Radiocarbon dating of artworks

Ines Krajcar Bronić, Nada Horvatinčić, Jadranka Barešić, Andreja Sironić

Ruđer Bošković Institute, Zagreb

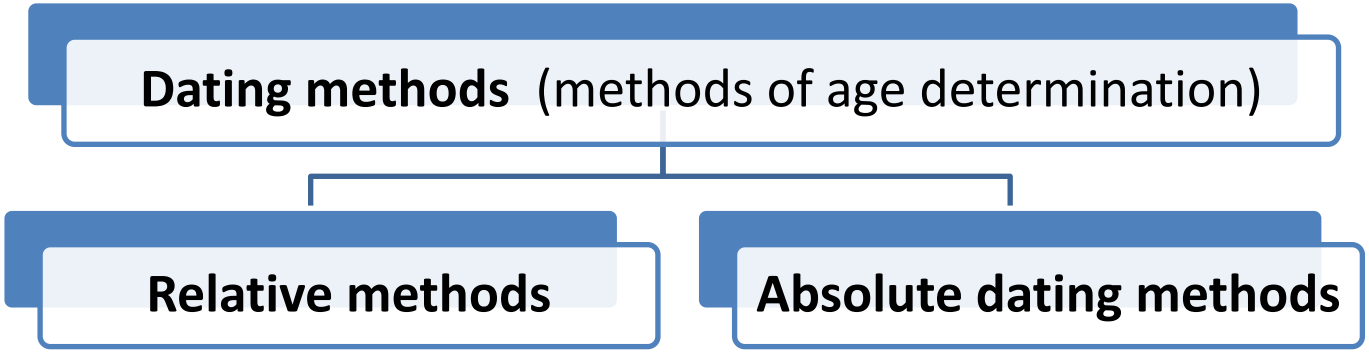
krajcar@irb.hr

SYMPOSIUM CroArtScia 2015
TECHNOLOGICAL INNOVATIONS: ART & SCIENCE

Dating – determination of the age of an object

Absolute dating of object of cultural heritage and art is one of the most important issues in art history studies and in archaeology.

Accurate dating in art history is essential for valuation of original objects of arts, for differentiation between the original works and later imitations and/or frauds and for recognition of reparation and restauration works.



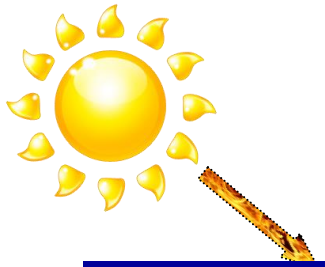
Relative dating provides relative order of past events, without necessarily determining their absolute age.

Absolute dating methods provide the absolute age of artefacts.
In archaeology and art history mostly used methods are **radiocarbon dating** and TL dating, and **dendrochronology**.

relative methods may complement information obtained by absolute dating

Radiocarbon (^{14}C) dating

- one of the most well-known radiometric methods of absolute dating
- it can be applied for dating materials of biogenic origin, such as wood, charcoal, bones, grains, paper, parchment, textile, etc.
- the range of ^{14}C age determination spans from 19th century up to ~60,000 years in the past
- the anthropogenic influence on the natural ^{14}C distribution during 20th century can be used for recognition of frauds



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

O_2

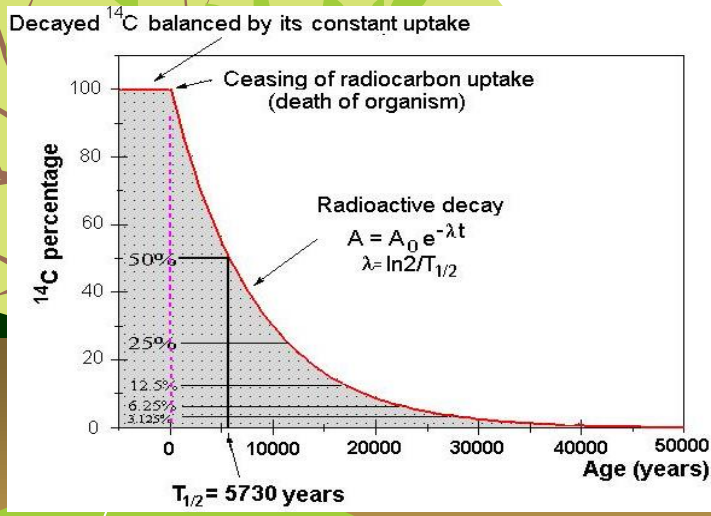
$^{14}CO_2$

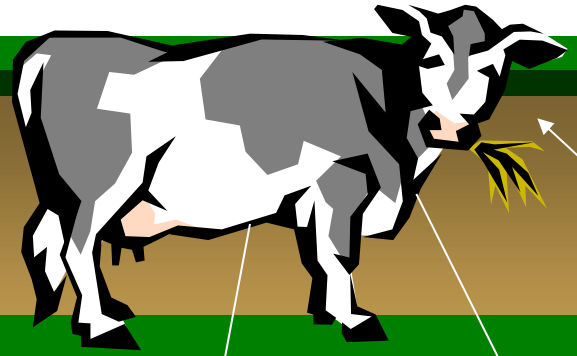
Carbon on Earth

^{12}C: 98.89 %

^{13}C: 1.1 %

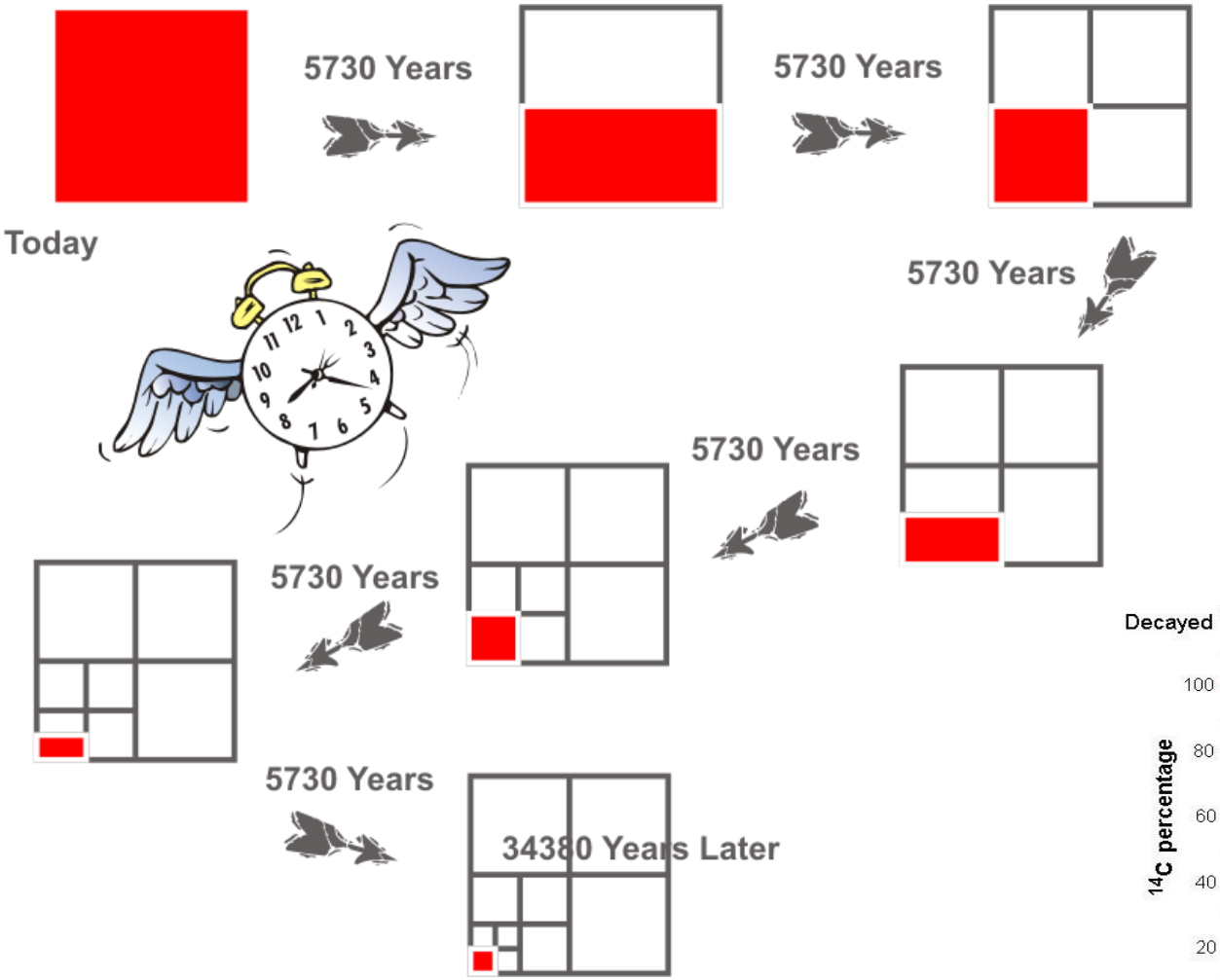
^{14}C: 1.18 x 10^{-10} %



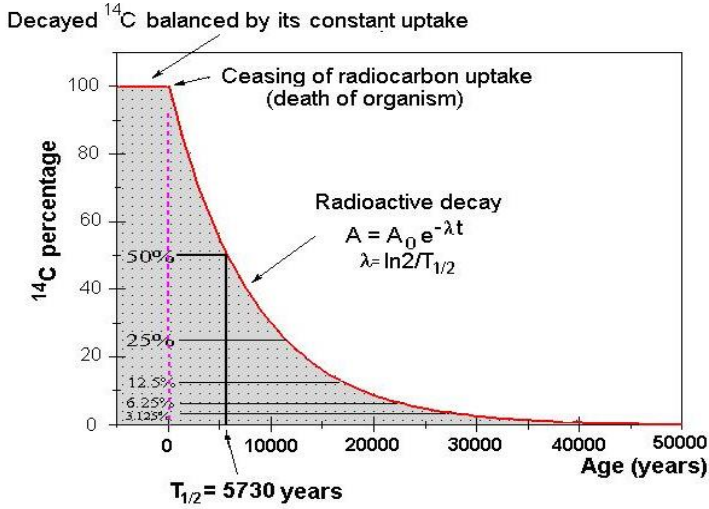


$^{14}C \rightarrow {}^{14}N + e + \bar{\nu}$

^{14}C Decay: a Clock



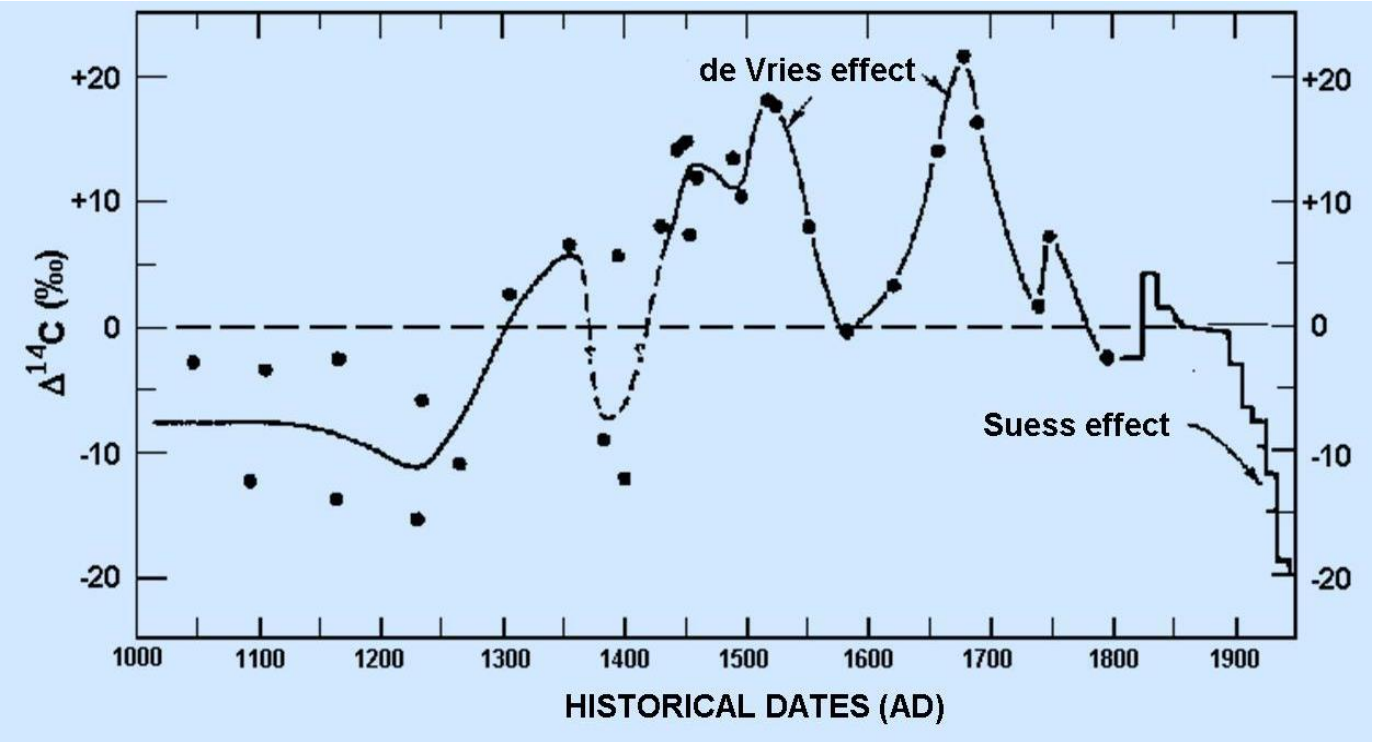
Assuming the ^{14}C level in the atmosphere has been constant, we can calculate how long ago an organism was in equilibrium with the atmosphere (= alive), if we measure the remaining ^{14}C level



Is the assumption of the constant ^{14}C level in the atmosphere correct?

Variations in ^{14}C production produce consistent differences between obtained radiocarbon ages and calendar ages.

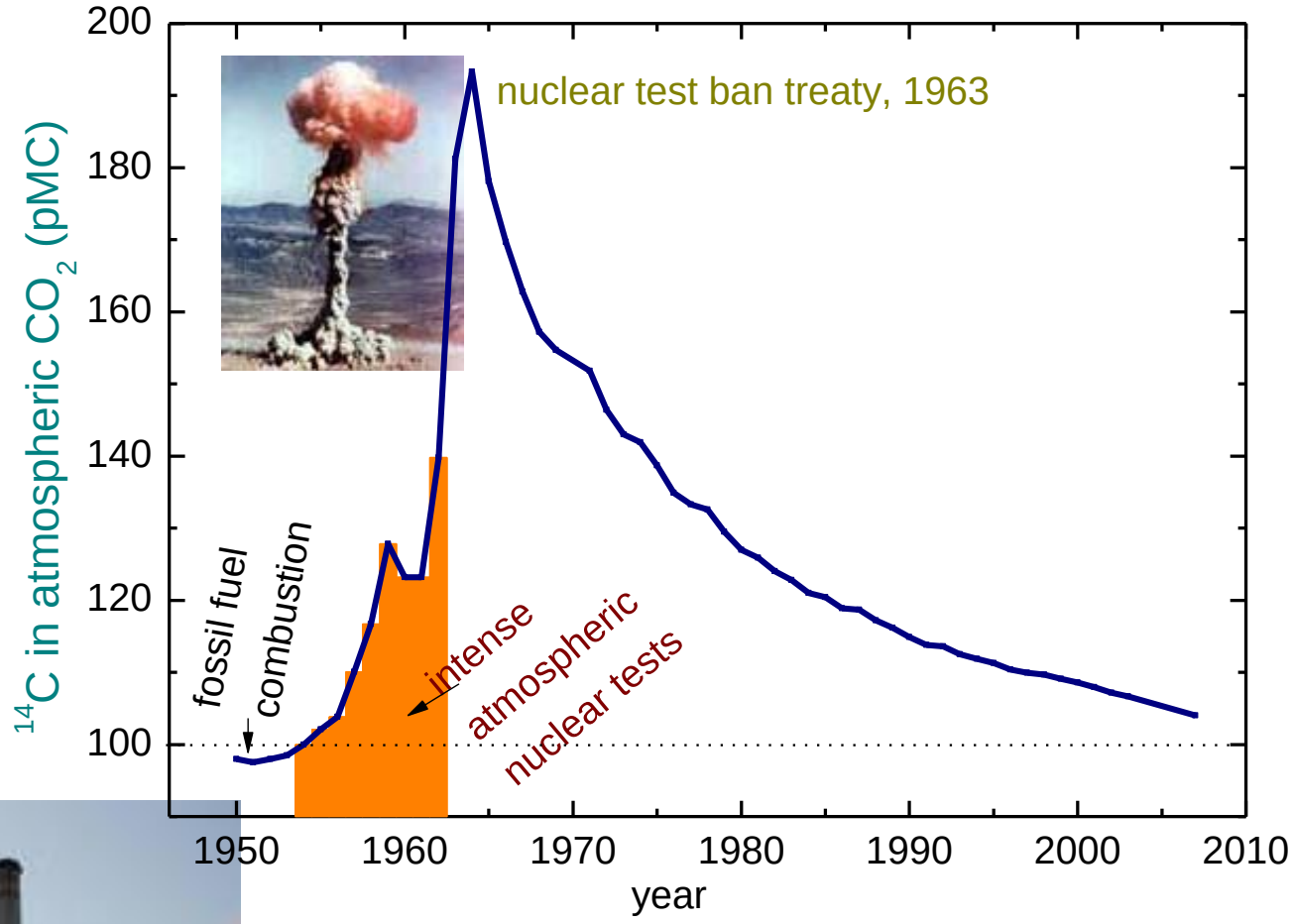
Natural variations caused by geomagnetic and solar modulation of the cosmic-ray flux



Fluctuations in radiocarbon activity of the atmosphere over last 1000 years

Anthropogenic activities

^{14}C in atmospheric CO_2 on the Northern Hemisphere



Techniques

Due to very low natural ^{14}C concentration the radiocarbon dating method requires special techniques for chemical preparation of samples and measurement of ^{14}C.

Particular care has to be taken for sample collection and/or storage as well as during sample pretreatment and chemical preparation.

Preparation of samples

- Extract all carbon from a sample (fractionation)
- All carbon only from the sample (contamination)

All sample pretreatment and preparation techniques, as well as measurement techniques of large efficiency

- **low relative abundance of ^{14}C atoms ($<10^{-10}$ %)**
- **low electron energy** (<156 keV)
- **low activity of** ^{14}C in natural materials, < 13 decays/min/g of carbon

Measurement techniques

Radiometric – number of decays per time (i.e., decay rate) of ^{14}C per mass of carbon

required mass of C: 1 - 5 g

Required mass of samples: 10 - 50 g

*Gas proportional counters (**GPC**)*

*Liquid scintillation counters (**LSC**)*

$^{14}C \rightarrow {}^{14}N + e^- + \nu$ **(156 keV)**

Accelerator Mass Spectrometry (AMS) – number of ^{14}C atoms is counted, together with the number of ^{12}C and ^{13}C

Required mass: <2 mg C, <1 g sample

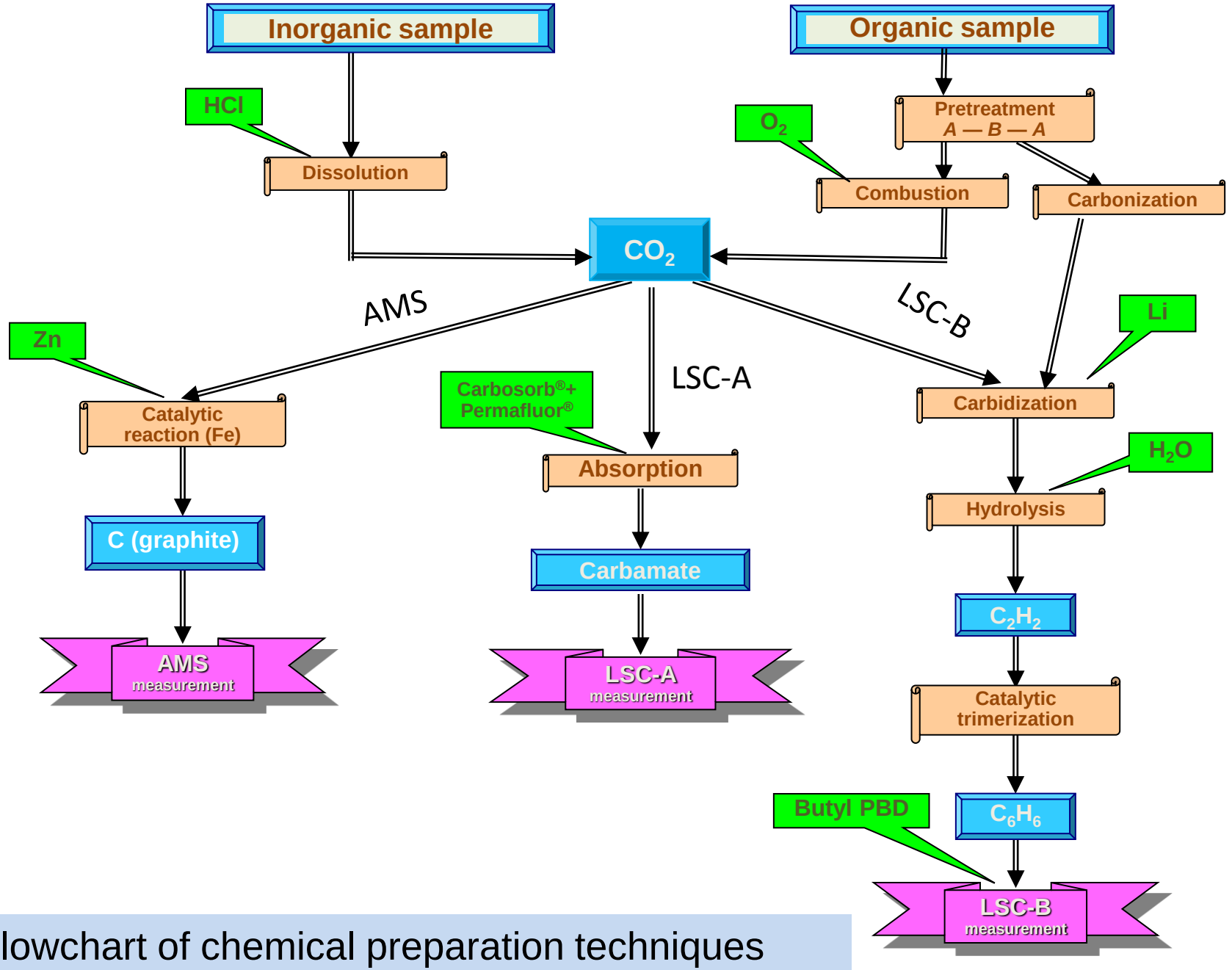
The main advantage of the AMS ^{14}C method is the possibility of measurement of very small amount of samples, but also a better accuracy is obtained

Radiocarbon Laboratory at the R. Bošković Institute

Laboratory for Low-level Radioactivity at the Ruđer Bošković Institute is the only radiocarbon laboratory in Croatia and in wider area, and has a long experience in radiocarbon dating (since 1968).

Two measurement techniques for ^{14}C dating are used:

1) sample preparation in form of benzene and measurement of ^{14}C activity by liquid scintillation counter (LSC) (Horvatinčić et al., 2004)
2) sample preparation in form of elemental carbon (graphite) and measurement of ^{14}C atoms by accelerator mass spectrometry (AMS) (Krajcar Bronić et al., 2010).
3) For monitoring purposes – absorption of CO_2
4) Determination of biogenic fraction in fuels

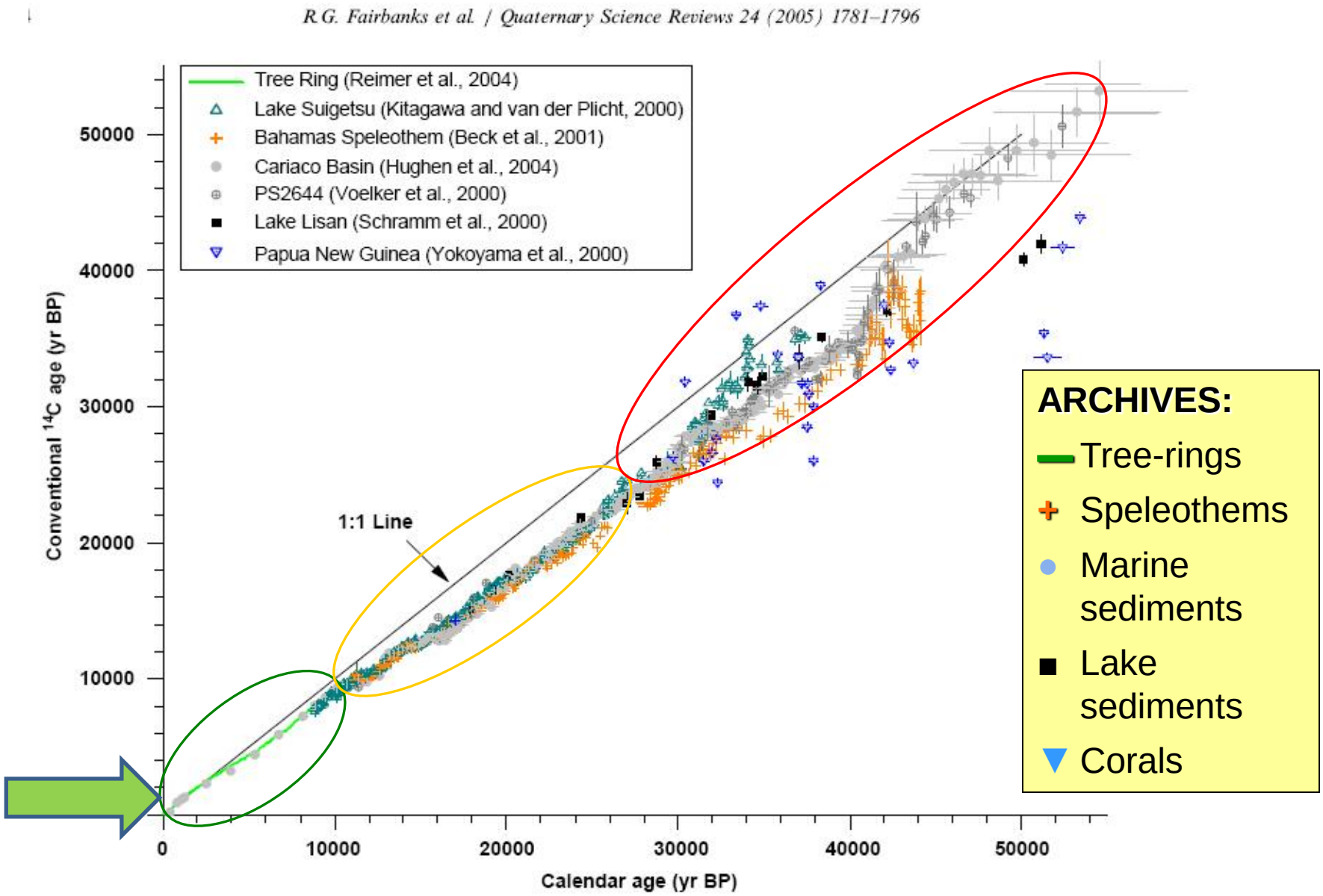


Flowchart of chemical preparation techniques for **AMS**, **LSC-A, LSC-B** methods

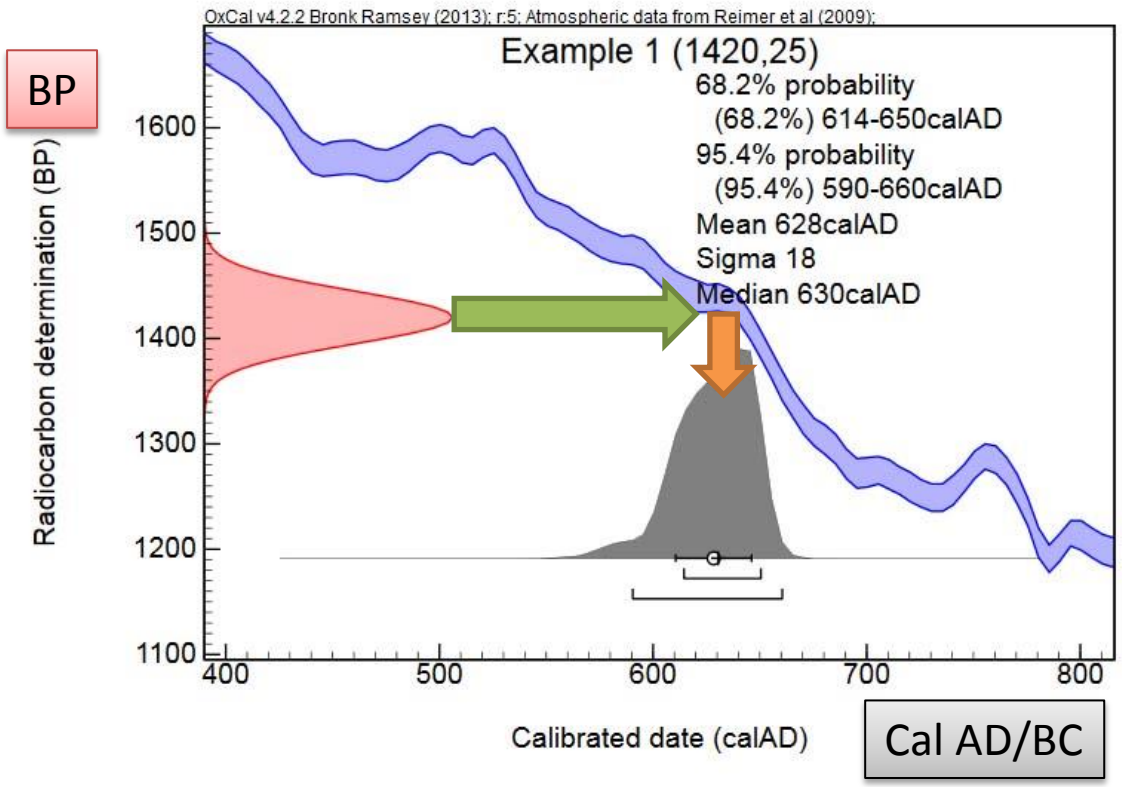
What is the results of the measurement?

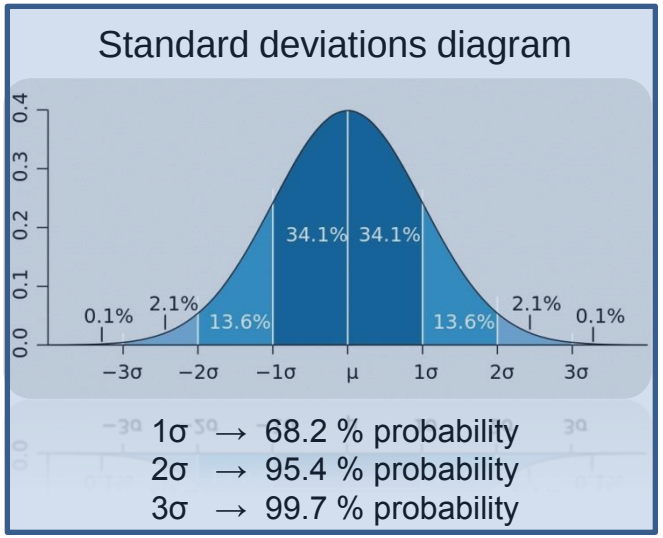
- **conventional radiocarbon age of the sample**, expressed in years Before Present (BP), where 0 BP = 1950 AD
- conventional ^{14}C years do not directly equate to calendar years because atmospheric ^{14}C concentration varies through time due to changes in the production rate
- a **calibration is required** to convert the conventional radiocarbon age to the calendar age
- accurate and precise **calibration curves** should be based on absolutely dated record that has carbon incorporated directly from the atmosphere at the time of formation

Radiocarbon calibration curves



Presentation of calibrated data





Example of a single calibrated date

Conventional radiocarbon ages (ordinate) in years BP are represented as the Gaussian curve with mean and standard deviation (uncertainty) being 1420 ± 25. Calibrated values, in calendar years, are obtained by transferring the values on ordinate over calibration curve to the abscissa. Results can be presented by 1σ, 2σ or 3σ probabilities and by mean or median values.

Several cases of ^{14}C dating of various objects of arts will be presented here.

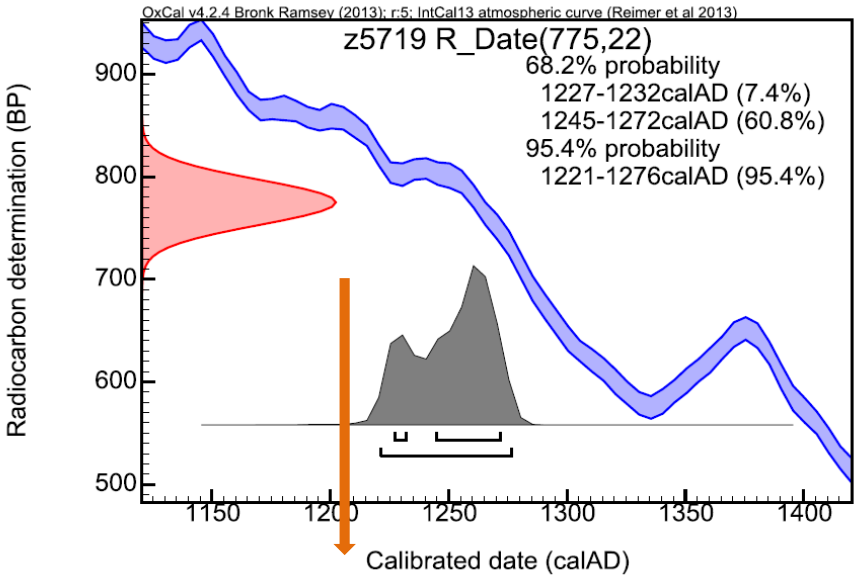
How to interprete radiocarbon dates and calibrated ages?

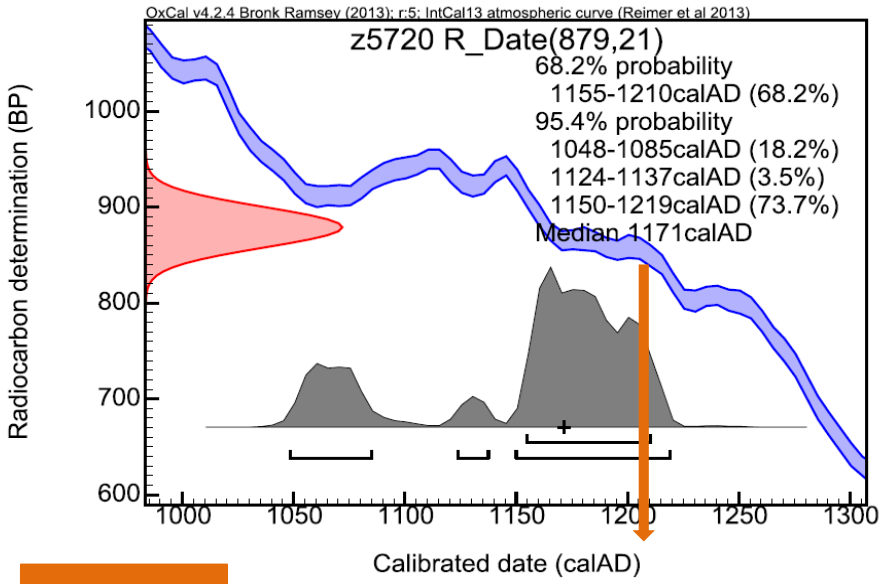
One has to keep in mind that radiocarbon dating gives the **age of material** (e.g., wood) and not the time of the creation of the art work, and that the creation of the art work cannot precede the formation of the material.

Case 1. a wooden object

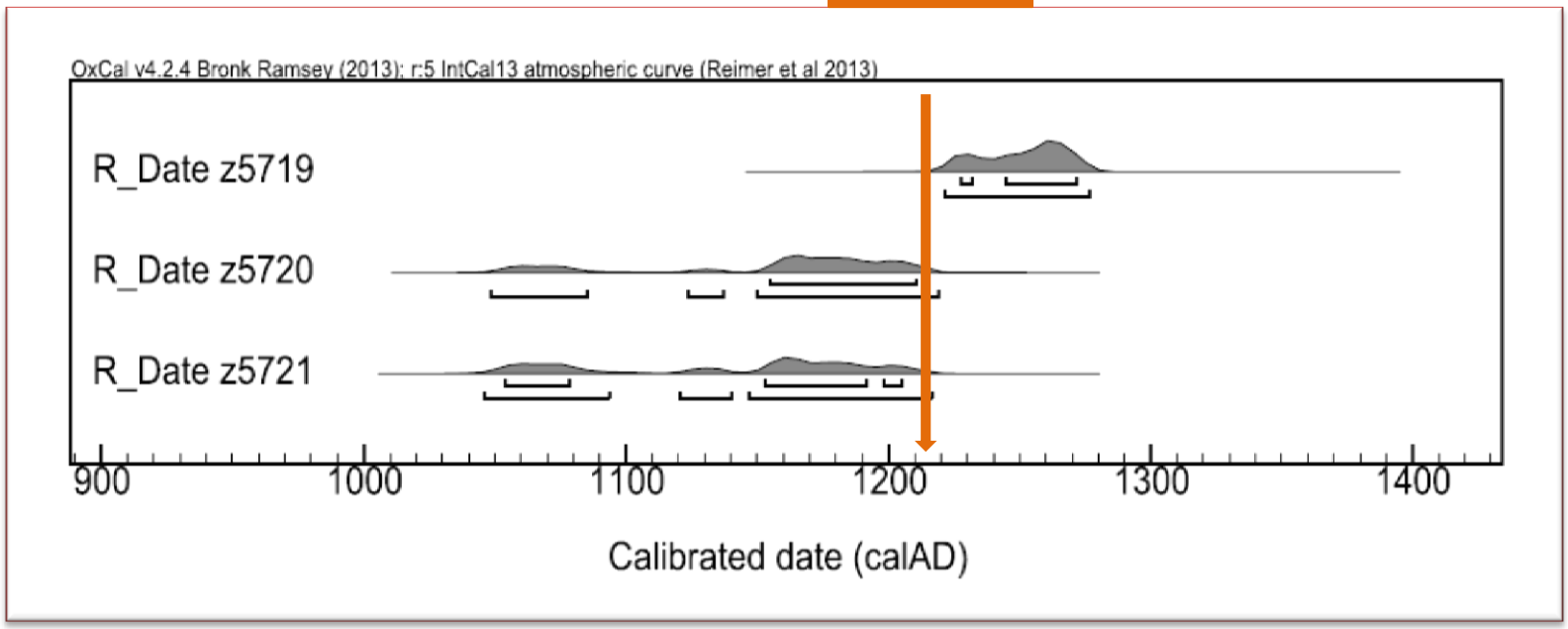
Expected date: 1214 AD
3 pieces of wood dated (AMS)

Z	A	Sample name	$\delta^{13}C$ **(‰)**	$a^{14}C$ (pMC)	**Conventional ^{14}C age (BP)**	**Calibrated age (calAD)**
5719	1105	Sample #1, walnut tree	-23.6	90.80±0.25	**775 ± 22**	**1245-1272 60.8%** 1227-1232 7.4% median 1254
5720	1107	Sample #2, walnut tree	-24.3	89.63±0.24	**879 ± 21**	**1155-1210 68.2%** median 1171
5721	1108	Sample #3, oak tree	-27.1	89.54±0.24	**887 ± 21**	**1054-1078 63.4%** 1198-1205 4.8% median 1159


OxCal v4.2.4 Bronk Ramsey (2013); r:5; IntCal13 atmospheric curve (Reimer et al 2013)
z5719 R_Date(775,22)
68.2% probability
1227-1232calAD (7.4%)
1245-1272calAD (60.8%)
95.4% probability
1221-1276calAD (95.4%)
Radiocarbon determination (BP)
Calibrated date (calAD)


OxCal v4.2.4 Bronk Ramsey (2013); r:5; IntCal13 atmospheric curve (Reimer et al 2013)
z5720 R_Date(879,21)
68.2% probability
1155-1210calAD (68.2%)
95.4% probability
1048-1085calAD (18.2%)
1124-1137calAD (3.5%)
1150-1219calAD (73.7%)
Median 1171calAD
Radiocarbon determination (BP)
Calibrated date (calAD)

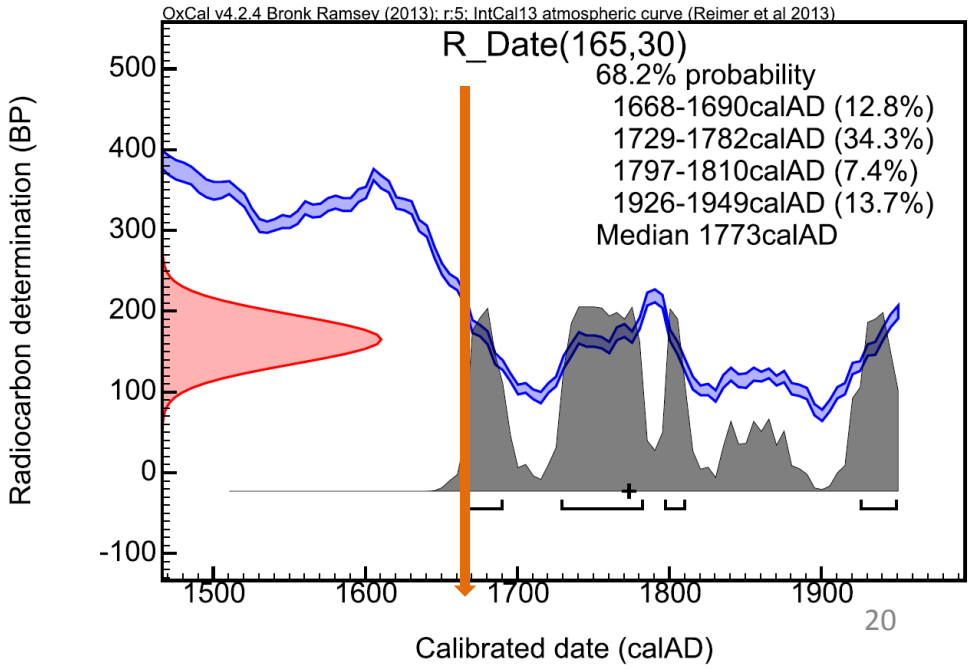
1214 AD


OxCal v4.2.4 Bronk Ramsey (2013); r:5 IntCal13 atmospheric curve (Reimer et al 2013)
R_Date z5719
R_Date z5720
R_Date z5721
Calibrated date (calAD)

Case 2. a violine

Assumed: Jacobus Steiner, 1665

A peg was ^{14}C dated (AMS)



Case 3. Ahd-Namah

Fojnica is a town and municipality in central Bosnia and Herzegovina, located west of the capital Sarajevo. The most important cultural site in Fojnica is the Holy Spirit Franciscan Monastery which houses an important part of the nation's cultural heritage, maintained by the Franciscan Province of Bosna Srebrena.

The Franciscan monastery in Fojnica has a large library of philosophical and theological works printed from the 16th to the 19th centuries, with some dating back to 1481.

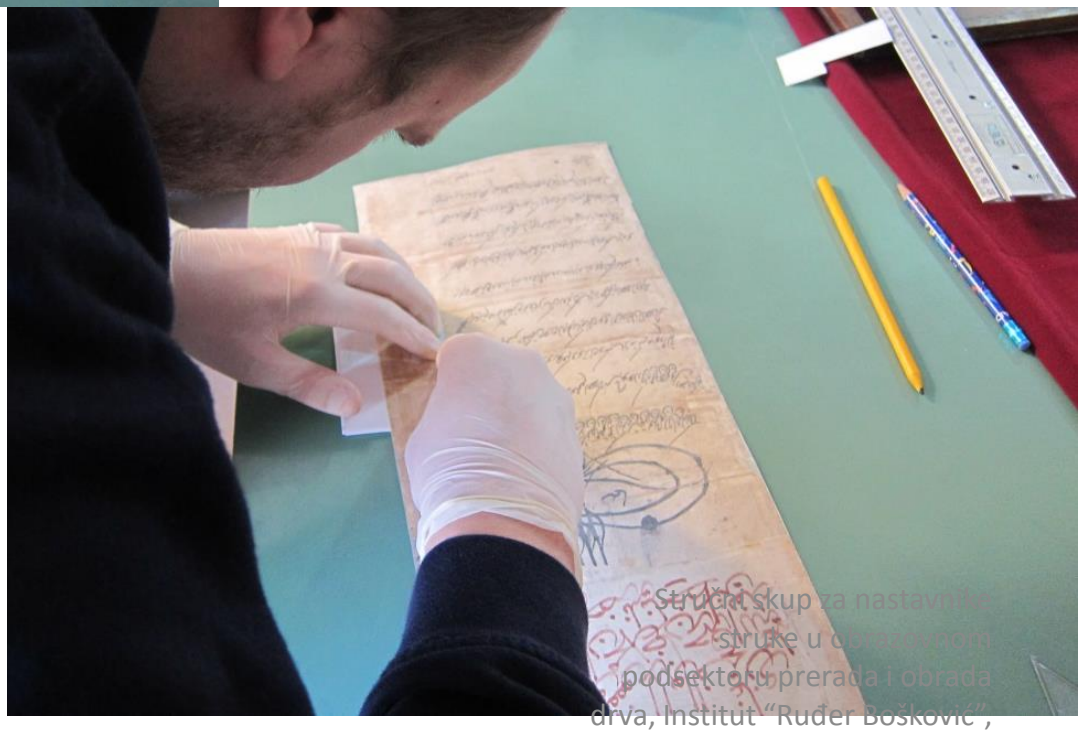
The monastery's museum collections hold the Ahd-Namah (the Order) of Sultan Mehmed II the Conqueror (1463 AD) guaranteeing security and freedom to the Franciscans. This document allowed the Franciscans of the day to preach freely among the Catholics in BiH, which in turn enabled the preservation of Bosnian Catholicism through the centuries.

In 2013 celebration of the 550th anniversary

Ahd-Namah and mantel from the museum collection in Fojnica Monastery (Ottoman Empire, Sultan Mehmed II, 1463 AD)

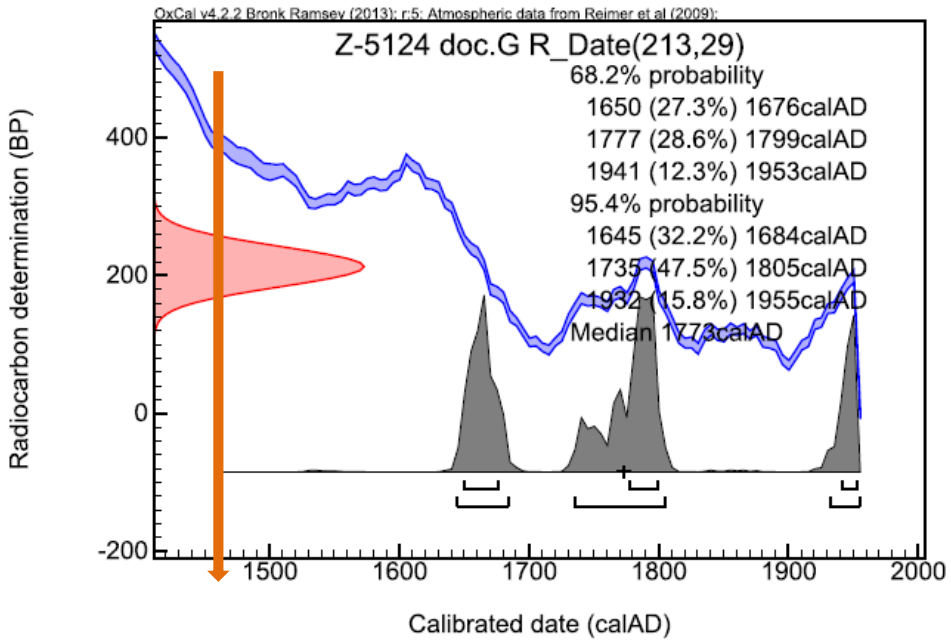
Paper sample taken from upper part of Ahd-Namah (sample #1)

Paper sample taken from lower part of Ahd-Namah (#2)



Sampling of linen of mantel from the same period (Fra Anđelo Zvizdović)

^{14}C age of Ahd-Namah

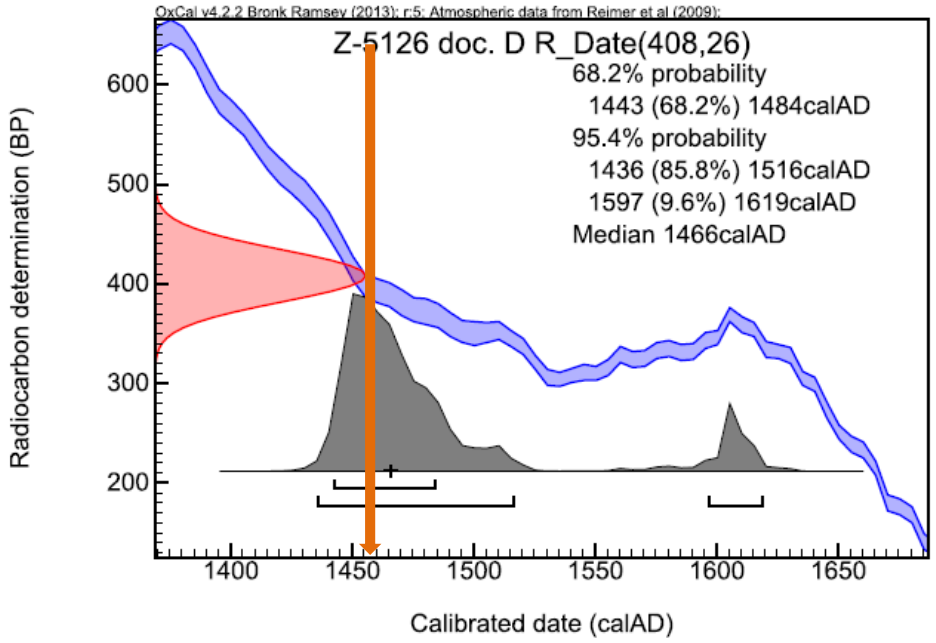


Upper part (#1)

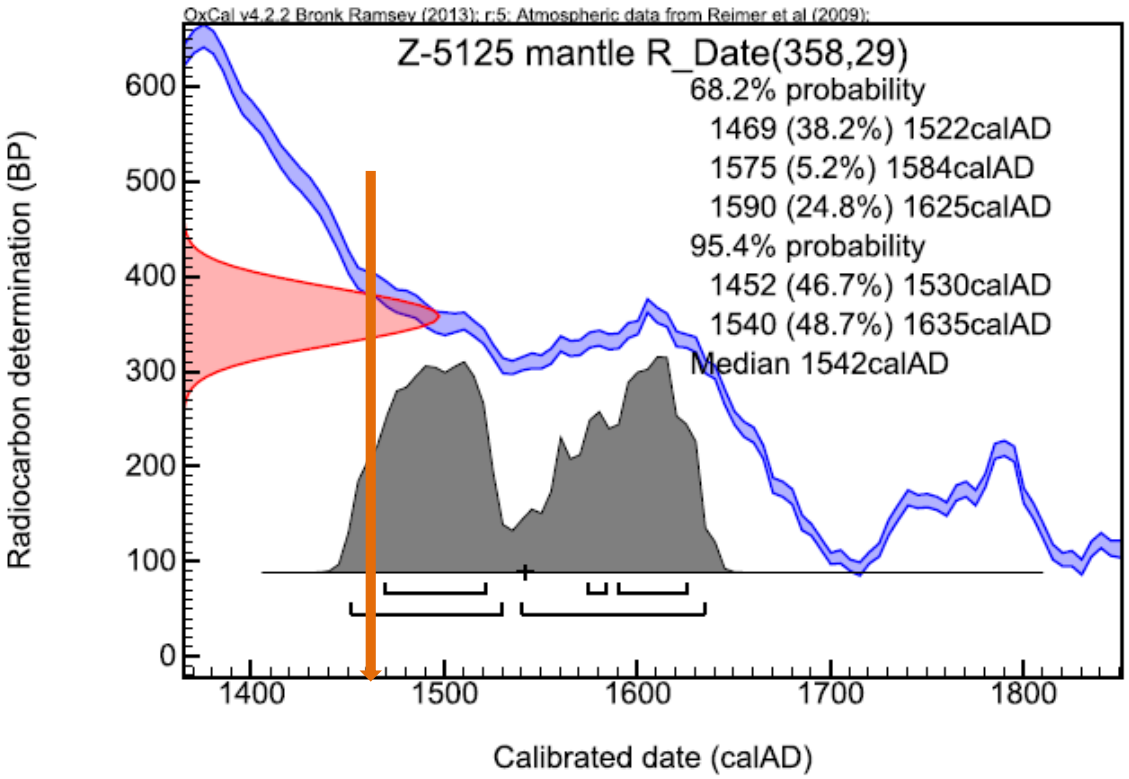
^{14}C conventional age (BP)	**215 ± 30**
Calibrated age (cal AD)	1650 – 1799 (55.9%)
Median cal AD	1773

Lower part (#2)

^{14}C conventional age (yr BP)	**410 ± 25**
Calibrated age (cal AD)	1443 – 1484 (68.2%)
Median cal AD	1466



^{14}C age of linen of mantel



^{14}C conventional age (yr BP)	**360 ± 30**
Calibrated age (cal AD)	1469 – 1625 (68,2%)
Median cal AD	1542

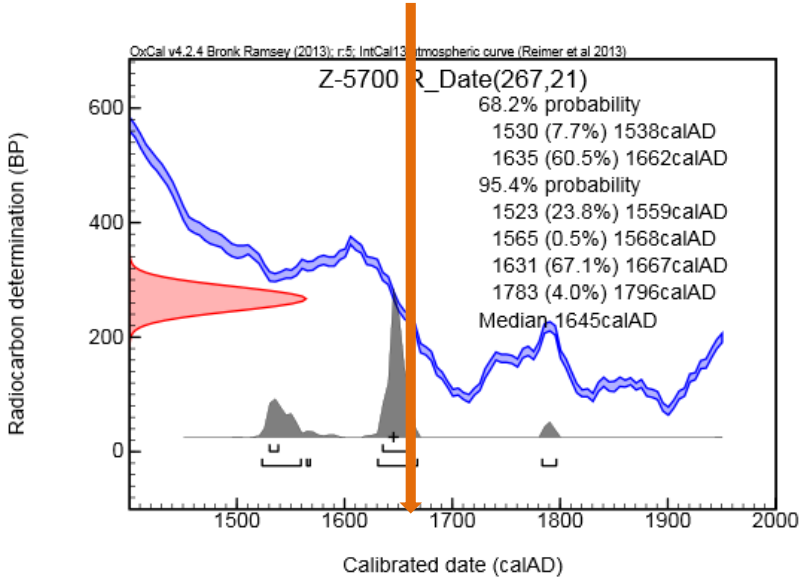
Case 4. Fojnica Armorial

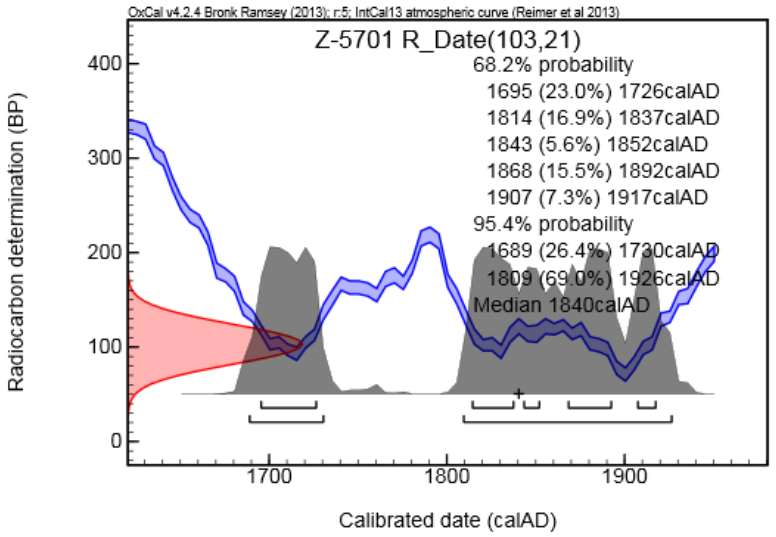
Fojnički grbovnik ***Fojnica Armorial***
an early modern roll of arms including heraldry of South Slavic history.
The manuscript is an important source of the classical heraldry of the Balkans peninsula.
The manuscript contains a total of 139 coats of arms.

Various estimates of its ages (from 1340 AD to 18th cent.)
Most probably dated to in between 1675 and 1688, i.e. in the context of the revolts against Ottoman rule during the Great Turkish War.

^{14}C dating – 2 samples, paper, AMS

ID	Sample name	Conventional ^{14}C age (BP)	$\delta^{13}C$ (‰)	Calibrated age (cal AD)	median cal AD
Z-5700 A1079	Papir (thick), #1	270 ± 20	-25,6	1635 – 1662 (60,5%)	1645
Z-5701 A1080	Papir (thin), #2	105 ± 20	-24,9	1695 – 1917 (68,2%)	1840





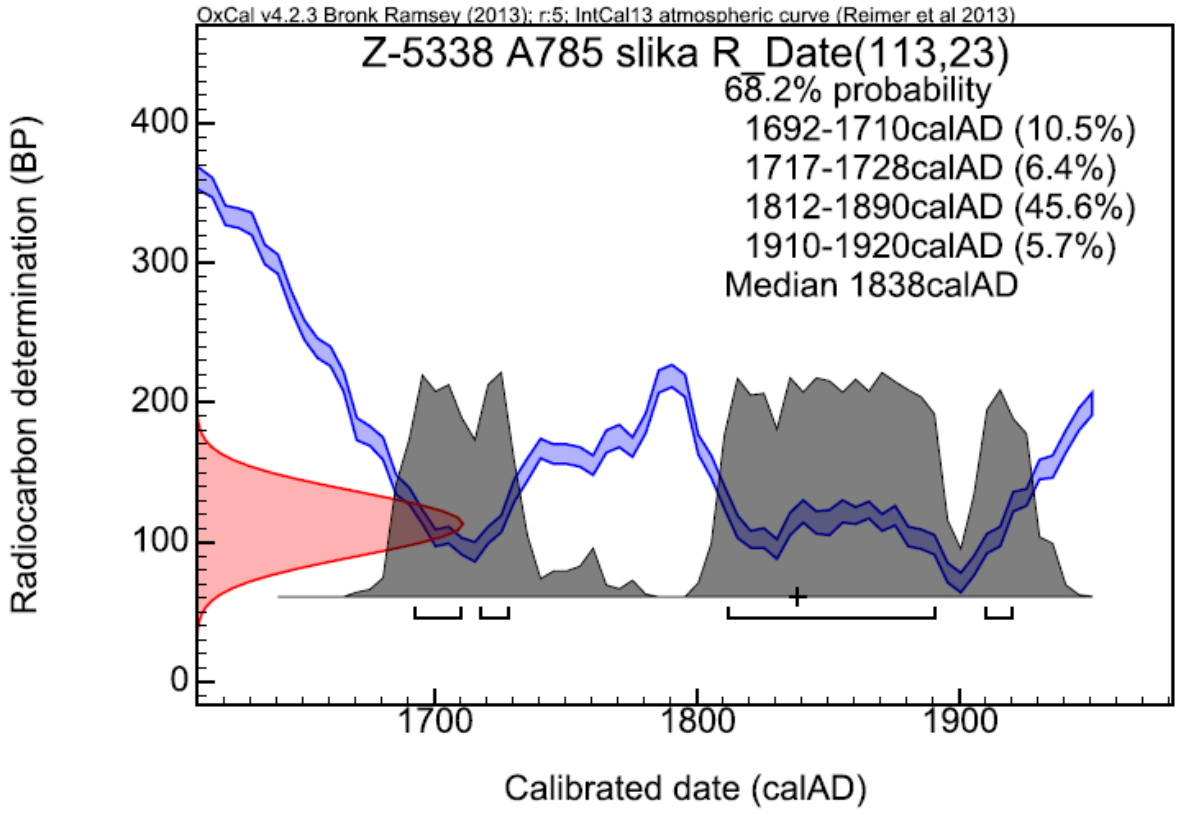
Confirmed hypothesis for the time of origin (17th century)

Case 4. painting

MILAN STEINER (1984 – 1918)

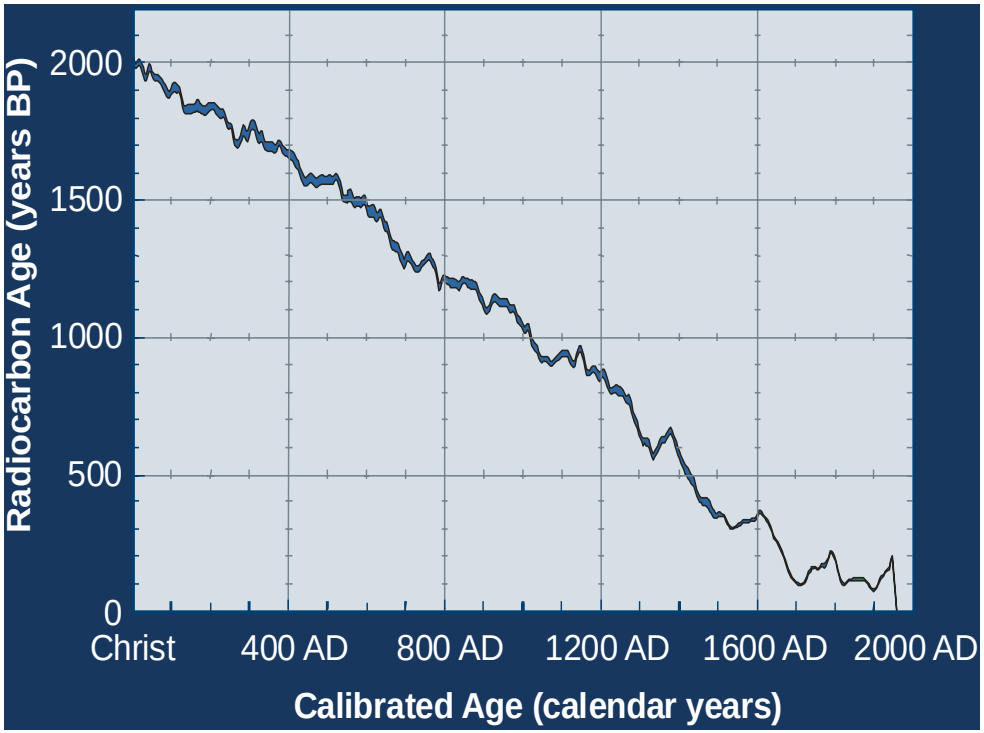
Was he the author of the painting?

The result support the hypothesis, or at least does not contradict it



Radiocarbon dating – Summary

1. Constant production of ^{14}C during last 60 000 years (calibration!)



2. Uniform distribution of ^{14}C in the biosphere (stationary, well-mixed reservoirs)
   – $\delta^{13}C$ normalization

3. Origin of carbon in a sample known („closed system”) (initial activity, contamination...)

Results

Results of radiocarbon measurements expressed as

BP

Conventional radiocarbon age

Years BP, 0 BP = 1950 AD

$\delta^{13}C$ normalization, Libby half-life 5568 yr

cal BC/AD

Calibrated age

Cal BC, Cal AD, probabilities and ranges

Calibration by common software

pMC

$F^{14}C$

Relative specific activity

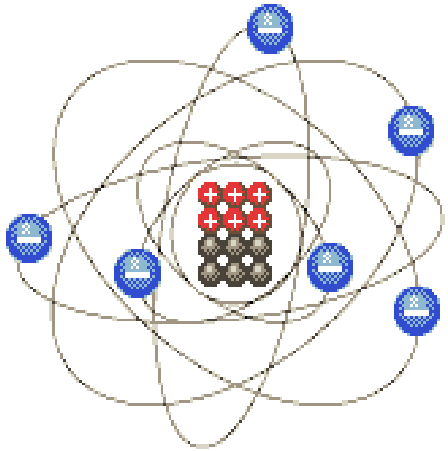
(more often in other applications)

pMC, permille, Fraction….

CONCLUSIONS

- Radiocarbon dating gives the age of material (e.g., wood, canvas… - the material of biogenic origin) and not the time of the creation of the art work - the creation of the art work cannot precede the formation of the material
- Radiocarbon dating cannot give a single year – a range of years is obtained with a certain probability, the width of the range depends on the measurement uncertainty and on the shape of the calibration curve
- Interpretation of results should be performed in close collaboration of art historian and radiocarbon specialists

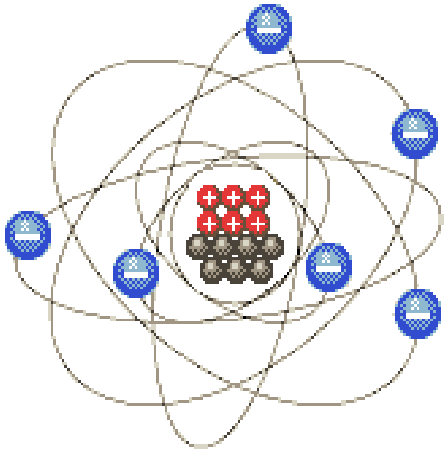
Carbon isotopes



^{12}C

98.89 %

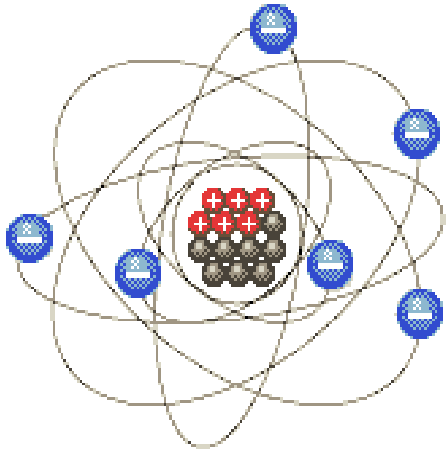
p = n = 6



^{13}C

1.11 %

n = 7



^{14}C

10^{-10} %

n = 8

$T_{1/2}$ = 5730 y

Comparison of ^{14}C AMS and LSC techniques at the Ruđer Bošković Institute

	^{14}C AMS	^{14}C LSC
mass of C in sample / g	$3.5 \cdot 10^{-3}$	4-5 (2.5)
form of prepared sample	graphite (+Fe)	benzene
Mass of prepared sample / g	$1.5 \cdot 10^{-3}$	4
Measurement accuracy / pMC	0.3	0.5
Detection limit / year BP	56 200	55 000
Time of measurement	<30 minutes	24 hours
No. of prepared samples per week	16	5