Setting up a ^{14}C dating method with solid targets of bulk sediments at the Dating and Ionizing Radiation Laboratory

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Objetives

- Setting up a ^{14}C dating method for organic matter in marine sediments using solid targetss
  - Prepare
  - Dating
  - Comparison

- Optimisation of the method
  - Obtain replicable results
  - Reduce the background

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^{14}C

- Source:

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

- C natural isotopes:

Isotope	Protons	Neutrons	Proportion (%)	$T_{1/2}$
^{12}C	6	6	99	Estable
^{13}C	6	7	1	Estable
^{14}C	6	8	10^{-10}	$5700(30)$ años

Table: Natural abundance of different carbon isotopes

Carbon cycle

- This carbon ^{14}C is distributed throughout the earth's reservoirs via the carbon cycle, but it takes time to reach the deep waters: Age of the reservoir.

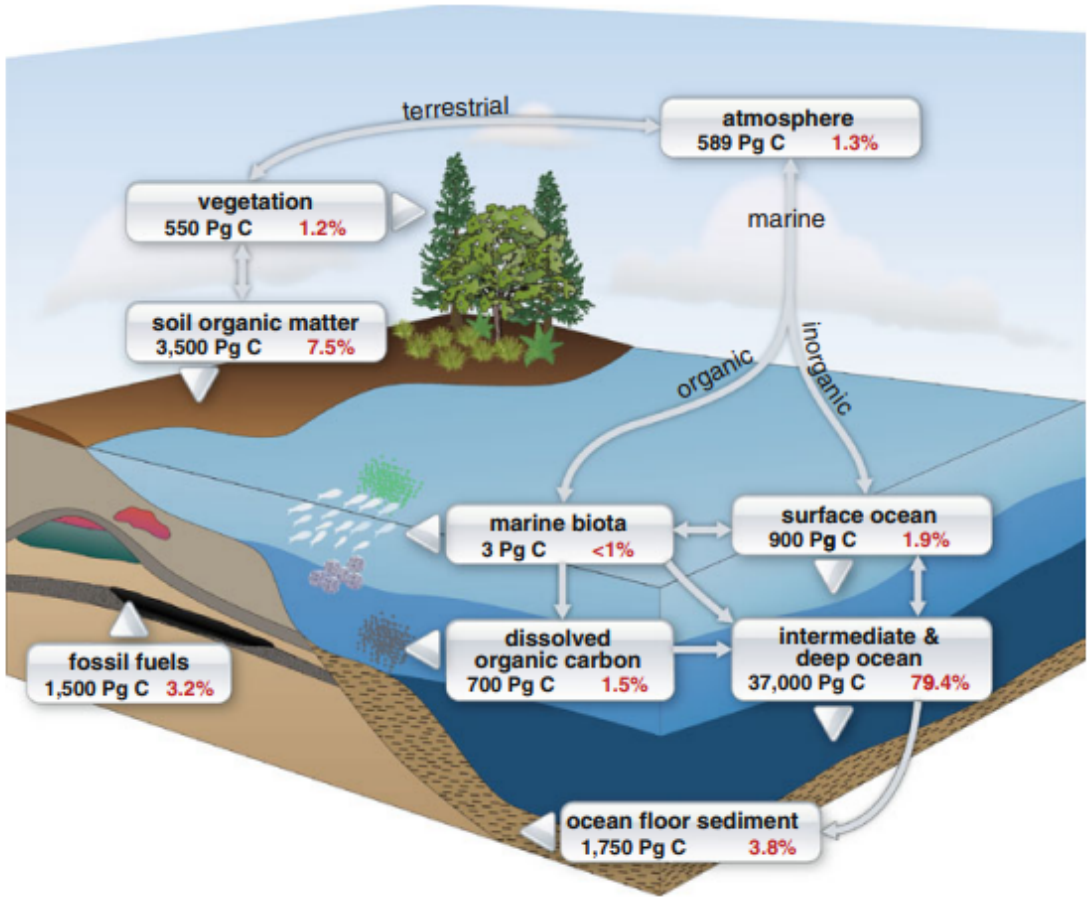

Figure: Carbon cycle

^{14}C assimilation

- ^{14}C is assimilated by living organisms through photosynthesis, plant consumption and animal consumption.

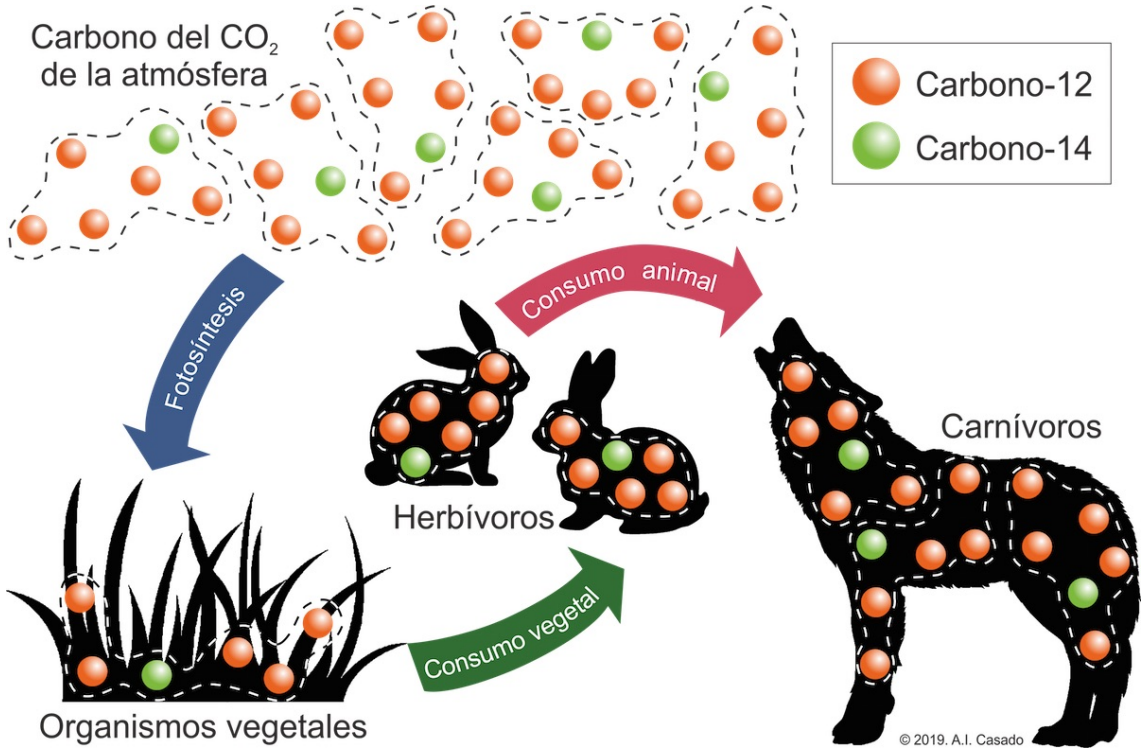

Figure: Incorporation of ^{14}C into living things.

Age calculation

- Developed by Willard Libby in 1950 for which he won the Nobel Prize in Chemistry in 1960.
- Living things stop exchanging ^{14}C when they die, which allows us to use it for dating: $A = A_0 e^{-\lambda t} \rightarrow T = -\frac{1}{\lambda} \cdot ln \frac{A}{A_0}$

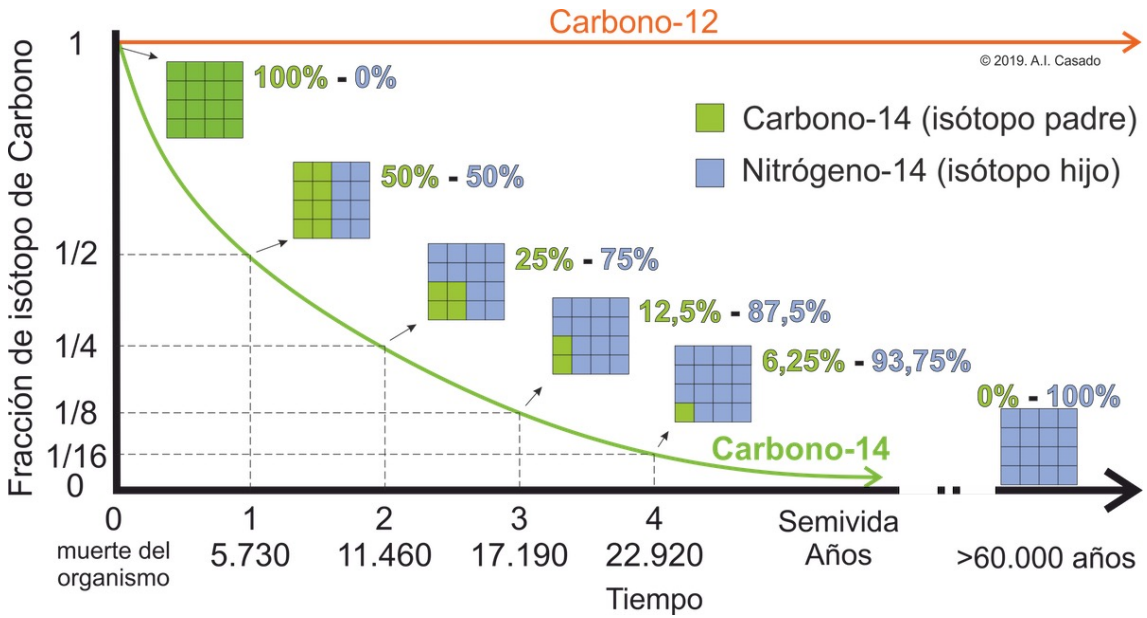

Figure: ^{14}C decay.

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$\Delta^{14}C$ over time

- The concentration of ^{14}C has varied over time:

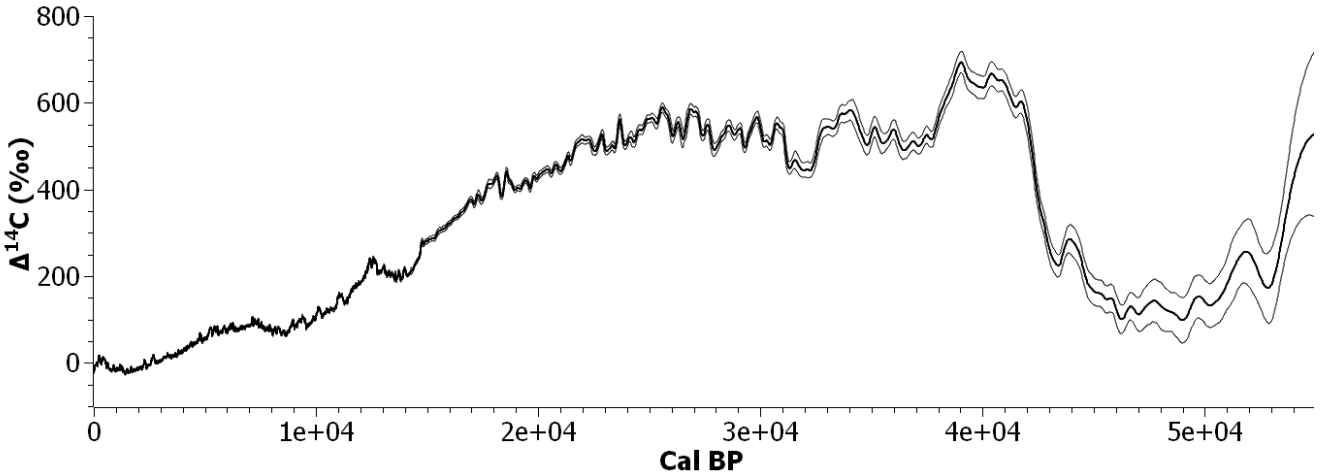
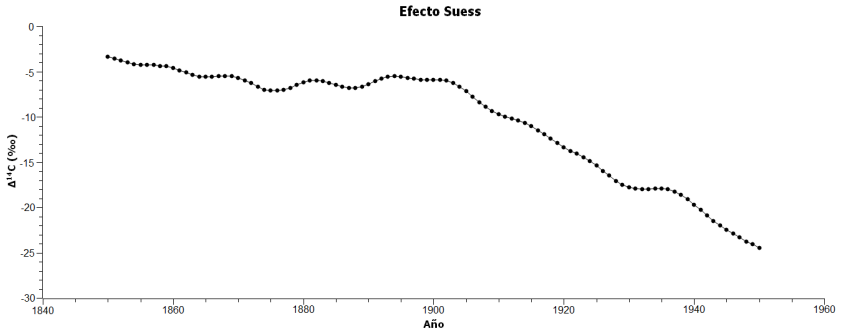


Figure: Variation of ^{14}C with time. CAL BP means years before 1950.

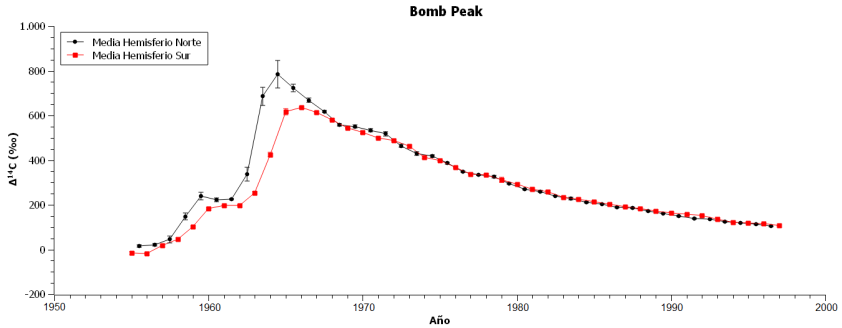
$$\Delta^{14}C(‰) = \left({}^{14}C/{}^{12}C \cdot e^{\lambda(1950-Y_C)} - 1\right) \cdot 1000$$

$\Delta^{14}C$ over time

- Anthropogenic effects:



(a) Suess efect



(b) Bomb Peak

Figure: Variation of ^{14}C due to human activity

- The fraction of ^{14}C is defined as: $F^{14}C = \frac{A_f}{A_0} = \frac{^{14}C_f/^{12}C}{^{14}C_0/^{12}C}$
- The year 1950 is 0 B.P: $F^{14}C\ (1950)\ = 1$
- ^{14}C Conventional age ^{14}C: $T = -\frac{1}{\lambda} ln\ \left(F^{14}C\right)$

Calibration curves

- The ^{14}C content of samples of known ages is measured.
- A calibration curve shows the calendar age on the x-axis and the conventional radiocarbon age on the y-axis.

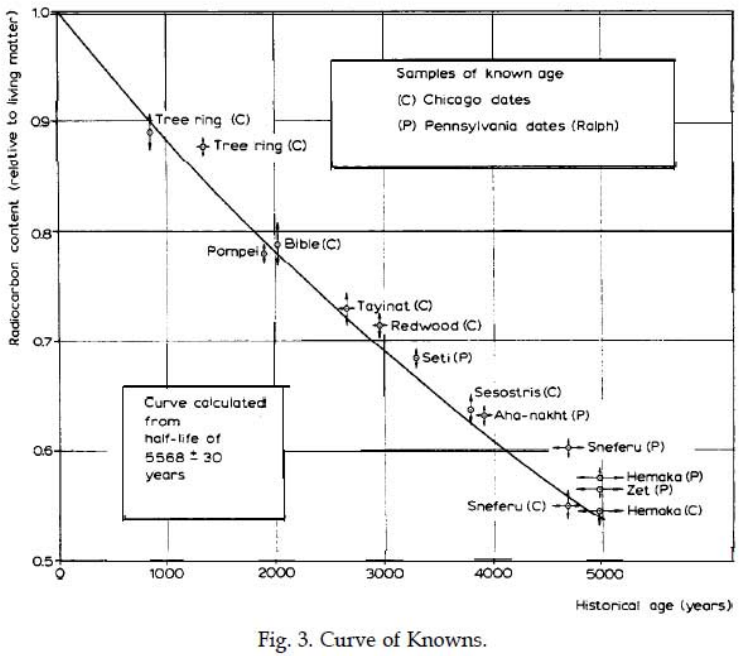
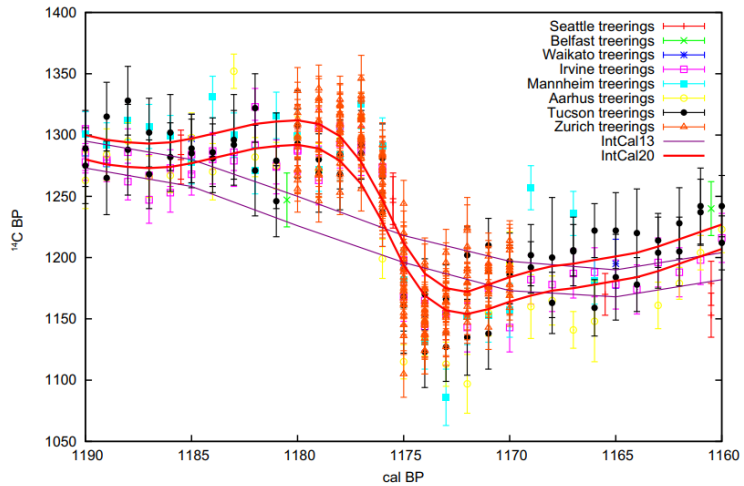


Fig. 3. Curve of Knowns.

(a) The first calibration curve reported by Willard Libby in 1950.



(b) Modern atmospheric calibration curve (IntCal20)

Figure: ^{14}C calibration curves

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Radiometric techniques and AMS

- There are two techniques: Radiometric (A) and Accelerator Mass Spectrometry (N):

$$A = \lambda N$$

- Accelerator mass spectrometry (AMS) is capable of obtaining good statistics in one hour, whereas radiometric techniques take days or even weeks.

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AMS

Figure: Photo of the AMS MICADAS at the University of Salamanca

^{14}C sample preparation laboratory

(a) (b)

Figure: ^{14}C sample preparation laboratory.

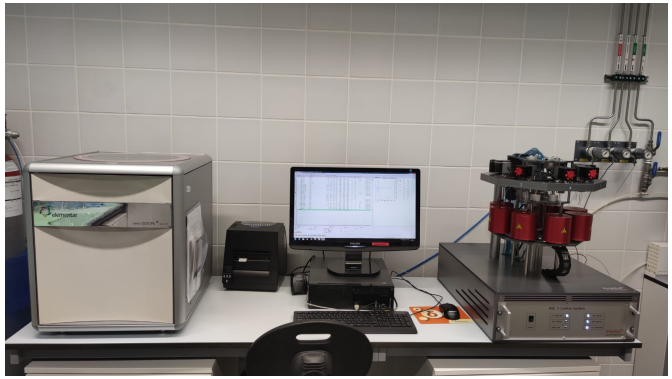

Figure: EA and AGE.

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Samples

- Background: without ^{14}C. We will use PhA.
- Standard: ratio $^{14}C/^{12}C$ known. We will use OxII, whose $F^{14}C\ (OxII) = 1.34057(45)$.
- Marine sediments: known age (Iberian Margin) and unknown age (Antarctica).
- Bone: Bone of an ovicaprine from the Roman Villa of Almenara-Puras in Valladolid.

Preparation: factors to consider

- Different samples, different preparations (wood, sediment, textile, bone...)
- Origin of the carbon to be dated.
- $C\%$ sample: We need 1 mg of final carbon.

Pretreatment of marine sediments: Fumigation

- Marine sediments are formed by: Eroded rocks, minerals, and inorganic (foraminifera) and organic remains of living things (foraminifera and other organisms).
- We want to date the organic matter.
- The objective of fumigation is to isolate organic carbon by removing inorganic carbon.
- A chemical attack is performed that dissociates the inorganic carbon, which combines with oxygen to form gaseous CO_2.
- Fumigation: 4 days of HCl + 4 days of NaOH at $60°C$

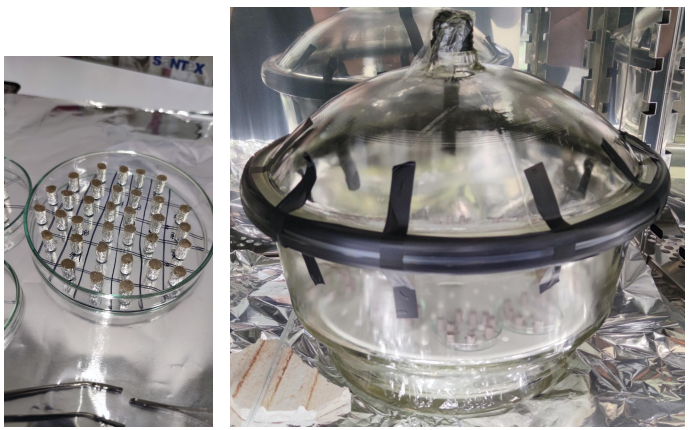


Figure: Fumigation method

Combustion and Graphitization

- The fumigated samples are combusted in an elemental analyzer to obtain carbon from the samples in the form of CO_2. Subsequently, they are reduced to carbon in the form of graphite according to $CO_2 + 2H_2 \rightarrow C + 2H_2O$.

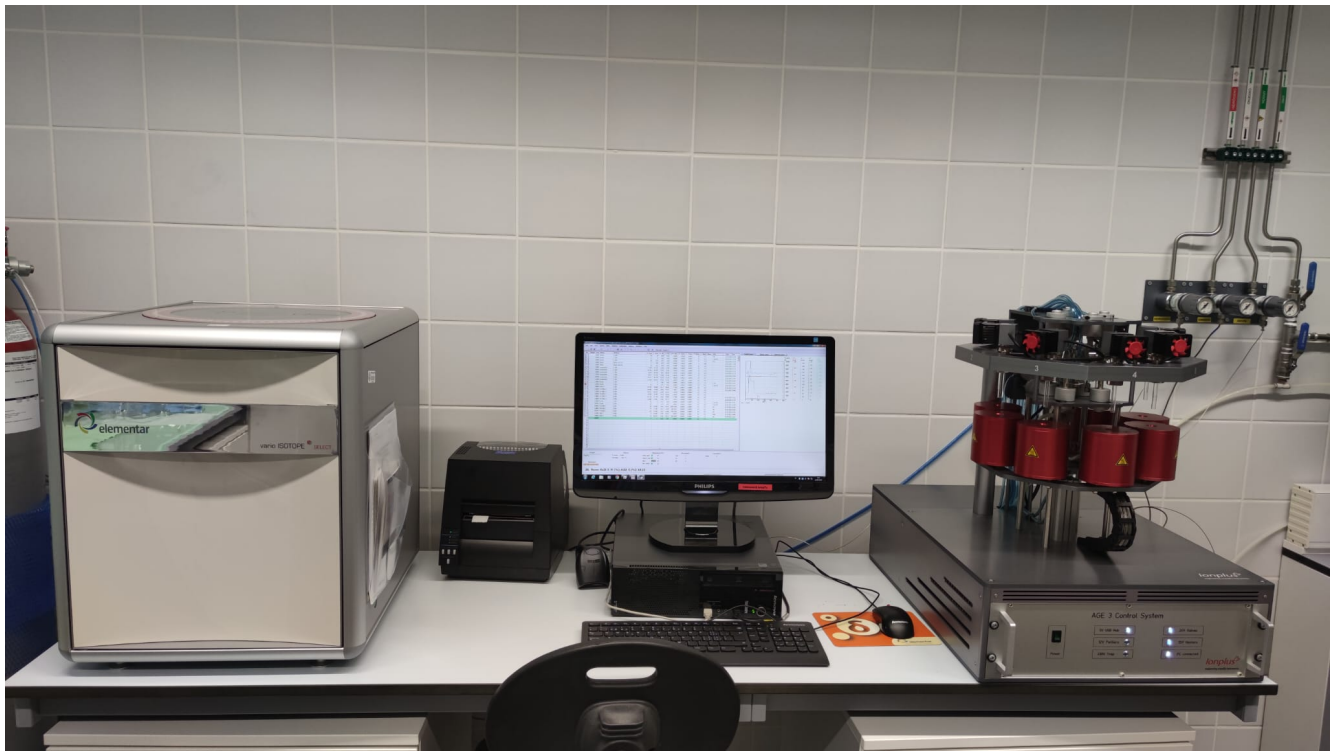
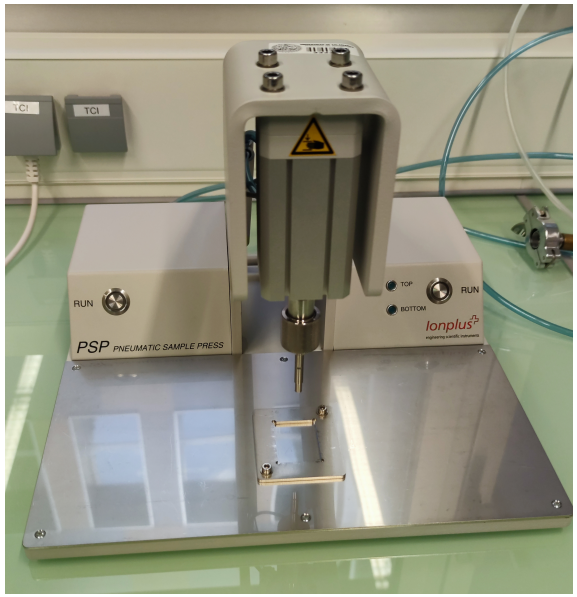


Figure: EA and AGE.

Pressing

- The graphite is pressed into metal cathodes, which will be introduced into the AMS.



(a) Pneumatic machine

(b) Cathodes

(c) Cathodes on a magazine

Figure: Pressing of samples into cathodes and how they are introduced into the AMS

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Measurement

- The AMS must be tuned before each measurement.
- Background and standard samples are measured in each magazine
- Ten passes are performed on each sample, with 10 cycles of 30 seconds each per pass (each sample is measured for a total of 3000 seconds).

Table: Samples measured on each magazine.

Magazine	Measured samples
221028LRI	Standard, Background, IM, Swiss Soil, Shale, TG-03 POWELL 2020
221031LRI	Standard, Background, IM, Swiss Soil, Shale, TG-03 POWELL 2020
221104LRI	Standard, Background, IM, Swiss Soil, Shale, TG-03POWELL 2020
221109LRI	Standard, Background, TG-01, TG-02 POWELL 2020
221110LRI	Standard, Background, TG-01, TG-02 POWELL 2020
221111LRI	Standard, Background, TG-01, TG-02 POWELL 2020
230203LRI	Standard, Background, Bone
230208LRI	Standard, Background
230210LRI	Standard, Background

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Results: AMS Background

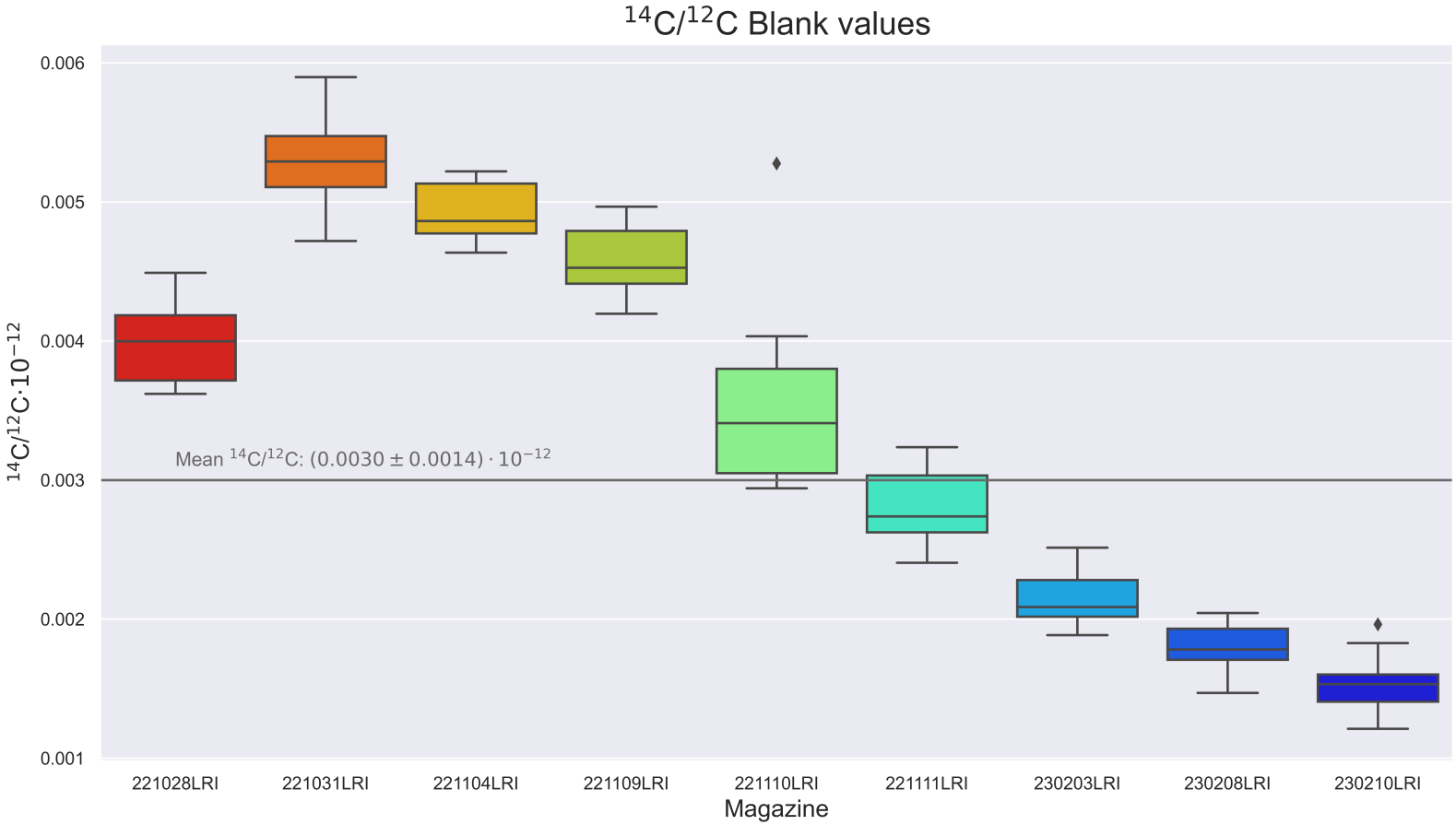

Figure: Evolution of background values over time

Results: Standard values

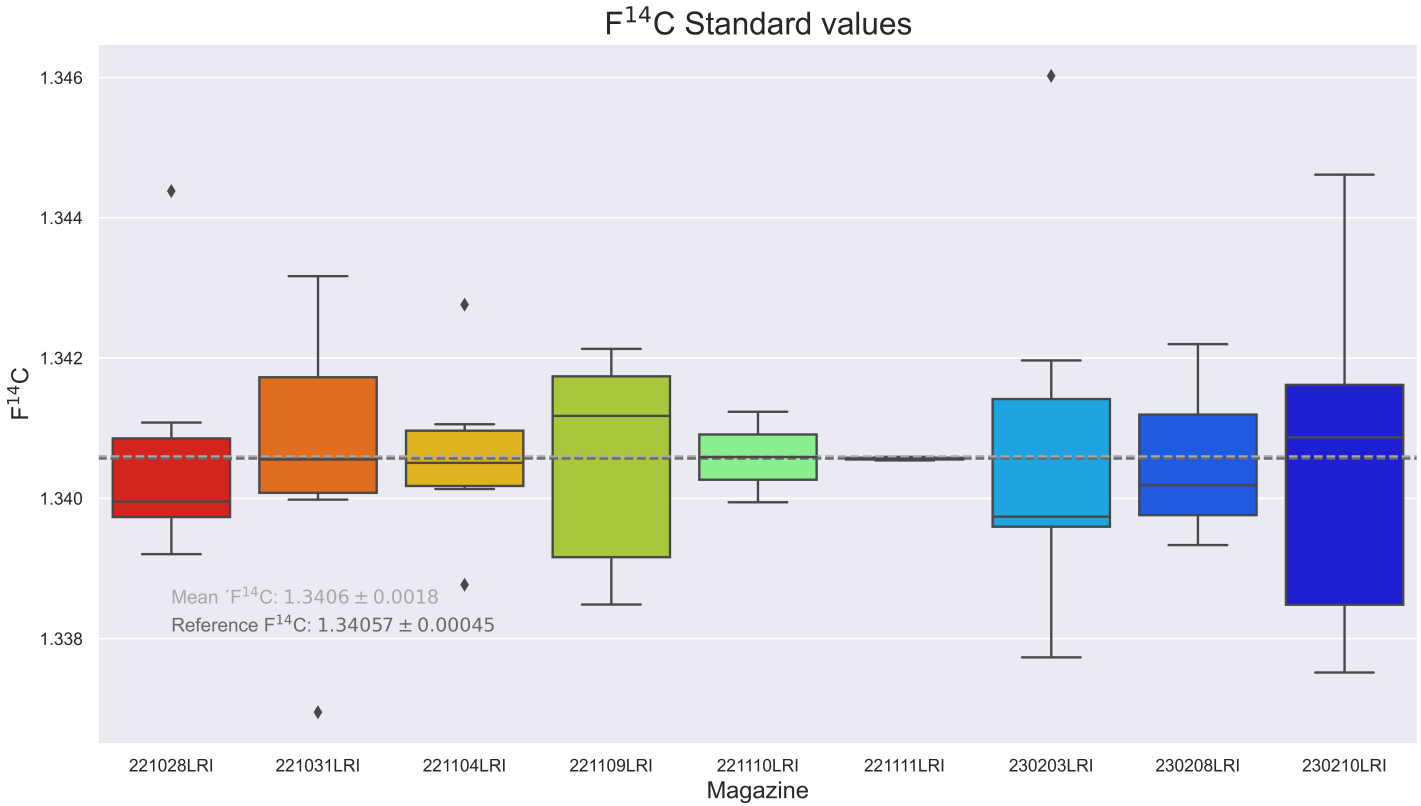

Figure: Evolution of the values of the standard samples over time

Results: Iberian Margin JC089

- Adequate values have been replicated for marine sediment samples dated at the ETH.

Table: Mean values of $F^{14}C$ of the samples analyzed.

Muestra	Tipo	$F^{14}C_{ETH}$	$F^{14}C_{CARBONUS}$
Shale	Sediment	0,0180(10)	0,01751(15)
Swiss Soil	Sediment	1,0660(10)	1,05356(90)
JC089 10 cm	Sediment	0,7381(61)	0,7051(10)
JC089 70 cm	Sediment	0,3302(51)	0,33089(51)
JC089 110 cm	Sediment	0,2153(29)	0,21834(41)

Results: POWELL 2020

- Dating of the TG-01 core POWELL 2020:

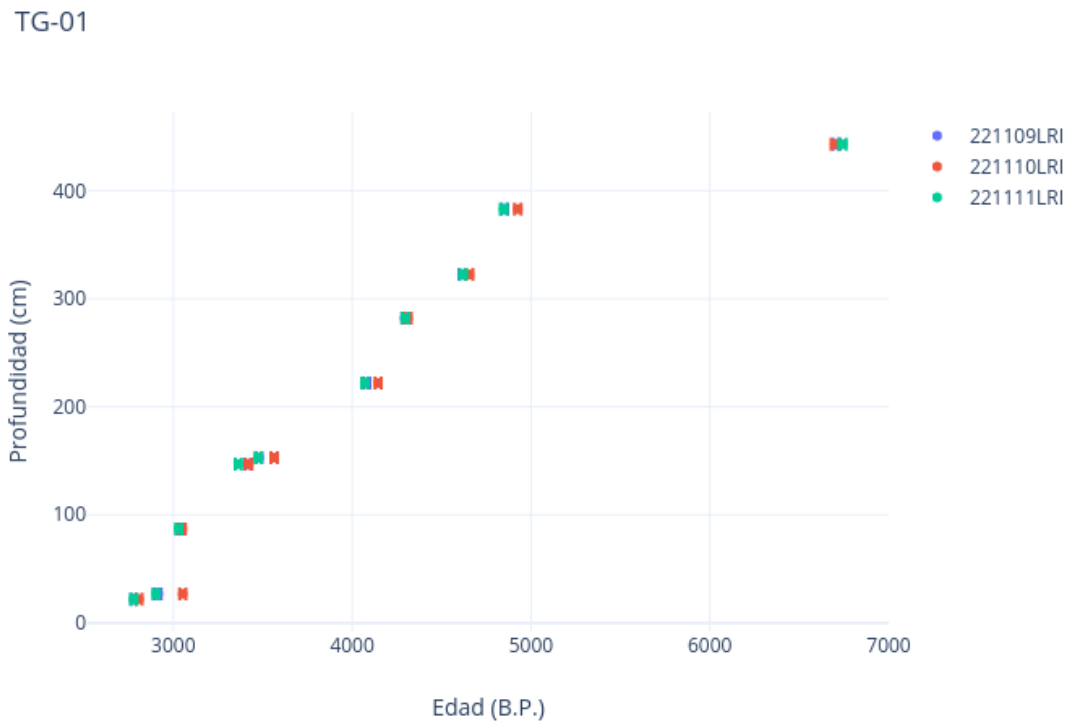

Figure: Results of the dating of core TG-01 from the POWELL 2020.

Results: POWELL 2020

- Dating of the TG-02 core POWELL 2020:

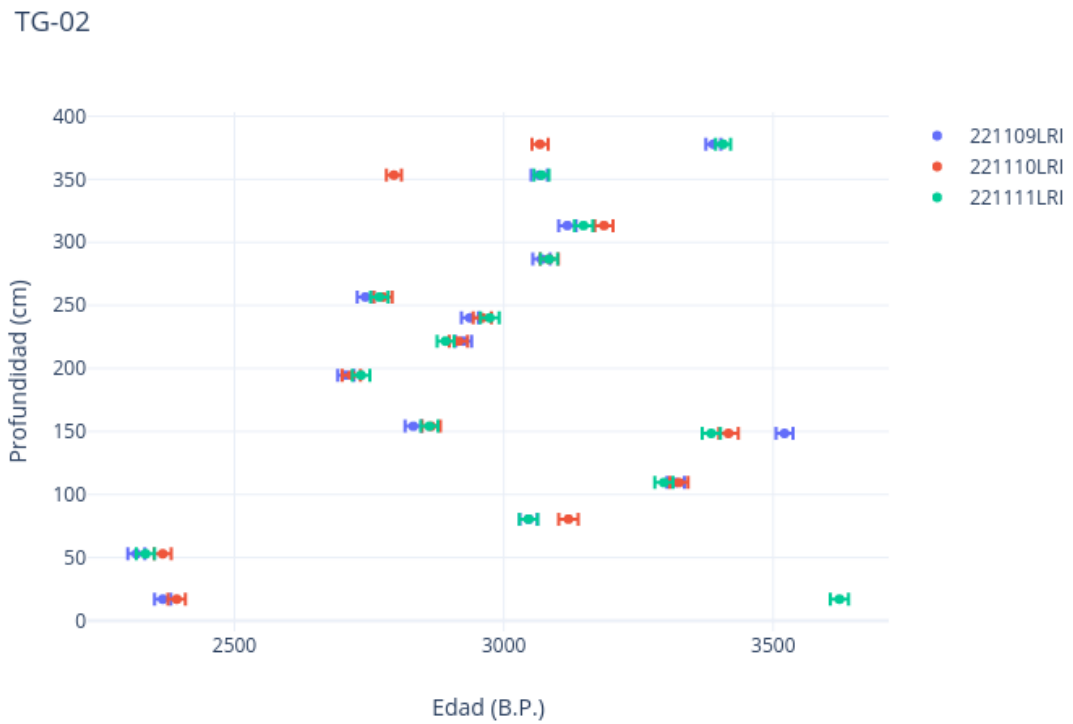

Figure: Results of the dating of core TG-02 from the POWELL 2020.

Results: POWELL 2020

- Dating of the TG-03 core POWELL 2020:

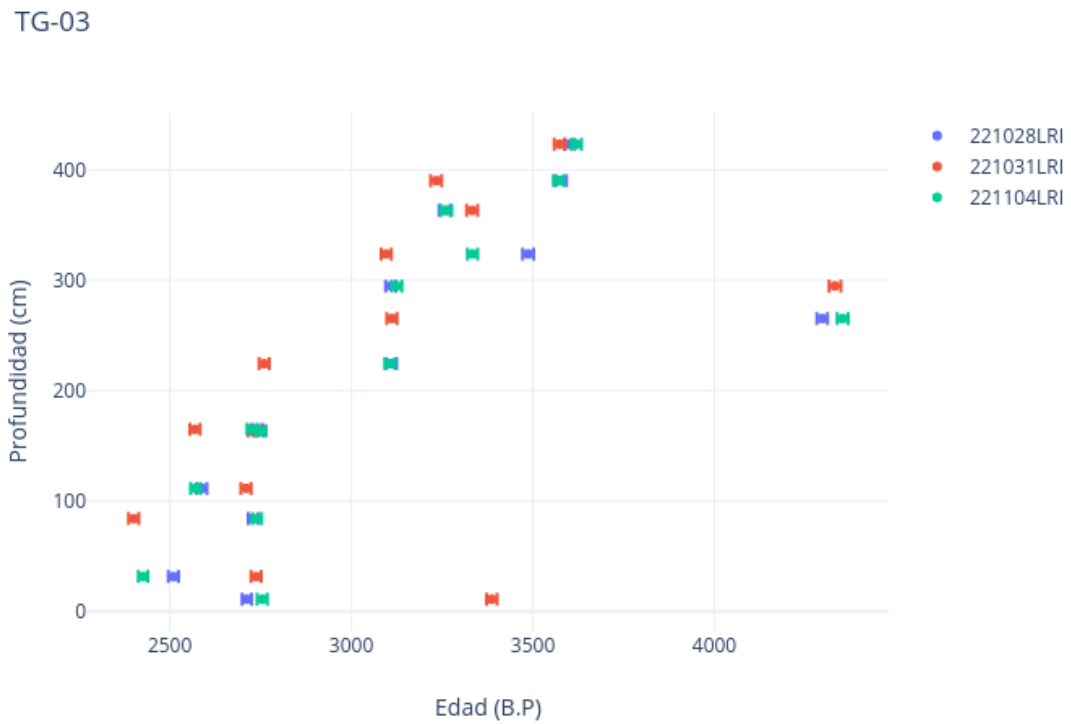

Figure: Results of the dating of core TG-03 from the POWELL 2020.

Results: Bone

- The dating results are consistent with the archaeological record:

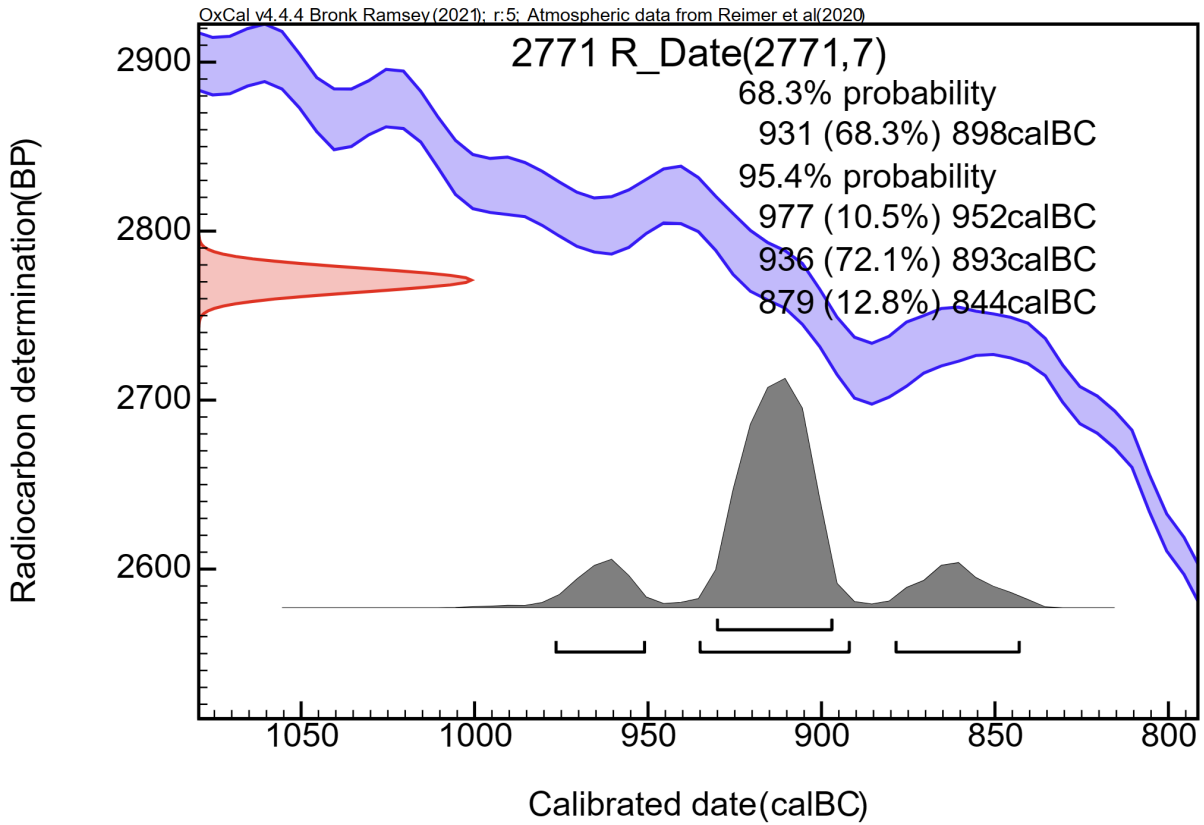

Figure: Calibration curve of the bone with a conventional mean age of $2771(7)\ yr\ B.P.$

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Conclusions

- It has been possible to replicate the appropriate values for standard samples while maintaining low background values.
- The fumigation method has been developed, obtaining comparable results.
- The first dating of samples of unknown age has been achieved.

Future

- Improve background values.
- Repeat sediment measurements from the POWELL 2020 campaign.
- Perform further intercomparison of fumigated samples with the ETH.

Thank you very much for your attention!