

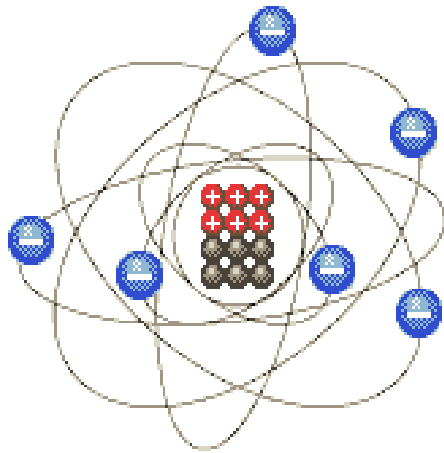
Određivanje starosti metodom ^{14}C

1. Uvod i neki primjeri datiranja

Ines KRAJCAR BRONIĆ
krajcar@irb.hr

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

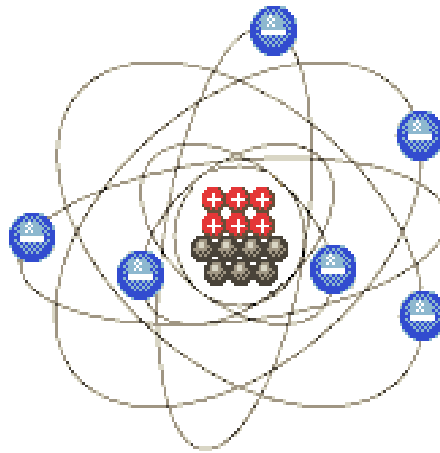
Izotopi ugljika



^{12}C

98.89 %

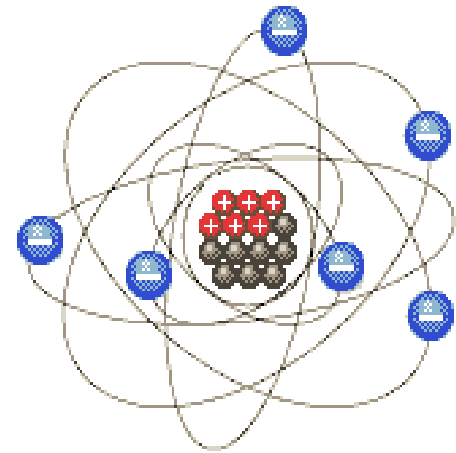
$p = n = 6$



^{13}C

1.11 %

$n = 7$



^{14}C

10^{-10} %

$n = 8$

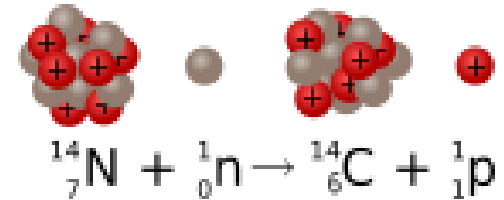
$T_{1/2} = 5730 \text{ y}$

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 ...

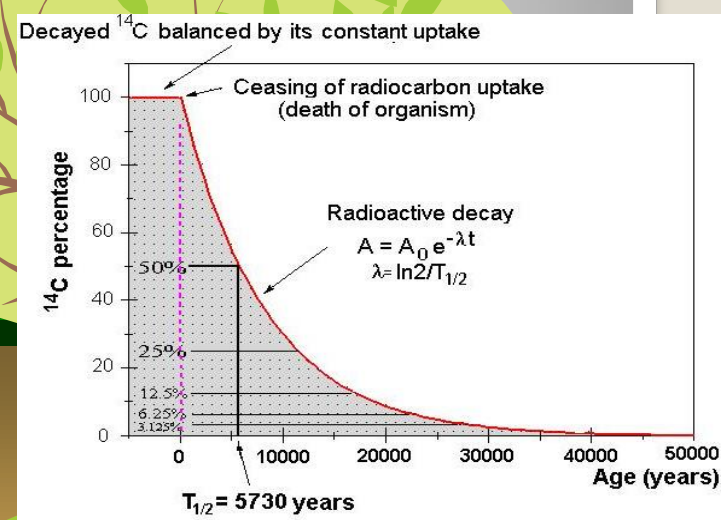
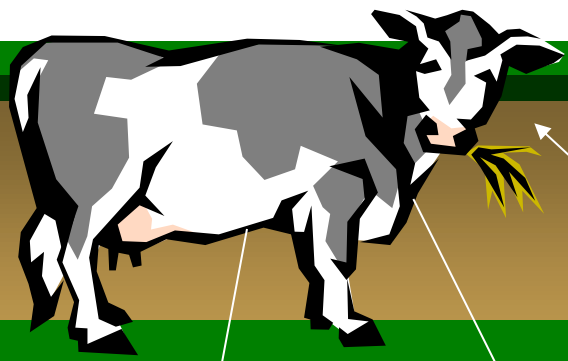
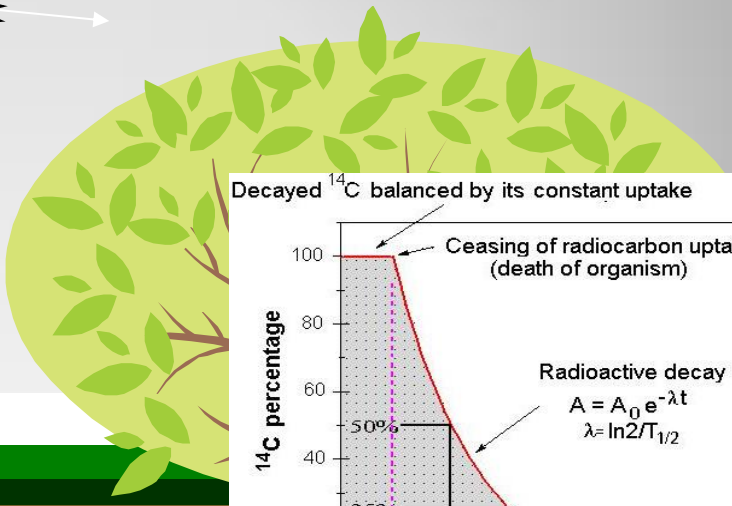
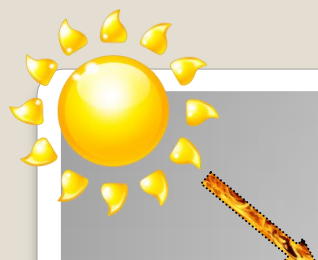
U Zemljinoj atmosferi	oko 220 PBq „prirodnog“ ^{14}C
Terestrijalni ^{14}C	oko 10000 PBq

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

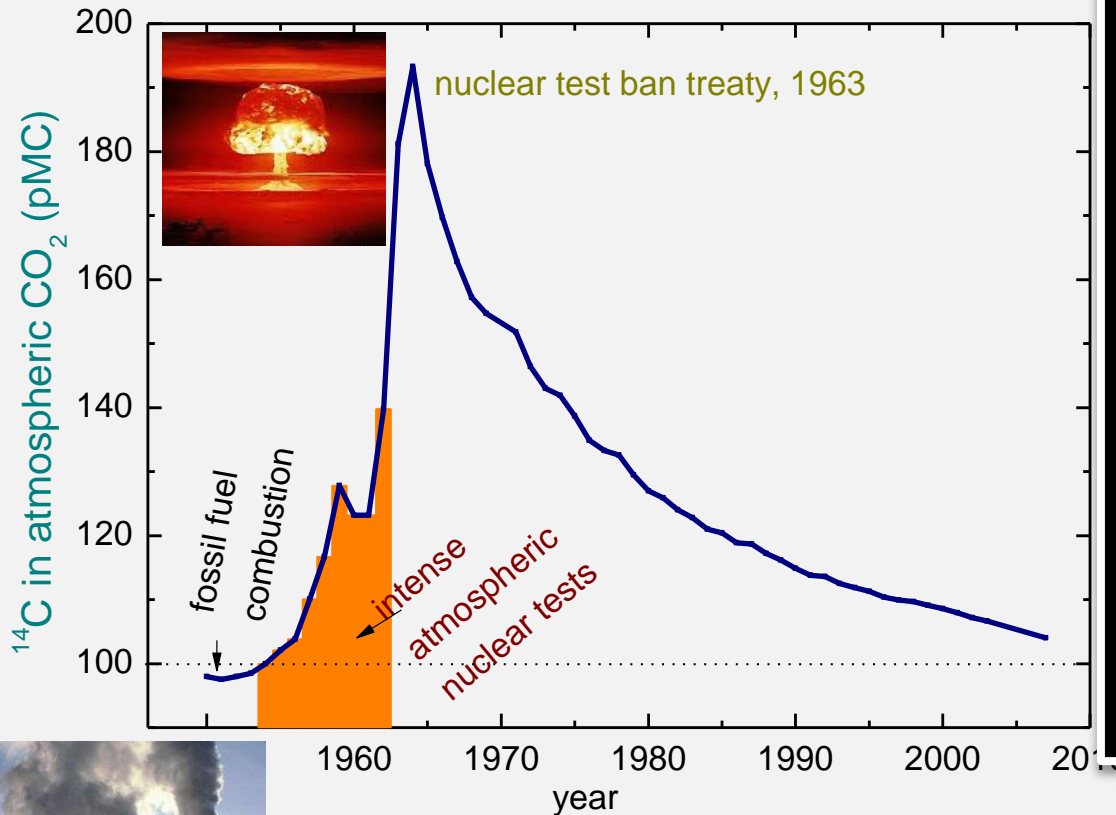
Nastaje interakcijama neutrona emitiranih u
atmosferskim nuklearnim eksplozijama

input 213 – 315 PBq,

udvostručena atm. specifična aktivnost ^{14}C

1963, nakon toga – pad

Anthropogenic ^{14}C

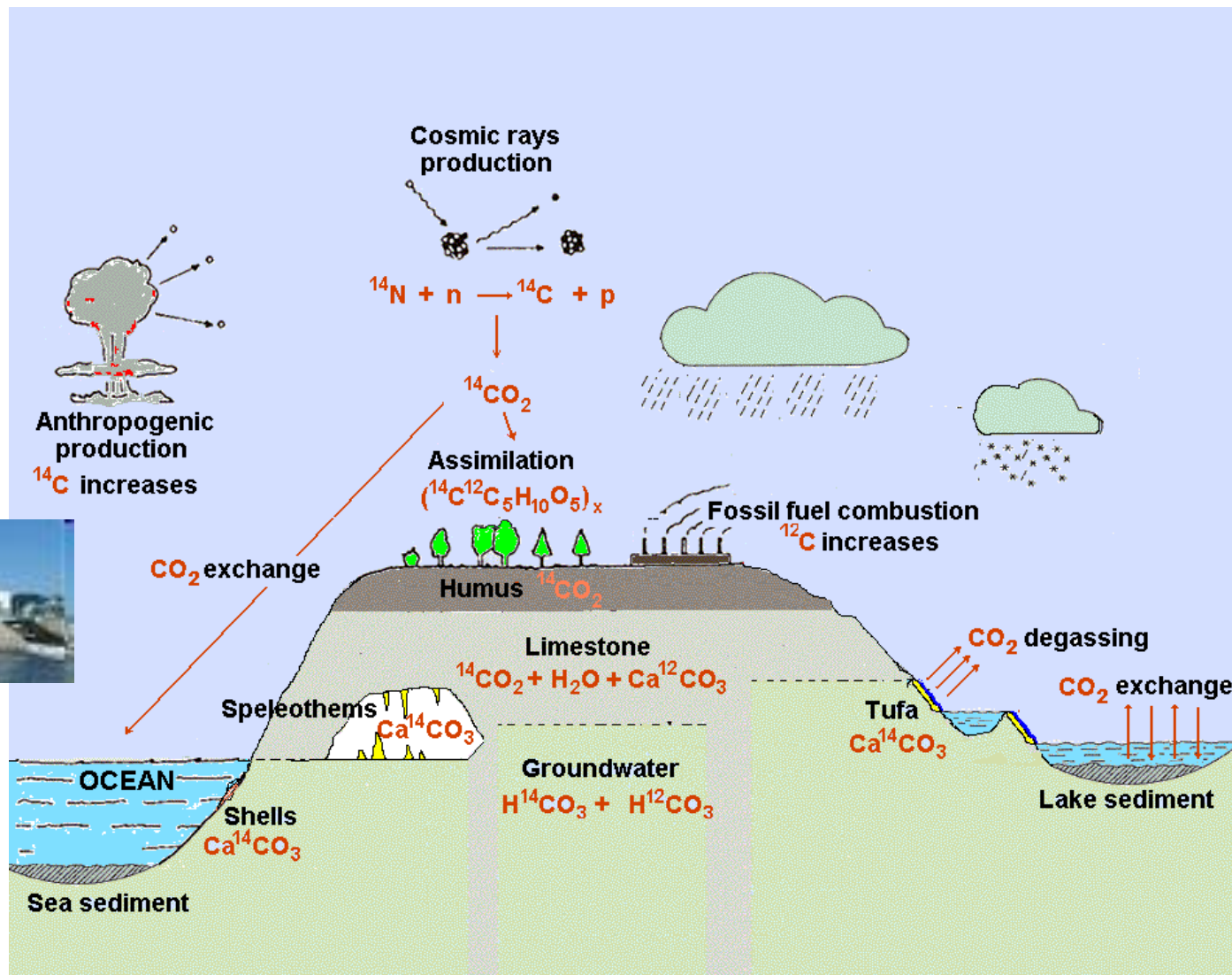


Anthropogenic activities disturbed the natural distribution of ^{14}C in the atmosphere through fossil fuel combustion (increasing of ^{12}C compared to ^{14}C) and atmospheric bomb tests (doubling the natural atmospheric ^{14}C activity in 1960-ties).

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



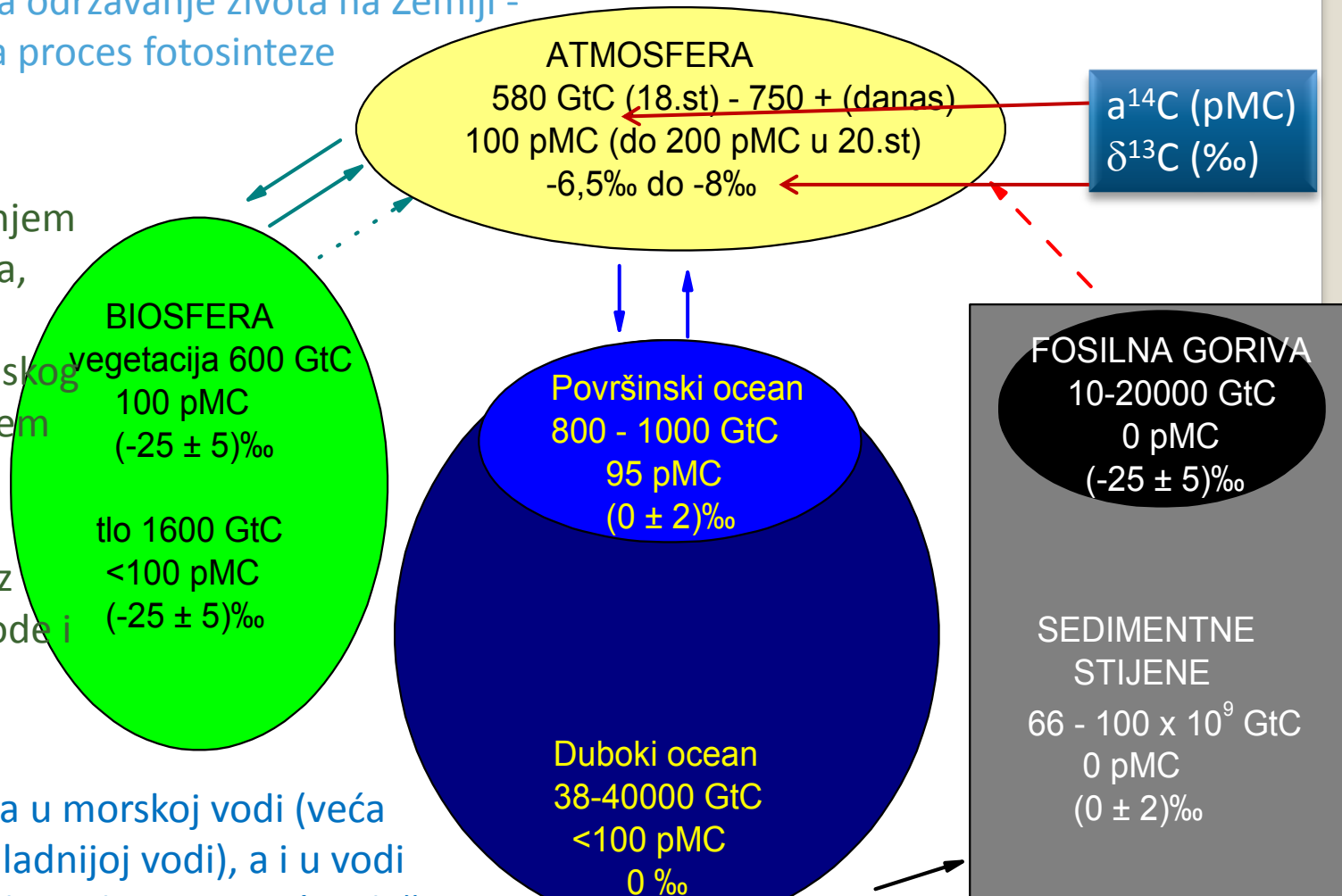
Raspodjela ^{14}C u prirodi



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

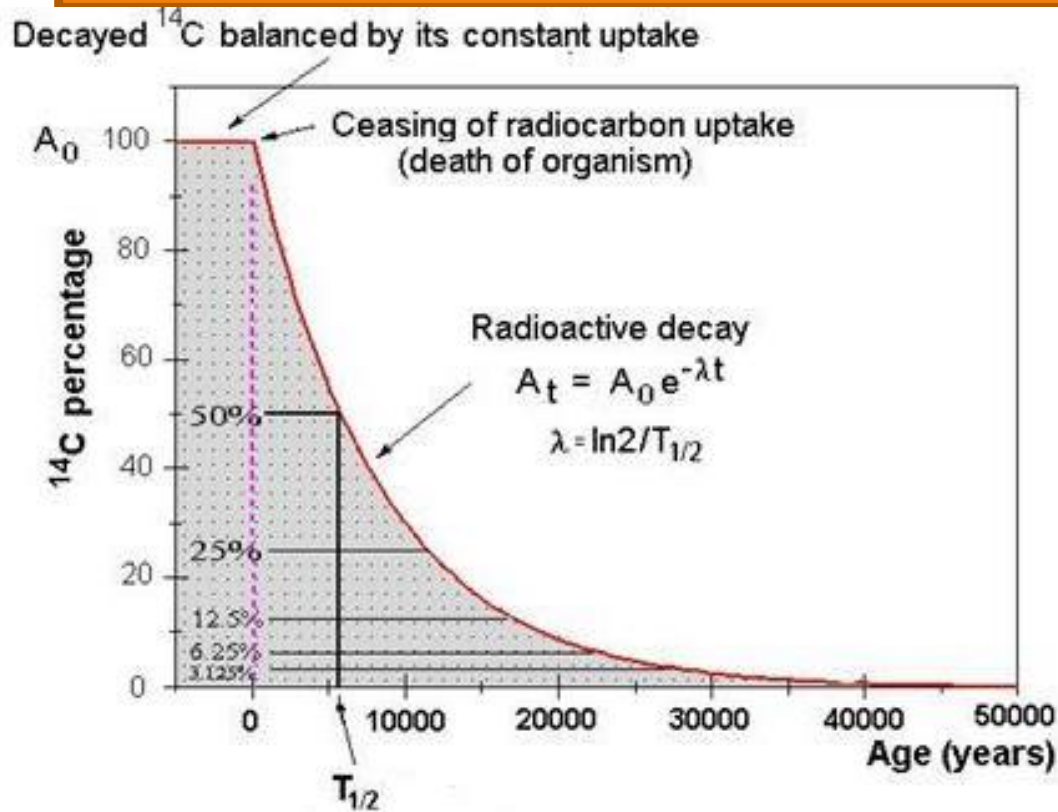
Vraća se u atmosferu disanjem biljaka i životinja, raspadanjem biljnog i životinjskog tkiva, spaljivanjem organskog materijala, oslobađanjem iz tople morske vode i vulkanskim erupcijama.

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.



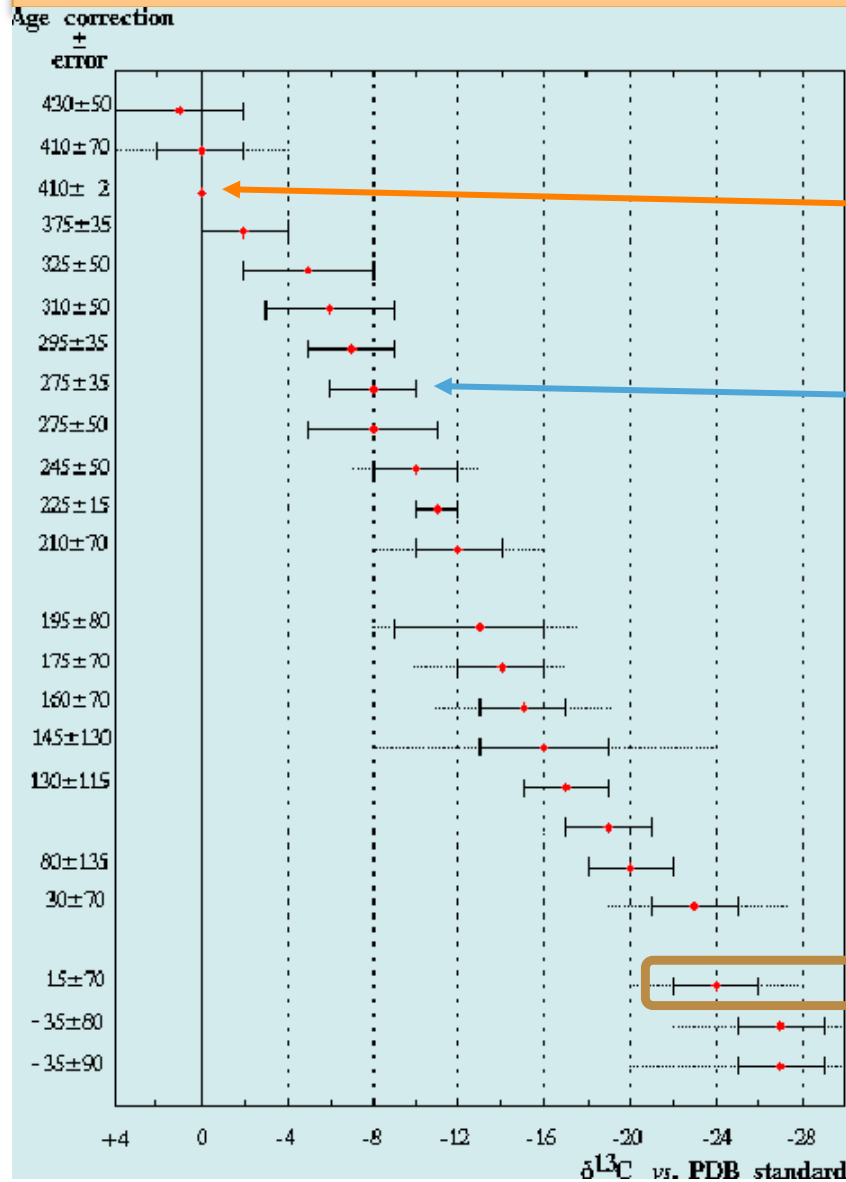
Izgaranjem fosilnih goriva oslobađa se ugljik koji je milijunima godina bio spremljen u litosferi.

Konvencijska ^{14}C starost



- 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



Marine HCO_3^- , CO_3
Saline lacustrine CO_3
PDB $\delta^{13}\text{C}$ standard

$$\delta^{13}\text{C} = 0\text{‰}$$

Bone apatite (C-4 diet)
Soil CO_3 (speleothems, nodules)

Freshwater shells
Bone collagen (C-4)

$$\delta^{13}\text{C} = -8\text{‰}$$

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

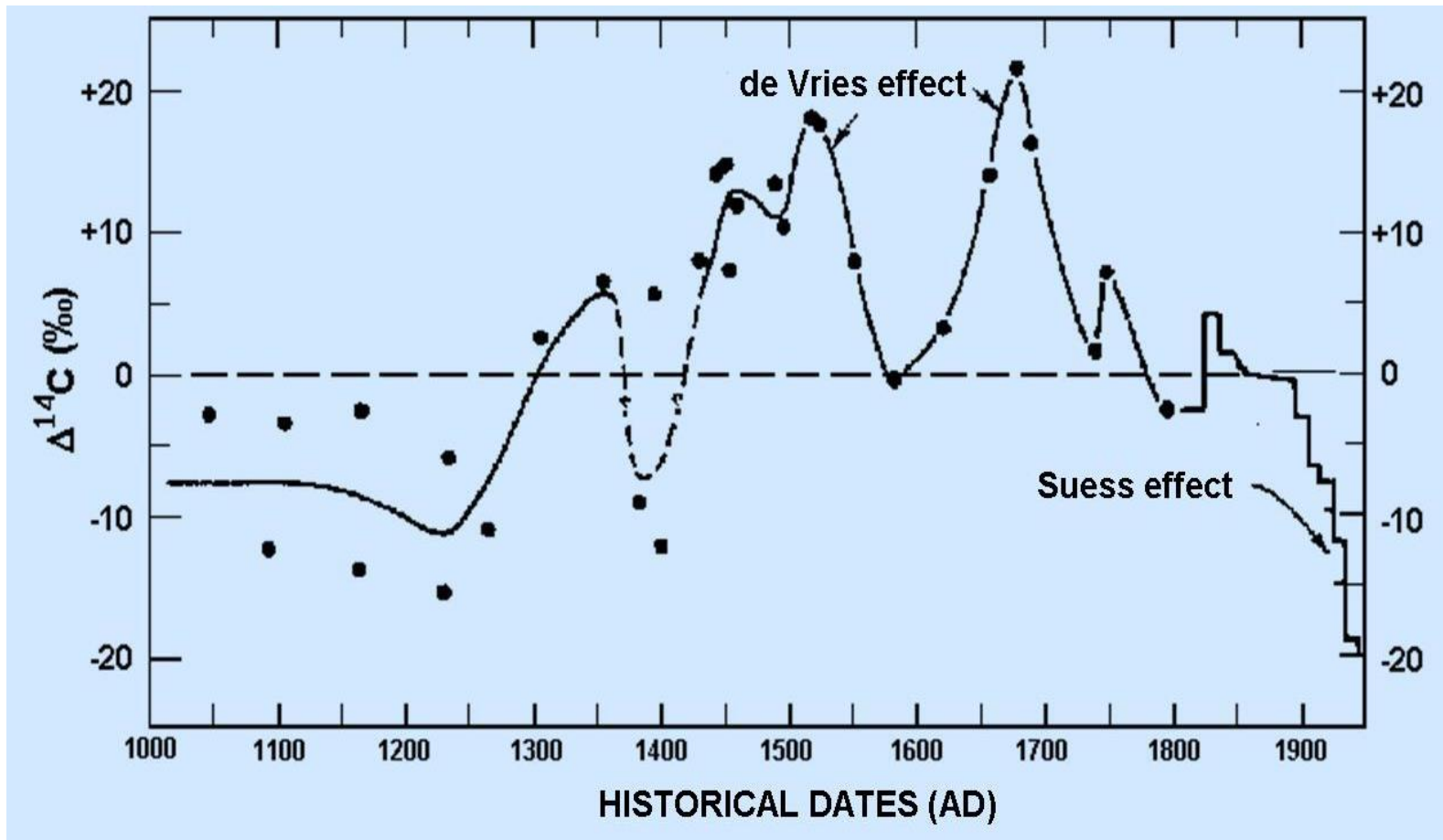
Wood, charcoal

$$\delta^{13}\text{C} = -25\text{‰}$$

Tree leaves, straw

Peats, humus

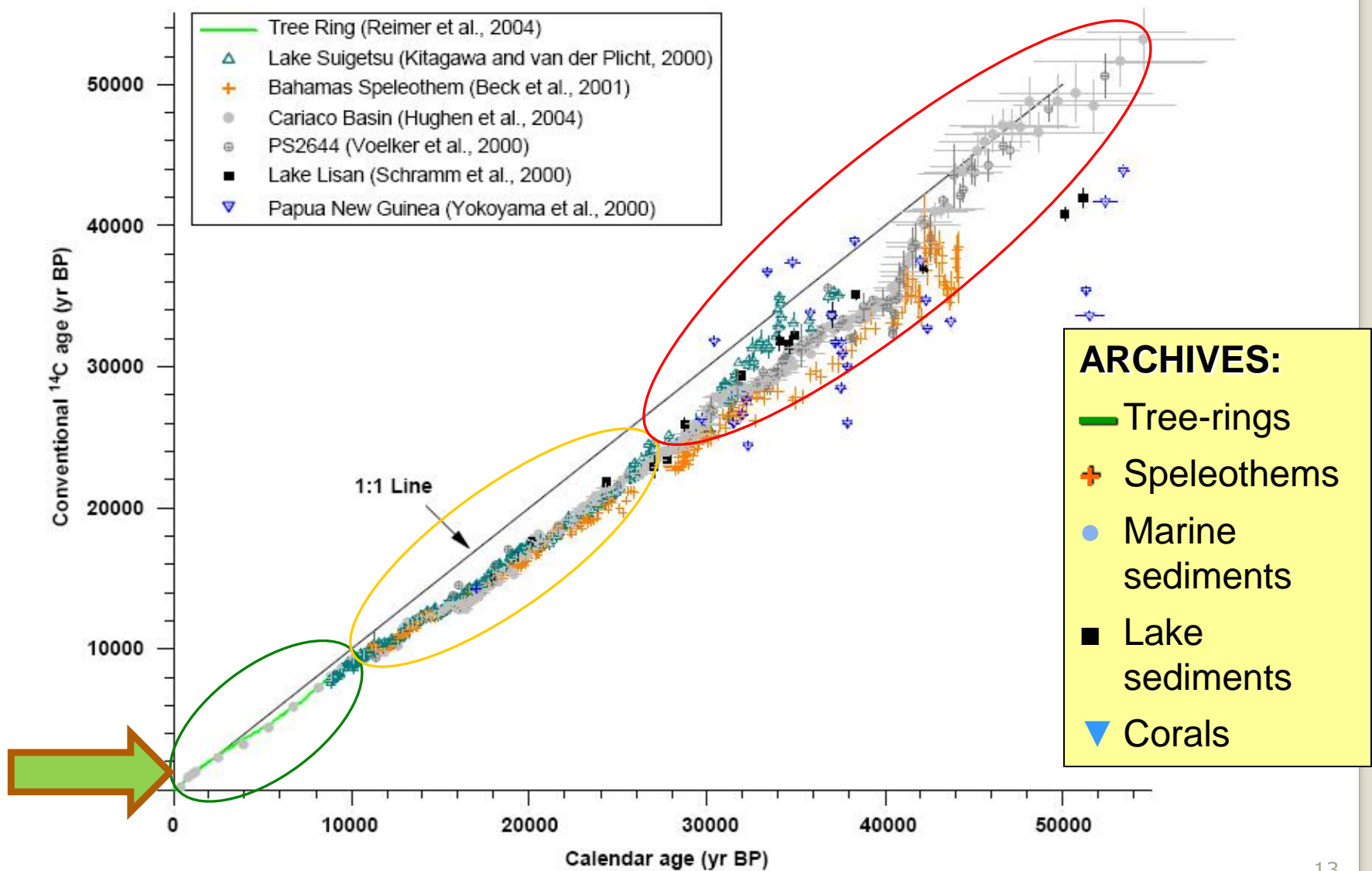
Primijećeno je da se atmosferska aktivnost ^{14}C mijenja u vremenu → potrebno kalibrirati izmjerenu (konvencijsku) ^{14}C starost, tj. pretvoriti ^{14}C godine u kalendarske godine



Fluctuations in radiocarbon activity over last 1000 years

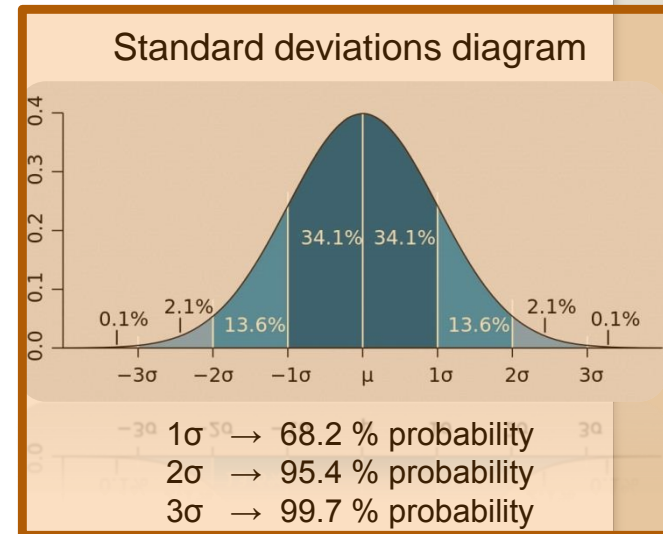
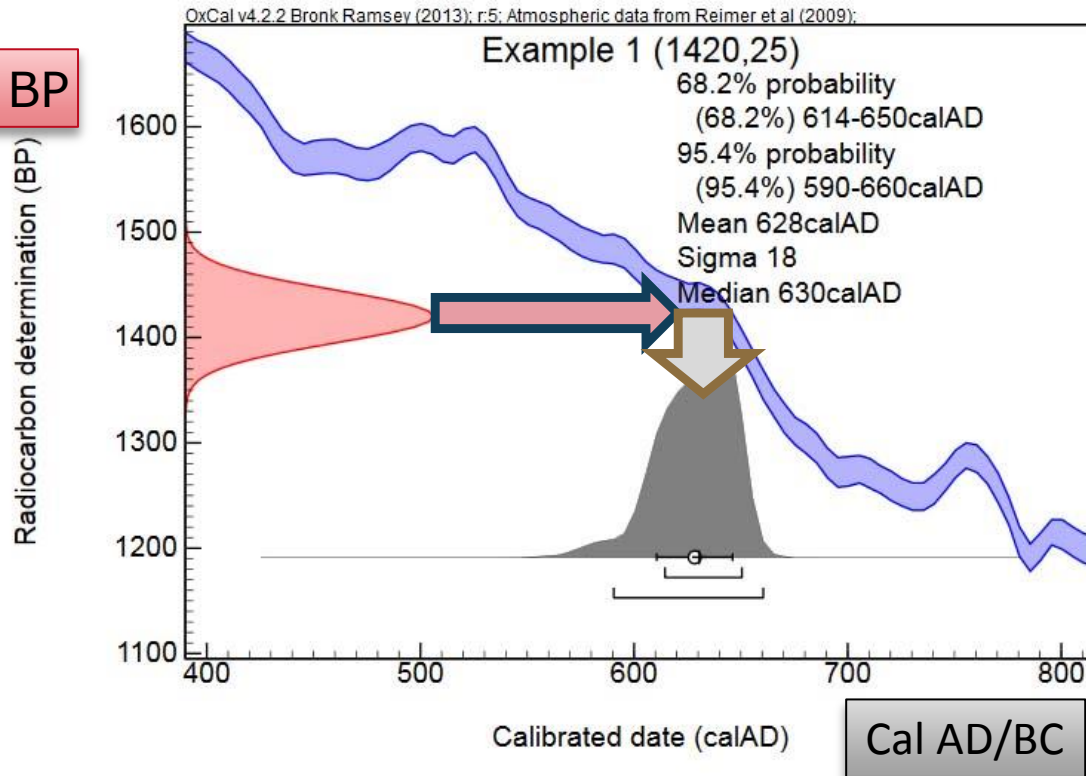
Radiocarbon calibration curves

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

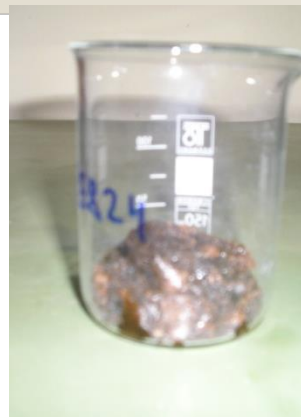
Priprema uzoraka ovisi

- o vrsti uzorka
- o mjernoj tehnici

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



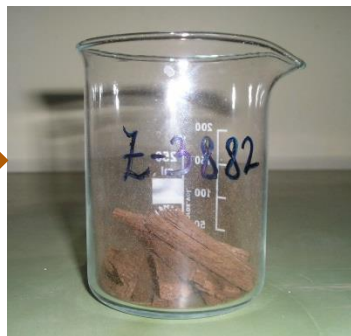
kost



kolagen



drvo



Nakon ABA obrade



sigla



Karboniziran uзорak

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

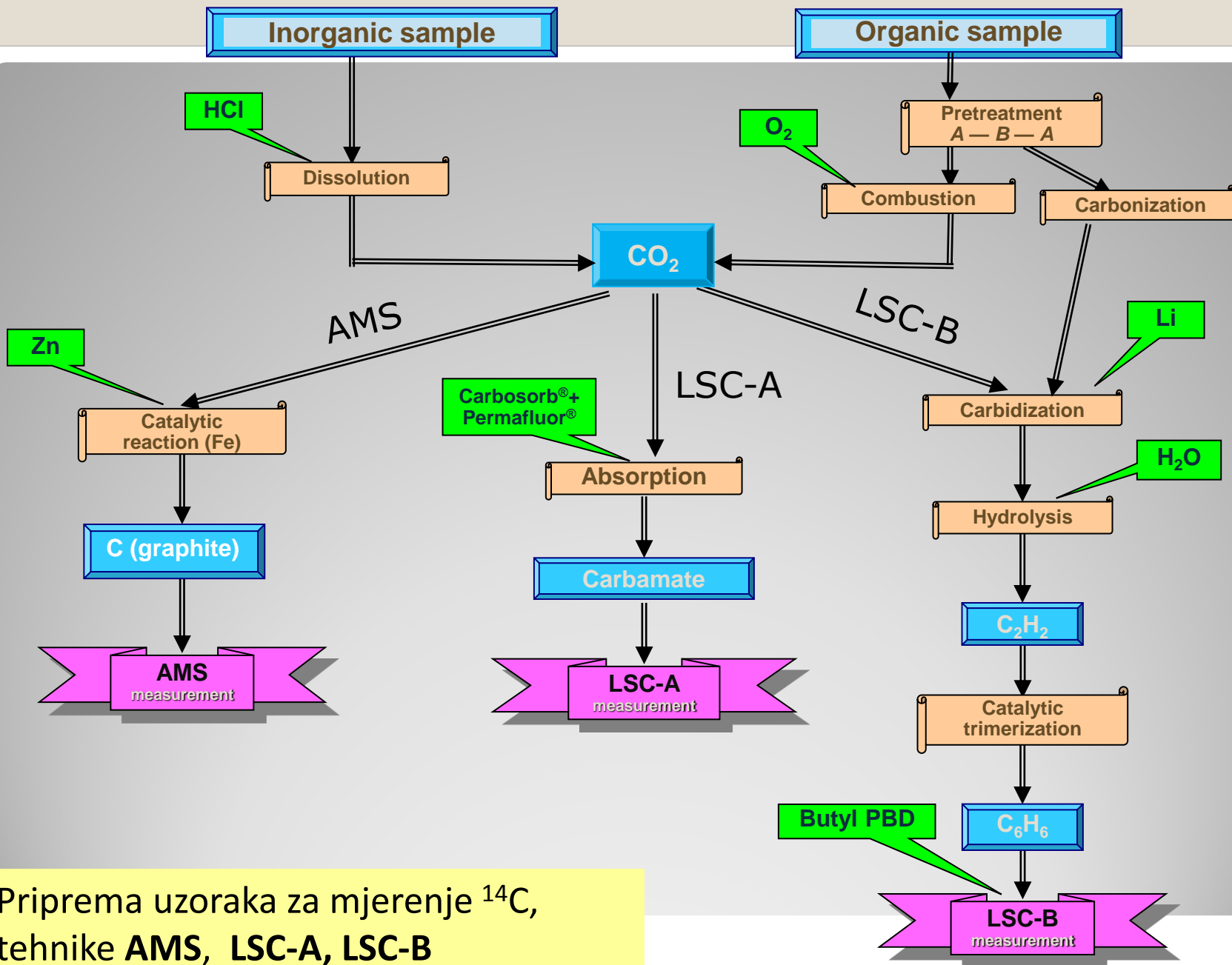
- Preparation of carbon samples for ^{14}C dating by the AMS technique - AMS 14C, FP6, 2007-2008
- Utjecaj klimatskih promjena i stanja u okolišu na biološko inducirano taloženje sedre i sedimentacijske procese u Plitvičkim jezerima, 2011 - 2013
- HRZZ 1623 - Reconstruction of the Quaternary environment 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

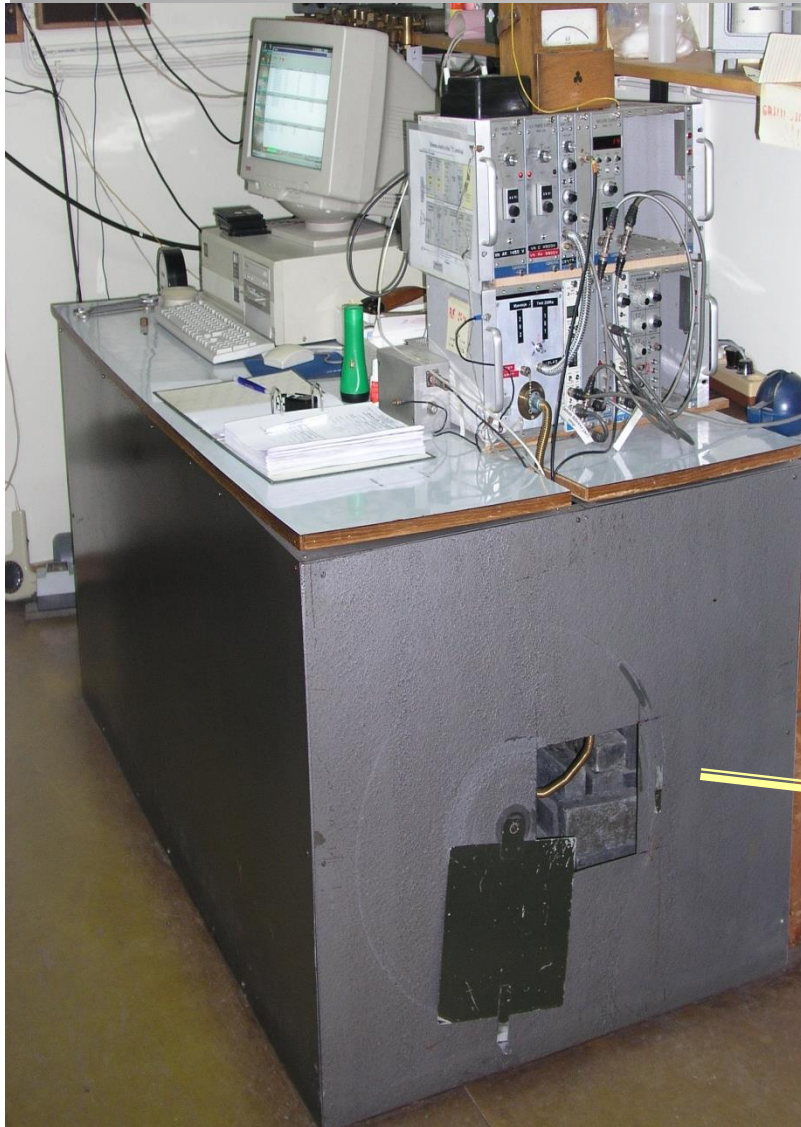
Bilateralni hrvatsko-srpski projekti

- **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

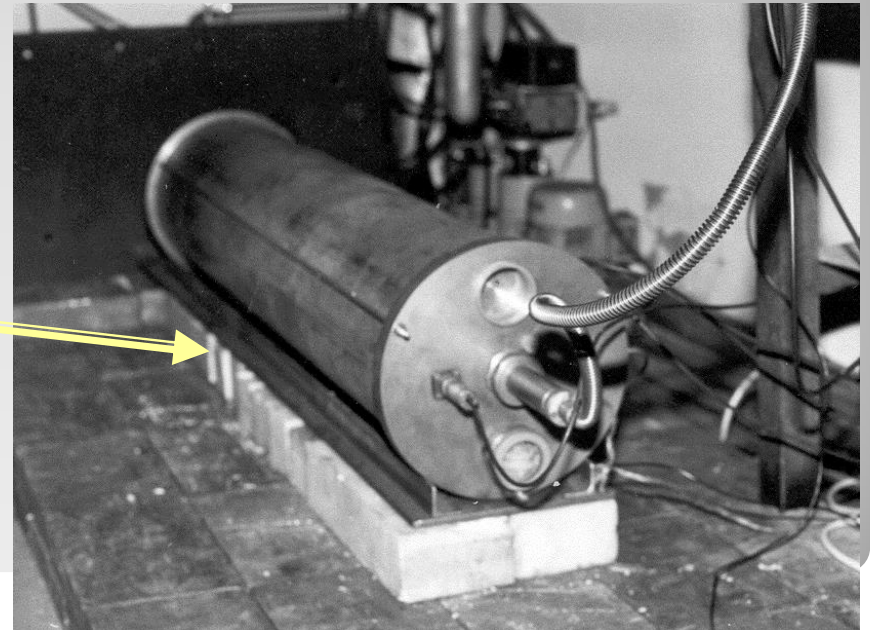


Priprema uzoraka za mjerenje ^{14}C ,
 tehnike **AMS**, **LSC-A**, **LSC-B**

GPC – Gas proportional counter

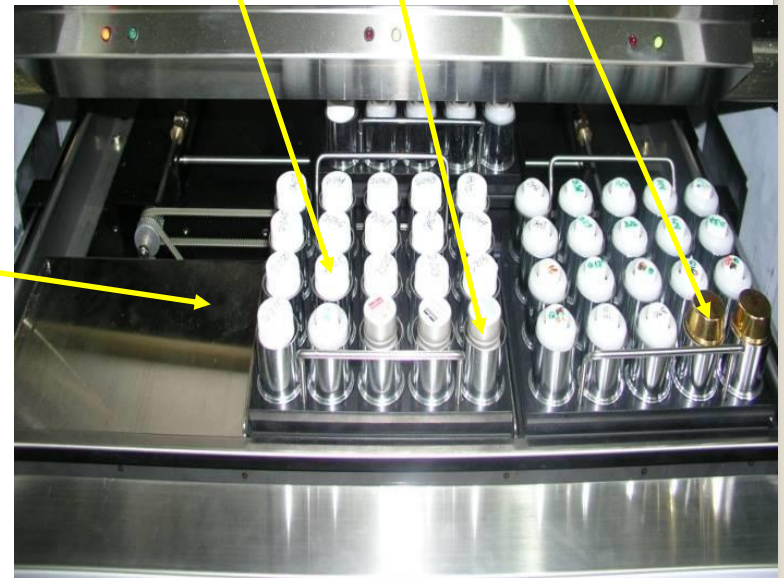


- Counting gas (CH_4) → sample and detection medium
- β particles from decay ionize gas → primary electrons
- electron avalanches are produced in strong electric field → signal



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

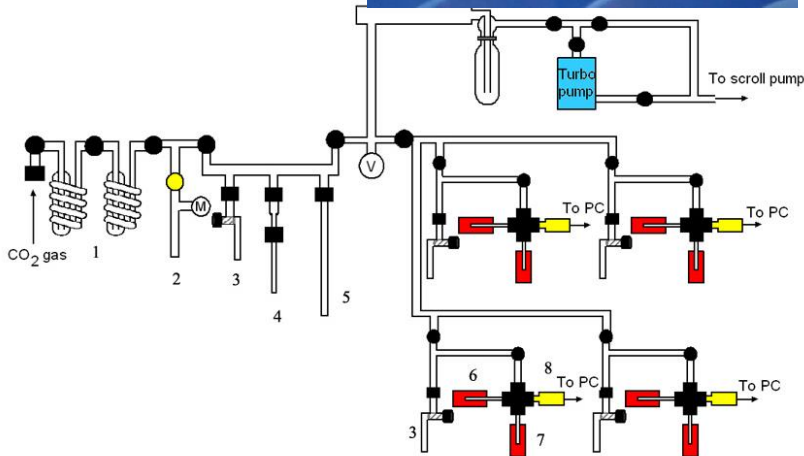
In cooperation with SUERC-UGLA, East Kilbride – Glasgow

AMS- ^{14}C

Ag

uzorak

CuO



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

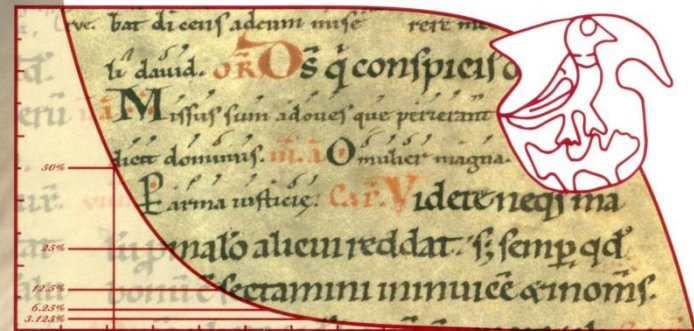
3/2015. – otkrivena neobilježena arhivska kutija s neevidentiranom arhivskom građom
Pet rukopisnih kodeksa na papiru,
6 pergamentnih listova s fragmentima rukopisa

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

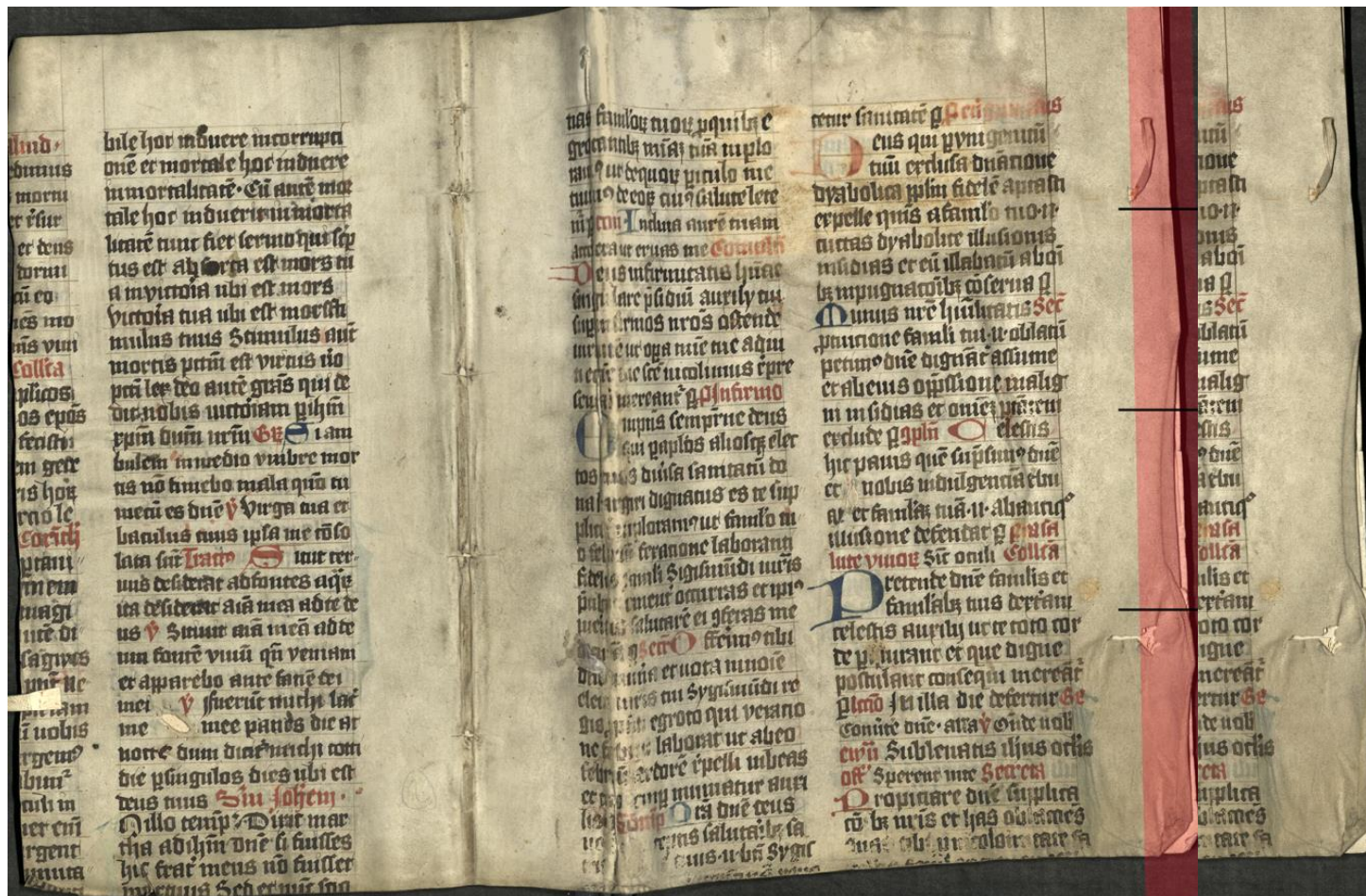


Pergament

rukopisi K3 i K4 – liturgijski tekstovi na latinskom

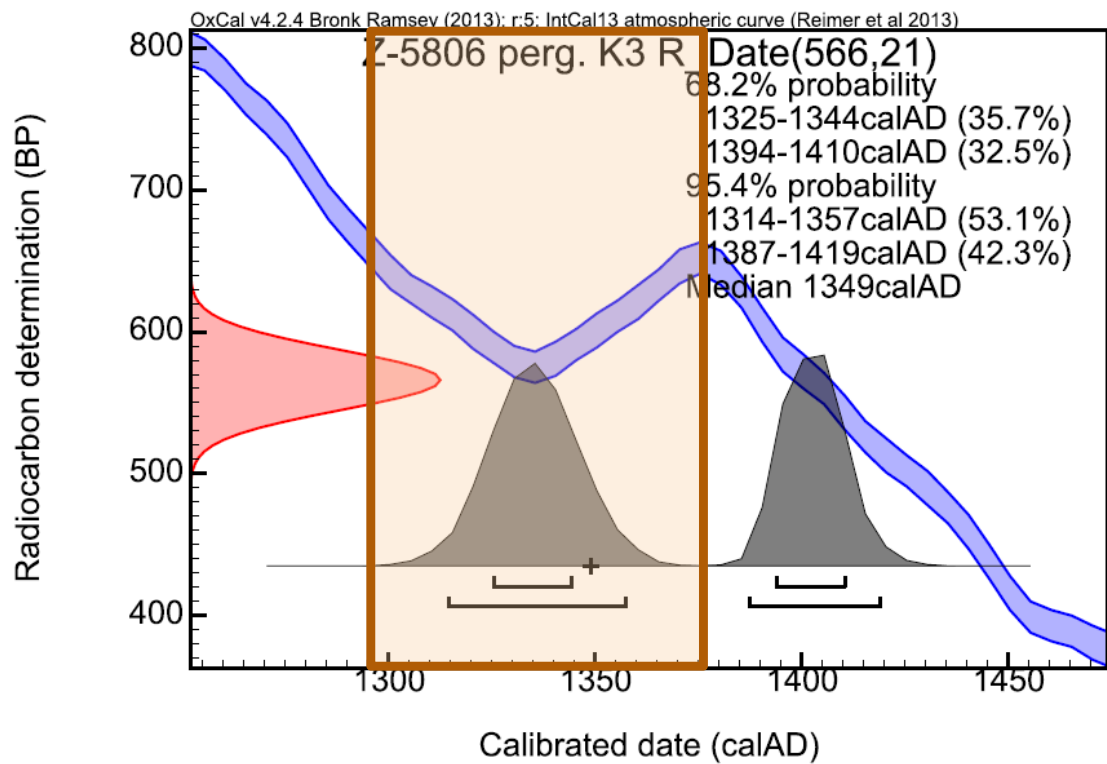
Arhiv Vojvodine, Novi Sad

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



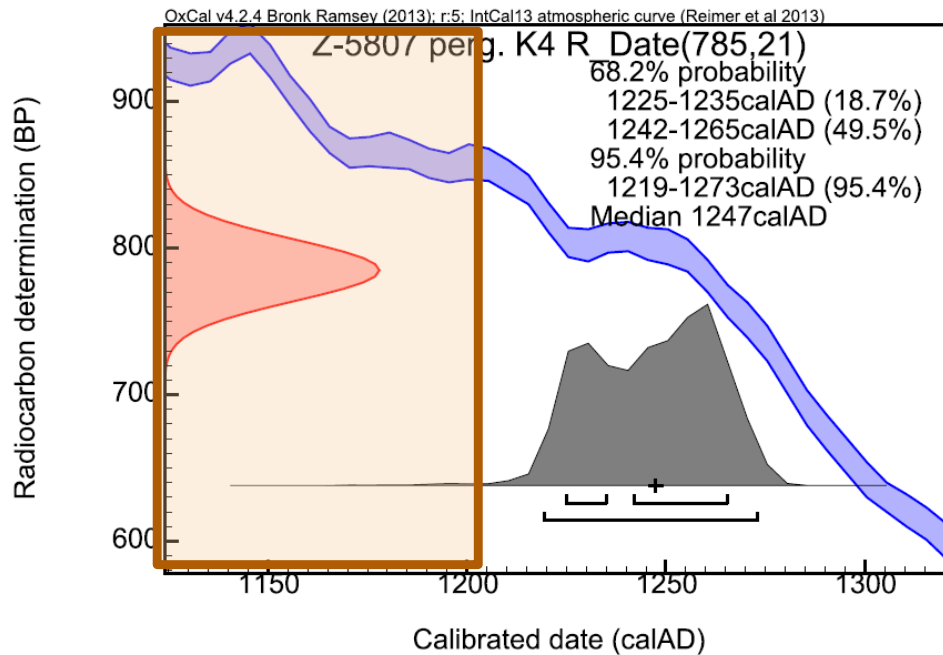
K3

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
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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