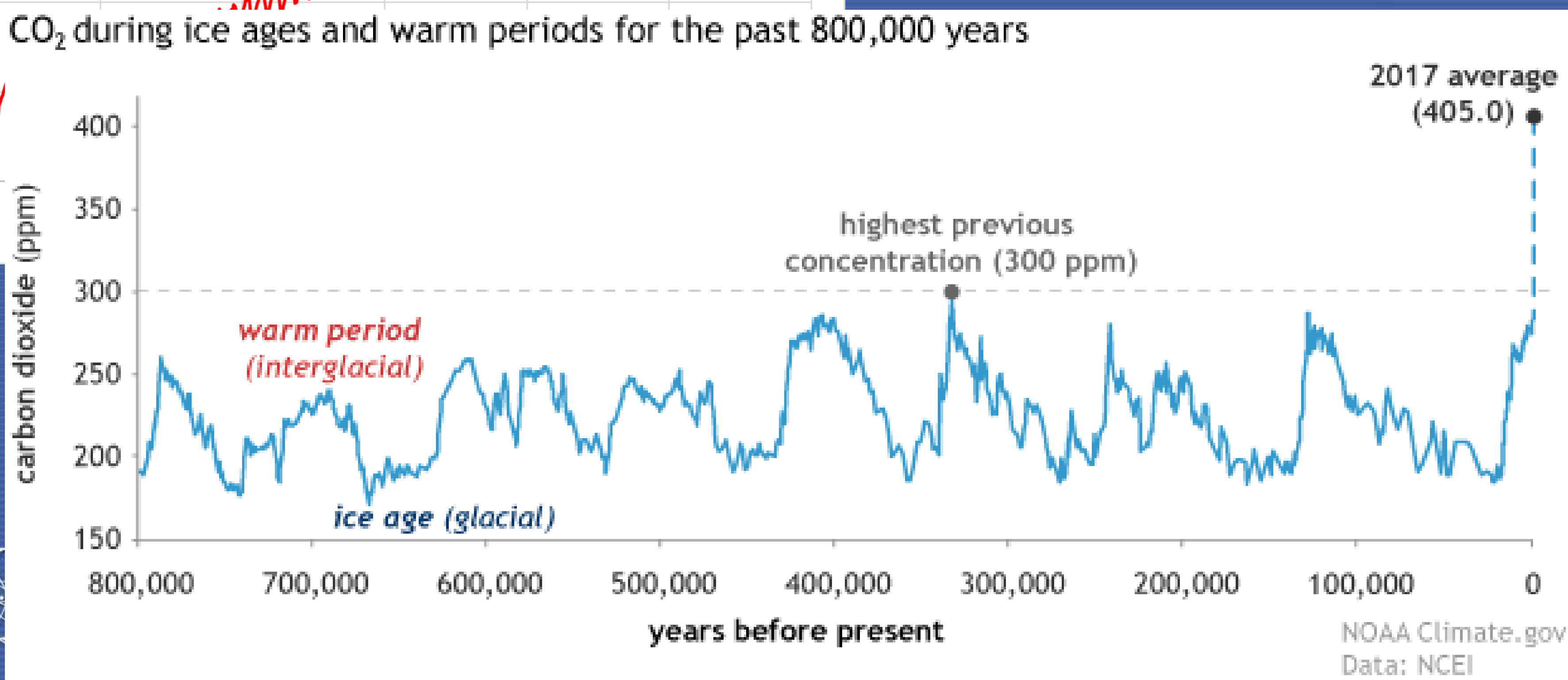



## IPCC – Report:

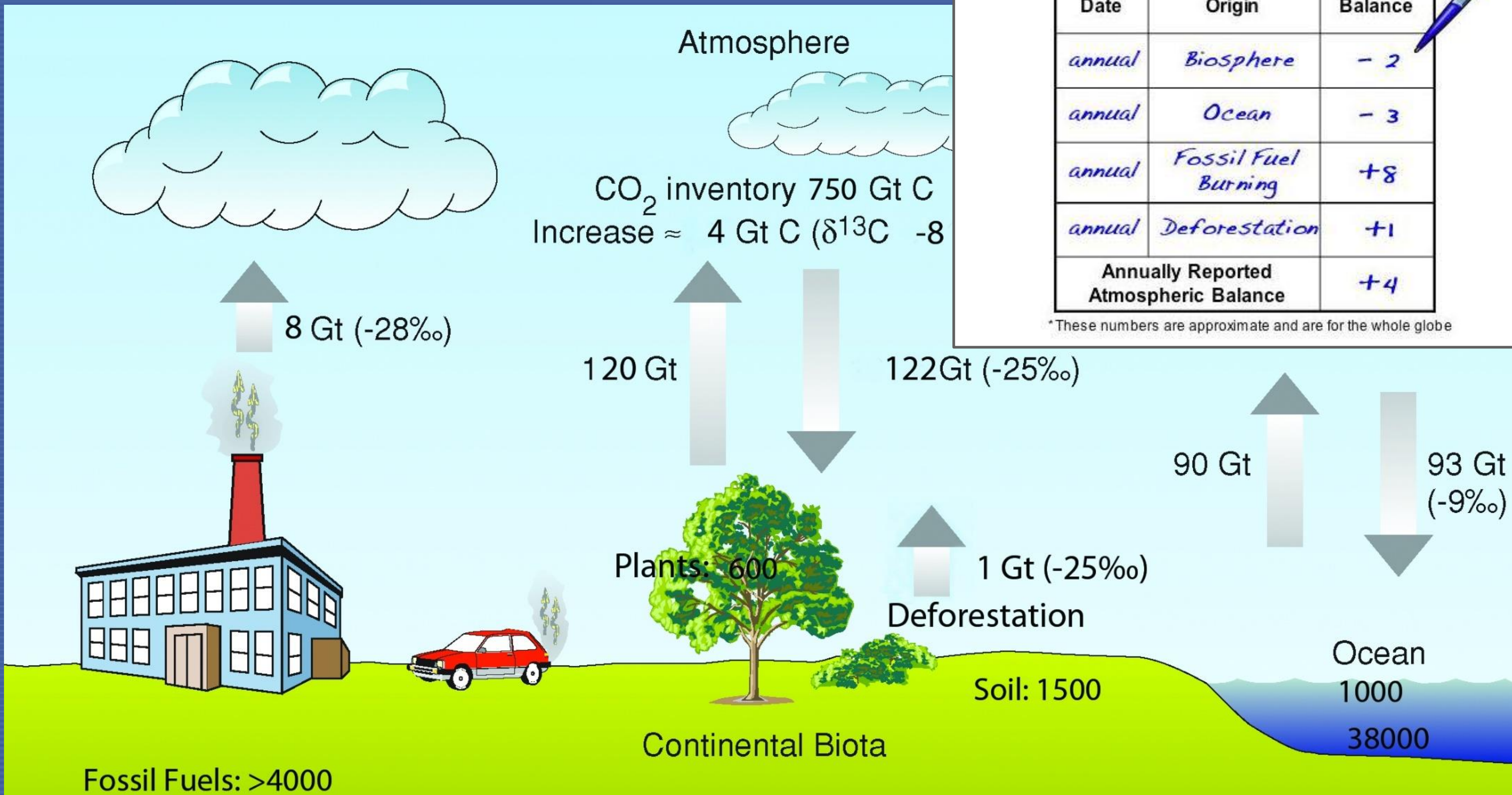
The New York Times

Oct. 7, 2018

*Major Climate Report Describes a Strong Risk of Crisis as Early as 2040*



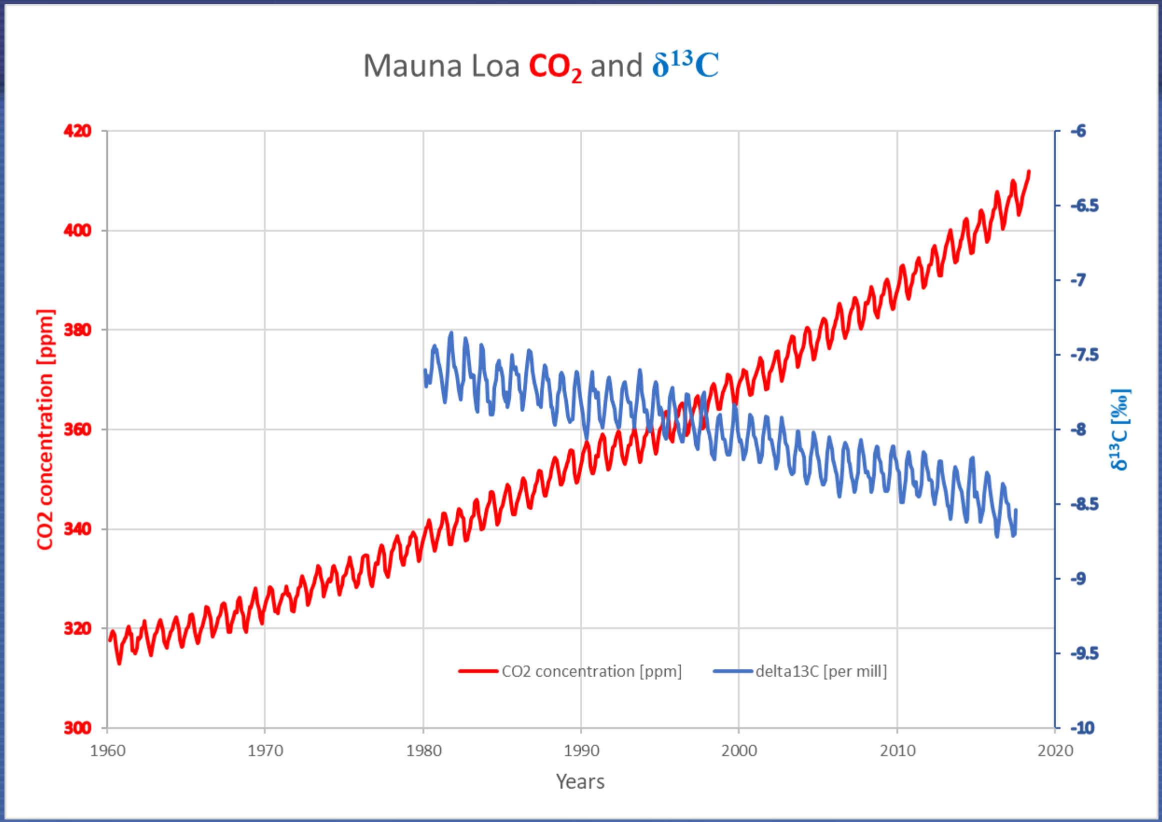
# Carbon Cycle

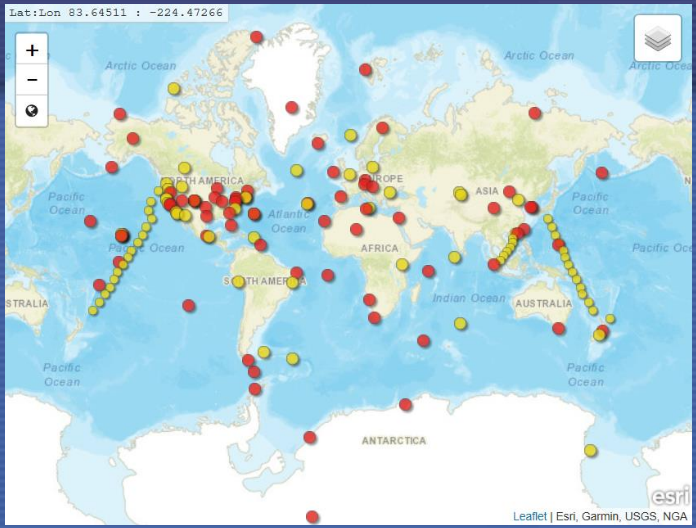



| Atmospheric $CO_2$ Account | | $10^{15}$ grams of carbon per year* |
|---|---|---|
| Date | Origin | Balance |
| annual | Biosphere | − 2 |
| annual | Ocean | − 3 |
| annual | Fossil Fuel Burning | +8 |
| annual | Deforestation | +1 |
| Annually Reported Atmospheric Balance | | +4 |

*These numbers are approximate and are for the whole globe

# Carbon Cycle - reference materials





Annual change in mean $\delta^{13}C$: ~0.02‰
Precision required for any laboratory: ±0.02‰ for 40 years!!!

**Ultra-stable reference material ⇒ IAEA-603 ±0.01‰**

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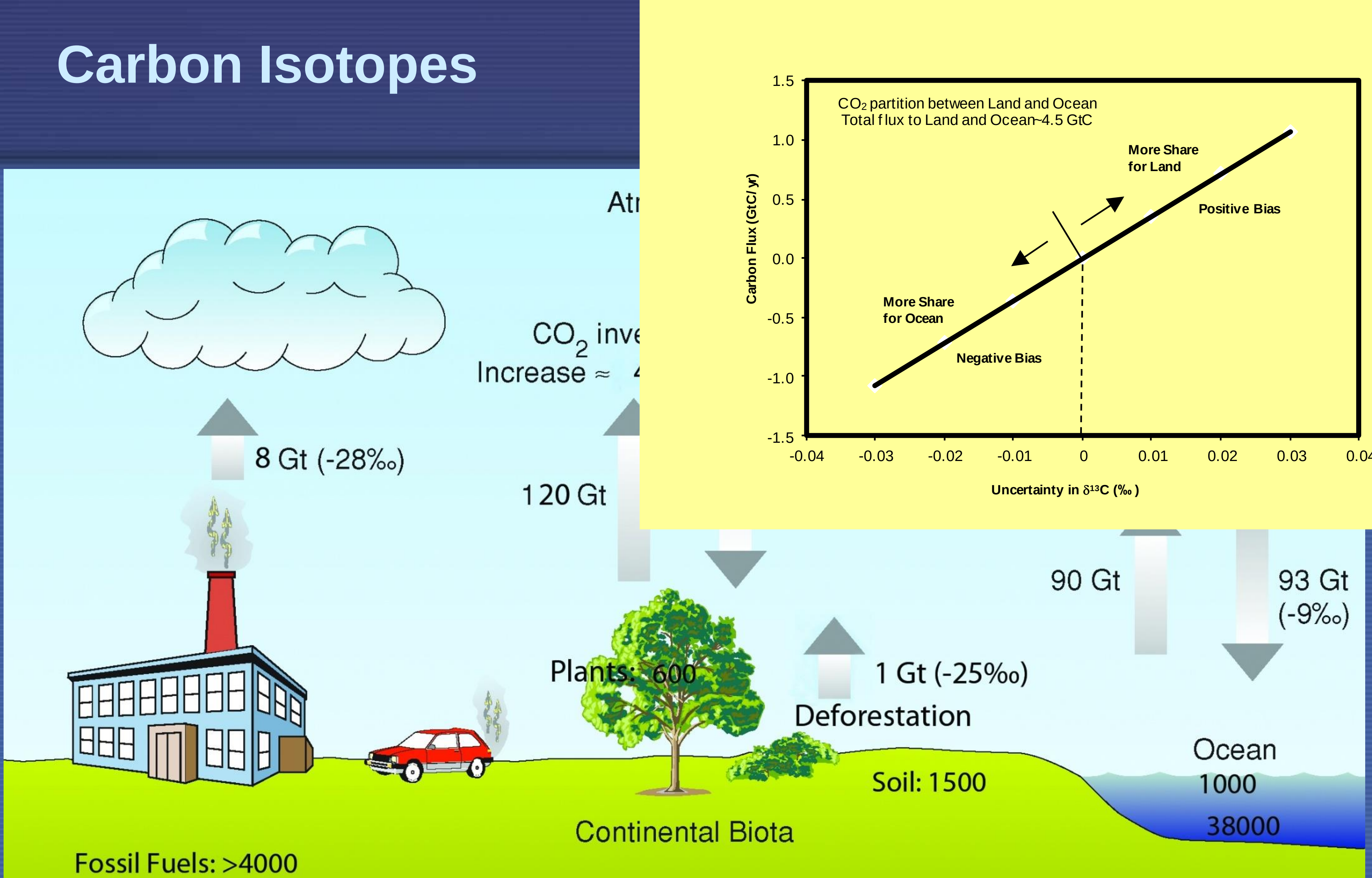
# Carbon Isotopes




**0.02‰ ≈ 1 Gt C**

**Ultra-stable reference material ⇒ IAEA-603 ±0.01‰**

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# Carbon Cycle – BIPM and IAEA

- New laser instruments – require new standardisation
- BIPM developed a $CO_2$ calibration strategy
- Measurement precision is achieved for $CO_2$
- Initiative for Comparison of $CO_2$ isotope ratios in 2020
- IAEA $CO_2$ / $CO_2$-in-air isotope ratio reference materials

- CCQM Isotope Ratio Working Group established

- ⇒ **Excellent cooperation for benefit of environmental monitoring worldwide**

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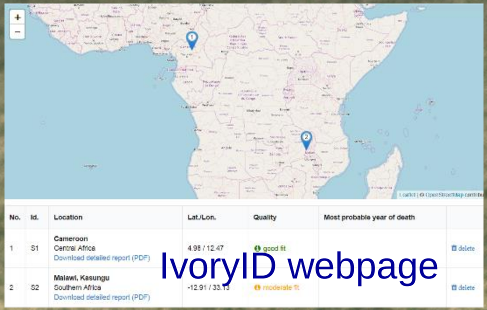
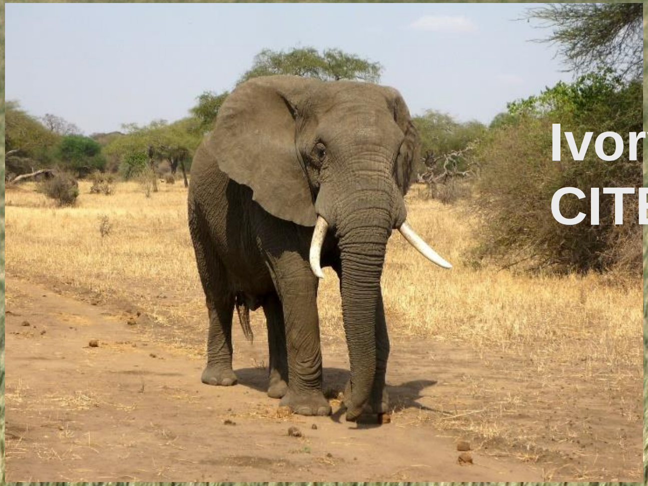
# Habitats / endangered species

Timber from concessions versus illegal sources – validation of origin

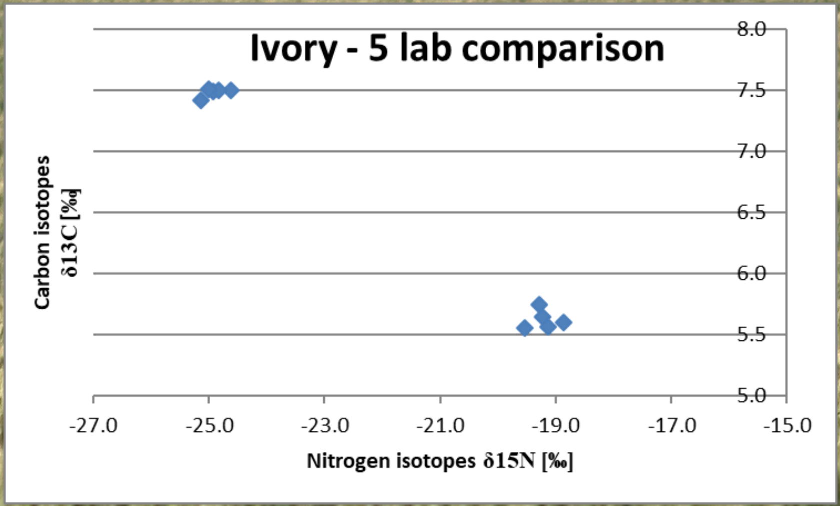
Work on Reference materials & on Sampling Guidelines



IvoryID webpage

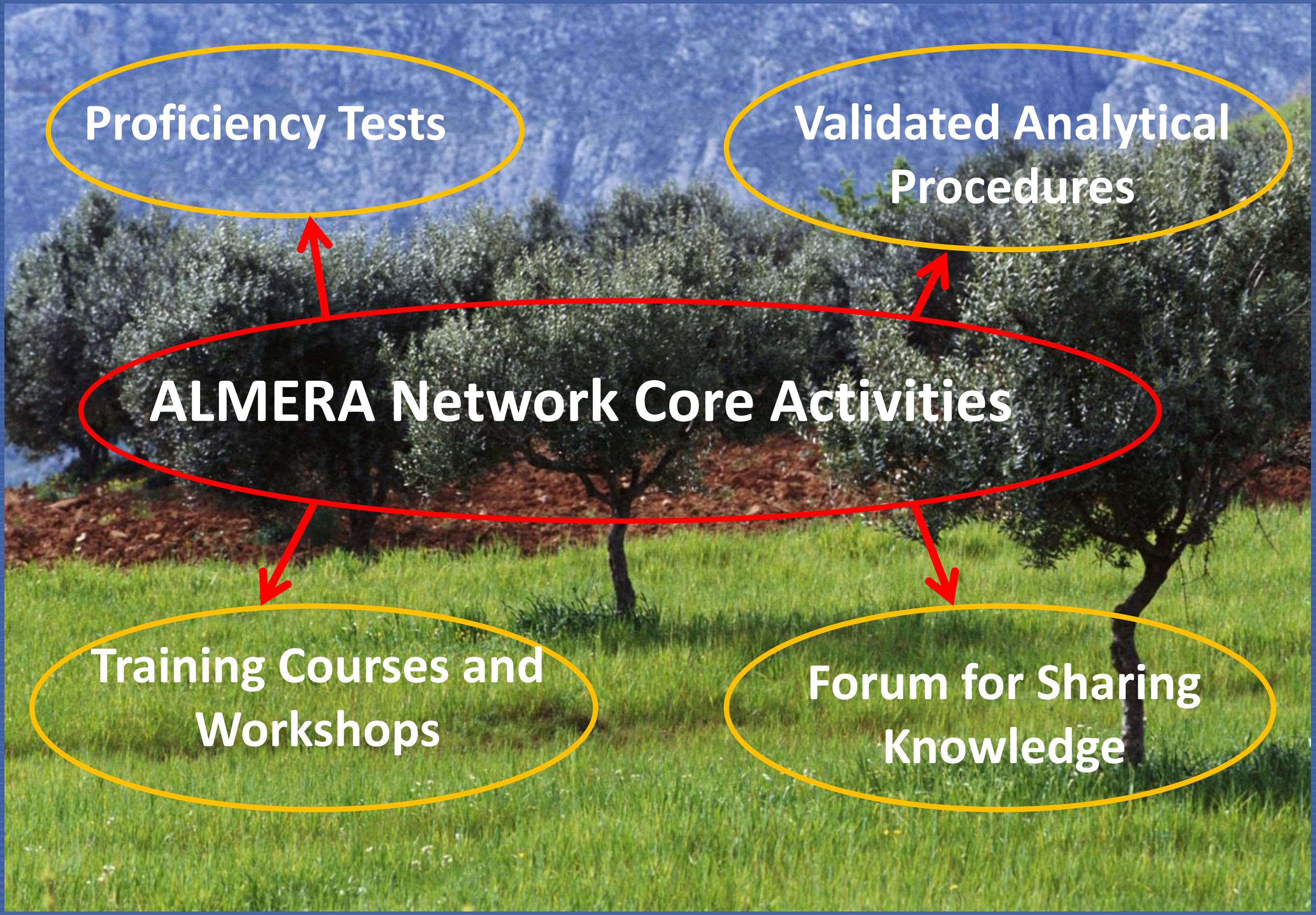


Ivory origin
CITES



# Radionuclides: ALMERA Network

- Analytical Laboratories for the Measurement of Environmental Radioactivity: Network of 177 laboratories in 89 countries

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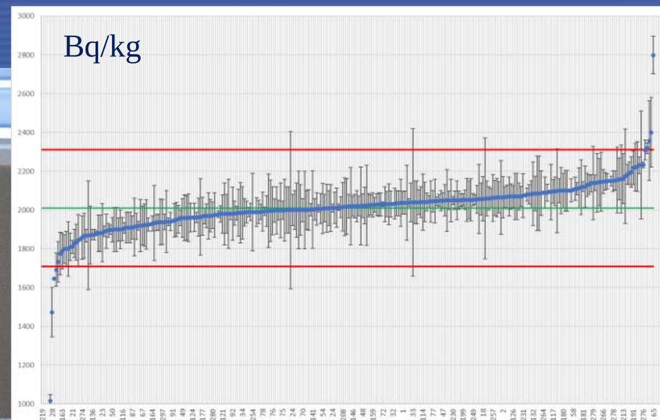
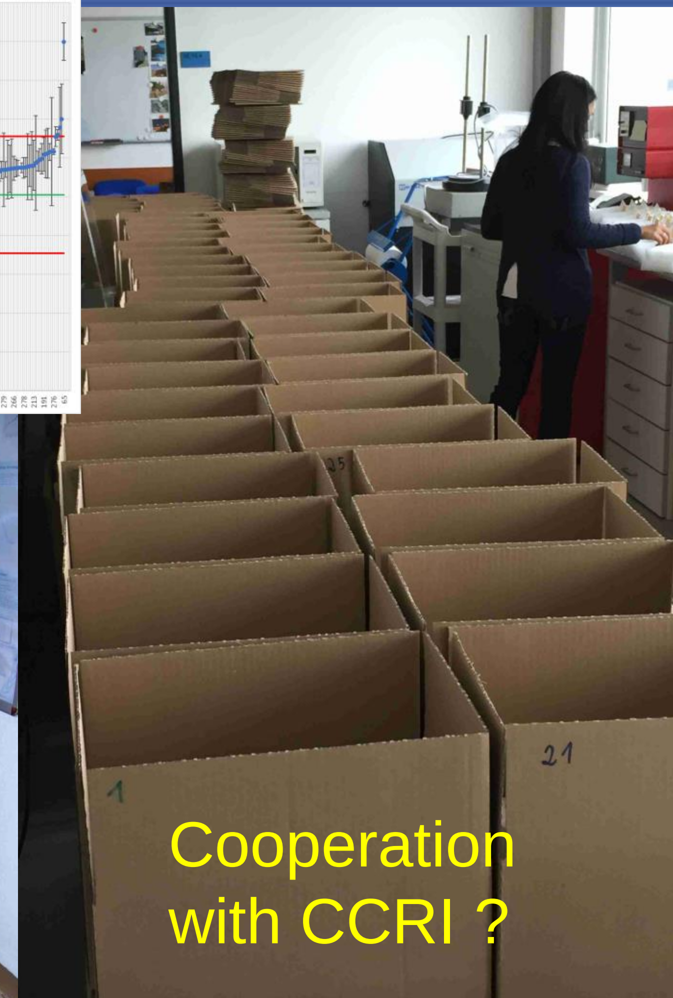
# Radionuclides: Support for Member State laboratories

Proficiency tests for 400 laboratories annually



Cooperation with CCRI ?

Thanks for your attention

E-Mail: m.groening@iaea.org