

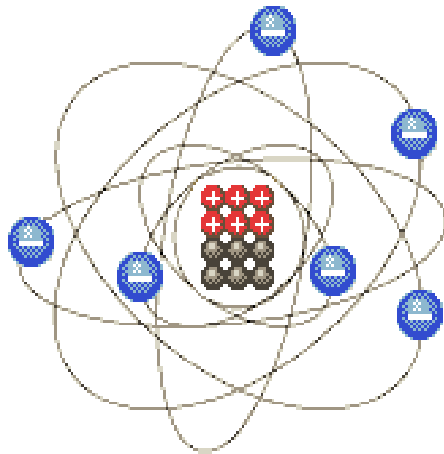
Određivanje starosti metodom ^{14}C

1. Uvod i primjer datiranja

Ines KRAJCAR BRONIĆ
krajcar@irb.hr

- ^{14}C metoda – osnove
- Mjerne tehnike
- Laboratorij IRB Zagreb
- Primjene - primjer

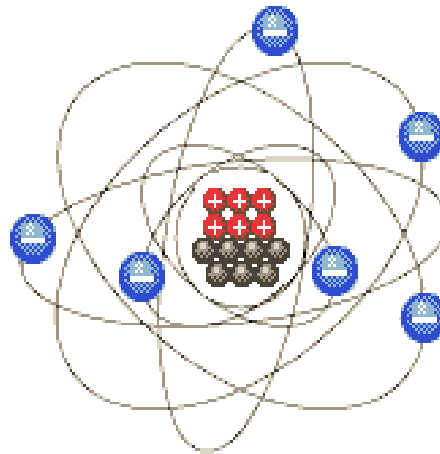
Izotopi ugljika



^{12}C

98.89 %

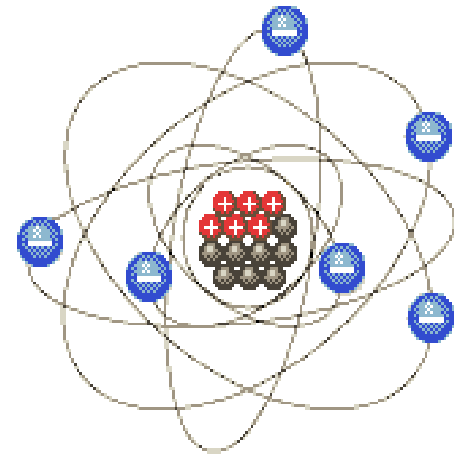
$p = n = 6$



^{13}C

1.11 %

$n = 7$



^{14}C

10^{-10} %

$n = 8$

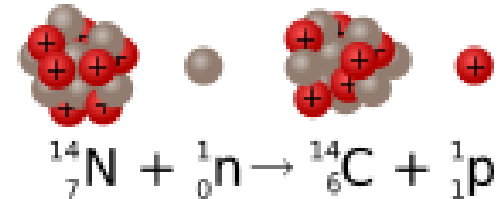
$T_{1/2} = 5730 \text{ y}$

Nastajanje ^{14}C (produkcija)

Kozmogeni i antropogeni izotop/radionuklid

Kozmogeni ^{14}C – prirodna produkcija

interakcija neutrona iz kozmičkog zračenja s ^{14}N



Produkcija 1.4 - 1.54 PBq/yr – nije jednolika zbog promjenjivog intenziteta kozmičkog zračenja, 11-godišnjeg sunčevog ciklusa, promjene zemljina magnetskog polja ...

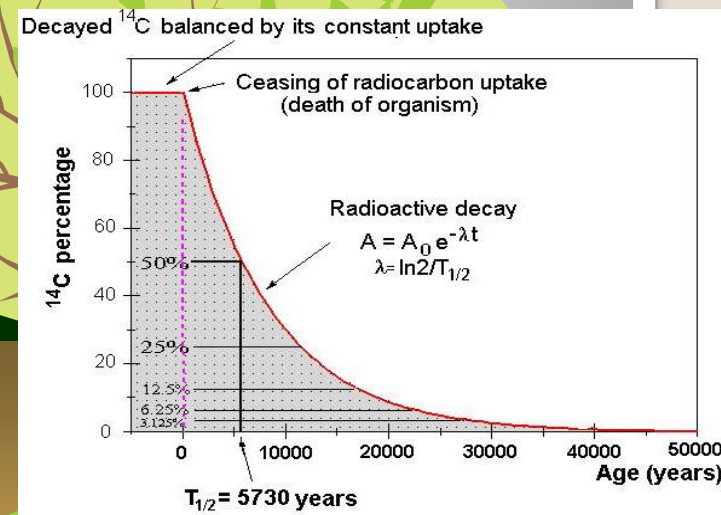
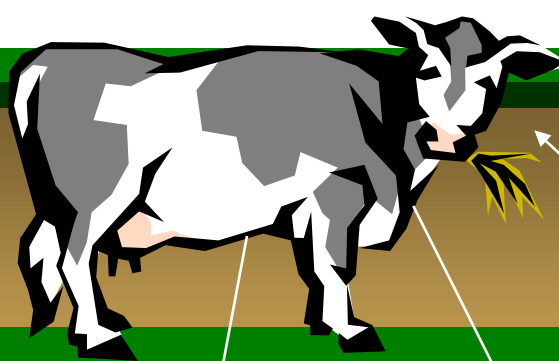
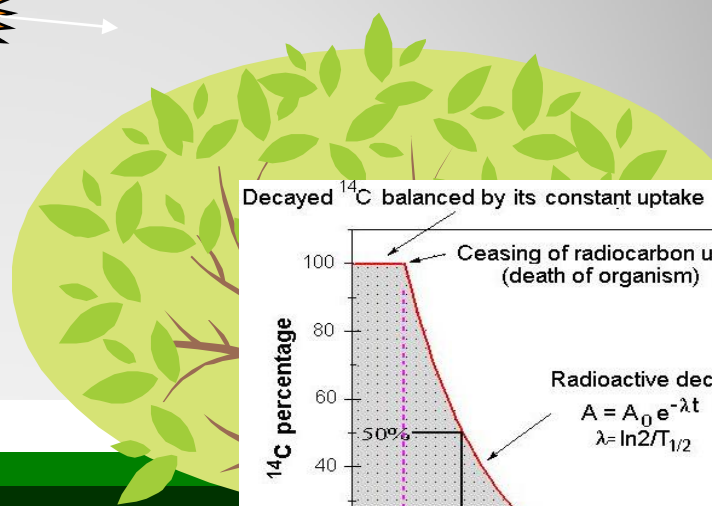
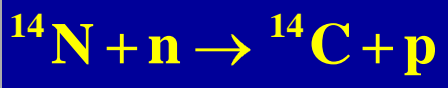
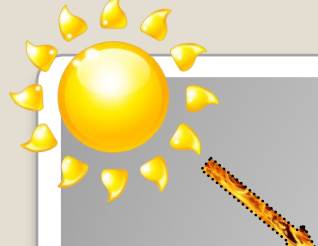
| | |
|-------------------------------|---|
| U Zemljinoj atmosferi | oko 220 PBq „prirodnog“ ^{14}C |
| Terestrijalni ^{14}C | oko 10000 PBq |

Carbon on Earth

^{12}C : 98.89 %

^{13}C : 1.1 %

^{14}C : 1.18×10^{-10} %



- Antropogeno

- „bomb” ^{14}C

- nuklearne elektrane

- drugi nuklearni objekti

- Fosilna goriva – razrjeđenje ^{14}C

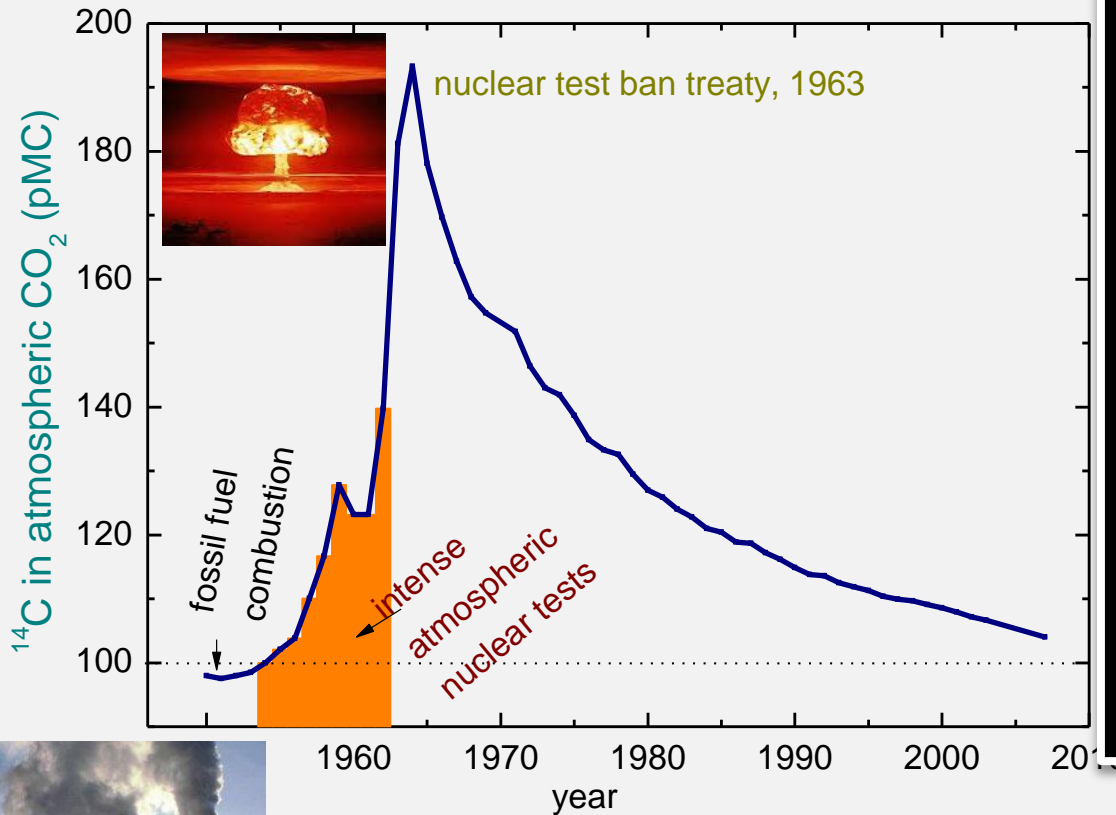
Nastaje interakcijama neutrona emitiranih u
atmosferskim nuklearnim eksplozijama

input 213 – 315 PBq,

udvostručena atm. specifična aktivnost ^{14}C

1963, nakon toga – pad

Anthropogenic ^{14}C

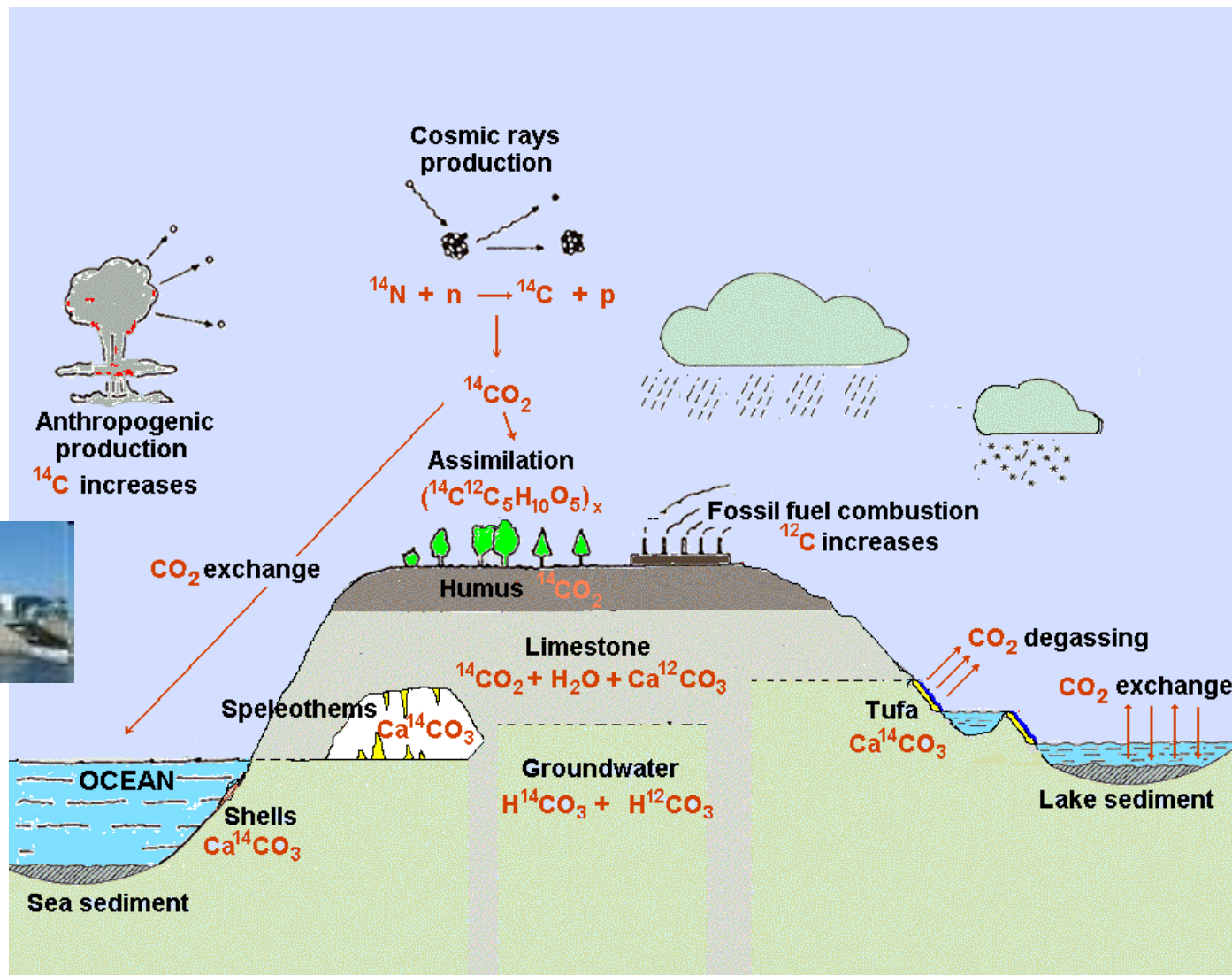


Anthropogenic activities disturbed the natural distribution of ^{14}C in the atmosphere through fossil fuel combustion (increasing of ^{12}C compared to ^{14}C) and atmospheric bomb tests (doubling the natural atmospheric ^{14}C activity in 1960-ties).

The „bomb-peak“ has served as an invaluable tracer to get insight into the global carbon cycle on the decadal time scale.



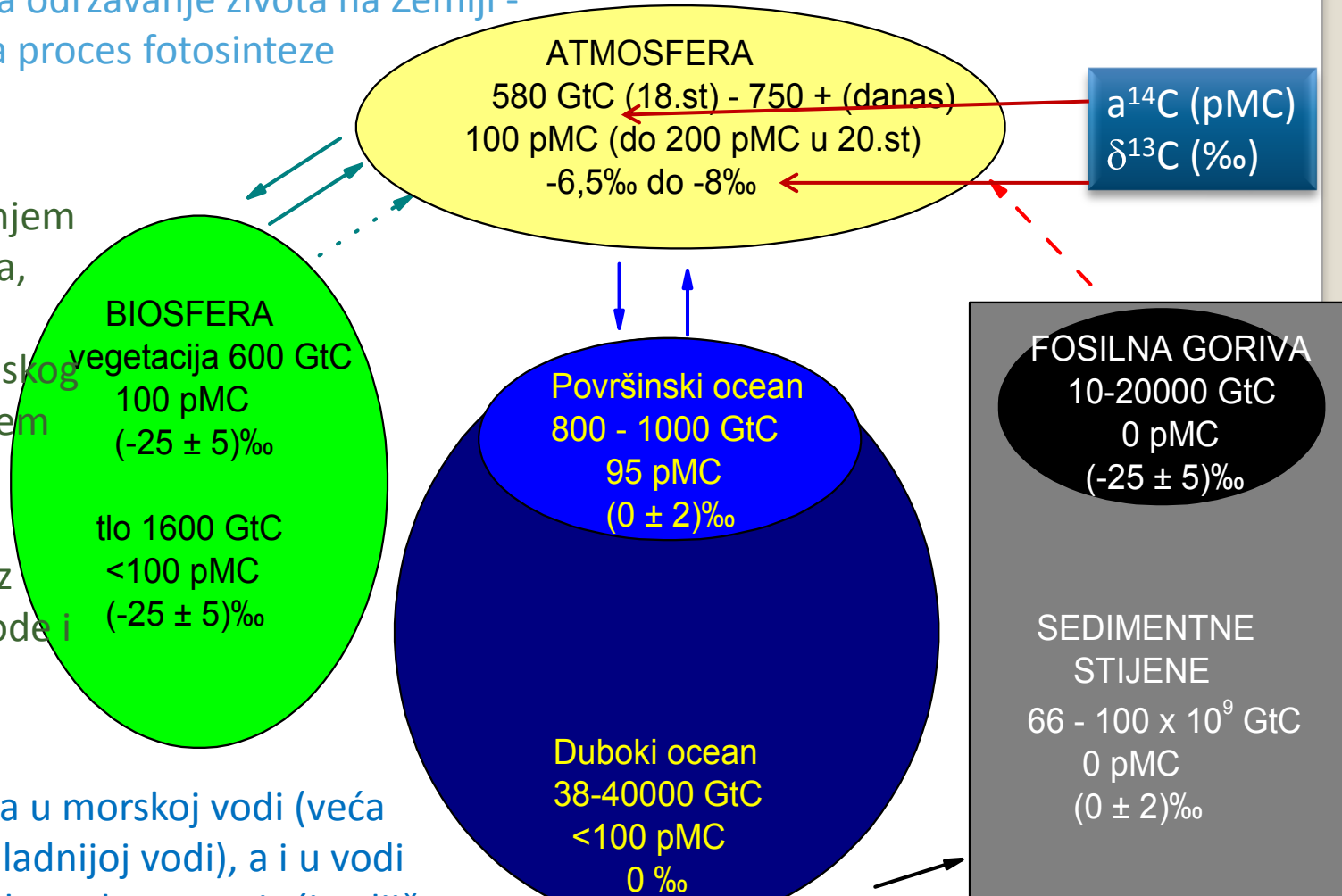
Raspodjela ^{14}C u prirodi



U atmosferi - uglavnom kao CO₂, 0,03 (0,04)% vol.
 - važna uloga za održavanje života na Zemlji -
 koriste biljke za proces fotosinteze

Vraća se u atmosferu disanjem biljaka i životinja, raspadanjem biljnog i životinjskog tkiva, spaljivanjem organskog materijala, oslobađanjem iz tople morske vode i vulkanskim erupcijama.

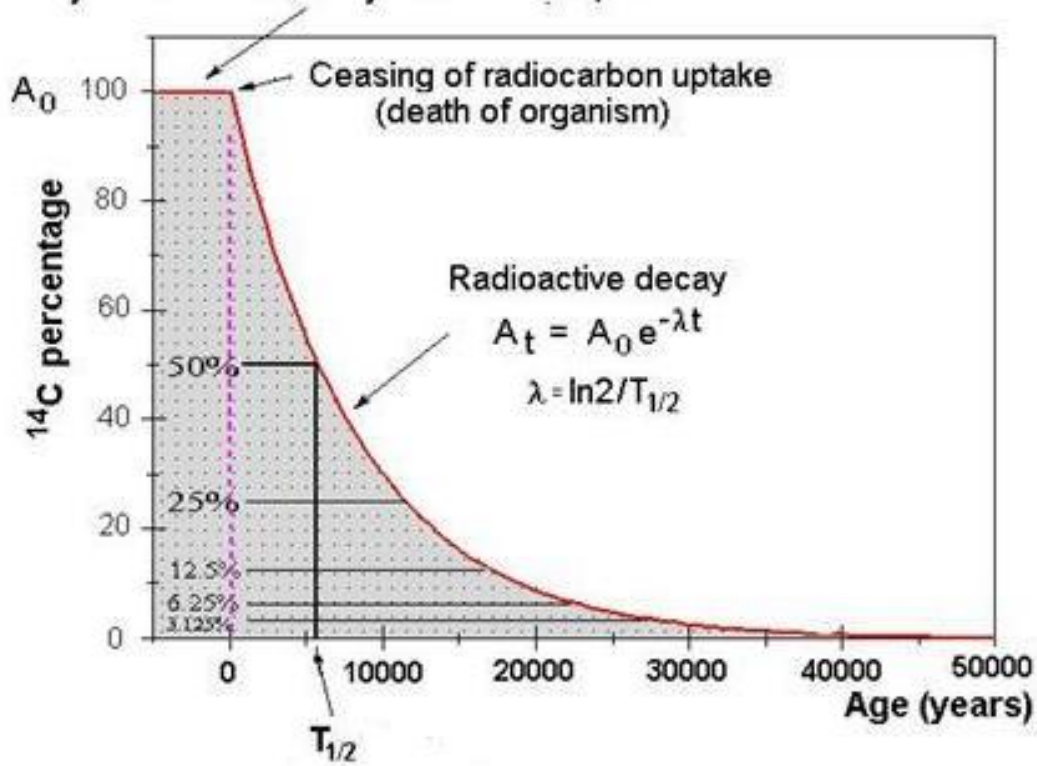
CO₂ se otapa u morskoj vodi (veća topivost u hladnijoj vodi), a i u vodi koja prolazi kroz tlo, stvarajući ugljičnu kiselinu, koja može otapati vapnenačke stijene.



Izgaranjem fosilnih goriva oslobađa se ugljik koji je milijunima godina bio spremljen u litosferi.

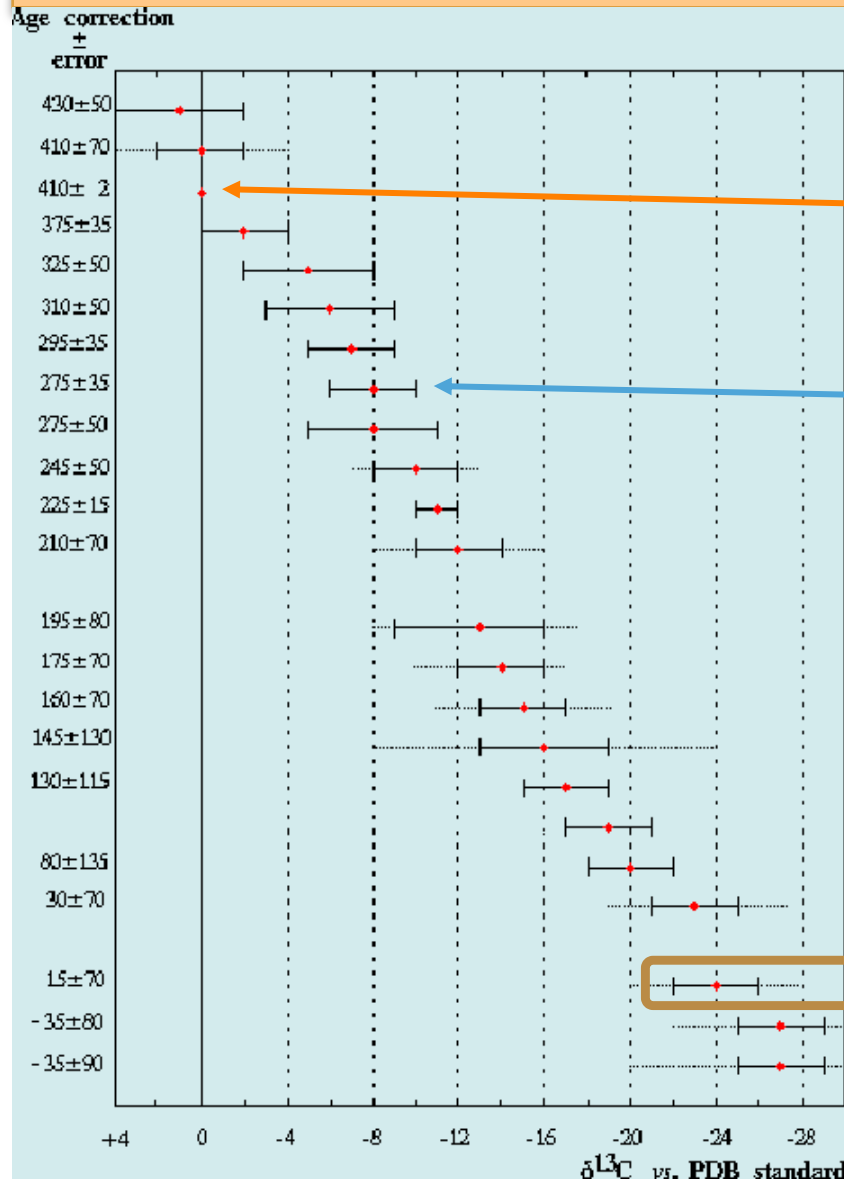
Konvencijska ^{14}C starost

Decayed ^{14}C balanced by its constant uptake



- a **half-life of 5568 years** (mean lifetime is 8030);
- correction for sample **isotopic fractionation** ($\delta^{13}\text{C}$);
- use of **1950 AD as 0 BP**, i.e. all ^{14}C ages head back in time from 1950;
- assumption that all ^{14}C **reservoirs** have remained **constant** through time.

Neke vrijednosti $\delta^{13}\text{C}$ različitih materijala koje se koriste za normalizaciju konvencijske starosti



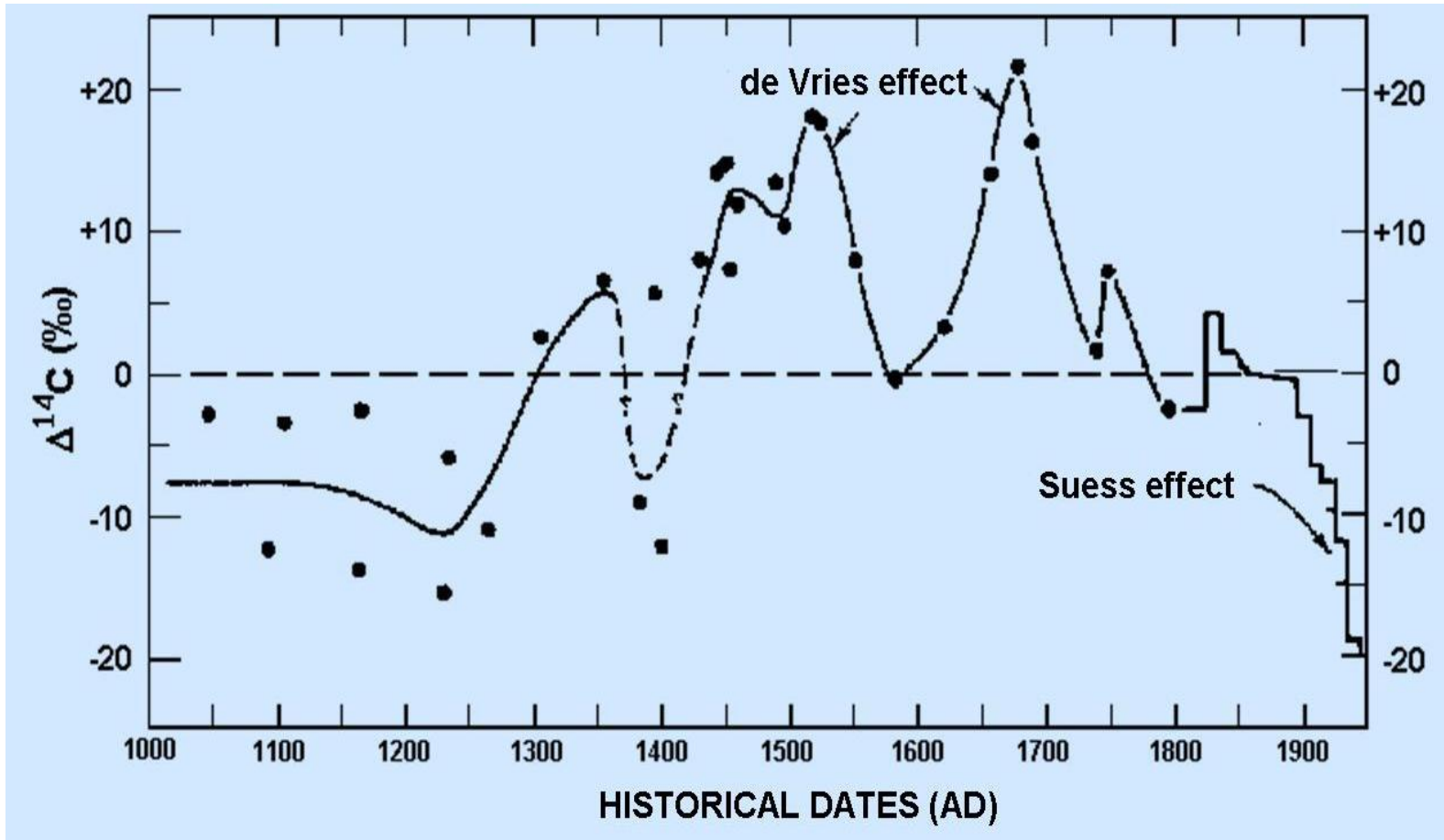
$\delta^{13}\text{C} = 0\text{‰}$

$\delta^{13}\text{C} = -8\text{‰}$

$\delta^{13}\text{C} = -25\text{‰}$

- Marine HCO_3^- , CO_3
- Saline lacustrine CO_3
- PDB $\delta^{13}\text{C}$ standard
- Bone apatite (C-4 diet)
- Soil CO_3 (speleothems, nodules)
- Freshwater shells
- Bone collagen (C-4)
- Atmospheric CO_2
- Terrestrial snail shells
- C-4 plants (maize, sorghum etc.)
- ANU sucrose (^{14}C standard)
- Bone apatite (C-3 diet)
- freshwater marine plants
- Grasses arid zone, sedges, papyrus
- Straws, flax
- Organic marine organisms
- Submerged freshwater plants
- Succulents (cactus, pineapple)
- Oxalic acid (^{14}C standard)
- Bone collagen, wood (C-3 diet)
- C-3 plants (wheat, oats, rice, etc.)
- graphite, coal
- Wood, charcoal
- Tree leaves, straw
- Peats, humus

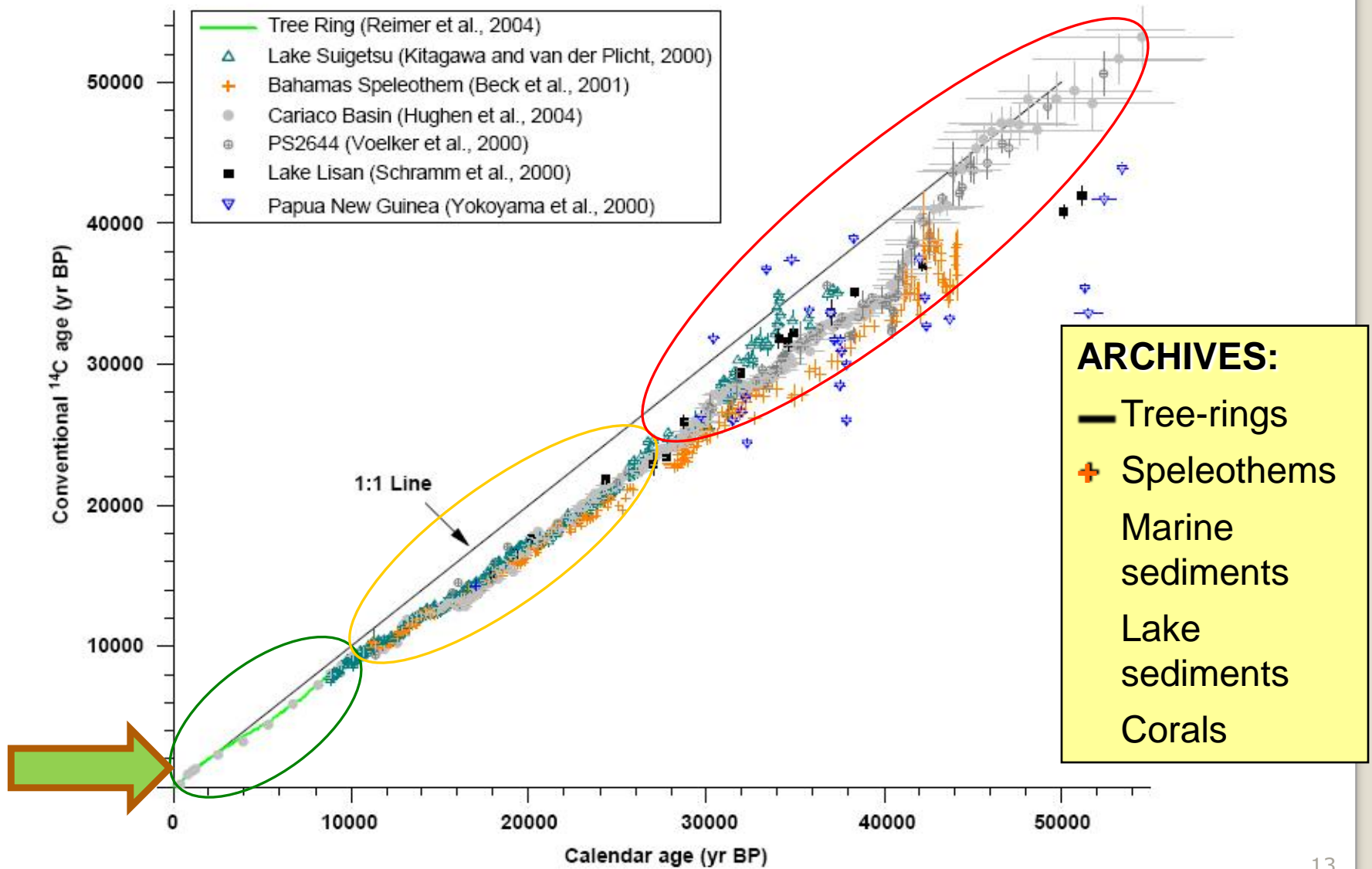
Primijećeno je da se atmosferska aktivnost ^{14}C mijenja u vremenu → potrebno kalibrirati izmjerenu (konvencijsku) ^{14}C starost, tj. pretvoriti ^{14}C godine u kalendarske godine



Fluctuations in radiocarbon activity over last 1000 years

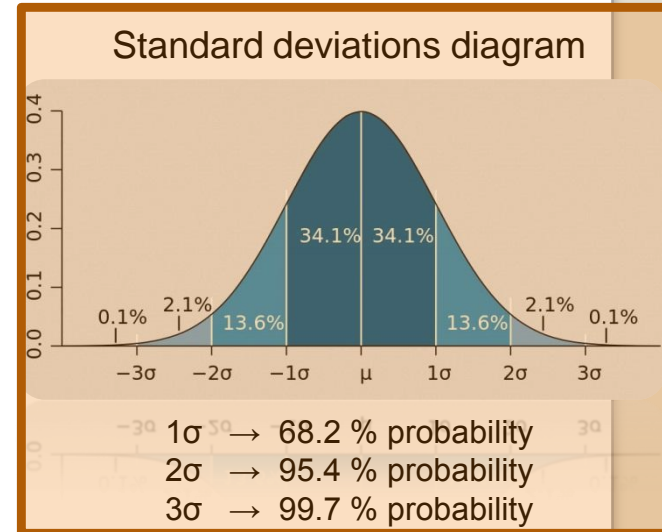
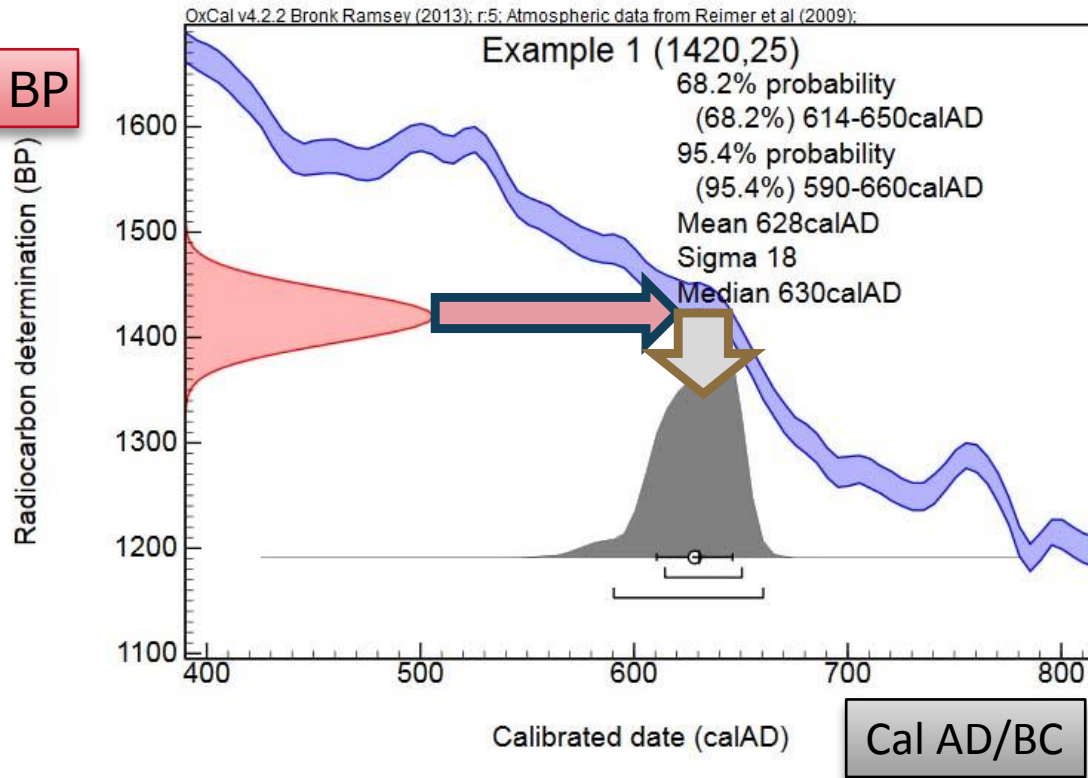
Radiocarbon calibration curves

R.G. Fairbanks et al. / *Quaternary Science Reviews* 24 (2005) 1781–1796



Kalibracija konvencijskih starosti

BP



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.

Rezultat

Može se izraziti kao

BP

Konvencijska ^{14}C starost

(godine) BP, 0 BP = 1950 AD
 $\delta^{13}\text{C}$ normalizacija, Libby half-life

cal BC/AD

Kalibrirana starost

Cal BC, Cal AD, vjerojatnosti i rasponi
dostupan software, kalibracijske krivulje

$a^{14}\text{C}$
 $F^{14}\text{C}$

Relativna specifična aktivnost ^{14}C
(često u geologiji, izučavanje atmosfere...)

$F = 1 \rightarrow a^{14}\text{C} = 100 \text{ pMC} \rightarrow 226 \text{ Bq/kgC}$

Priprema uzoraka i mjerenje

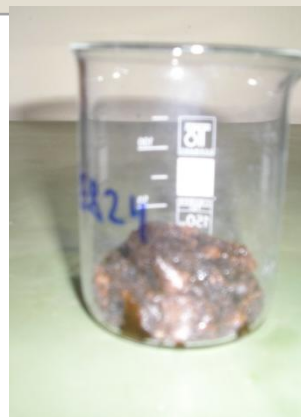
Priprema uzoraka ovisi

- o vrsti uzorka
- o mjernoj tehnici

- Izdvojiti sav ugljik iz uzorka (frakcionacija)
- Sav ugljik dolazi samo iz uzorka (kontaminacija)



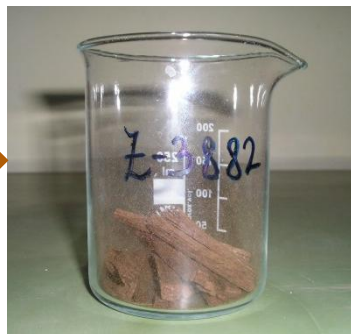
kost



kolagen



drvo



Nakon ABA obrade



siga



Karboniziran
uzorak

Mjerne tehnike

Radiometrijske – broje se raspadi ^{14}C (po jedinici mase
u jedinici vremena)



potrebna masa C: **1 - 5 g**

Potrebna masa uzorka: 10 - 50 g

Gas proportional counters (GPC)

Liquid scintillation counters (LSC)

Accelerator Mass Spectrometry (AMS)

– broje se atomi ^{14}C , ^{12}C i ^{13}C

Potrebna masa: **<2 mg C, <1 g uzorka**

IRB – laboratorij za ^{14}C

Laboratorij za mjerenje niskih radioaktivnosti (Radiocarbon and Tritium Laboratory)

Zavod za eksperimentalnu fiziku

Institut Ruđer Bošković , Zagreb, Hrvatska

<http://www.irb.hr/zef/c14-lab>

lna@irb.hr

Razvoj metode ^{14}C započeo 1968.

Plinski proporcionalni brojač - Gas proportional counting - GPC (CH_4)

Tekućinski scintilacijski brojač - Liquid scintillation counting – LSC

(benzen LSC-B, apsorpcija CO_2 LSC-A)

Accelerator Mass Spectrometry - AMS

priprema grafita

>6200 uzoraka

(3700 GPC, 700 LSC-A, 1400 LSC-B, 1300 AMS)

Suradnici

- Nada Horvatinčić, znanstvena savjetnica, kemičar
- Ines Krajcar Bronić, znanstvena savjetnica, fizičar
- Jadranka Barešić, znanstvena suradnica, kemičar
- Ivanka Lovrenčić Mikelić, znanstvena suradnica, geolog
- Martina Rožmarić Mačefat, znanstvena suradnica, kemičar
- Andreja Sironić, viša asistentica, kemičar
- Damir Borković, stručni suradnik, fizičar
- Matea Krmpotić, doktorandica, kemičar
- Anita Rajtarić, tehnička suradnica
- Bogomil Obelić, znanstveni savjetnik u mirovini, fizičar, vanjski

Projekti

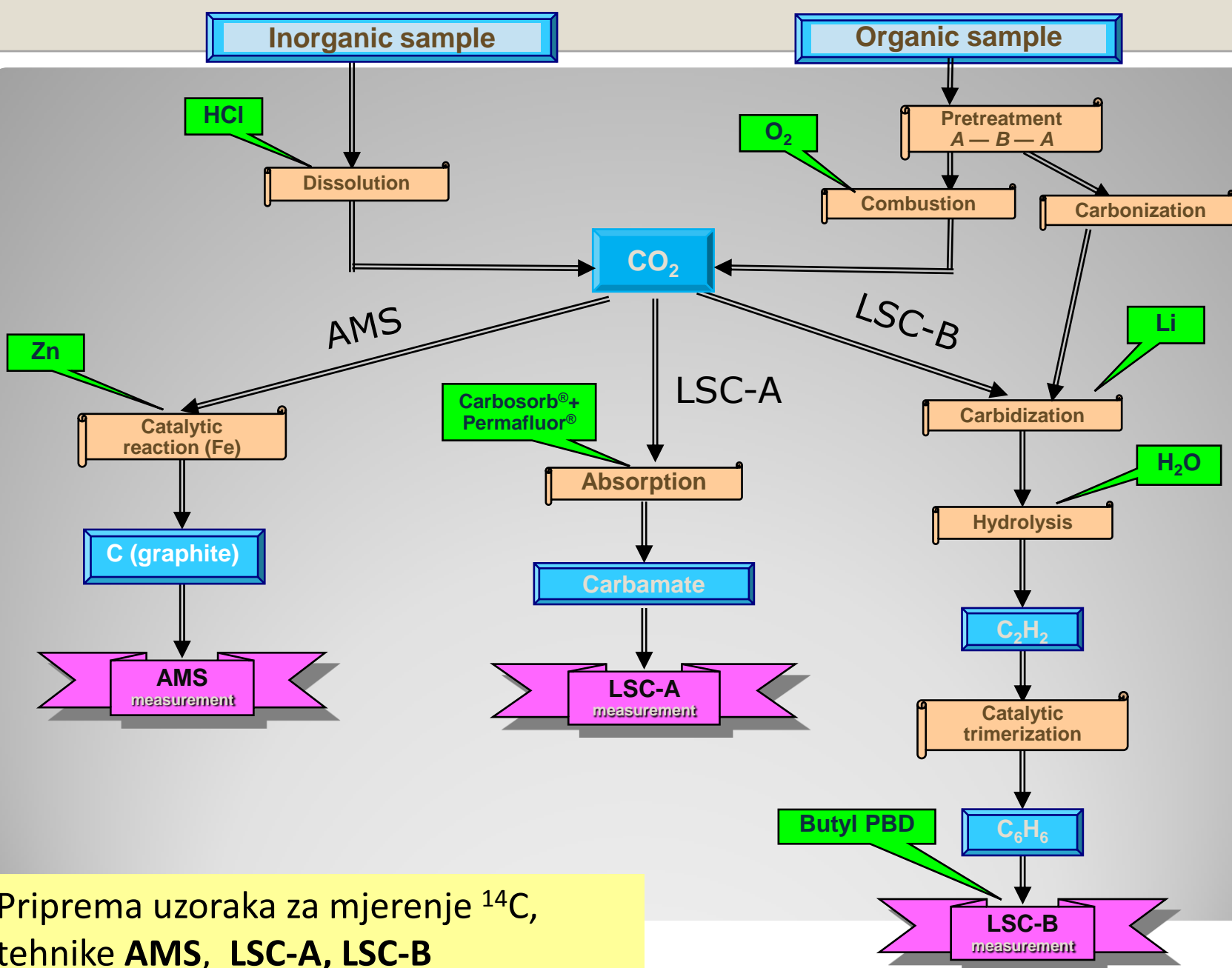
- Preparation of carbon samples for ^{14}C dating by the AMS technique - AMS 14C, FP6, 2007-2008
- Utjecaj klimatskih promjena i stanja u okolišu na biološko inducirano taloženje sedre i sedimentacijske procese u Plitvičkim jezerima, 2011 - 2013
- HRZZ 1623 - Reconstruction of the Quaternary environment in Croatia using isotope methods – REQUENCRIM
- IAEA TC projekt CRO/1/007 "Isotope Investigation of the Groundwater-Surface Water Interaction at the Well Field Kosnica in the Area of the City of Zagreb, 2016-2017
- FP5, 3 FP6, FP7 projekti
- IAEA – TC projekti, CRP – RC, organizacija Training Course
- Bilateralni projekti



Projekti

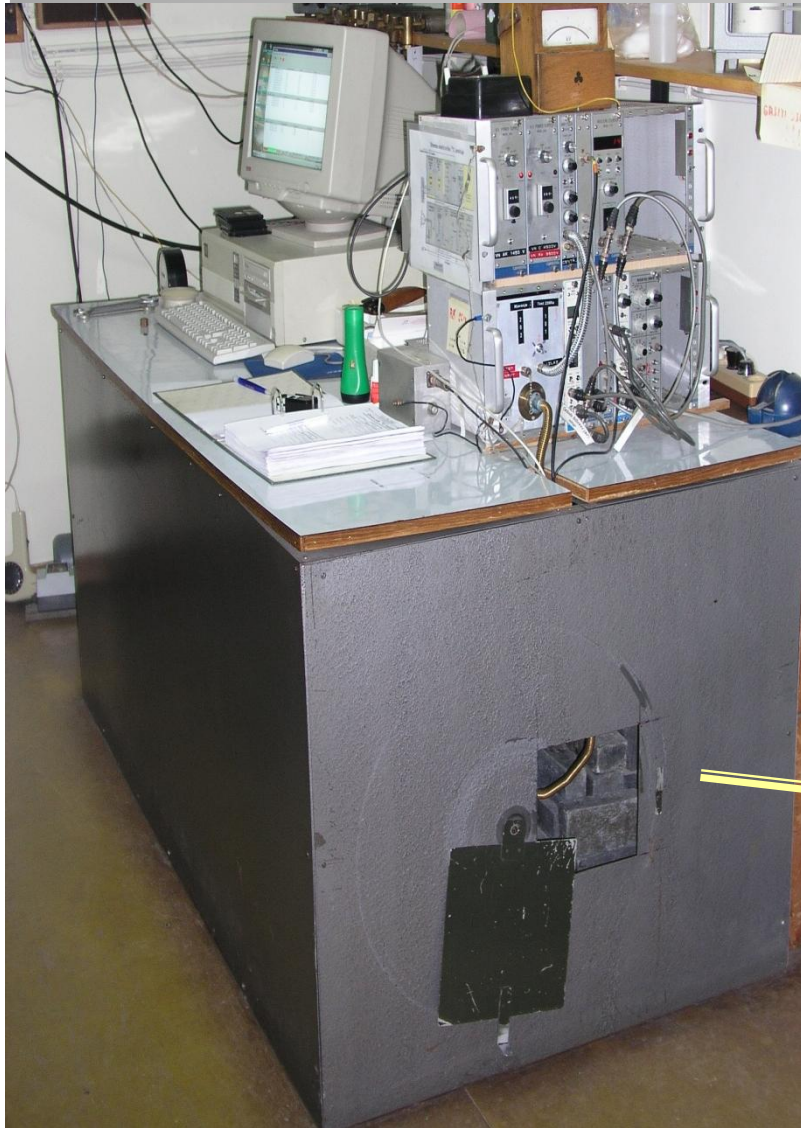
Bilateralni hrvatsko-srpski projekti

- **Optimizacija metoda mjerenja radioaktivnosti (^3H , ^{14}C , ^{90}Sr , ^{222}Rn) u uzorcima iz okoliša** - Institut Ruđer Bošković i Prirodno-matematski fakultet, Univerzitet u Novom Sadu, 2016-2017
- **^{14}C i ^{137}Cs u sedimentima - usporedba metoda i primjena na recentne sedimente**, Institut Ruđer Bošković i Prirodno-matematski fakultet, Univerzitet u Novom Sadu, 2011 – 2012

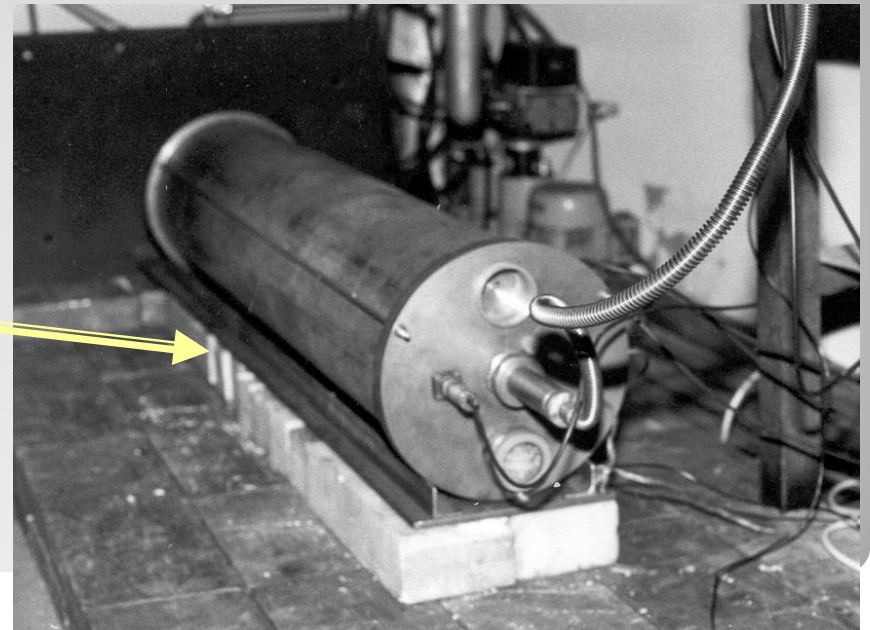


Priprema uzoraka za mjerenje ^{14}C ,
 tehnike AMS, LSC-A, LSC-B

GPC – Gas proportional counter

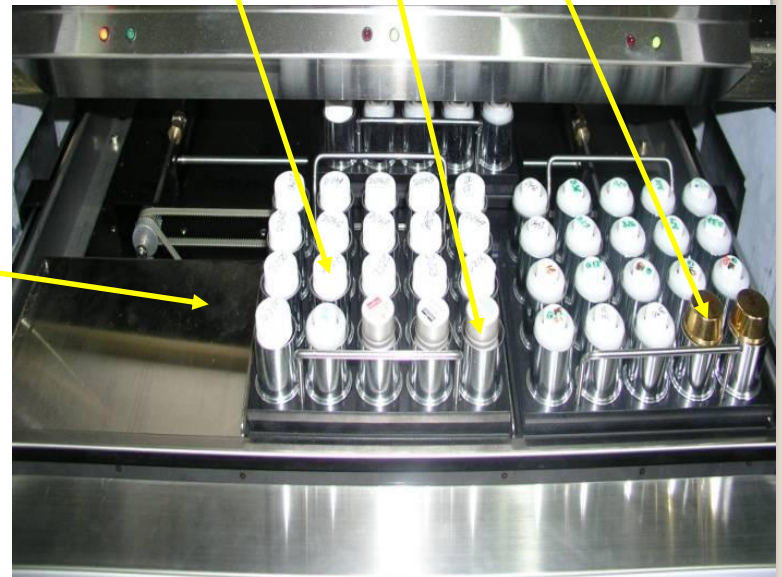


- Counting gas (CH_4) → sample and detection medium
- β particles from decay ionize gas → primary electrons
- electron avalanches are produced in strong electric field → signal



LSC – Liquid scintillation counter

Ultra-low-level *Quantulus 1220*



^{14}C sample preparation for AMS

ABA pretreatment

Collagen extraction

Combustion to CO_2

Reduction to C

Preparation of targets

AMS measurement

Organic carbon

Preparation of carbon samples for ^{14}C dating by the AMS technique – AMS-14C

SSA WBC 043584, 1.1.2007. – 31.12.2008.

Co-ordinator: Ines Krajcar Bronić

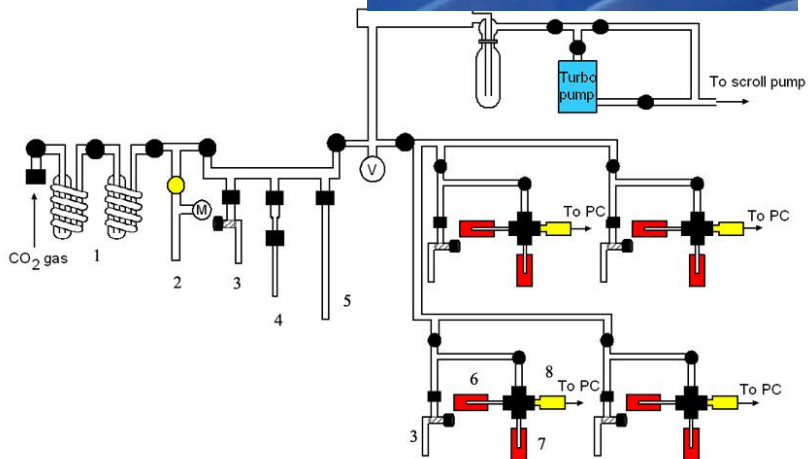
In cooperation with SUERC-UGLA, East Kilbride – Glasgow

AMS- ^{14}C

Ag

uzorak

CuO



IAEA.org
International Atomic Energy Agency

TC programme CRO/8/006
"Application of isotope techniques in investigation of water resources and water protection in the Karst area of Croatia" (2005-2007)
Principal investigator:
Nada Horvatinčić

Graphitization line

Usporedba nekih karakteristika mjernih tehnika ^{14}C (AMS i LSC) na Institutu Ruđer Bošković

| | ^{14}C AMS | ^{14}C LSC |
|-----------------------------------|---------------------|---------------------|
| masa C / g | $2 \cdot 10^{-3}$ | 4 (2) |
| Oblik pripremljenog uzorka | graphite (+Fe) | benzene |
| Preciznost / pMC | 0.3 | 0.5 |
| Granica detekcije / year BP | 56 200 | 55 000 |
| Trajanje mjerenja | >30 minuta | 24 sata |
| Broj pripremljenih uzoraka tjedno | 16 | 5 |
| Cijena / kn | 3000 | 1650 |

Primjene ^{14}C

- **Datiranje (određivanje starosti) organskih uzoraka** (biljke, drvo, žito, sjemenke, drveni ugljen, koža, platno/tekstil, kosti, zubi, slonovača, rogovi, pergament, papir, treset, tlo, organski sedimenti, DOC - dissolved organic carbon...)
- **Datiranje sekundarnih karbonata** (anorganski/karbonatni sediment, šljunač, školjke, koralji, školjke, DIC - dissolved inorganic carbon) – **potrebno poznavati tzv. početnu aktivnost ^{14}C**
- **Ciklus ugljika u prirodi**
- **Monitoring okoliša** (okolina nuklearnih postrojenja)
- Oceanologija, klimatologija
- Forenzika
- Medicinske, biokemijske, farmakološke primjene
- Određivanje udjela biogene komponente

ZAPAMTITI!

- ❖ Metoda datiranja pomoću ^{14}C daje **starost materijala biogenog porijekla** (drvo, platno, papir), a ne vrijeme stvaranja npr. umjetničkog djela
- ❖ Metoda datiranja pomoću ^{14}C ne daje kao rezultat pojedinačnu godinu, već **raspon godina** (s određenom vjerojatnošću)
- ❖ Interpretaciju rezultata potrebno je raditi **u suradnji s drugim istraživačima** (arheolozi, povjesničari umjetnosti, geolozi...)

Arhiv Vojvodine, Novi Sad

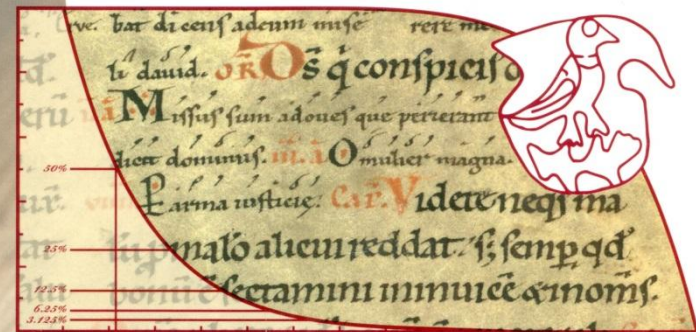
3/2015. – otkrivena neobilježena arhivska kutija s neevidentiranom arhivskom građom
Pet rukopisnih kodeksa na papiru,
6 pergamentnih listova s fragmentima rukopisa

Pergament korišten kao omot bilježnica iz 16. st (1569-70 AD, 1590 AD)

„traganje za izgubljenom istinom” opisano u knjizi „Put dokumenta”

Novi Sad, 2016,
ISBN 978-86-80017-39-6

ПУТ ДОКУМЕНТА

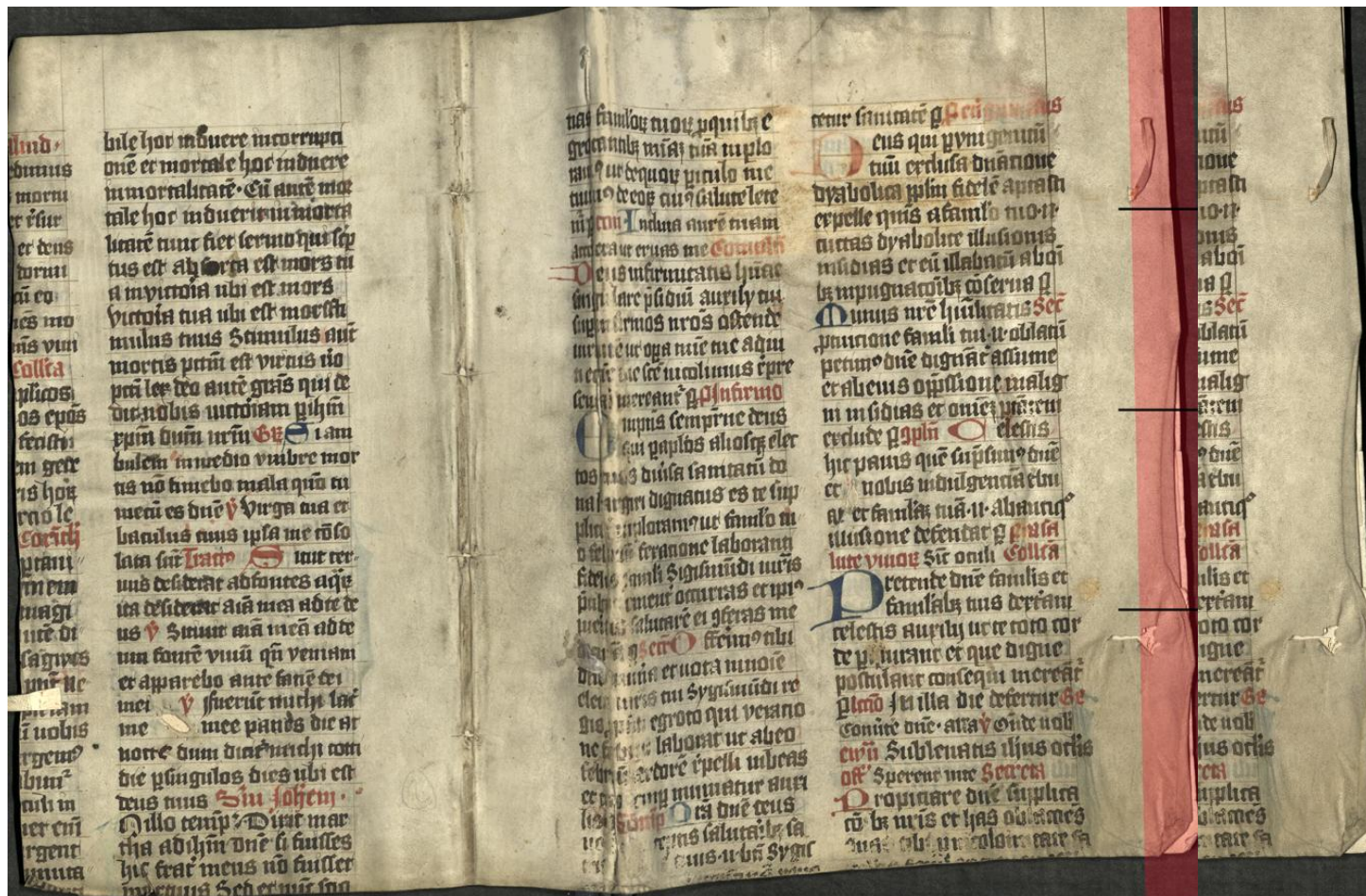


Pergament

rukopisi K3 i K4 – liturgijski tekstovi na latinskom

Arhiv Vojvodine, Novi Sad

Pergament korišten kao omot bilježnica iz 16. st (1569-70 AD, 1590 AD)



K3

K4

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 inquit me a. lxx.

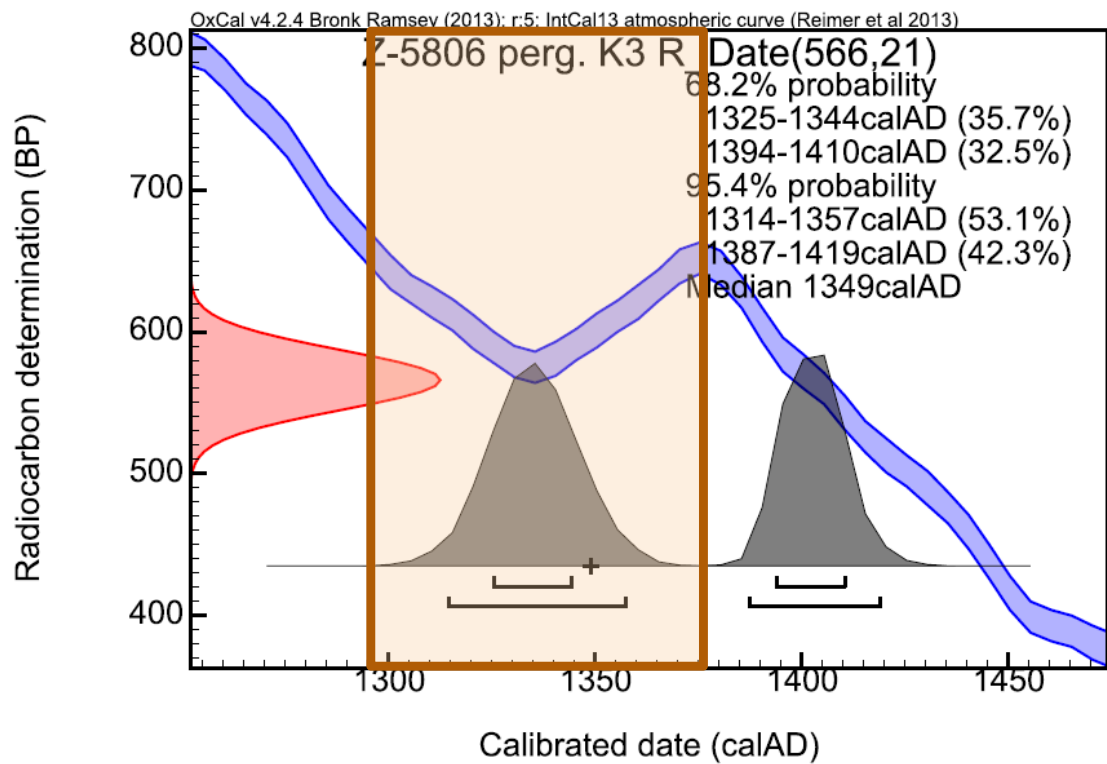
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 autem quod
 inquit me qua
 Deus
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 inquit patres nostri
 inquit me a. lxx.

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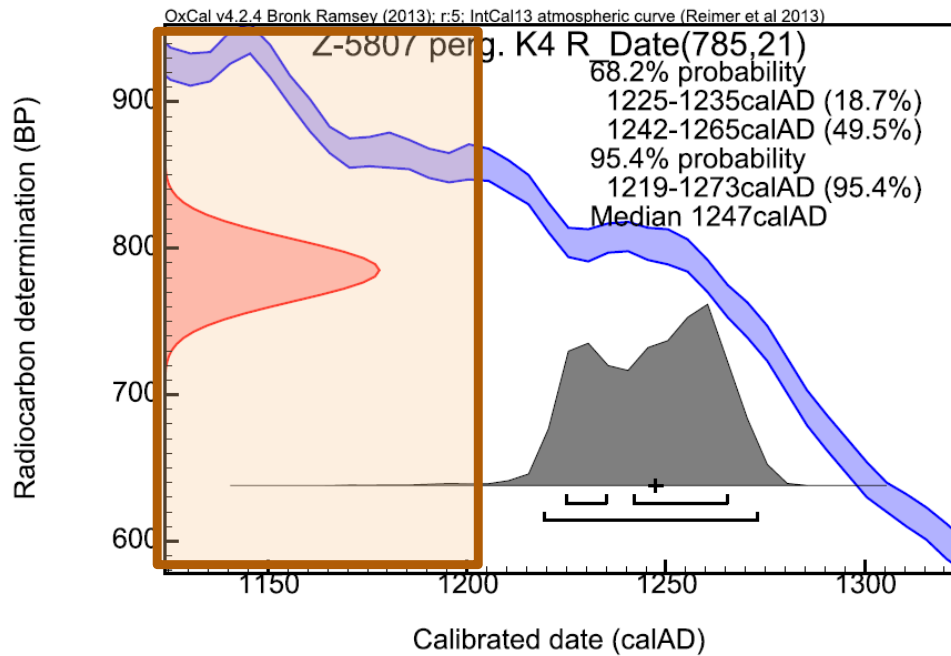
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| Lab. no | Naziv uzorka | Konvencijska ^{14}C starost (BP) | $\delta^{13}\text{C}$ (‰) | Raspon kalibriranih godina (cal AD) | medijan cal AD | Očekivani period |
|-----------------|--------------|---|---------------------------|-------------------------------------|----------------|------------------|
| Z-5806 A1140 | Pergament K3 | 565 ± 20 | -21.0 | 1325 – 1410 (68.2%) | 1349 | 14th c. |
| Z-5807 A1141 | Pergament K4 | 785 ± 20 | -21.4 | 1225 – 1265 (68.2%) | 1247 | 12th c. |



K3 – rezultat datiranja podudara se s arheografsko-paleografskim rezultatima, 14.-15. st.

| Lab. no | Naziv uzorka | Konvencijska ^{14}C starost (BP) | $\delta^{13}\text{C}$ (‰) | Raspon kalibriranih godina (cal AD) | medijan cal AD | Očekivani period |
|-----------------|--------------|---|---------------------------|-------------------------------------|----------------|------------------|
| Z-5806 A1140 | Pergament K3 | 565 ± 20 | -21.0 | 1325 – 1410 (68.2%) | 1349 | 14th c. |
| Z-5807 A1141 | Pergament K4 | 785 ± 20 | -21.4 | 1225 – 1265 (68.2%) | 1247 | 12th c. |



K4 –arheografsko-paleografski rezultati 12. st.
 U Arhivu dokumentiran s vremenom porijekla 12.-13.st.

- Najstariji u Arhivu Vojvodine
- Jedan od najstarijih dokumenata u svim arhivima R. Srbije,
- spada u red raritetnih dokumenata kulturne baštine