APPLICATIONS OF ACCELERATOR MASS SPECTROMETRY RADIOCARBON DATING IN FORENSICS

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OUTLINE

- Introduction: the Centre for Dating and Diagnostics at Unisalento
- How ^{14}C-dating can be used in forensics
- Potentialities, drawbacks and open issues
- Field of applications: analysis of human remains, ivory and cultural heritage
- The CRP F11021 of IAEA Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences: objectives and status
- Conclusions and outlook

UNIVERSITÀ DEL SALENTO

CEDAD

CEDAD Centro di Datazione e Diagnostica

CEDAD is a multidisciplinary research and service center

Cultural Heritage

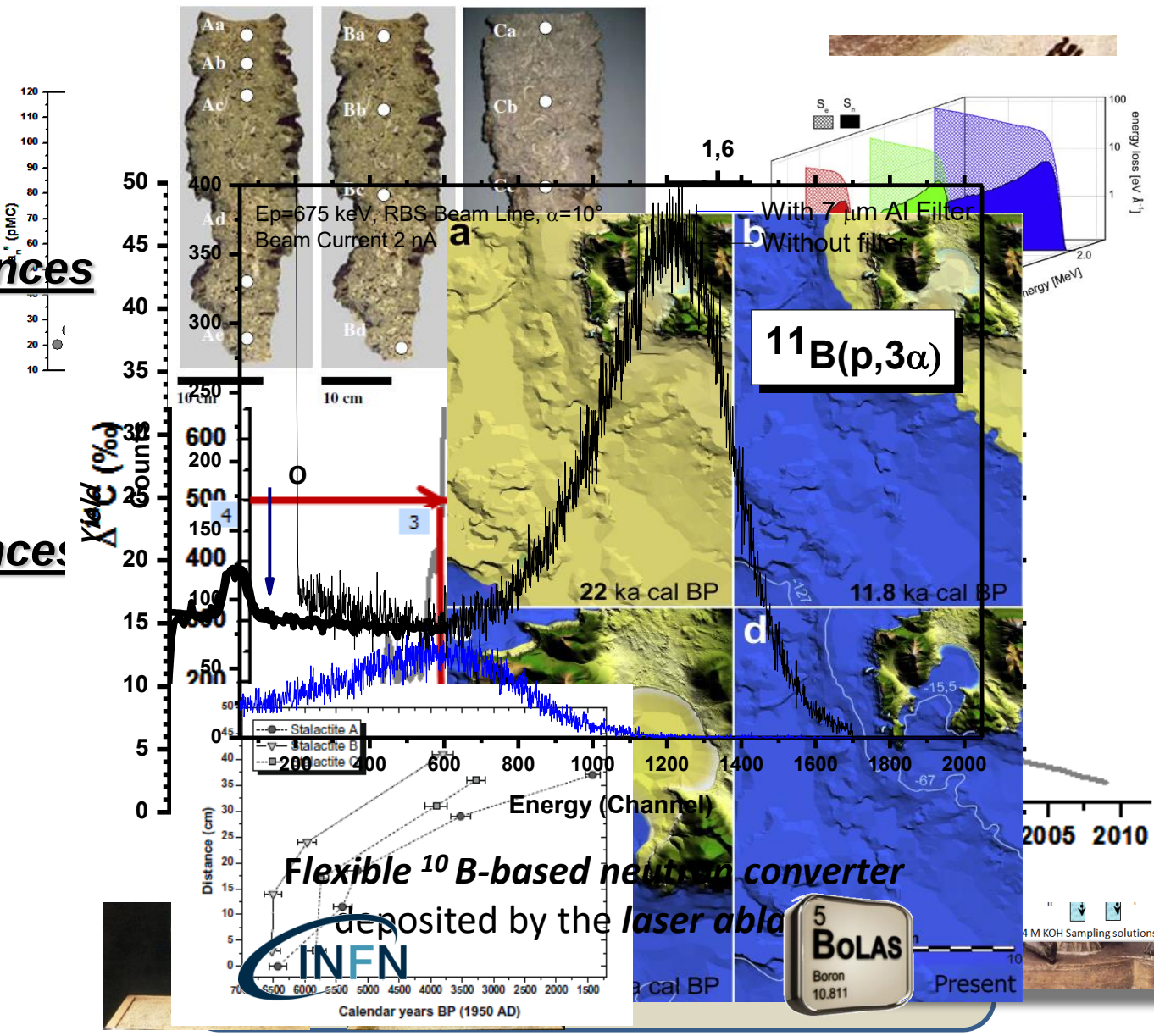
Environmental Sciences

Forensics

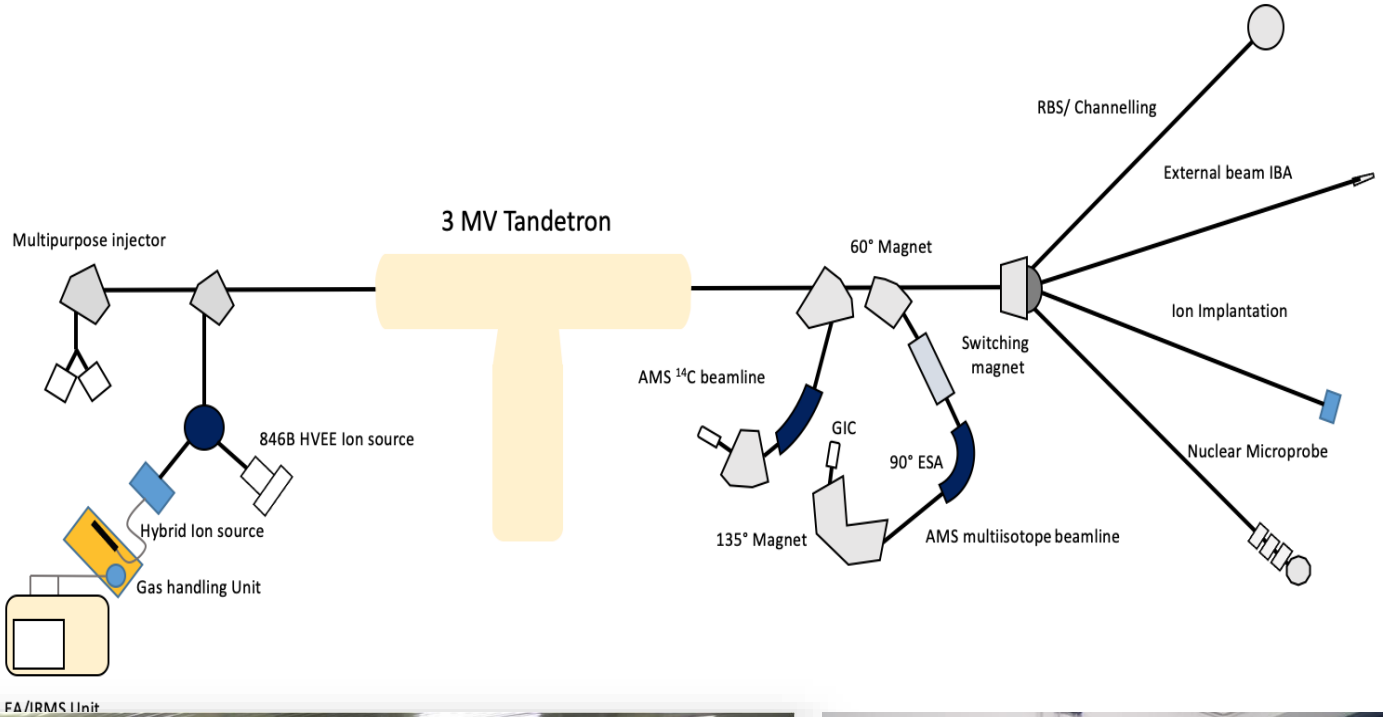
Earth and Life Sciences

Material Sciences

Nuclear Physics



THE 3 MV TANDETRON ACCELERATOR



^{14}C DATING: BASIC PRINCIPLES

Once produced it is oxidised to $^{14}CO_2$ entering the different terrestrial reservoirs: the biosphere, the hydrosphere and the cryosphere

Nuclear reactions

$$p + N,O,Ar \rightarrow n + \ldots.$$

$$^{14}_{7}N + n \rightarrow {}^{14}_{6}C + p$$

$^{14}C/^{12}C=10^{-12}$

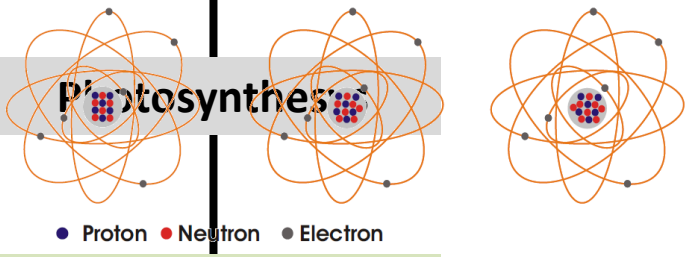
Atmosphere (2% global ^{14}C inven

Chemical reactions

$$^{14}_{6}C + O_2 \rightarrow {}^{14}_{6}CO + O$$

$$^{14}_{6}CO + OH^* \rightarrow {}^{14}_{6}CO_2 + H$$

^{12}C ^{13}C ^{14}C



Photosynthesis

Dissolution

Air trapping

Biosphere (~5%)

Hydrosphere (~93%)

Cryosphere (<0.1 %%)

Natural carbon isotopes

^{14}C DATING: DECAY LAW

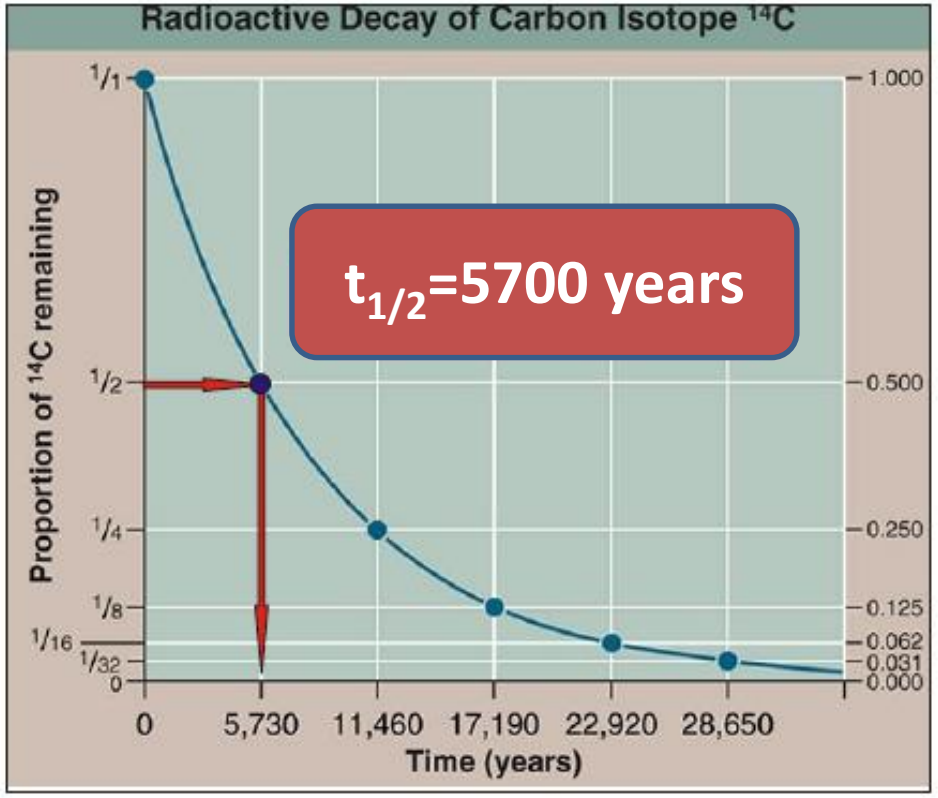
When the exchanges with the environment stop because of the death of the organism the ^{14}C concentrations decreases following the radioactive decay law with a half life of 5730 years

THE RADIOCARBON DECAY

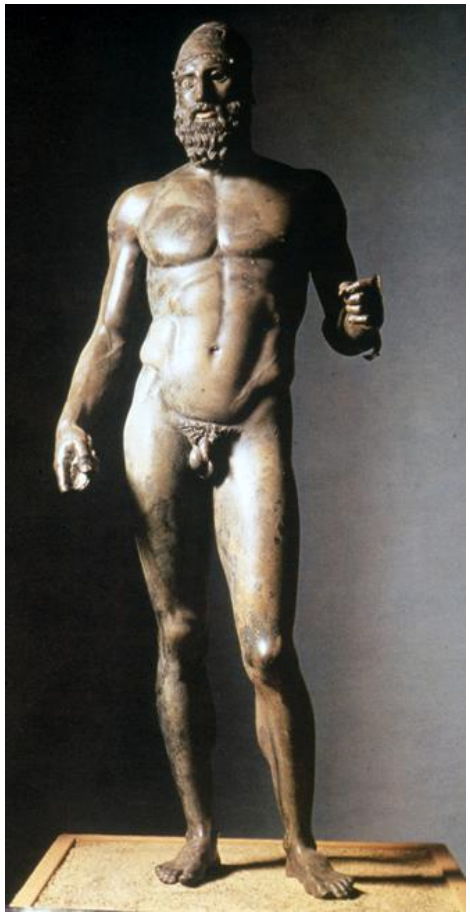
$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + e^{-} + \bar{\nu}$$

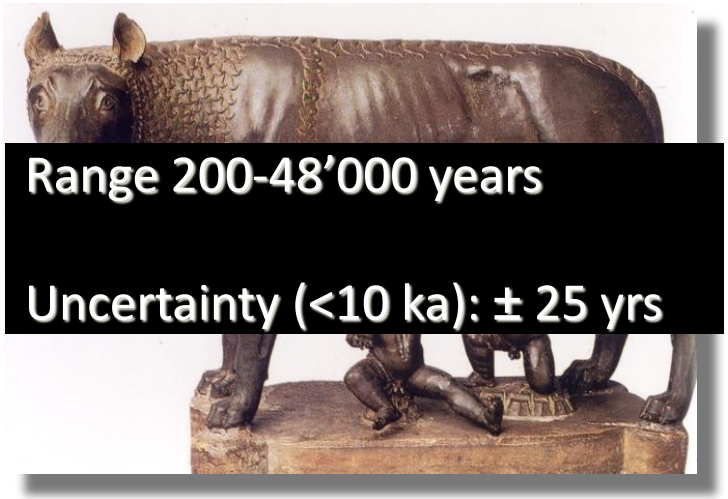
$$N = N_0 e^{-\lambda t}$$

The measurement of the ^{14}C concentration in the samples allows to calculate the time passed since its death.



$$t = -\frac{1}{\lambda} \ln\left(\frac{N}{N_0}\right)$$





Range 200-48’000 years

Uncertainty (<10 ka): ± 25 yrs

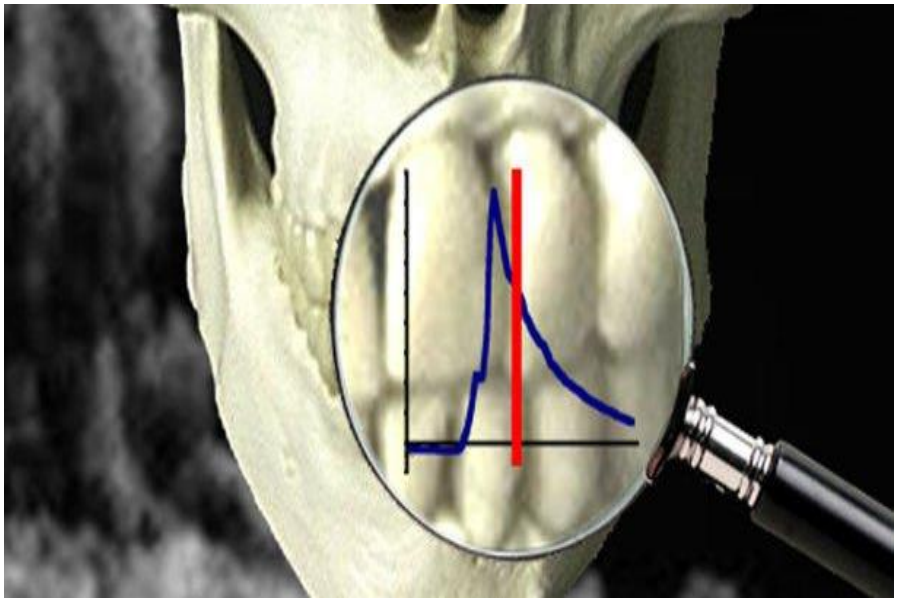
^{14}C DATING AT CEDAD

- Dating for external "customers": 30'000 samples
- Development of new protocols for "non standard" samples: cremated bones, mortars, water, pigments
- Applications of ^{14}C from nuclear fallout in forensics
- Determination o… such as plastics, fu…
- Instrumental de…

Tipologia di campioni:

- Charcoal
- Bones
- Sediments
- Hairs
- Wood
- Vegetal remains
- Organic inclusions in pottery
- Textiles
- Shells
- Eggs
- Leather
- Canvas

The role of ^{14}C in forensics



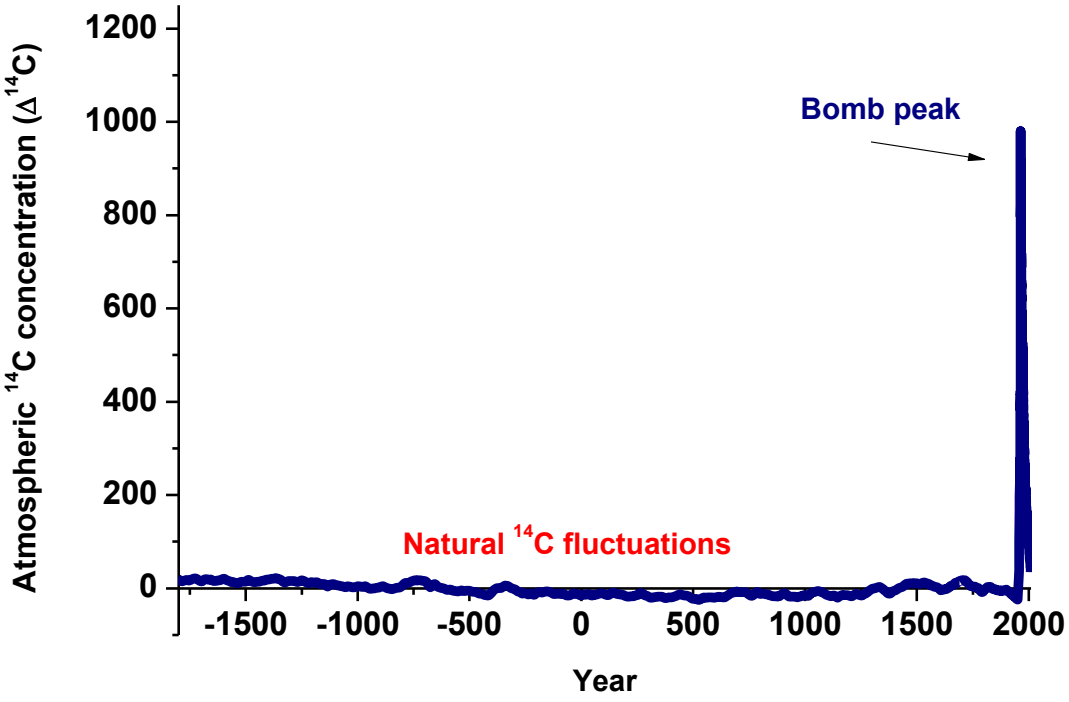
“Recent” samples

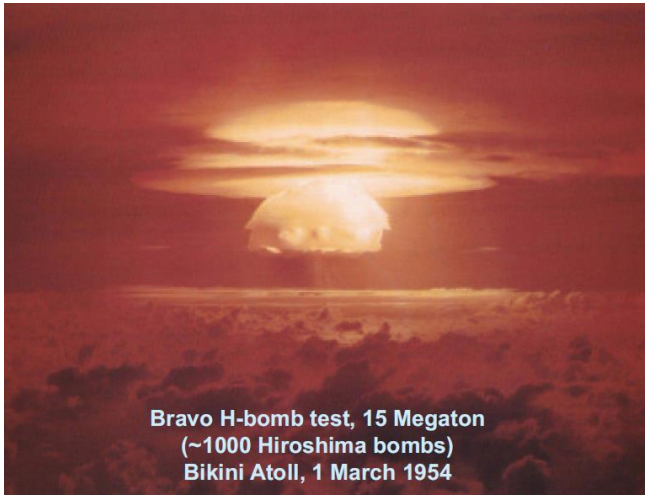
High resolution

THE "BOMB PEAK"

Atmospheric nuclear detonation tests carried out in the atmosphere after 1950 CE resulted in a tremendous increase of the ^{14}C concentration

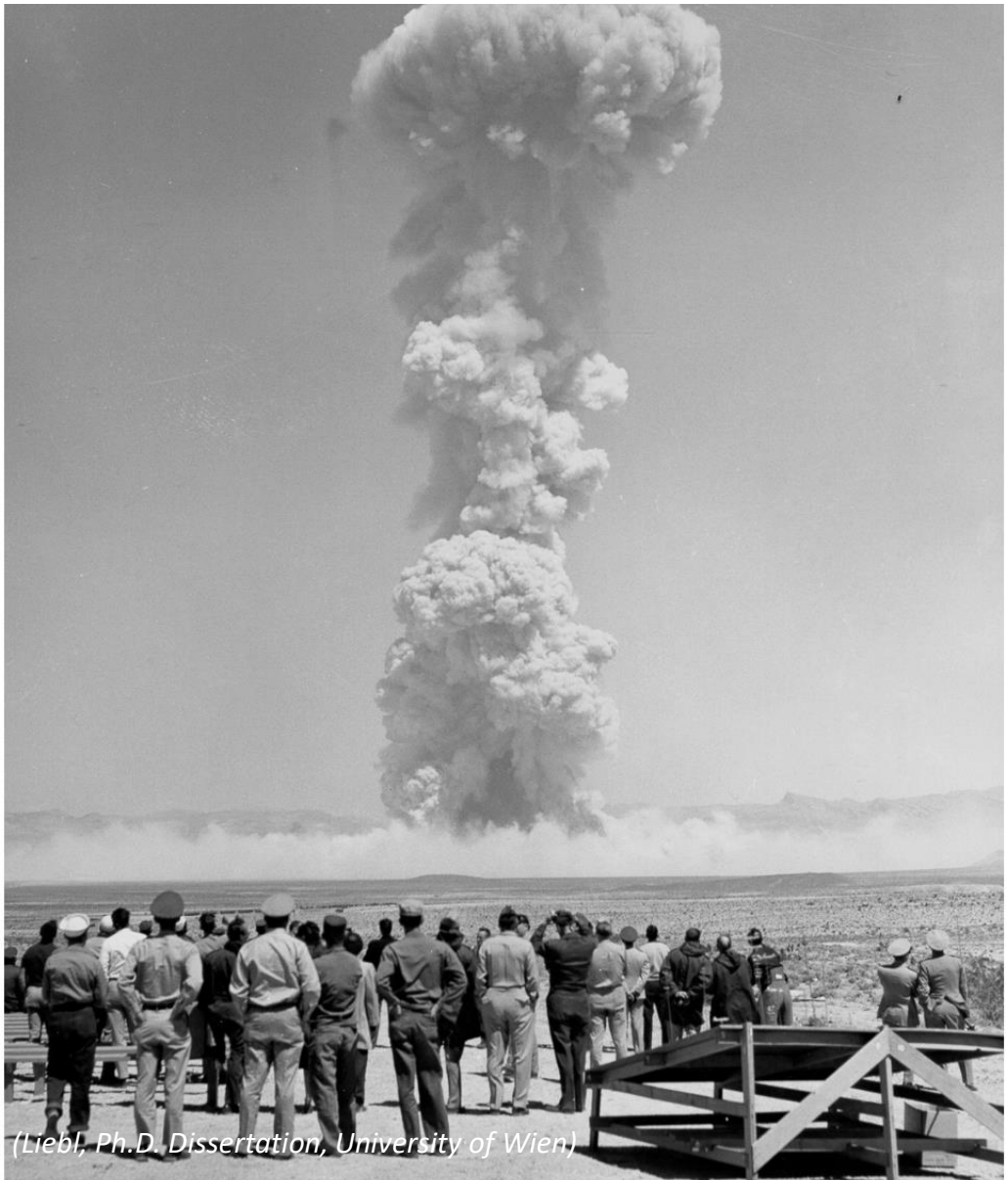
$$^{14}N + n \rightarrow {}^{14}C + p$$





Anthropogenic ^{14}C

Mushroom cloud reaching the stratosphere. **MET** ***atomic test at Nevada Test Site, April 15, 1955.***

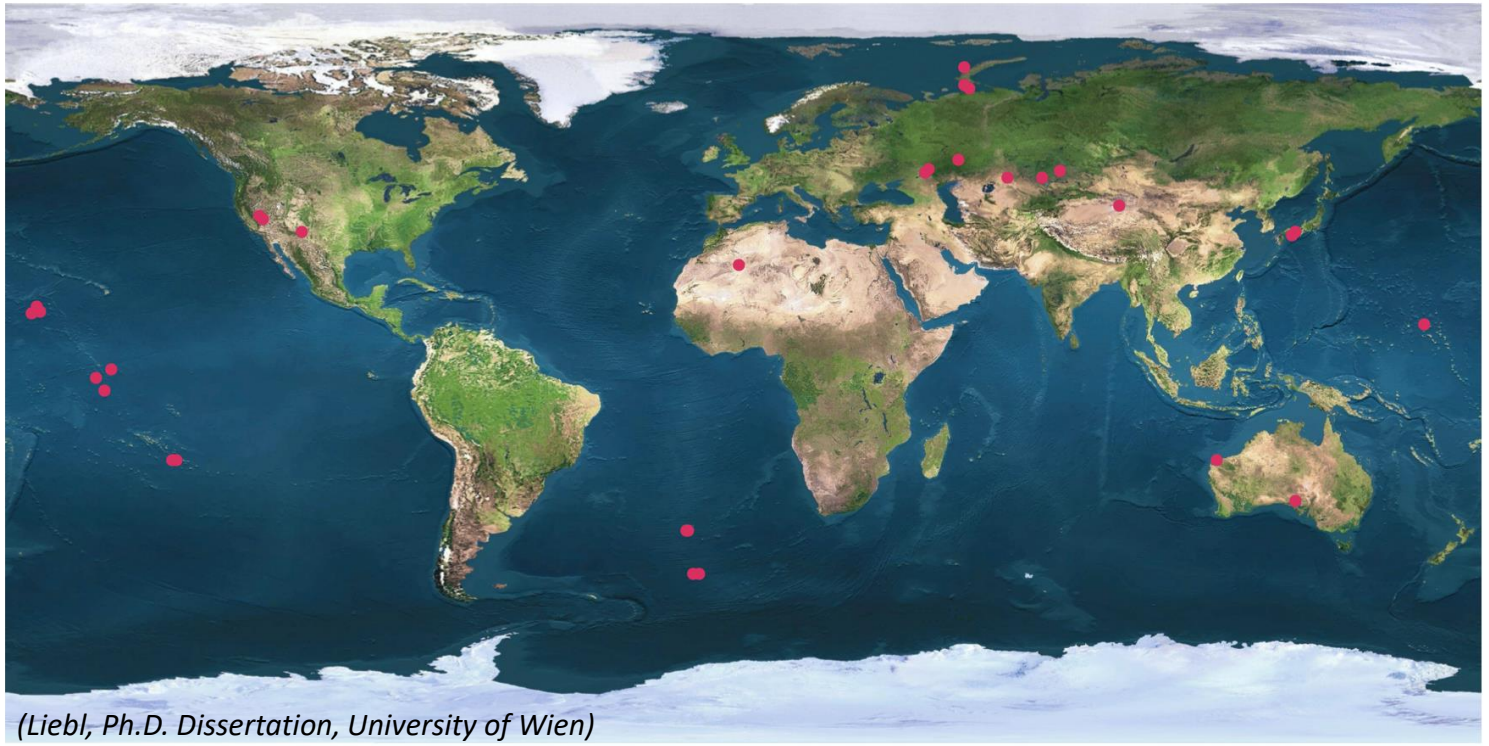


Anthropogenic ^{14}C

Natural ^{14}C production	
Cosmic ray production	*2.9 - 3.3 x 10^{26} atoms/a*
Anthropogenic ^{14}C production	
Atmospheric nuclear weapons tests	*598 – 632 x 10^{26} total*
Nuclear industry (in 2005)	*0.57 x 10^{26} atoms/a*

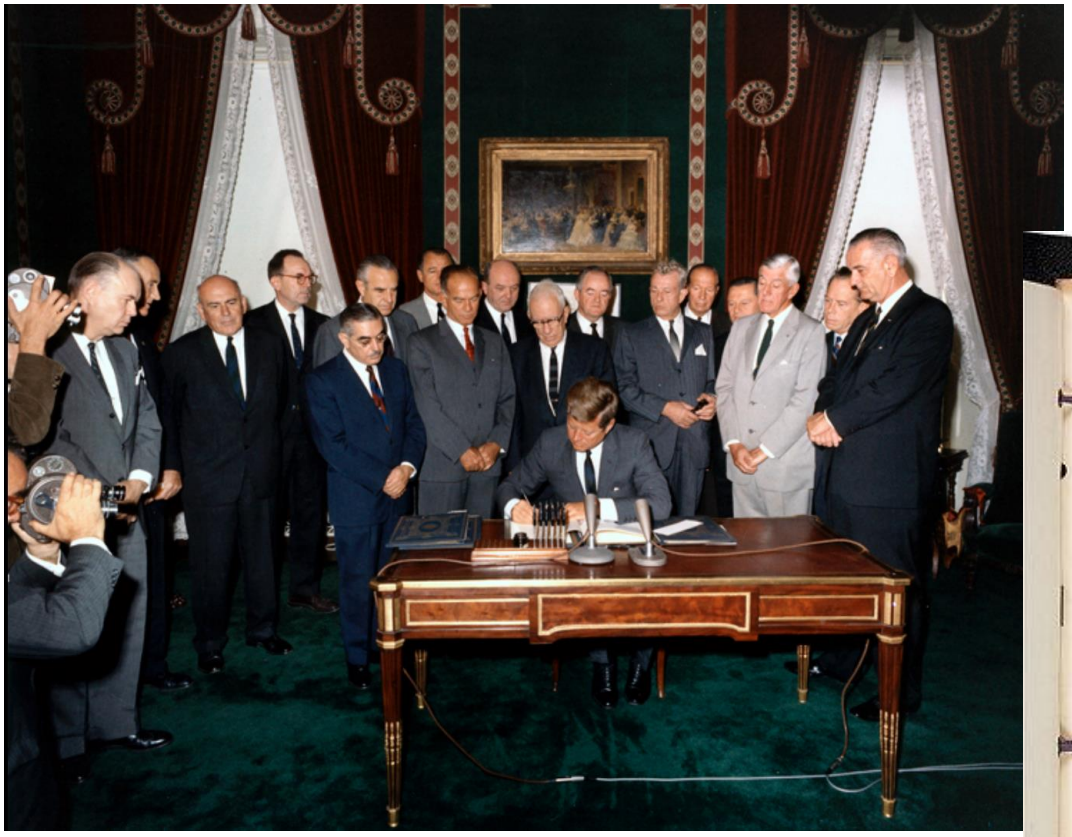
(From: Naegler and Levin 2006)

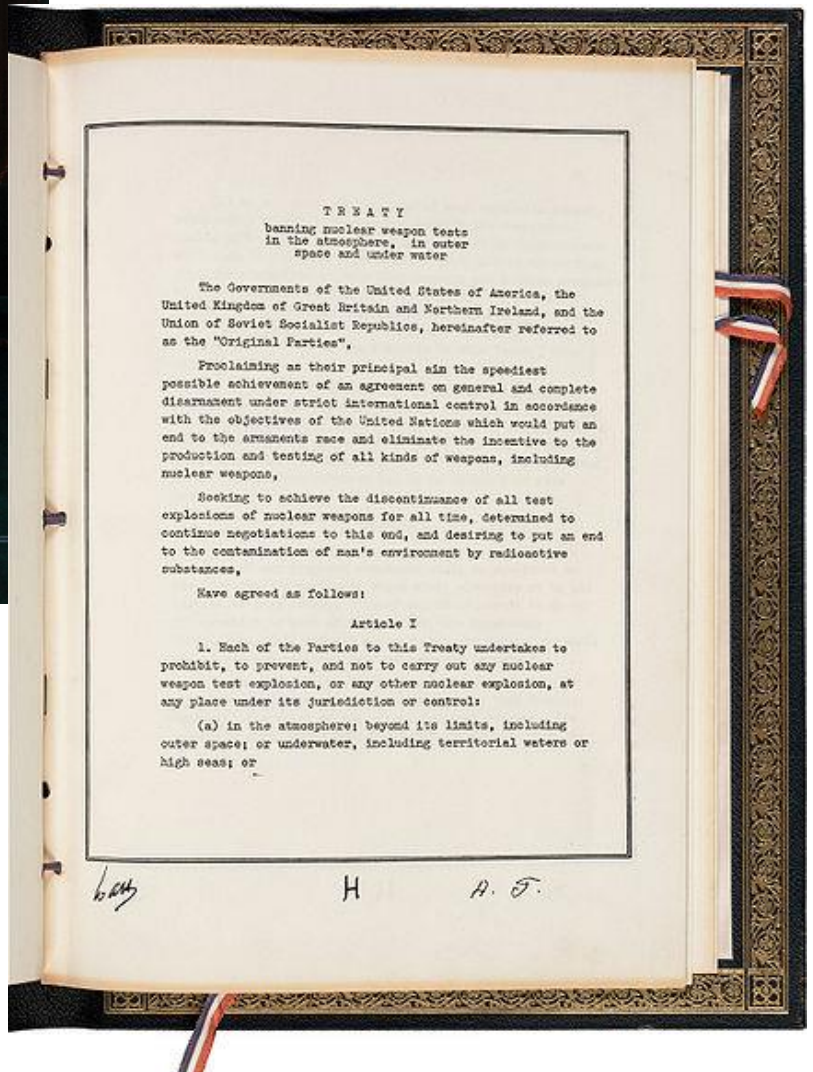
Atmospheric nuclear weapons tests sites (incl. WWII)



(Liebl, Ph.D. Dissertation, University of Wien)

Anthropogenic ^{14}C





TREATY
banning nuclear weapon tests
in the atmosphere, in outer
space and under water

The Governments of the United States of America, the United Kingdom of Great Britain and Northern Ireland, and the Union of Soviet Socialist Republics, hereinafter referred to as the "Original Parties",

Proclaiming as their principal aim the speediest possible achievement of an agreement on general and complete disarmament under strict international control in accordance with the objectives of the United Nations which would put an end to the armaments race and eliminate the incentive to the production and testing of all kinds of weapons, including nuclear weapons,

Seeking to achieve the discontinuance of all test explosions of nuclear weapons for all time, determined to continue negotiations to this end, and desiring to put an end to the contamination of man's environment by radioactive substances,

Have agreed as follows:

Article I

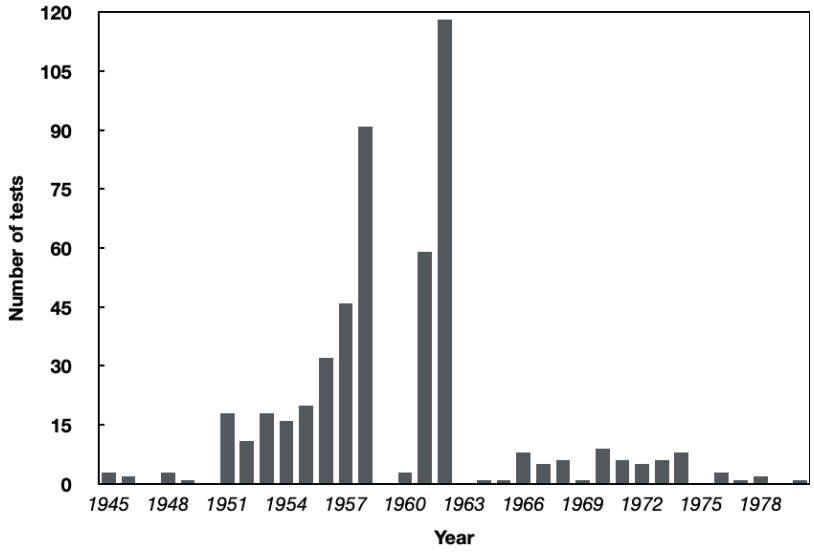
1. Each of the Parties to this Treaty undertakes to prohibit, to prevent, and not to carry out any nuclear weapon test explosion, or any other nuclear explosion, at any place under its jurisdiction or control:

(a) in the atmosphere; beyond its limits, including outer space; or underwater, including territorial waters or high seas; or

H

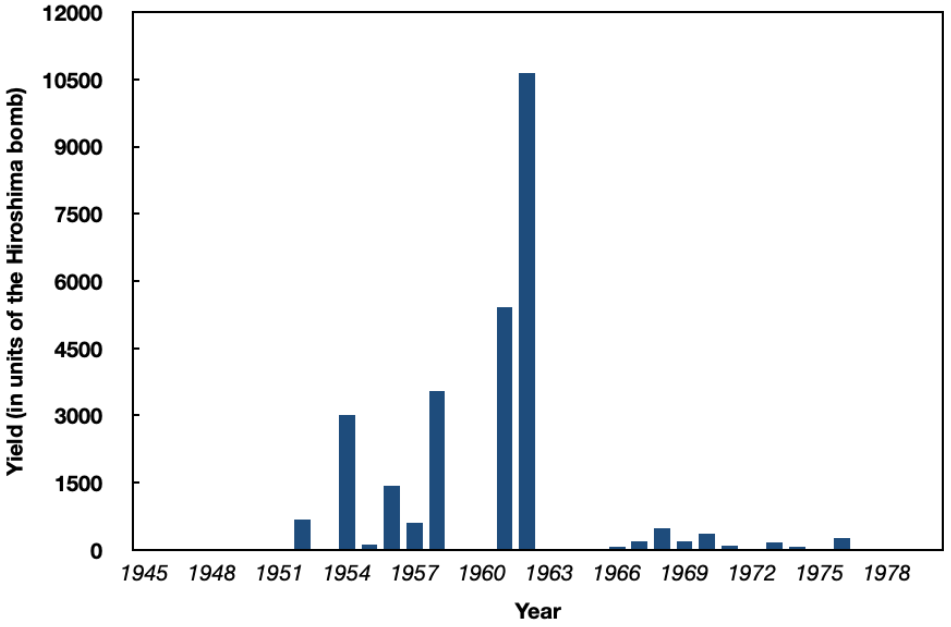
The President John F. Kennedy signs the "Limited Nuclear test ban treaty" in October 1963

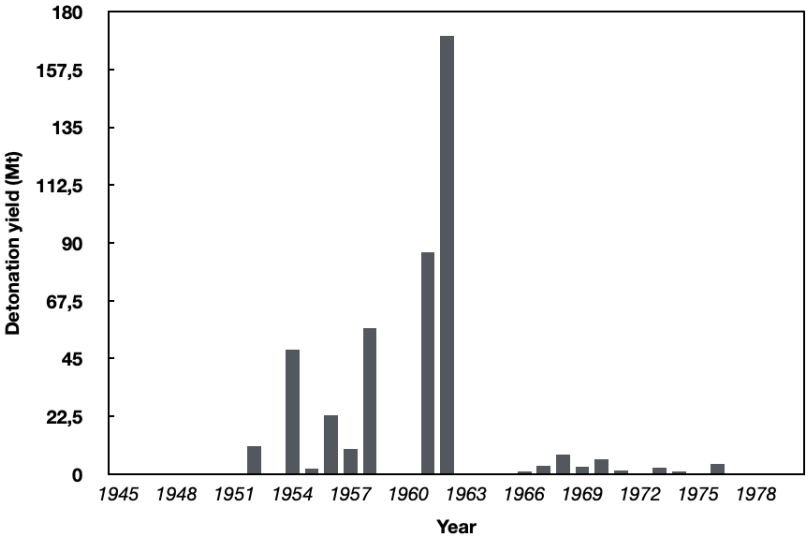
Anthropogenic ^{14}C



Number of nuclear atmospheric tests

Overall yield > 27'500 Hiroshima bombs



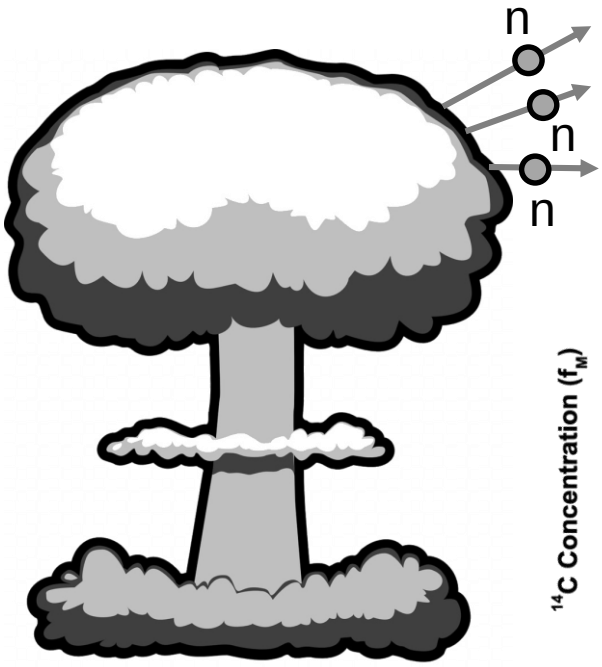


Corresponding yield in Megaton

The ^{14}C atmospheric concentration almost doubled in the mid 1960's

Interhemispheric differences

How we do it?

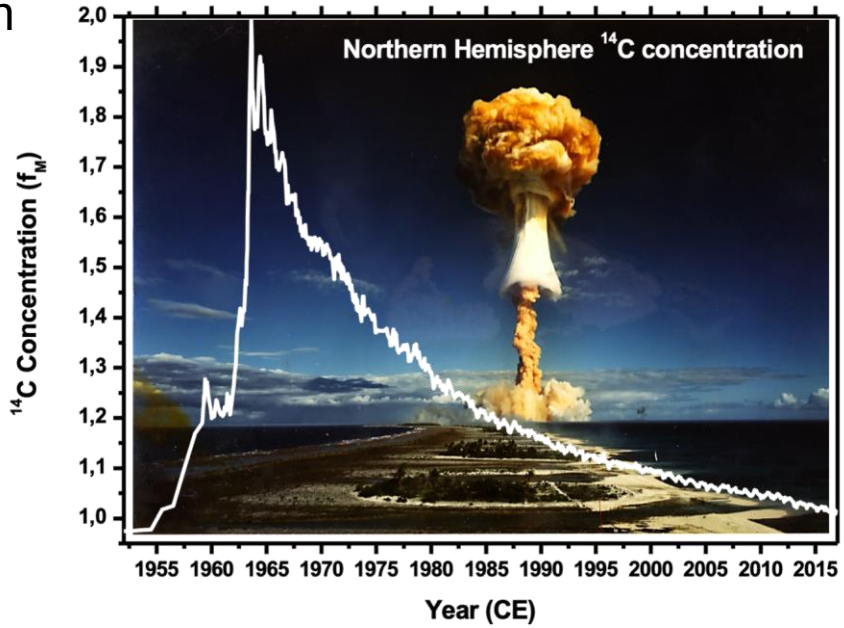


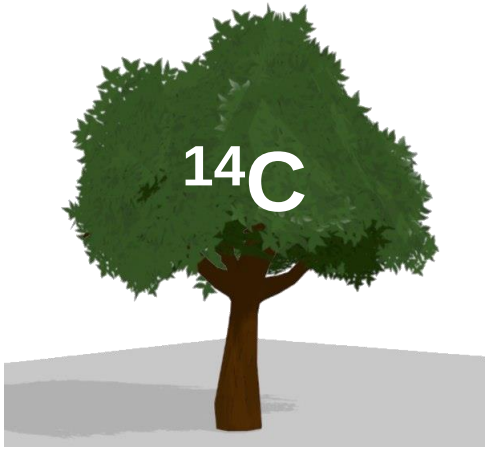
Atmospheric nuclear test

$$n + {}^{14}N \rightarrow {}^{14}C + p$$

Anthropogenic ^{14}C production

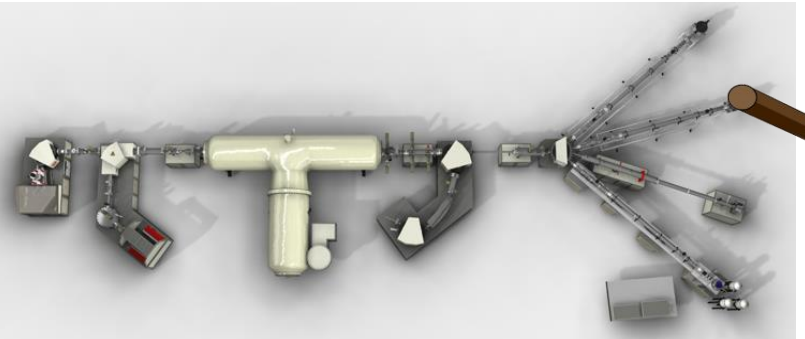
$$^{14}CO_2$$

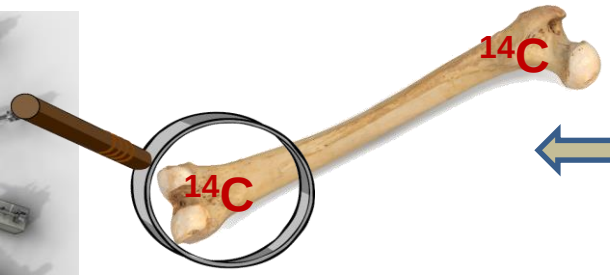




Uptake in living organis

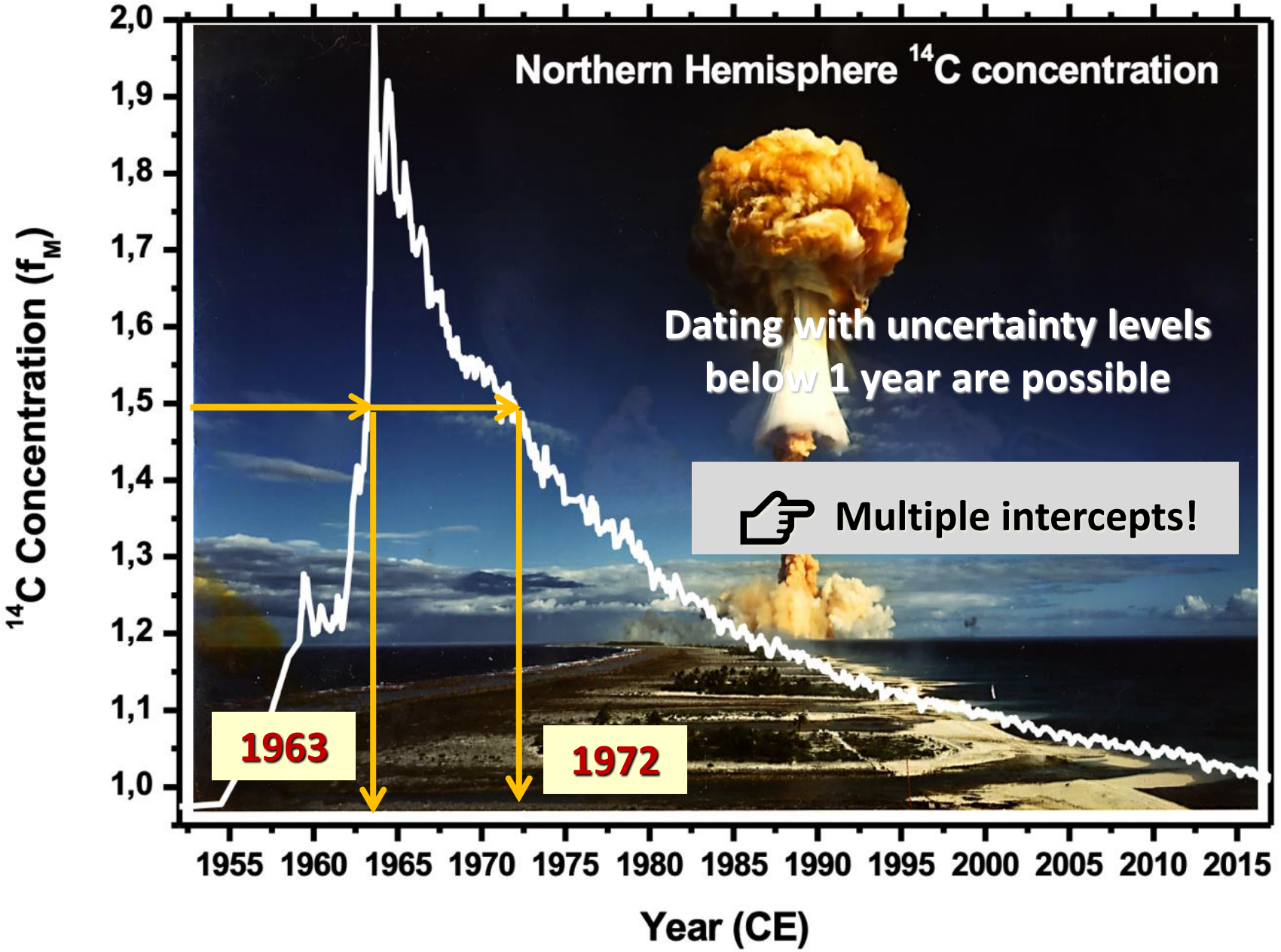
AMS





^{14}C labelling

“BOMB PEAK DATING"



FORENSICS APPLICATIONS OF THE BOMB PEAK

The use of ^{14}C-bomb peak dating is a very powerful tool in forensics

- ✓ **High resolution is possible**
- ✓ **Bomb peak curve very well known (weekly resolution)**
- ✓ **Calibration software freely available**
- ✓ **Scarce sensitivity to environmental factors (humidity, light….)**

- ✓ **Multiple intercepts**
- ✓ **Data interpretation can be complex as related to carbon turnover**
- ✓ **Complex instrumentation (accelerators)**

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CASE STUDIES

FORENSICS: a recent case study

In spring 2010 a body (white, male) was found in an artificial lake in Italy.
The autopsy revealed that the person had been shot in the face.
Different samples were taken and submitted to AMS radiocarbon dating at CEDAD

Sample no.	Element	Type of Tissue
M hair	Head hair	Hair keratin
M tooth 43	Mandibular right canine	Dental enamel
M tooth 47	Mandibular right second molar	Dental enamel
M pubic symphysis	Pubic symphysis	Trabecular bone
M base of skull	Base of skull	Cortical bone

Tissues have been provided by Prof. C. Cattaneo, LABANOF-*Dipartimento di Morfologia Umana e Scienze Biomediche* (DMU), University of Milano, Italy

RESULTS

1. Canine is formed before the molar: the first intercepts with the curve can be excluded
2. Death year: 2009 AD
3. Carbon turnover rate is faster for trabecular than for cortical bone

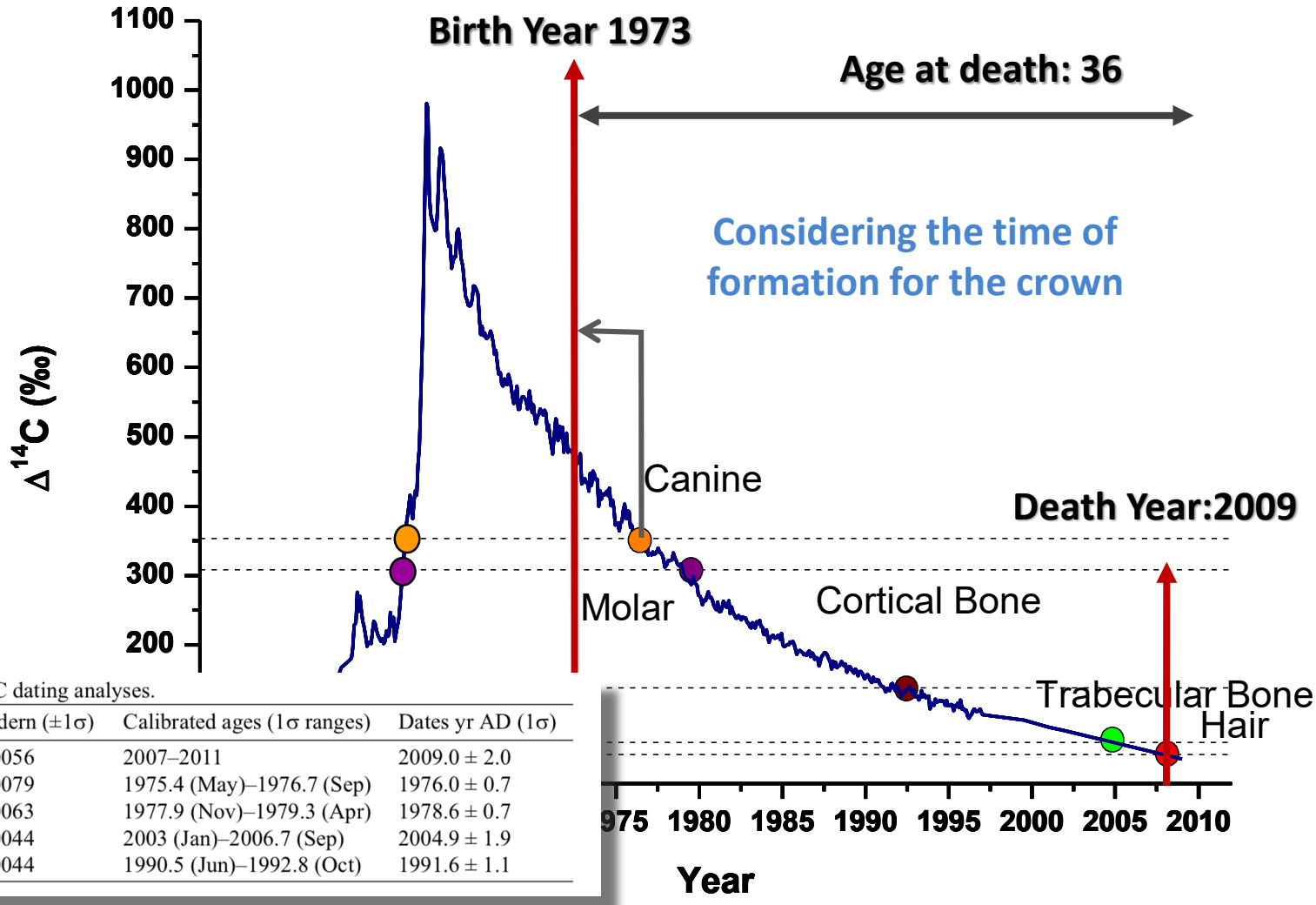

Table 2 Results of AMS ^{14}C dating analyses.

Sample ID	Fraction modern (±1σ)	Calibrated ages (1σ ranges)	Dates yr AD (1σ)
S1	1.0493 ± 0.0056	2007–2011	2009.0 ± 2.0
S2	1.3632 ± 0.0079	1975.4 (May)–1976.7 (Sep)	1976.0 ± 0.7
S3	1.3182 ± 0.0063	1977.9 (Nov)–1979.3 (Apr)	1978.6 ± 0.7
S4	1.0674 ± 0.0044	2003 (Jan)–2006.7 (Sep)	2004.9 ± 1.9
S5	1.1463 ± 0.0044	1990.5 (Jun)–1992.8 (Oct)	1991.6 ± 1.1

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RADIOCARBON AND THE PROTECTION OF ENDANGERED SPECIES:

The case of Elephant Ivory

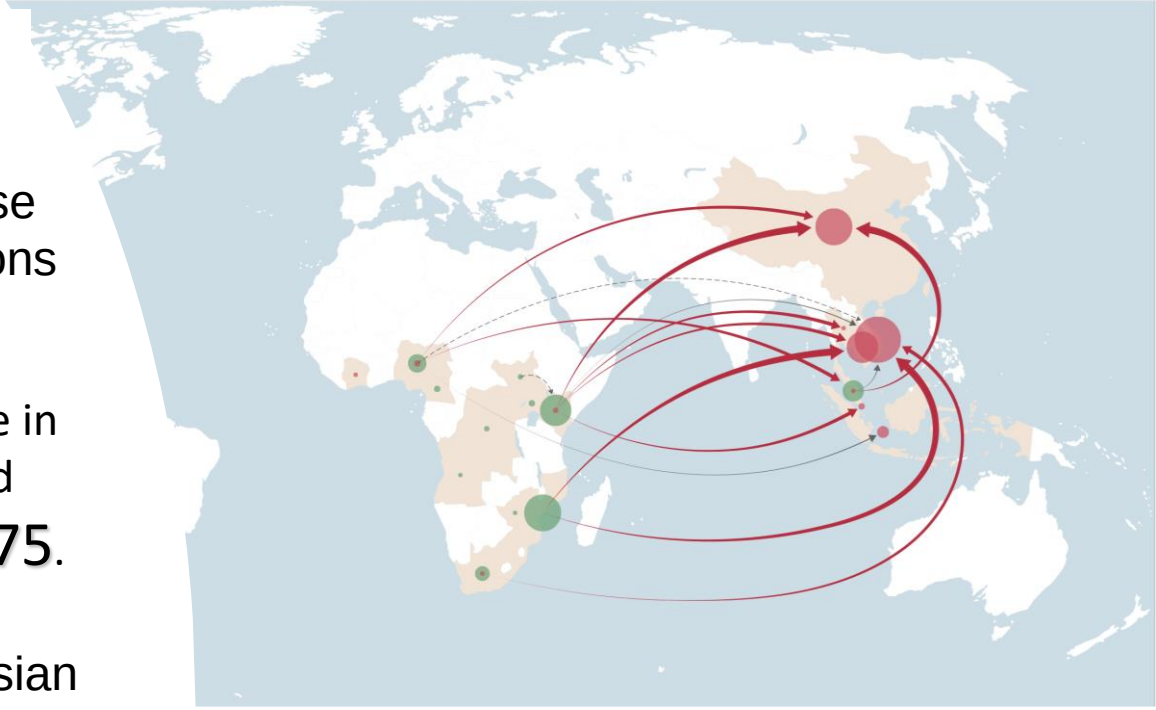
The problem

The illegal trade of ivory is the cause of the decline of Elephant populations due to poaching

The Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) entered into force in 1975.

In 1989 African Elephants joined Asian Elephants in CITES with the highest level of protection

Total BAN of ivory trade after 1990



WHO?

Wildlife protection agencies
Border control services
Police corps
Private citizens

^{14}C

ASK US TO:

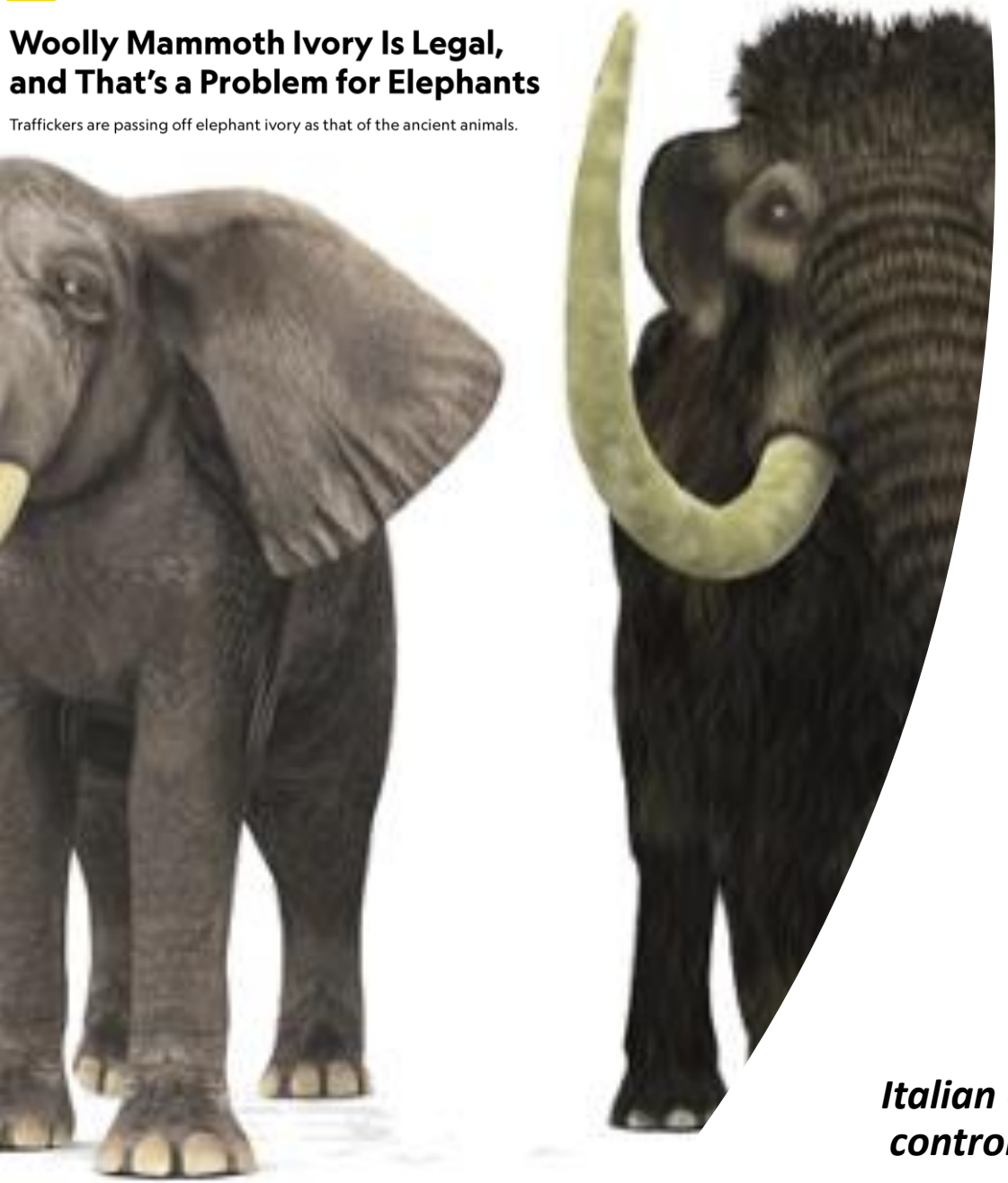
Certificate pre-CITES samples

(When was the Elephant killed?)

NATIONAL GEOGRAPHIC

Woolly Mammoth Ivory Is Legal, and That's a Problem for Elephants

Traffickers are passing off elephant ivory as that of the ancient animals.



MAMMOTH OR ELEPHANT IVORY?

^{14}C AGE

46306 ± 850 years BP

46973 ± 870 years BP

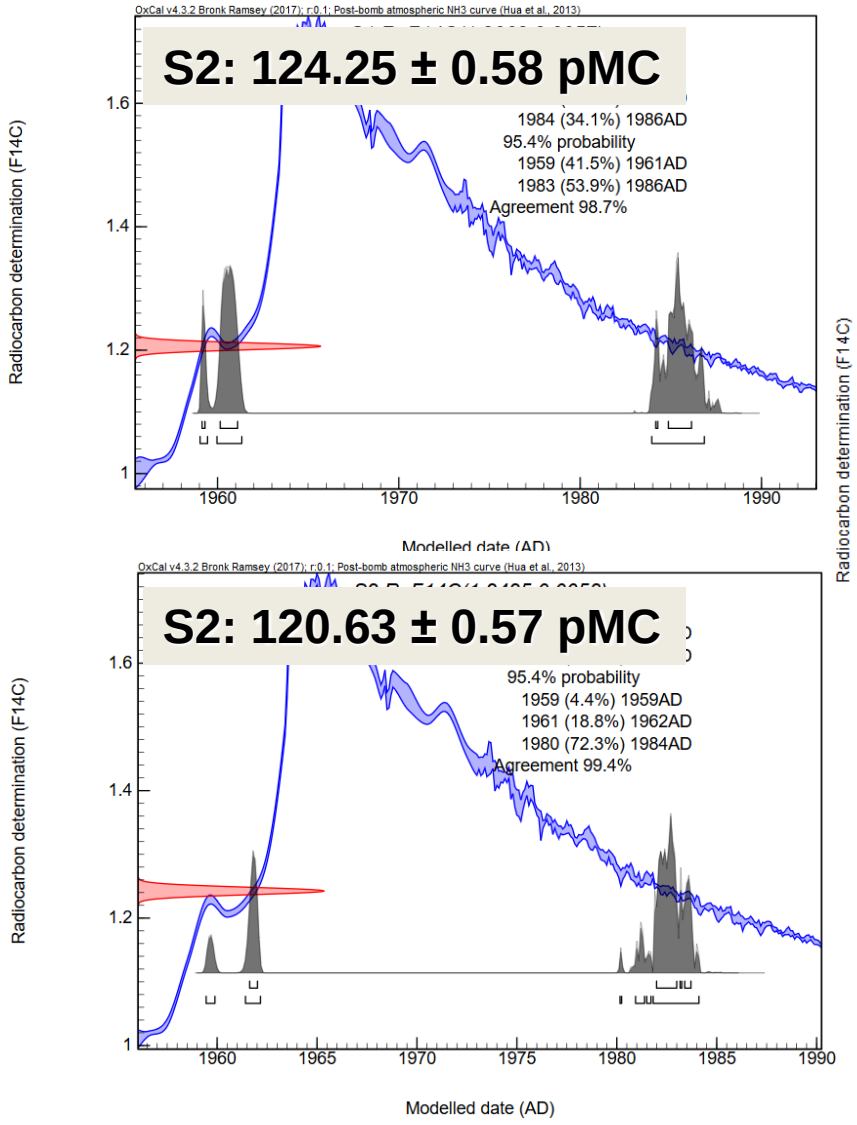
↓

MAMMOTH

Italian Customs control service

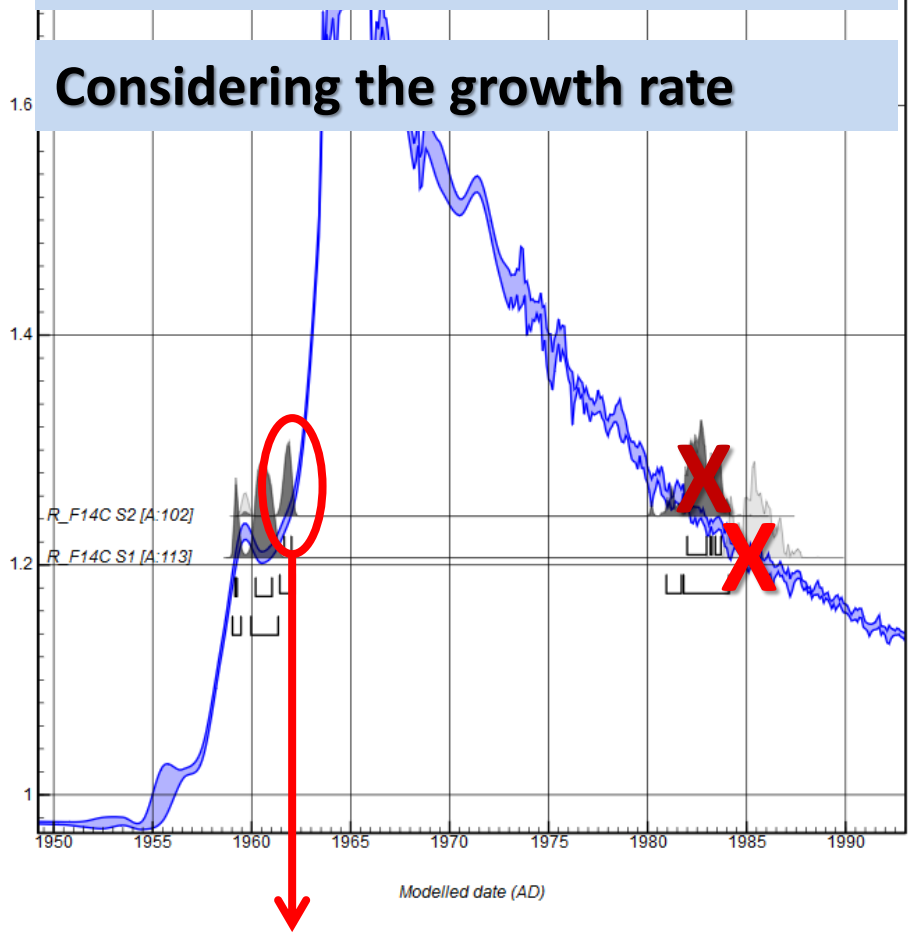
IVORY EXAMPLE: POST BOMB

Two samples (from the same tusk) were submitted for dating. Provenance: Somalia (NHZ3)



But S2 is younger than S1 (5 cm)

Considering the growth rate



Age: 1961-1962 AD (base of the tusk)

Buying date: 15 January After 1984

Impact

A new tool is available to law enforcement agencies

^{14}C dating is required routinely during investigations

^{14}C provides critical information to law enforcement, conservation, government and policy organizations and agencies

^{14}C was used to assess the time lag between animal death and ivory seizures

UNODC
United Nations Office on Drugs and Crime

"No evidence that long-term government or other stockpiles contributed significantly to the illegal trade while poached ivory was being rapidly moved into the illegal trade".

Cerling et al., PNAS, 2016

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The role of ^{14}C dating in the identification of missing persons in Cyprus

Collaboration with: T. Eleftheriou, I. Engin, L., CMP, Cyprus

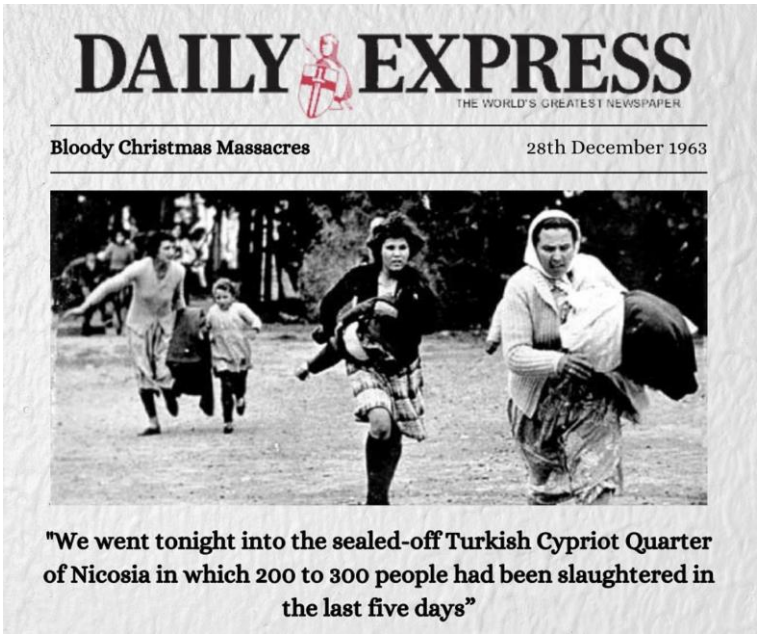
CMP COMMITTEE ON MISSING PERSONS IN CYPRUS

Intercommunal fighting in Cyprus

Two waves of violence hit Cyprus starting from the 1960's

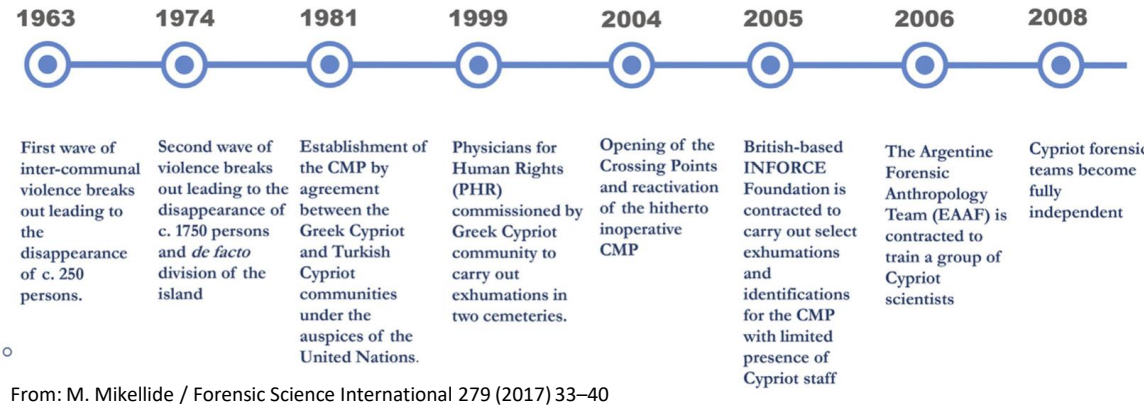
The first period of violence between the Greek Cypriot and Turkish Cypriot communities broke out in **1963 and lasted until 1967**, leading to the disappearances of approximately 250 persons.

A second wave of violence broke out in the summer of **1974**, which led to the disappearance of approximately 1750 persons and to the de facto division of the island


DAILY EXPRESS
THE WORLD'S GREATEST NEWSPAPER

Bloody Christmas Massacres 28th December 1963

"We went tonight into the sealed-off Turkish Cypriot Quarter of Nicosia in which 200 to 300 people had been slaughtered in the last five days"



From: M. Mikellide / Forensic Science International 279 (2017) 33–40

CMP COMMITTEE ON MISSING PERSONS IN CYPRUS

The Committee on Missing Persons in Cyprus (CMP) is a bi-communal body established in 1981 by the Greek and Turkish Cypriot communities with the participation of the UN.

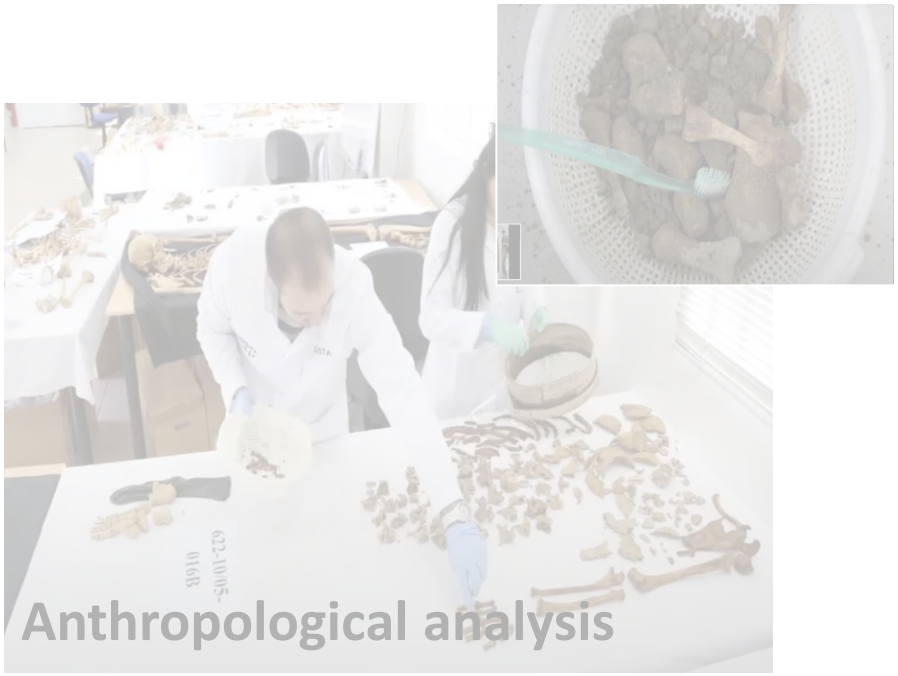
Its objective is to recover, identify, and return to their families, the remains of **2002** persons (492 Turkish and 1,570 Greek Cypriots) who **went missing** during the inter-communal fighting in 1963-64 and the events of 1974.

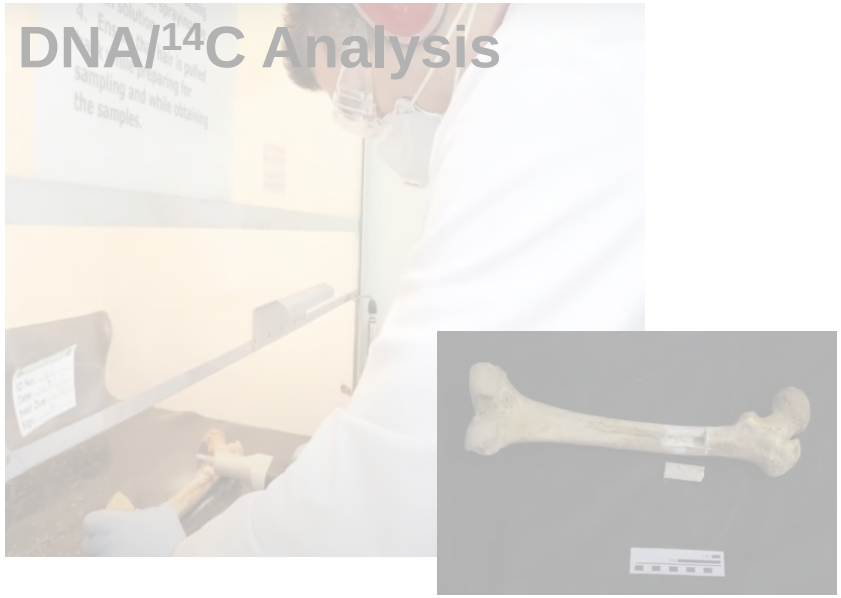
The mandate of the CMP is humanitarian and does not attempt to establish the cause of death or attribute responsibility for the death of missing persons

The CMP employs a forensic team of more than 60 Cypriot archaeologists, anthropologists and geneticists, who conduct excavations throughout the island and anthropological and genetic analyses of remains at the CMP Anthropological Laboratory.

"Image Rights: CMP".

The CMP identification process





The role of ^{14}C dating

During the anthropological phase, skeletal samples are also selected for radiocarbon dating analysis to determine the antiquity of the remains

^{14}C Dating → >200 yrs → **Not relevant for the CMP's mandate**

Further investigations needed

- **Bomb carbon detected**
- **^{14}C Ages <200 yrs**

^{14}C dating is being used on >130 samples as pre-screening

Issues

Sometimes the rests were intentionally mixed with pre-existing remains (cemeteries or archaeological sites)

Some rests were left unburied and went mixed with archaeological findings

Everyone is allowed to ask CMP support and often no context information is available

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CMP COMMITTEE ON MISSING PERSONS IN CYPRUS

The role of ^{14}C dating-Simple but not easy

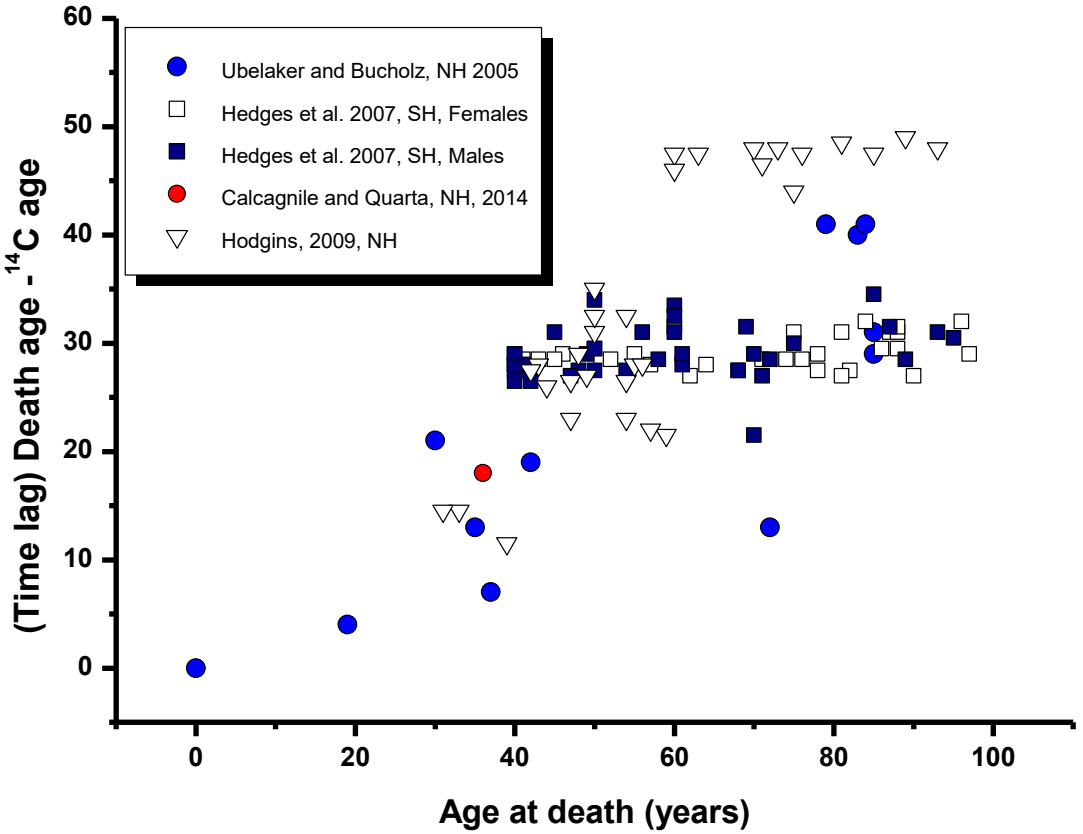
Interpretation of radiocarbon data has to carefully takes into account different aspects:

- **Local deviations** of the bomb curve from the global average;
- **Dietary effects** (consumption of marine food);
- **Multiple intercepts** with the bomb peak curve;
- Difference between the ^{14}C content measured in the analyzed tissue and in the atmosphere in the year of death (time lag)

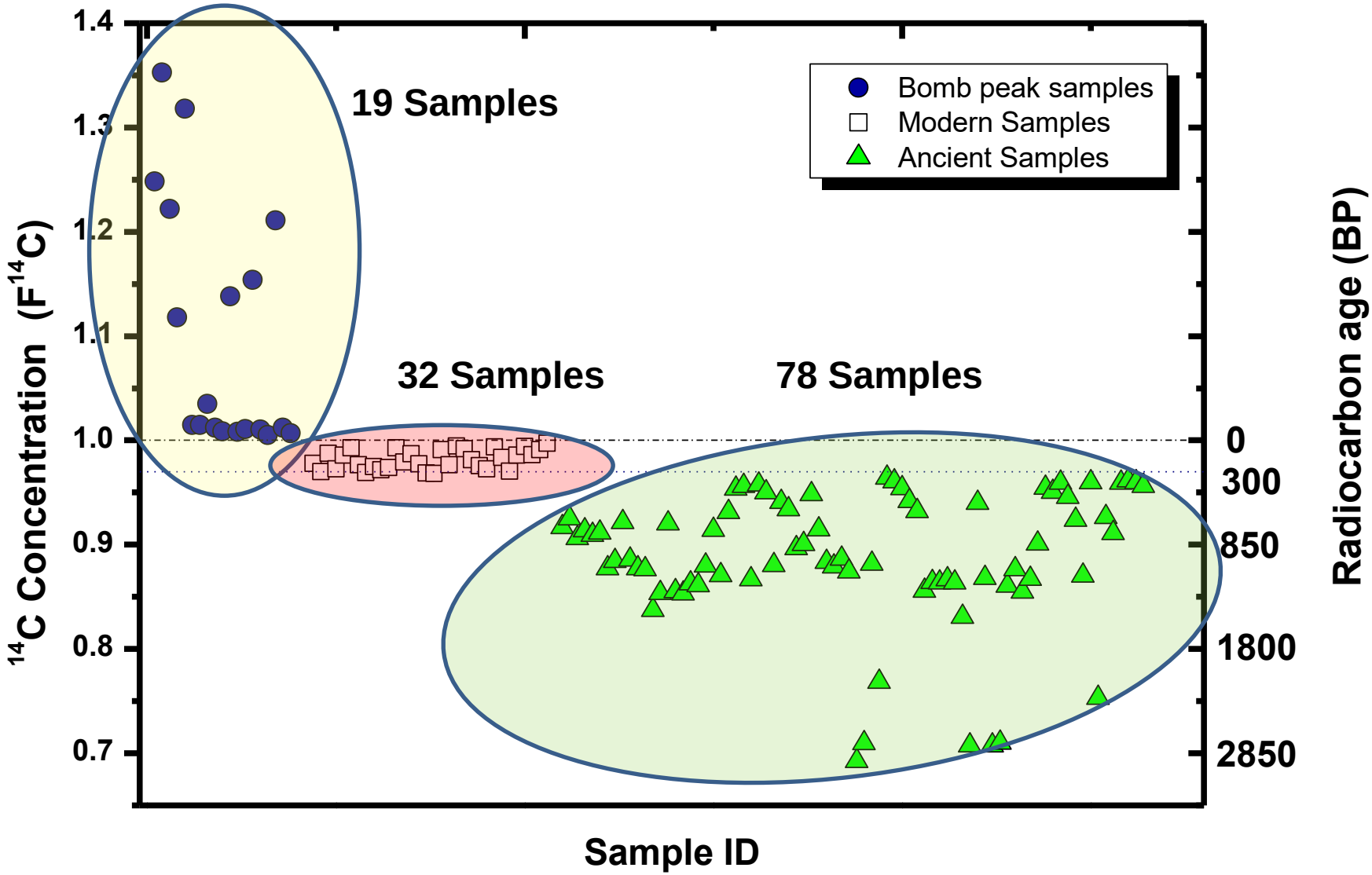
Time lag depends on:

- **Age at death**
- **Analyzed tissue**

Variability between different individuals



Radiocarbon results



CASE REPORT

According to witness information, a skull belonging to a young soldier was removed from its initial burial site and was thrown to a pit inside the old cemetery. The primary burial was excavated in 2012 in an open field by the CMP and commingled remains belonging to a Minimum Number of two Individuals were recovered.

Expected death year is 1974

Case

The skull was recovered in 2013 by the archaeologists of CMP at 35 cm depth together with other bones which did not associate together.

The anthropological examination

The skull belonged to an **elderly** and **edentulous male** individual. Age > 60 years

Genetic analysis

The DNA analysis performed on **8 skeletal samples from the cemetery site** showed a **MNI of 5 individuals** that **did not match with any of the family reference samples of the missing persons**. In addition, the genetic analysis did not show **any association** between the remains found from the two different burial sites (the open field and the cemetery)

^{14}C analysis

For a sample extracted from the skull a ^{14}C concentration of **1.0108± 0.0047 was measured**

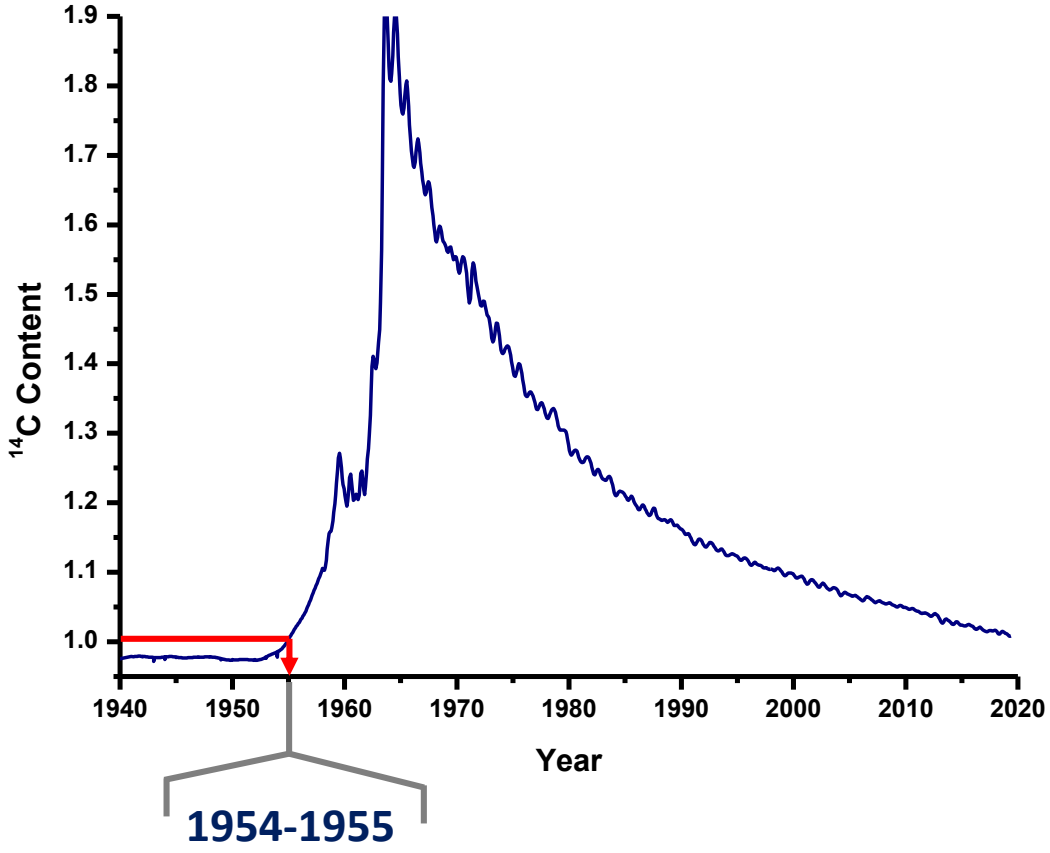
Can the skull be dated (death year) to

1963-1964 or **1974**?

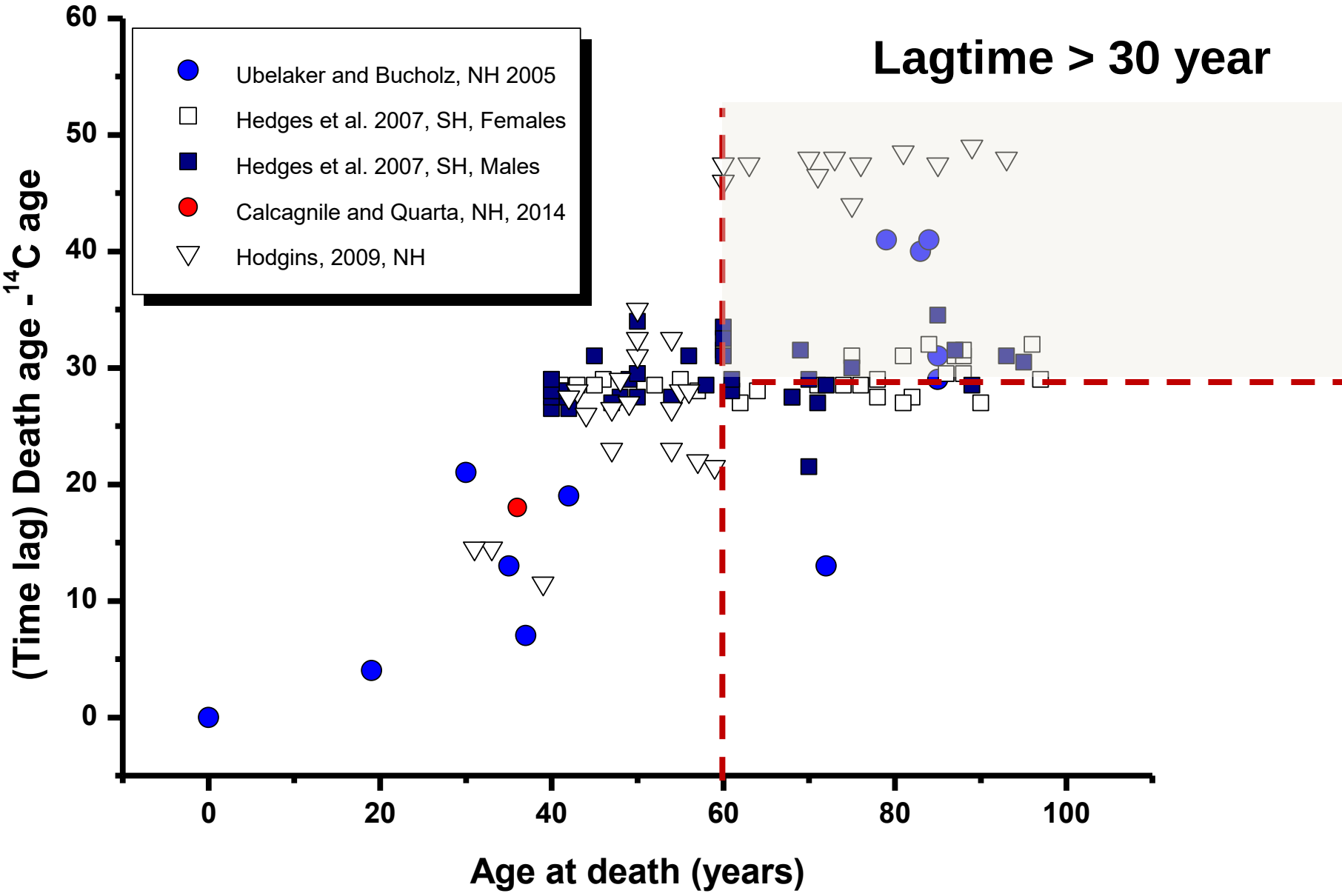
^{14}C data interpretation

A post-bomb ^{14}C concentration of **$F^{14}C$=1.0108± 0.0047** was measured

Age at death: > 60 yrs



^{14}C data interpretation

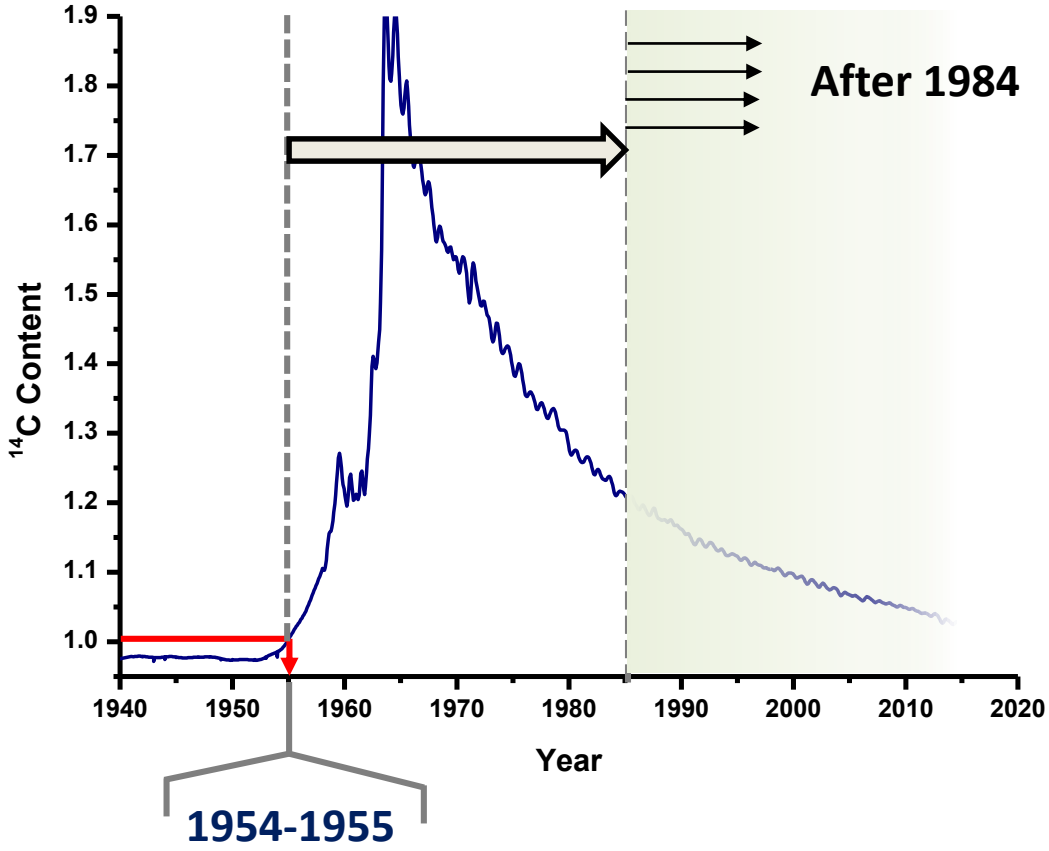


^{14}C data interpretation

A post-bomb ^{14}C concentration of **$F^{14}C$=1.0108± 0.0047** was measured

Age at death: > 60 yrs

Lagtime: > 30 yrs

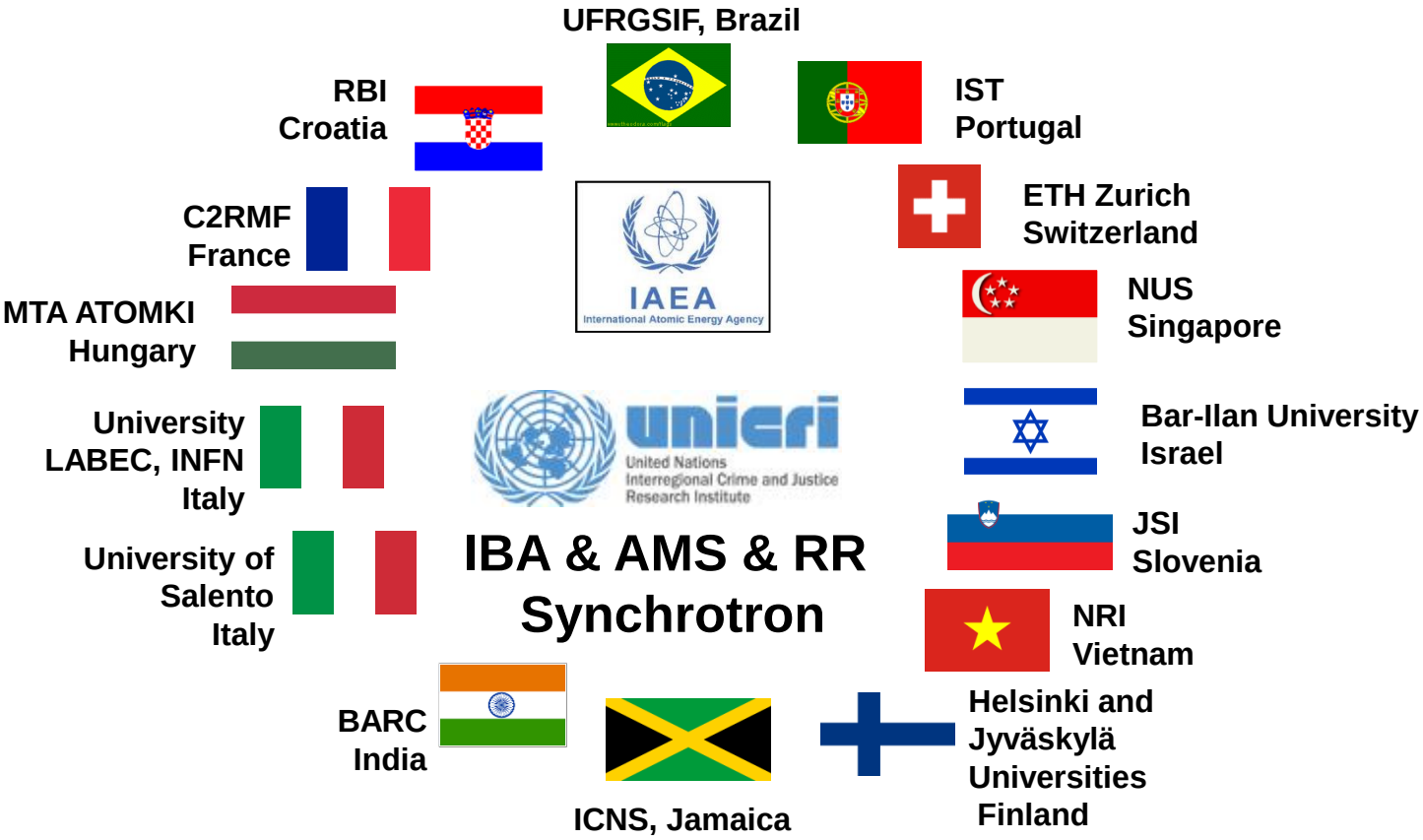


The interest for the
<u>CMP Project can be ruled out</u>


"For families of missing persons,
time does not heal - answers do"

The IAEA CRP F11021

Coordinated Research Project
"Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Science"
(2017-2021)



Courtesy by Dr. Aliz Simon, IAEA

IAEA
International Atomic Energy Agency
Atoms for Peace

The IAEA CRP F11021-2nd MEETING

The IAEA CRP F11021

Goals

- ✓ **To develop and utilize** the unique capabilities of nuclear analytical techniques towards recognized needs of forensic sciences that could not be efficiently addressed by other methods;
- ✓ **To contribute to capacity building** and long term collaboration and networking between the practitioners of nuclear analytical techniques and forensic science stakeholder communities resulting in demonstrable societal gains and enhanced public recognition.

To bridge the gap between the practitioners of nuclear analytical techniques and forensic science stakeholder communities, by facilitating the establishment of long-term cooperation and networking between them;

- WP1. Forensics glass analysis
- WP2. Food authentication and proveneancing
- WP3. Nuclear techniques in heritage forensics
- WP4. Radiocarbon for forensics

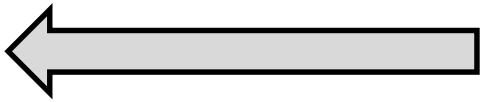
OPEN ISSUES AND WP4 STARTING POINTS

- Define **common guidelines** on the application of ^{14}C-dating in forensics

  I. Quality assurance protocols
  II. Ethical issues
  III. Calculation procedures
  IV. Interpretation of the data
  V. Achievable precision levels
  VI. Robustness of the analyses

- Combined use of accelerator (and non-accelerator) based techniques (i.e. AMS+IBA+NAA+FTIR+RAMAN+SEM)

- Intercomparison exercises on real, complex cases



- Shared and common way of reporting results

Inter-comparison 2019

DIFFERENT KIND OF SAMPLES WERE SELECTED:

Different ages from >40 ka to contemporary

Animal Bones

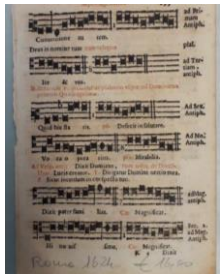
Ivory samples

Paper and textiles

Cofees and wines

All the samples were split in three parts and sent to the participating laboratories

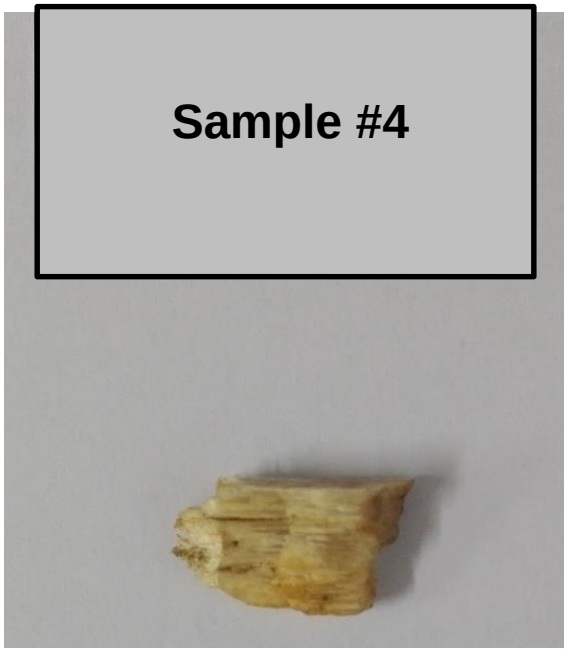
Material	Code	Description
coffee bean	coffee bean	Powder from Brazil
paper	AS1	Arches paper
paper	AS2	Arches paper
paper	1561AD	paper
paper	Rome1624	paper
textile	Old BOX	textile
paper	Paris	paper
leaves	Tel Aviv	leaf
Parchment	Parchment	Parchment
bone	At_1	Modern pig leg bone
bone	At_2	Tibia of an Eurasian aurochs
bone	At_3	Mandible of a woolly mammoth
Ivory	Sample A	pre-bomb
Ivory	Sample B	after 1950
Ivory	Sample C	after 1950

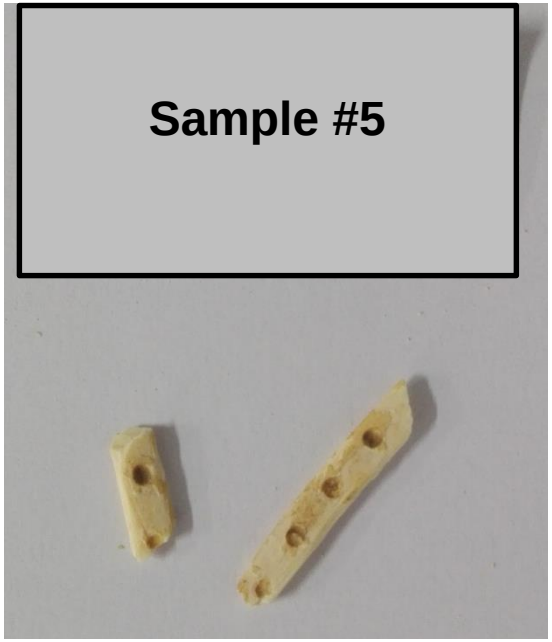


^{14}C intercomparison on ivory samples

Ivory samples submitted to CEDAD for forensics analyses

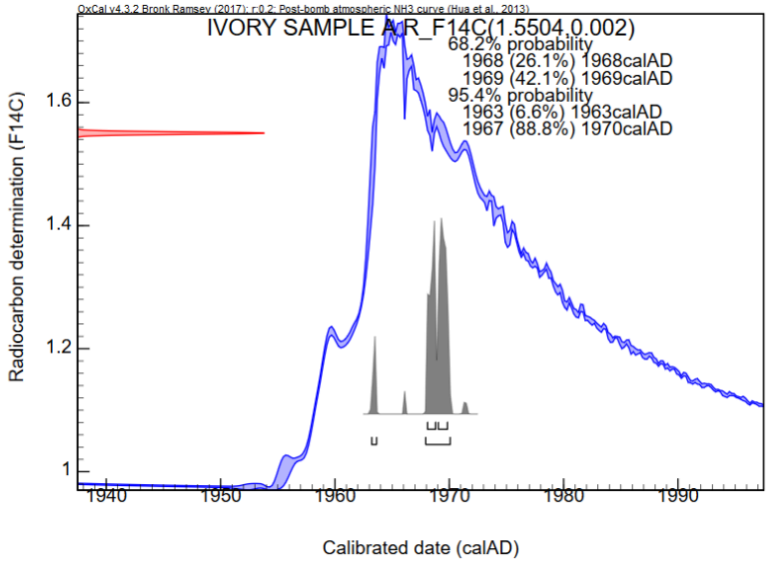
Sample A. Expected age: Pre-bomb sample
Sample B. Expected age: After 1950 AD (post-bomb sample)
Sample C. Expected age: After 1950 AD (post-bomb sample)

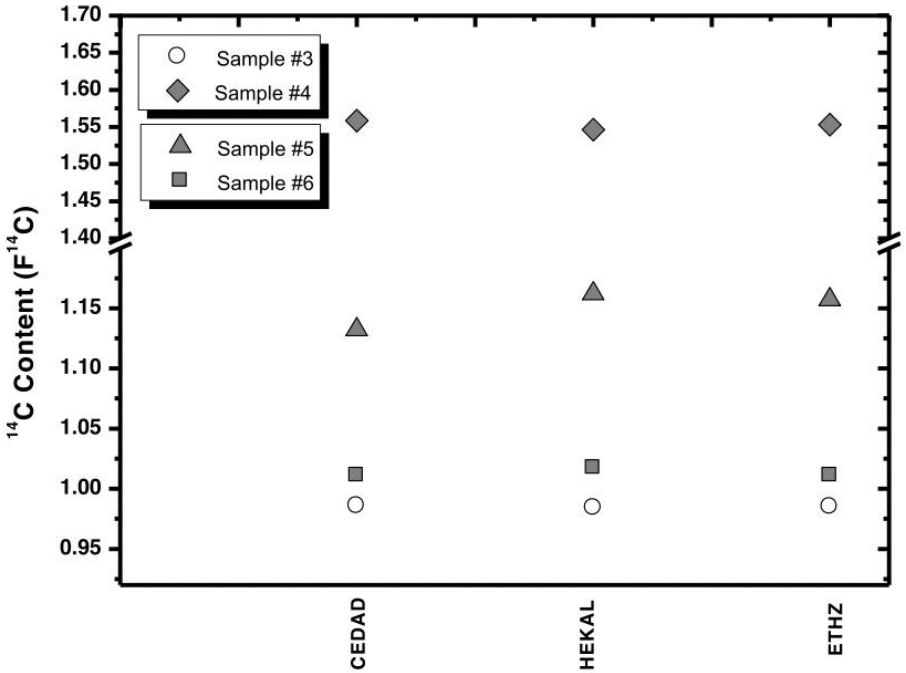


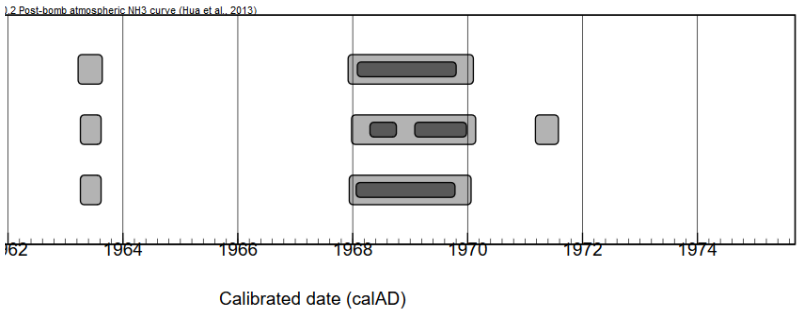


^{14}C intercomparison on ivory samples

Lab	#4	#5	#3
ETH	1.5530 (0.0041)	1.1570 (0.0032)	0.9850 (0.0028)
Atomki	1.5466 (0.0038)	1.1621 (0.0025)	0.9843 (0.0023)
CEDAD	1.5516 (0.0055)	1.1322 (0.0052)	0.9859 (0.0055)







Fully consistent results:

1969 ± 1

Full details in…..

Sample ID	Sample description	Expected age
Sample #1	Mandible of a woolly mammoth	Background (>50 ka)
Sample #2	Tibia fragment of a Eurasian aurochs	~6800 yr
Sample #3	Ivory sample A	Pre-bomb
Sample #4	Ivory sample C	Post-bomb
Sample #5	Ivory sample B	Post-bomb
Sample #6	Modern pig leg	Sampled in 2018

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^{14}C INTERCOMPARISON EXERCISE ON BONES AND IVORY SAMPLES: IMPLICATIONS FOR FORENSICS

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ABSTRACT. The application of accelerator mass spectrometry radiocarbon (AMS ^{14}C) dating in forensics is made possible by the use of the large excursion of the ^{14}C concentration in the post-WWII terrestrial atmosphere due to nuclear testing as a reference curve for data calibration. By this approach high-precision analyses are possible on samples younger than ~70 years. Nevertheless, the routine, widespread application of the method in the practice of forensics still appears to be limited by different issues due to possible complex interpretation of the results. We present the results of an intercomparison exercise carried out in the framework of an International Atomic Energy Agency (IAEA) CRP-Coordinated Research Project between three AMS laboratories in Italy, Hungary, and Switzerland. Bone and ivory samples were selected with ages spanning from background (>50 ka) to 2018. The results obtained allow us to assess the high degree of reproducibility of the results and the remarkable consistency of the experimental determinations.

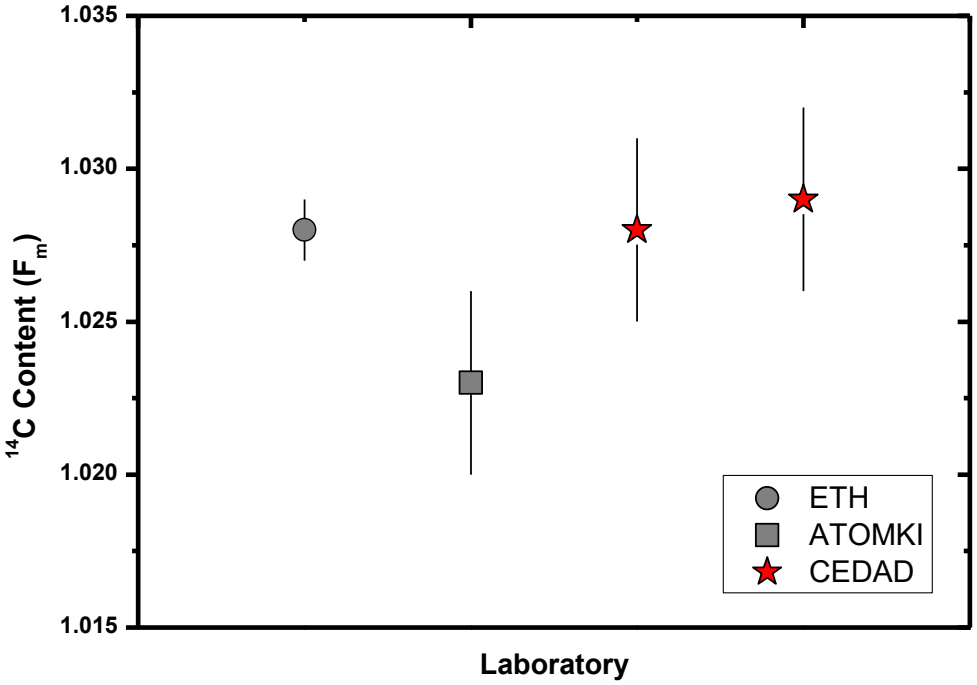
KEYWORDS: bomb-peak dating, bones, forensics, intercomparison.

Analysis on foodstuff (coffes and wines)

- **WP2: Food authentication and provenancing**
- Methodological development of nuclear analytical techniques for the detection of adulteration of foodstuff
- Development of a full profile of some food supplements to serve as starting point for forensic scientists
- Coffee, tea, milk and its derivatives, food supplement, fruits

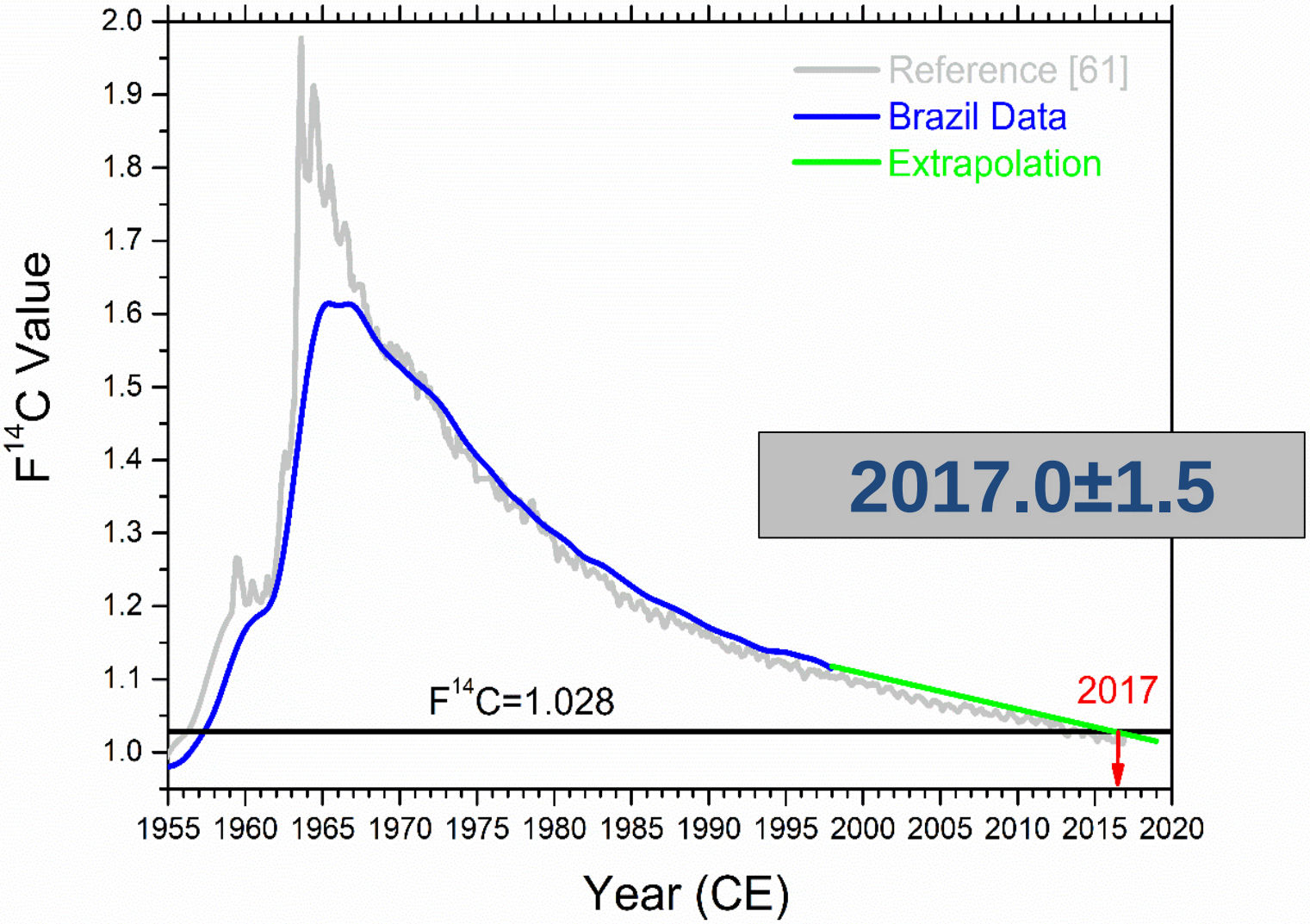
^{14}C intercomparison on Brazilian coffee-First sample

Lab	Lab Code	$F^{14}C$
ETH	coffee bean (powdered)	1.028±0.001
Atomki	I/1780/1	1.023±0.003
CEDAD	Unprocessed	1.028±0.003
CEDAD	AAA processing	1.029±0.003



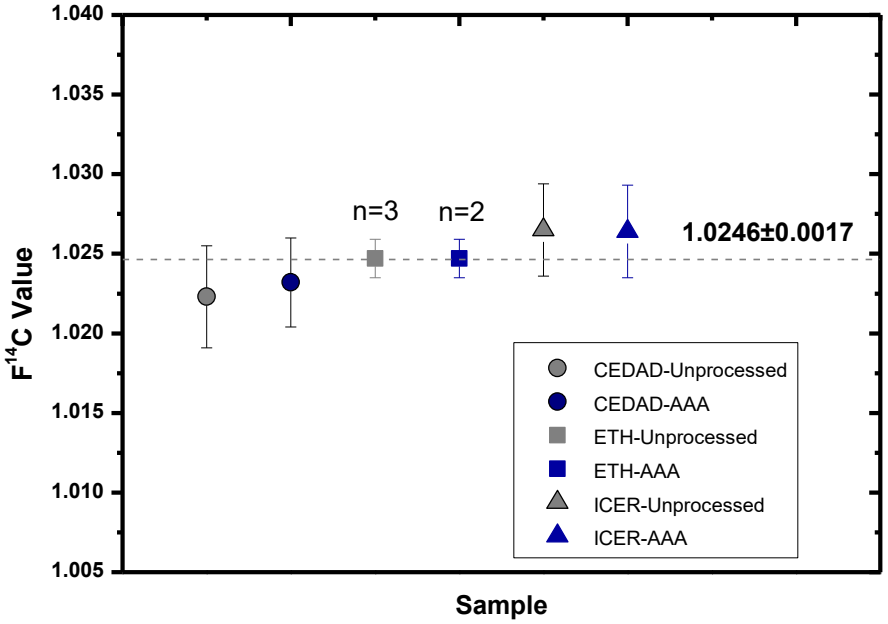
Fully consistent results!

^{14}C intercomparison on Brazilian coffee:calibration

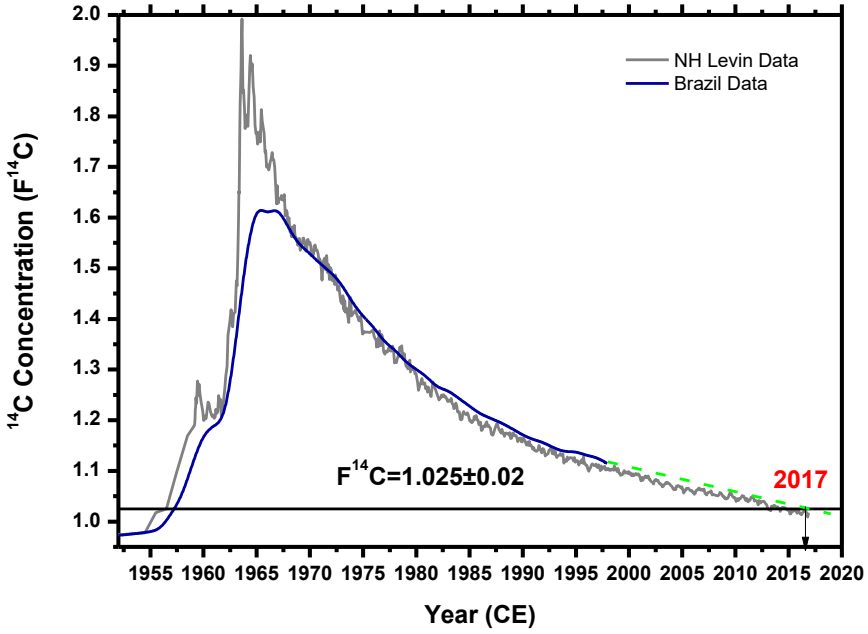


Data from: G. M. Santos et al. Annual growth rings in a sample of Paraná pine (*Araucaria angustifolia*): towards improving the ^{14}C calibration curve for the Southern Hemisphere, Quaternary Geochronology 25 (2015) 96 – 103.

^{14}C intercomparison on Brazilian coffee-Second sample



Fully consistent results!



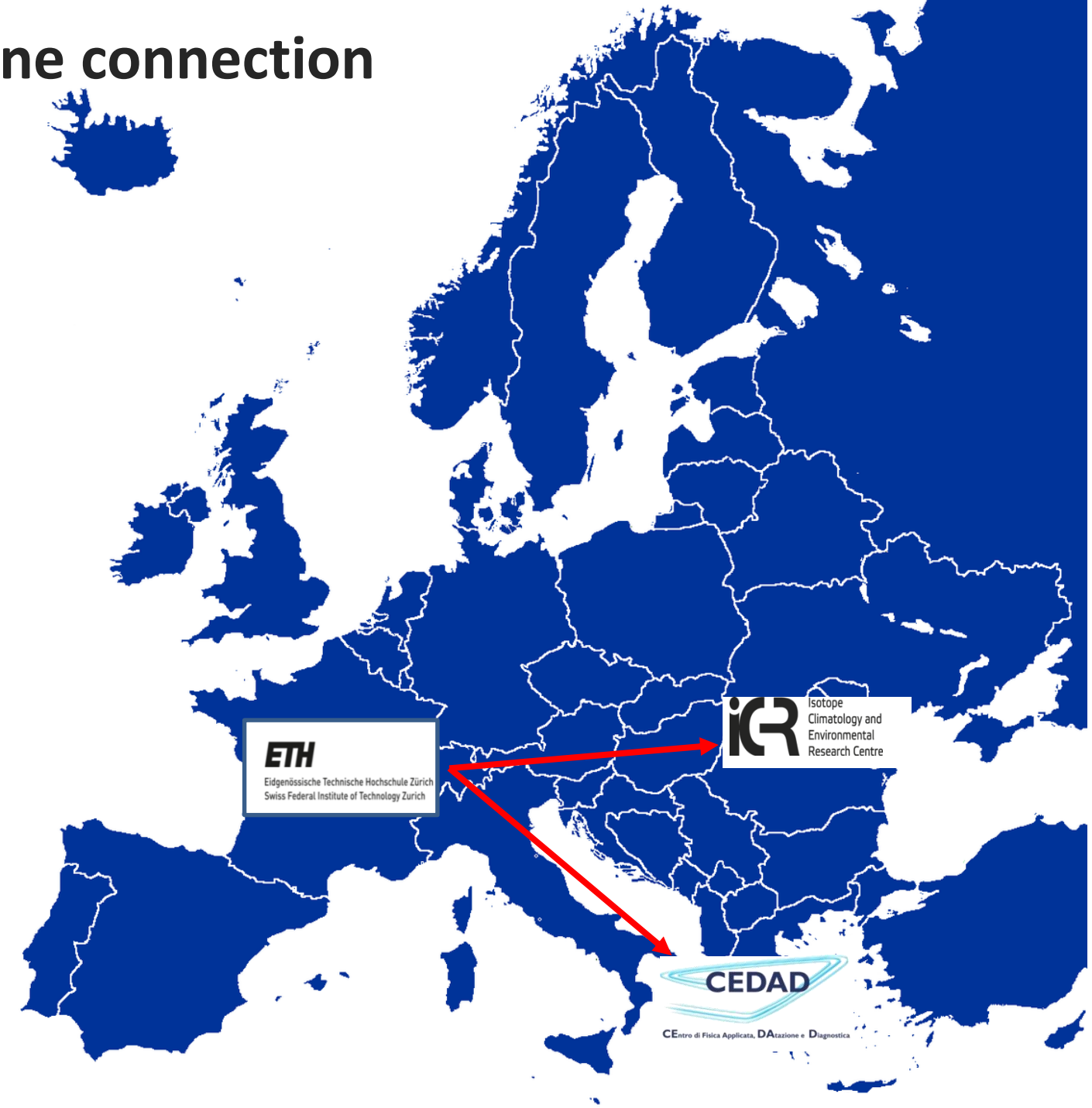
Analysis of wine samples

Analyzed samples

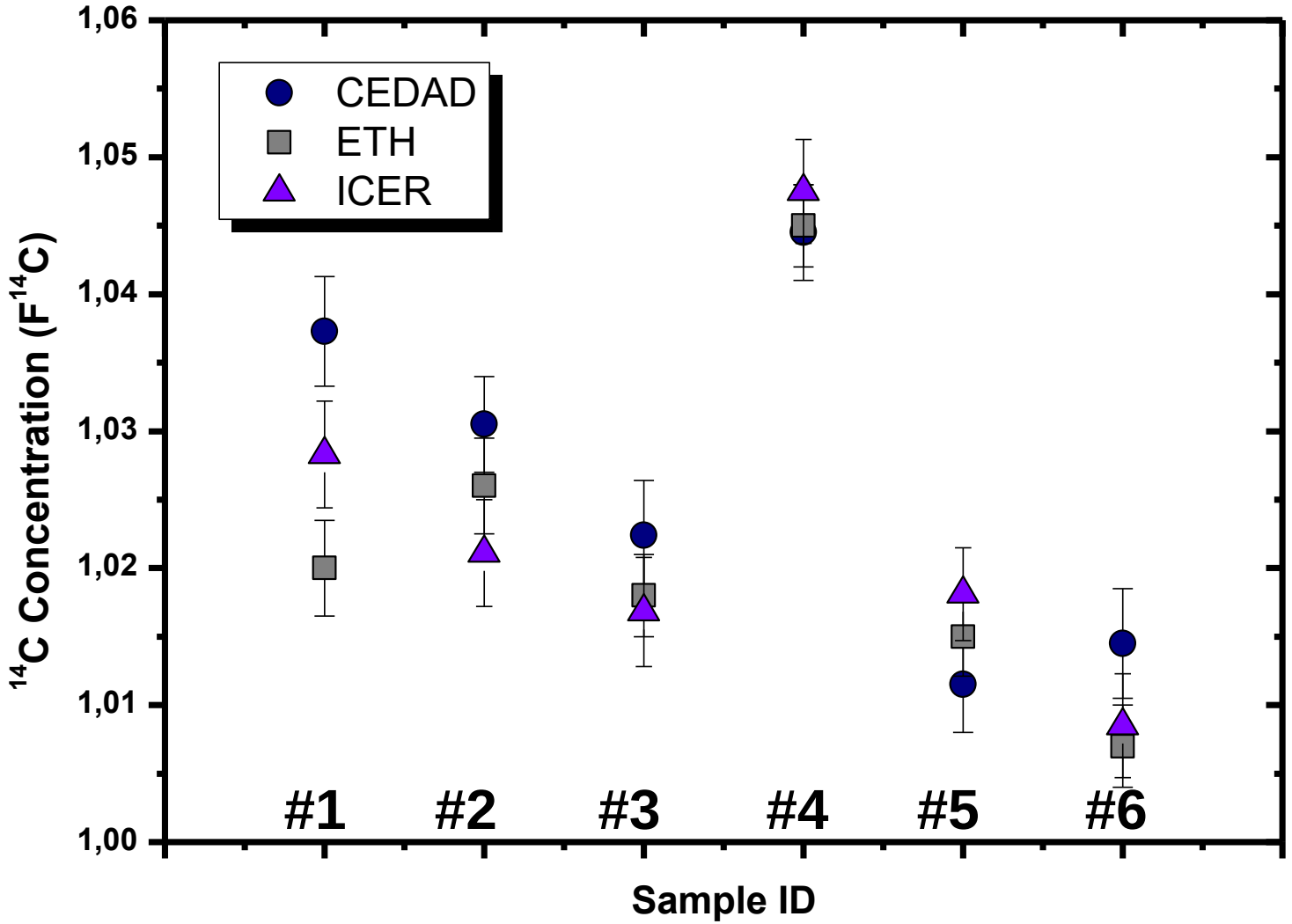
		Wine	Brand	Provenance	Year
	#6	Cabernet	Nals Margreid	Nalles Sud Tirol-Italy	**2017**
	#5	Moscato	Casa Santos Lima	Lisbon, Portugal	**2019**
	#4	Montessu	Agricola Punica	Sardinia (Sulcis), Italy	**2011**
	#3	Reserva	Gran Feudo	Cintruénigo, Navarra, Spain	**2014**
	#2	Cave Merlot	Boscato	Serra Gaucha, Brazil	**2015**
	#1	Cave Merlot	Boscato	Serra Gaucha, Brazil	**2008**

Three aliquots were sampled

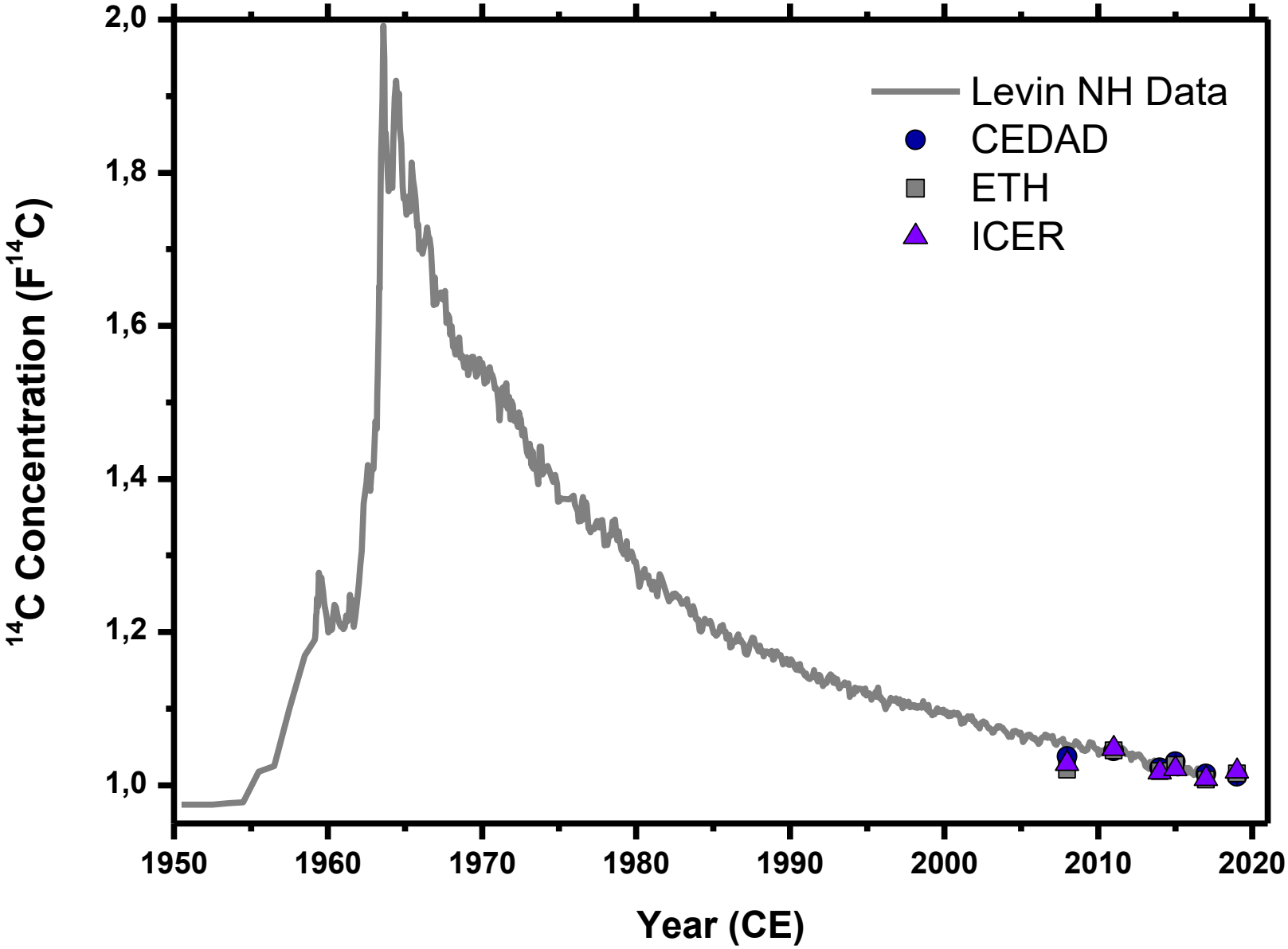
The wine connection



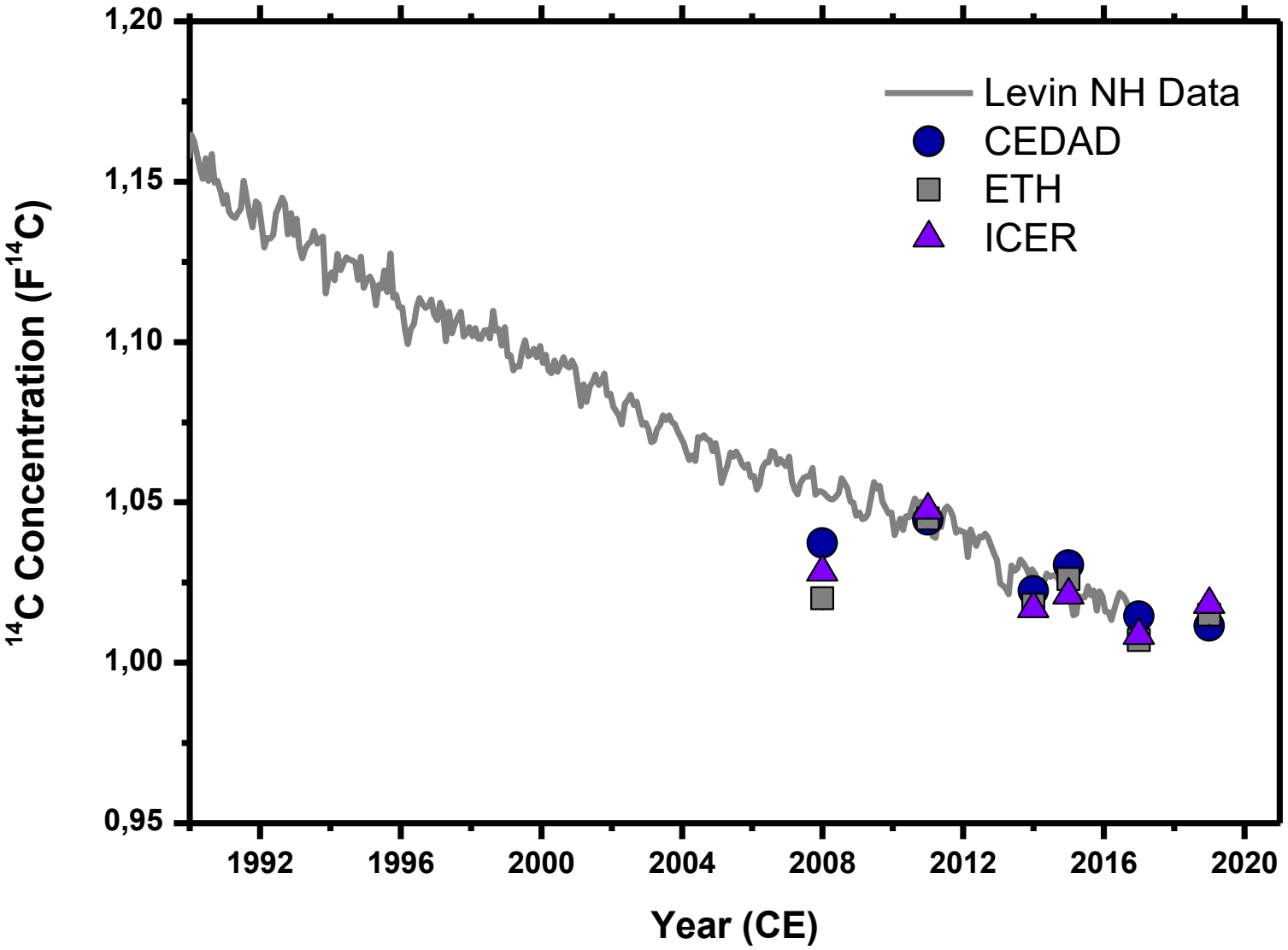
^{14}C intercomparison on wines: Results



^{14}C intercomparison on wines: comparison with atmospheric data



^{14}C intercomparison on wines: comparison with atmospheric data



CONCLUSIONS

- ✓^{14}C dating has a large potential in forensics
- ✓Different methodological aspects have to be properly addressed
- ✓The outcomes of the IAEA CRP has been presented
- ✓Results of an intercomparison exercise have been presented

The 4th International Radiocarbon in the Environment Conference

in 2024 in LECCE, Italy

Gianluca QUARTA-Lucio CALCAGNILE

Thank you!