The Abdus Salam
International Centre for Theoretical Physics

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SCHOOL ON ION BEAM ANALYSIS AND ACCELERATOR APPLICATIONS

13 - 24 March 2006

^{14}C dating with accelerator mass spectrometry

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SCHOOL ON ION BEAM ANALYSIS AND ACCELERATOR APPLICATIONS

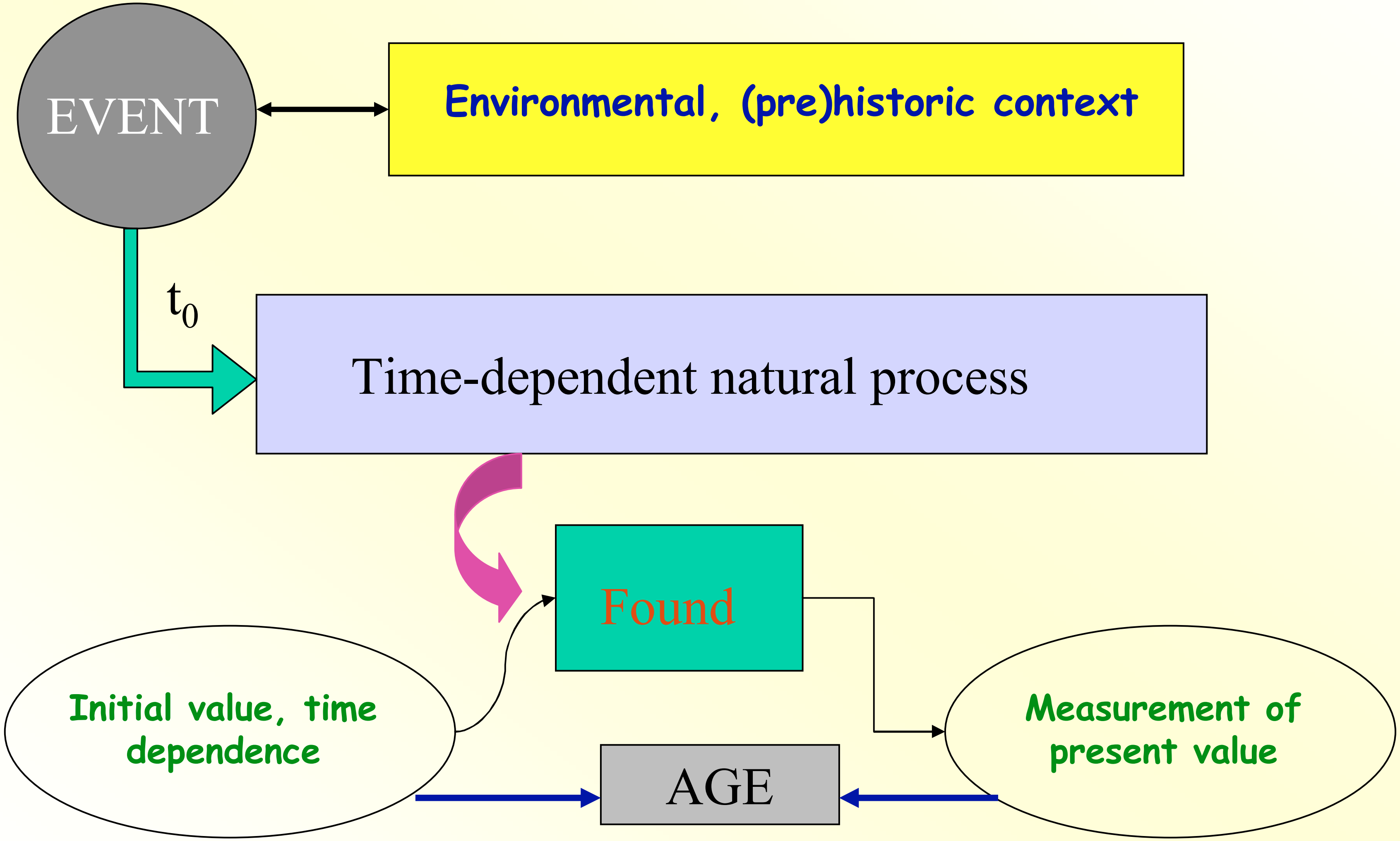
Trieste, March 2006

^{14}C DATING WITH ACCELERATOR MASS SPECTROMETRY

(Filippo Terrasi; Dipartimento di Scienze Ambientali, Seconda Università di Napoli, Caserta)

- Relative and absolute dating. ^{14}C as natural chronometer.
- Basic assumptions. Decay counting and atom counting
- Measurement of the isotopic ratio. Suppression of interferences
- Background, fractionation and calibration corrections
- AMS and Nuclear Astrophysics

DATING (RELATIVE AND ABSOLUTE)



Willard F. Libby …

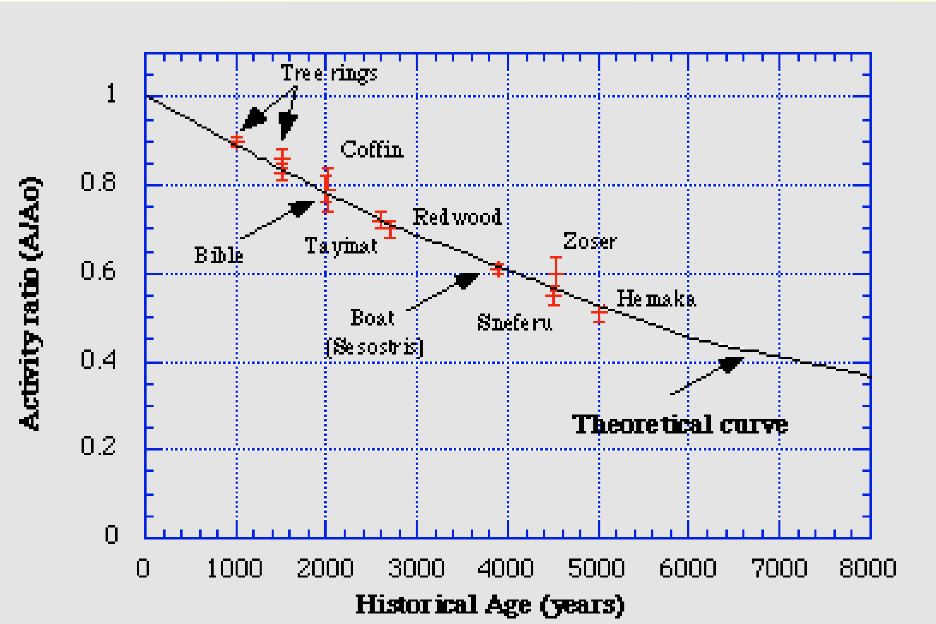
Birth of Radiocarbon Dating

W. F. Libby (ca. 1952)

"Seldom has a single discovery in chemistry had such an impact on the thinking in so many fields of human endeavor."

-*Nobel Committee (1960)*

[1]



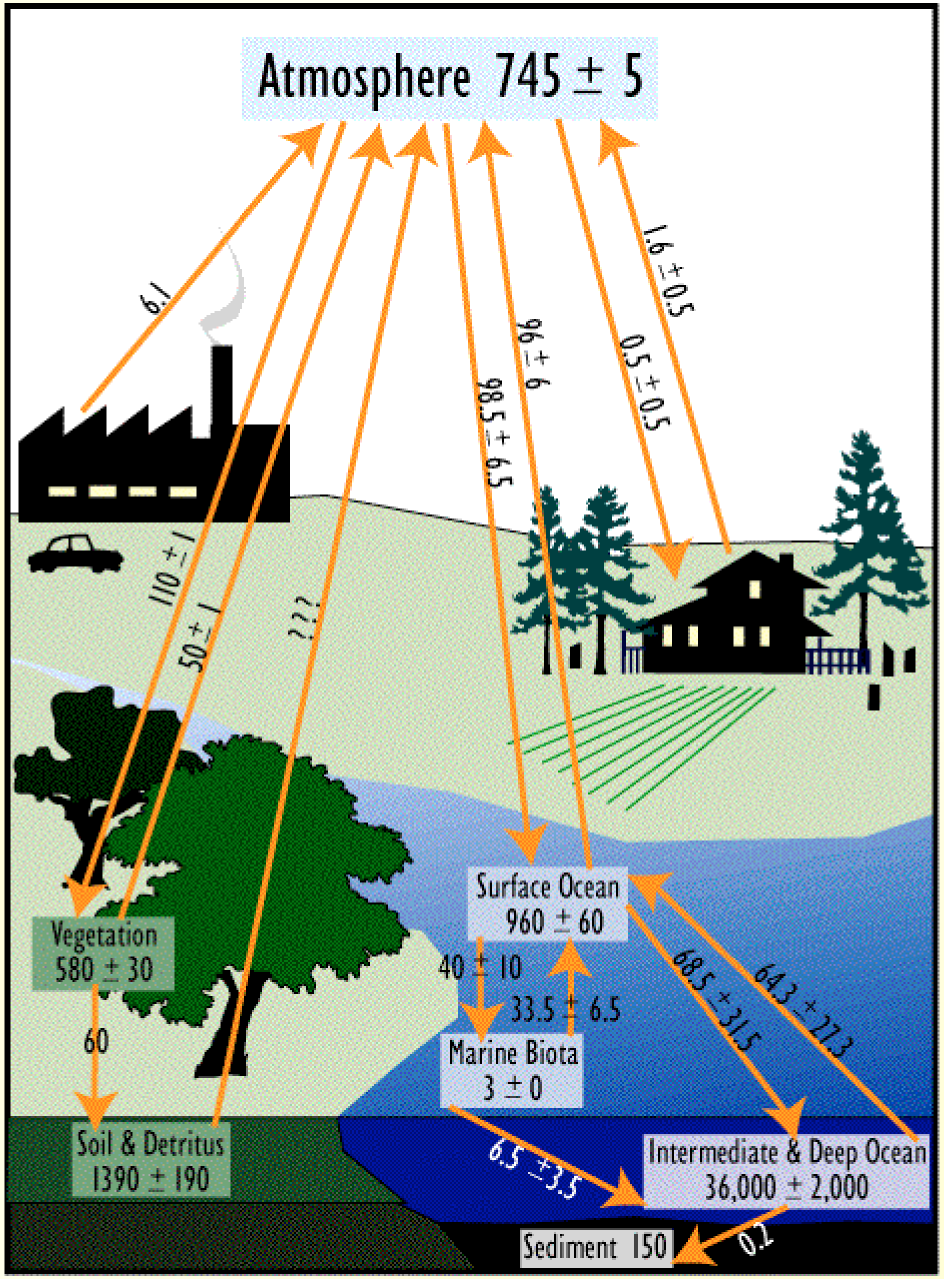
"The curve of knowns"

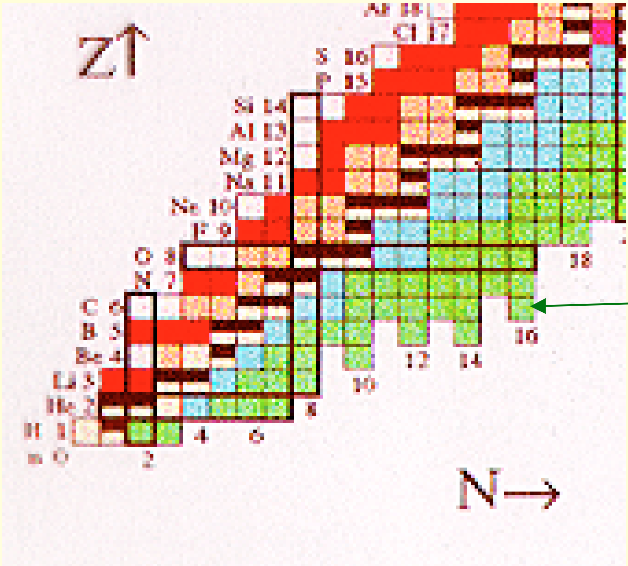
The global carbon cycle

- C is the 4th abundant element in the solar system
- C is about 20% of biosphere

Stores in PgC or GTC(10^{15} g)

Fluxes in PgC/year





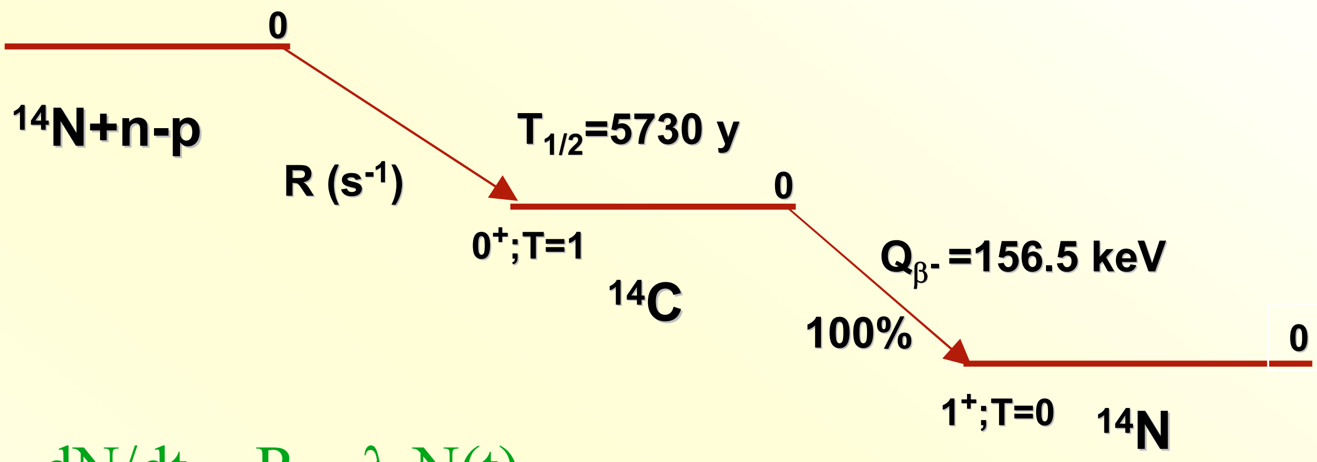
^{12}C (98.9%)

^{13}C (1.1%)

^{14}C radioactive

^{14}C production in the atmosphere

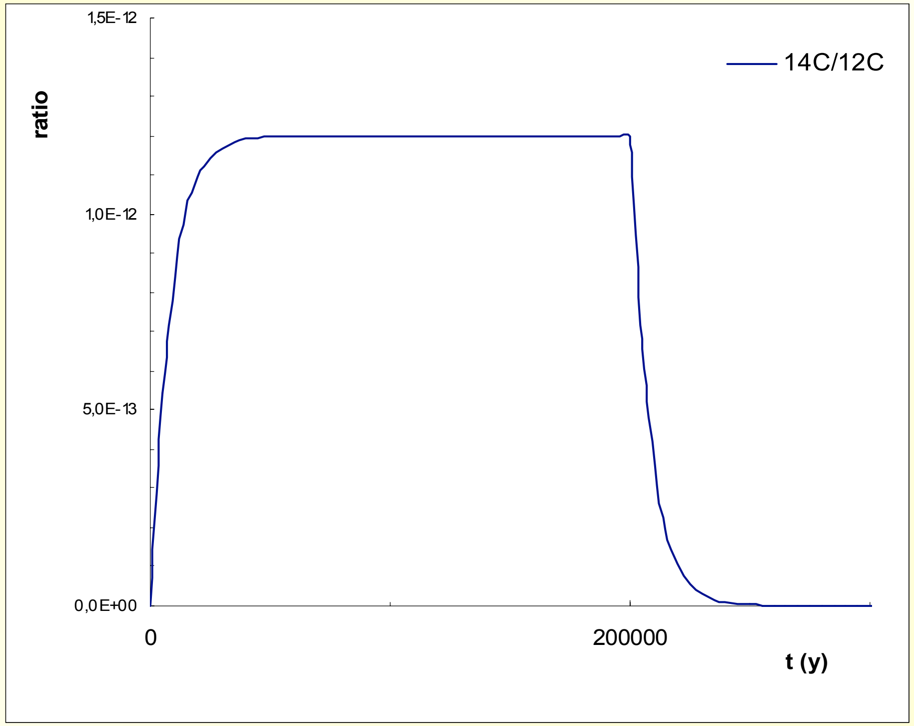
- Cosmic-ray primary protons produce secondary neutrons by spallation on N and O; neutrons are thermalized
- In the low stratosphere the reaction $^{14}N(n, p)^{14}C$ takes place (σ ~ 1.8 b, average prod. rate 2.2 at/cm^2/s, but latitude dependent)
- If the production rate is constant, after a few half lives ($T_{1/2}$ = 5730 y) production and decay reach equilibrium
- ^{14}C is oxidized to $^{14}CO_2$ and, mixing with stable CO_2, enters the global carbon cycle



$$dN/dt = R - \lambda\, N(t)$$

If at t=0 N(0)=0

$$N(t) = R/\lambda\ (1-e^{-\lambda t})$$



Example: ^{14}C production started at time 0 and stopped 200000 years later.

SCHEMATIC ASSUMPTIONS

1. ^{14}C is rapidly uniformly distributed in atmosphere -> "mixing and residence time"
2. The isotopic composition of atmospheric C is constant at least since the last 60,000 years and is known -> "constant production rate"
3. C in living organisms is exclusively of atmospheric origin (or from a known "reservoir") and does not contain spurious C -> "contamination"
4. The isotopic composition of C in the living organism is the same of the atmospheric C (fractionation!) -> "equilibrium system – reservoir"

SCHEMATIC ASSUMPTIONS (cont)

5. After the death the exchange of C with the atmosphere (and other compartments) ceases and the system is closed
6. The half life of ^{14}C is precisely known -> "adopted value: (5730±40 y)"

$$t = \tau \ln[C_0/C(t)];\ \Delta t = \tau\ \Delta C/C$$

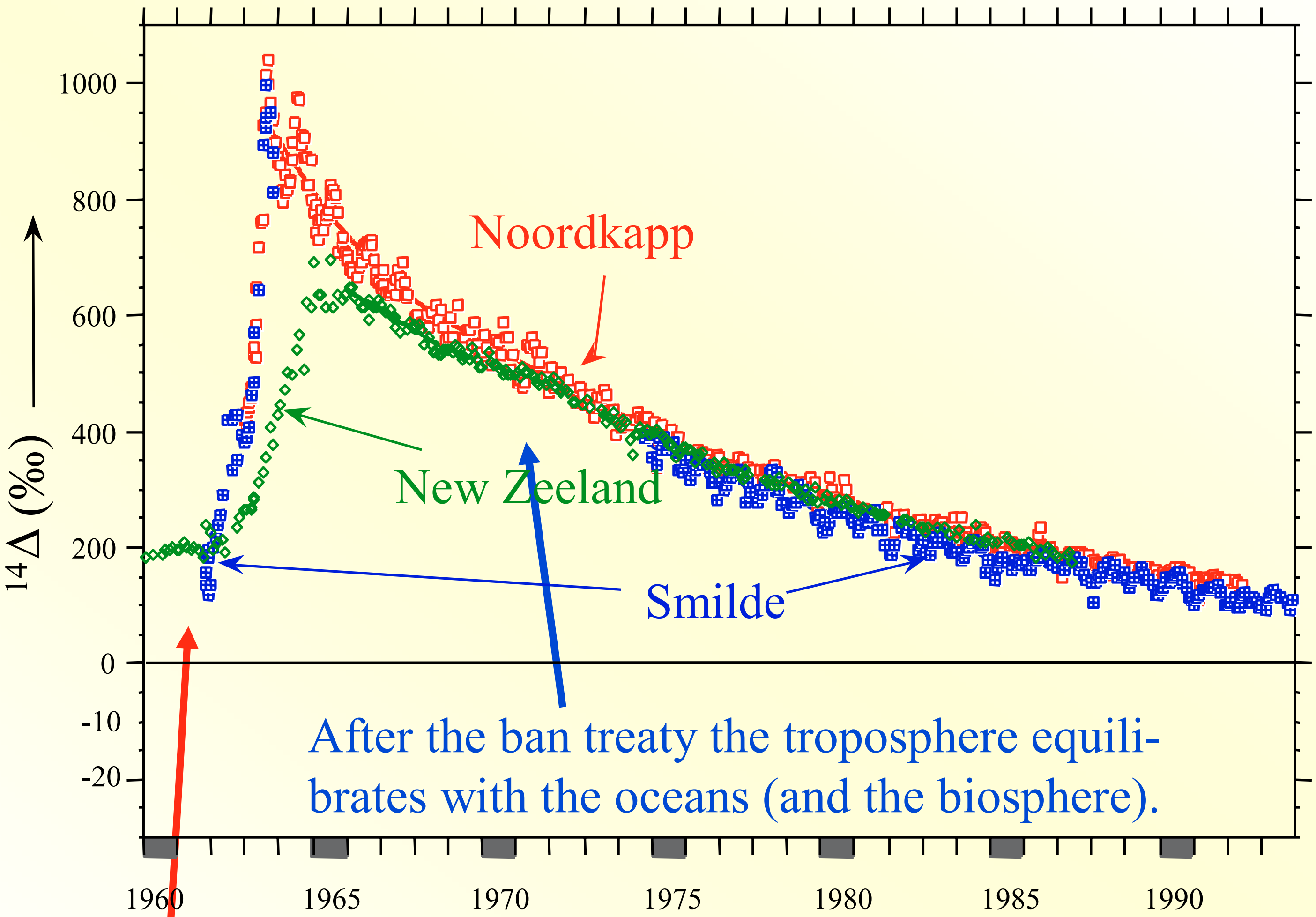
but:

3 → Background subtraction

4 → Fractionation correction

2-6 → Calibration

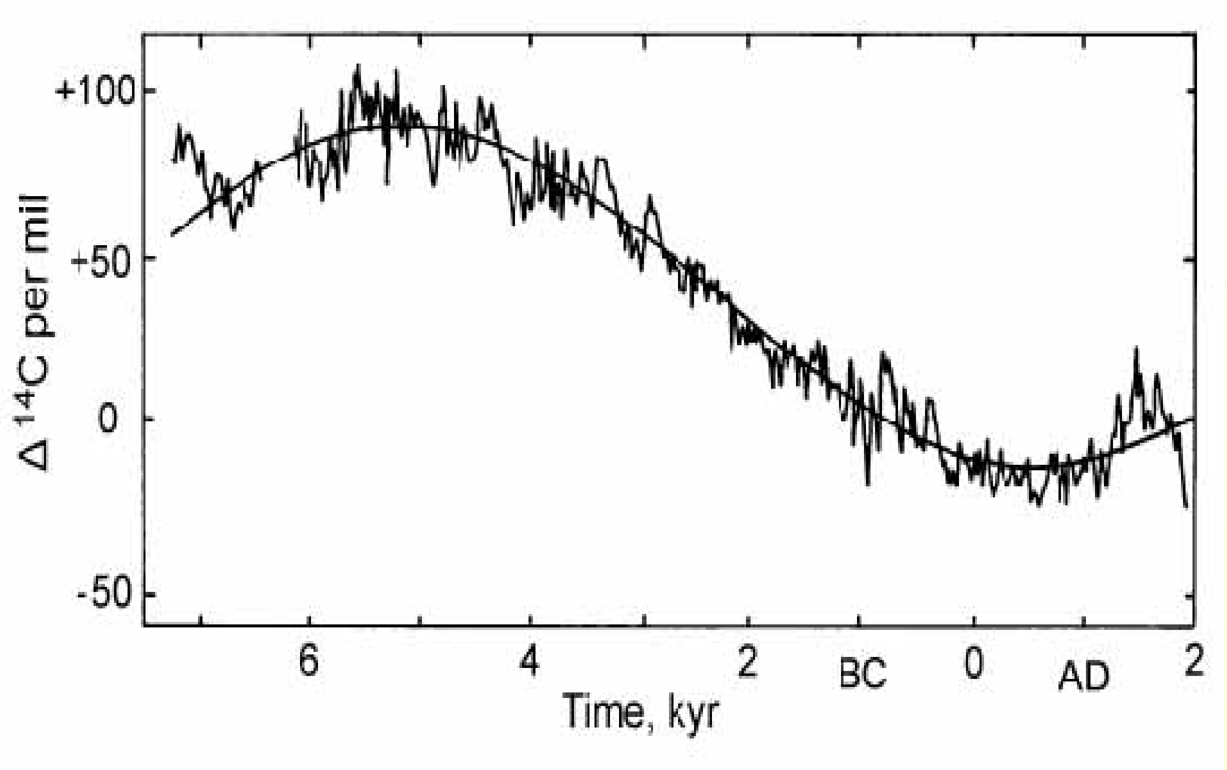
1) "mixing and residence time"



Above-ground nuclear bomb tests produce huge amounts of ^{14}C in the stratosphere

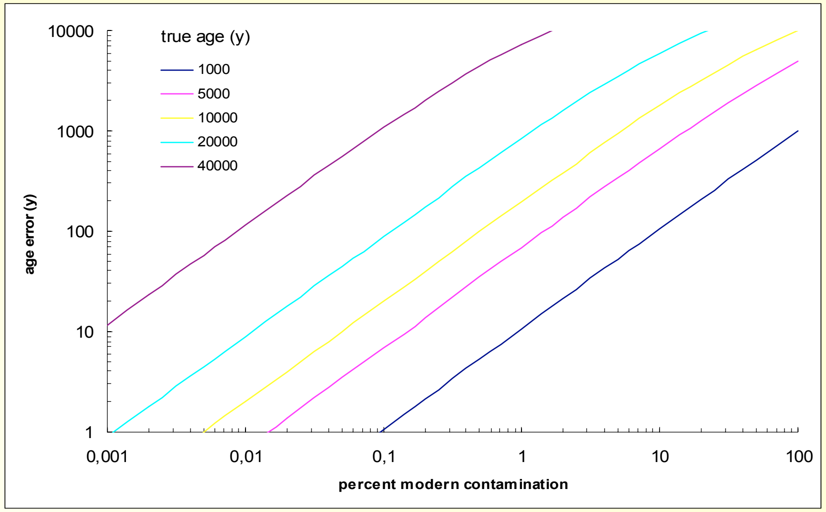
2) constant production rate

Difference of the past atmospheric ^{14}C concentration with respect to “present” vs age



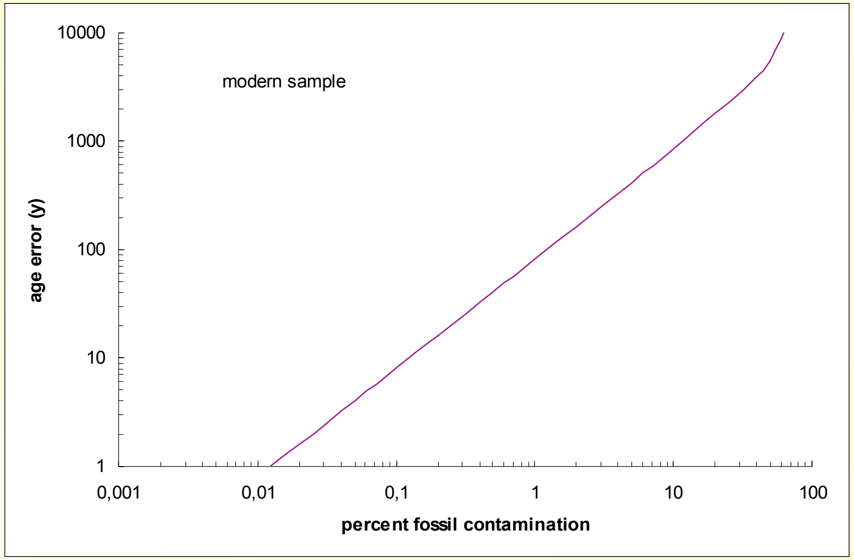
Variations of geomagnetic field and solar activity

3) contamination



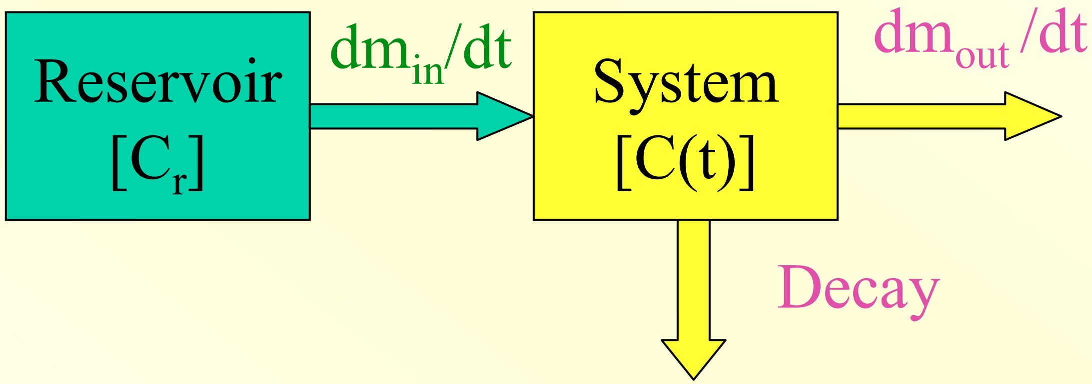
Effect of modern C contamination on the apparent age

Effect of fossil C contamination on the apparent age



4) equilibrium system – reservoir

Photosynthesis and metabolic processes



Constant mass: $dm_{in} = dm_{out}$ -> $\nu = dm_{in}/dt = dm_{out}/dt$

$$N(t) = m\,C(t)$$

$$dN/dt = \alpha\, C_r\, \nu - N(t)\,(\nu/m + \lambda)\ ;\quad \nu/m + \lambda \approx \nu/m$$

$t >> v/m \quad C(t) \rightarrow \alpha\, C_r$

Measurement of ^{14}C concentration

Pre-bomb atmosphere $^{14}C/^{12}C = 1.2\ 10^{-12}$

Decay counting

1g C **5 10^{22} atoms ^{12}C**

6 10^{10} atoms ^{14}C

$\lambda N = 0.25\ s^{-1}$

10^5 counts ⇨ 110 h

$M\ t\ (0.3\%) = 110\ g\ h$

Atom counting

1mg C **1.9 10^{14} p/s ^{12}C (30 μA)**

220 p/s ^{14}C

$\varepsilon = 50\%$

10^5 counts ⇨ 0.25 h

60 million ^{14}Catoms in the sample

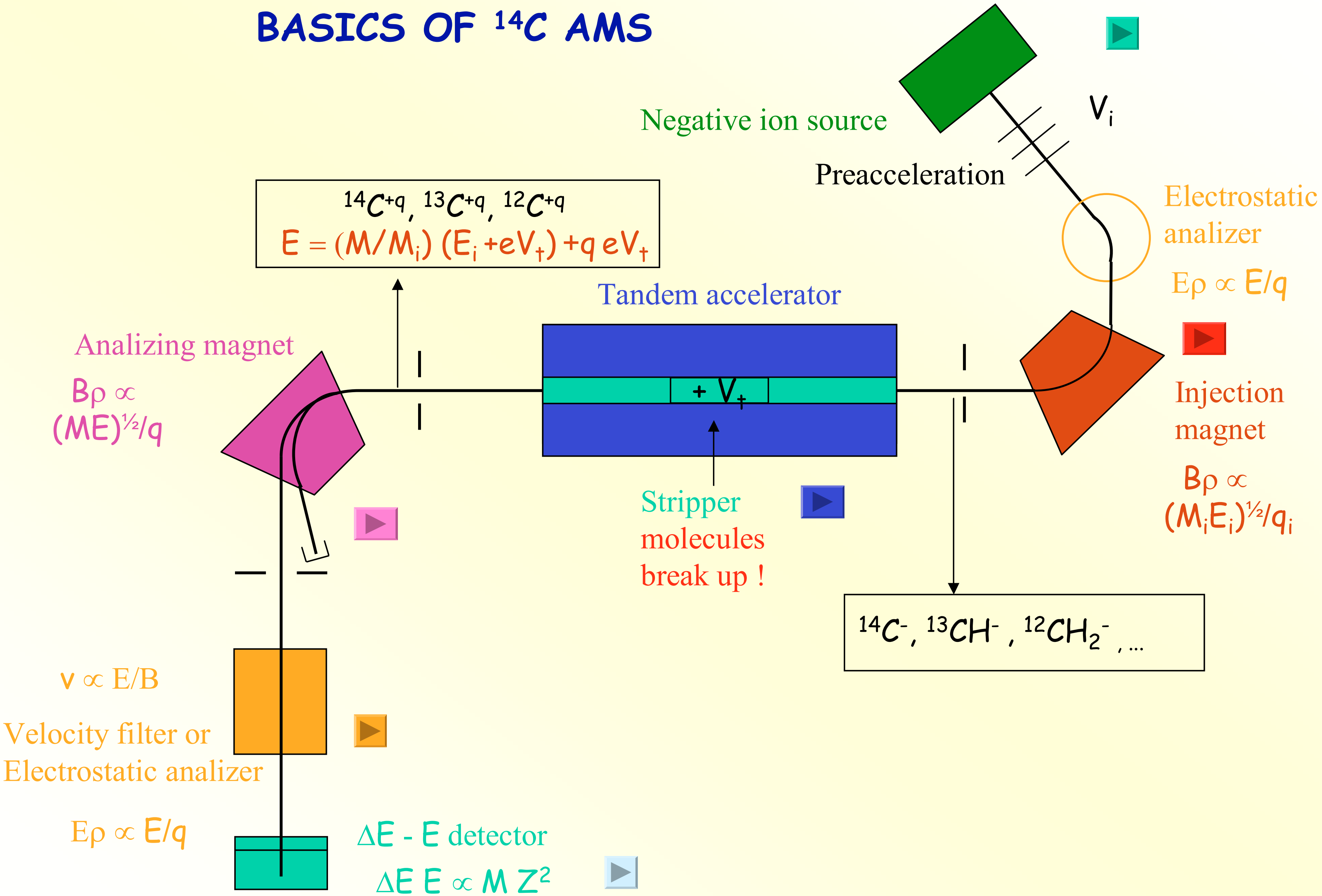
$M\ t\ (0.3\%) = 2.5\ 10^{-4}\ g\ h$

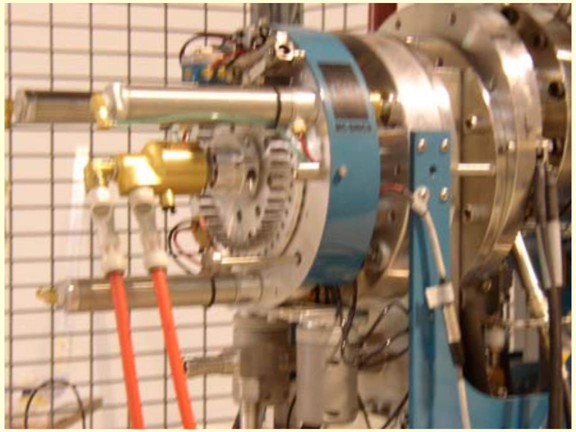
$\Delta M/M \sim$ 1/80000 $^{14}C - ^{14}N$

1/1000 $^{14}C - ^{12}CH_2$

1/2000 $^{14}C - ^{13}CH$

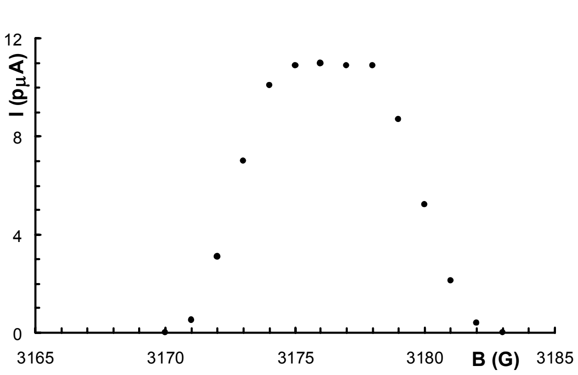
BASICS OF ^{14}C AMS





Negative ion sputtering source

- Sputtering of target material by a focused Cs^+ beam produced by thermal ionization
- Graphite targets yield up to > 100 μA C^- → need for sample treatment (alternative: development of gas ion sources)
- N does not form stable negative ions: isobaric interference elimination
- Preacceleration to ~ 100 keV
- Sputter energy tail: E/q selection by electrostatic analysis



Low energy mass analysis

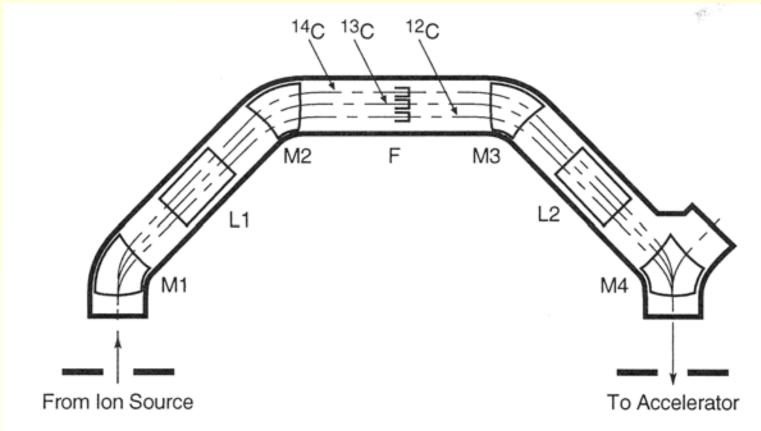
moderate resolution, high stability, double focusing, flat top transmission

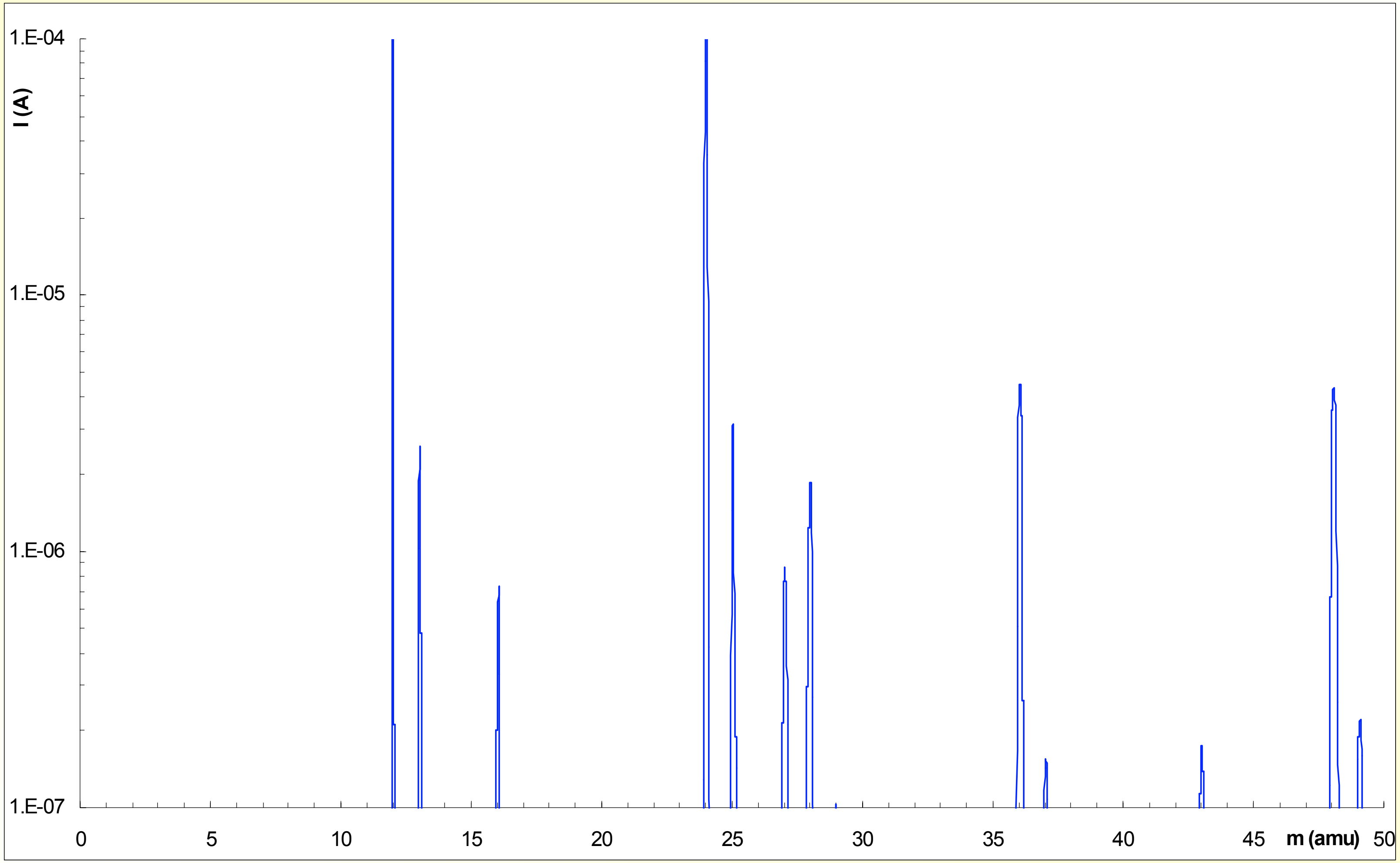
- Fast sequential injection

Bouncing voltages applied to the insulated magnet chamber M ($V_{inj}+V_{bou}$) = const → fast (<100 μs) switching of injection on the accelerator axis of the three isotopes at constant B and with the same injection energy. While injecting mass M, mass M-1 is detected in an offset Faraday cup

- Simultaneous injection

Recombinator





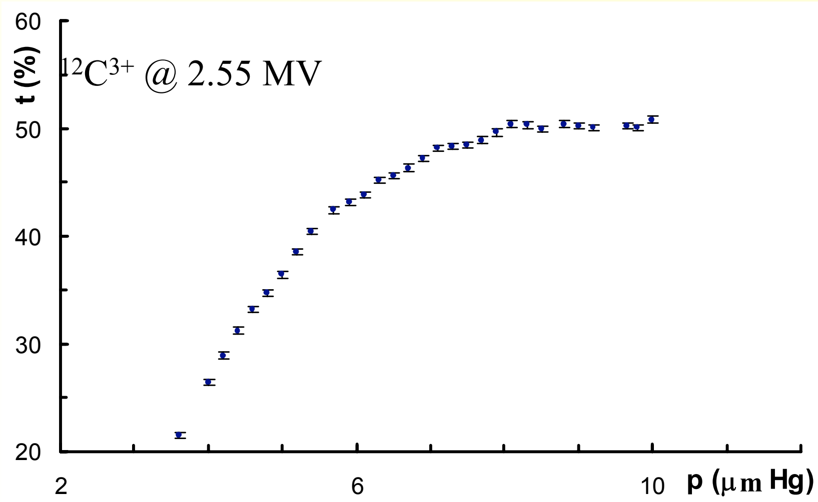
le mass spectrum

Tandem accelerator

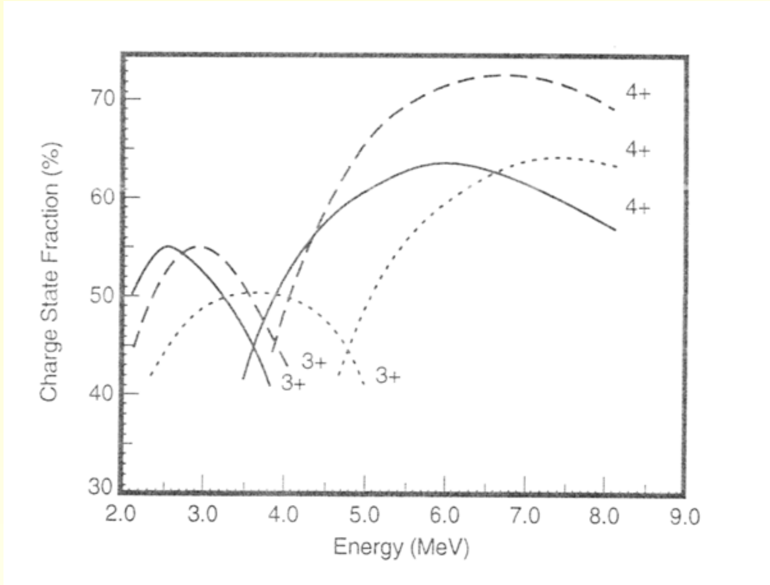
High energy (> 10 MeV) mass spectrometry allows:

- Rejection of molecular interferences by electron stripping
- Reduction of isobaric interferences by mass and charge identification
- Minimization of scattering and charge exchange processes

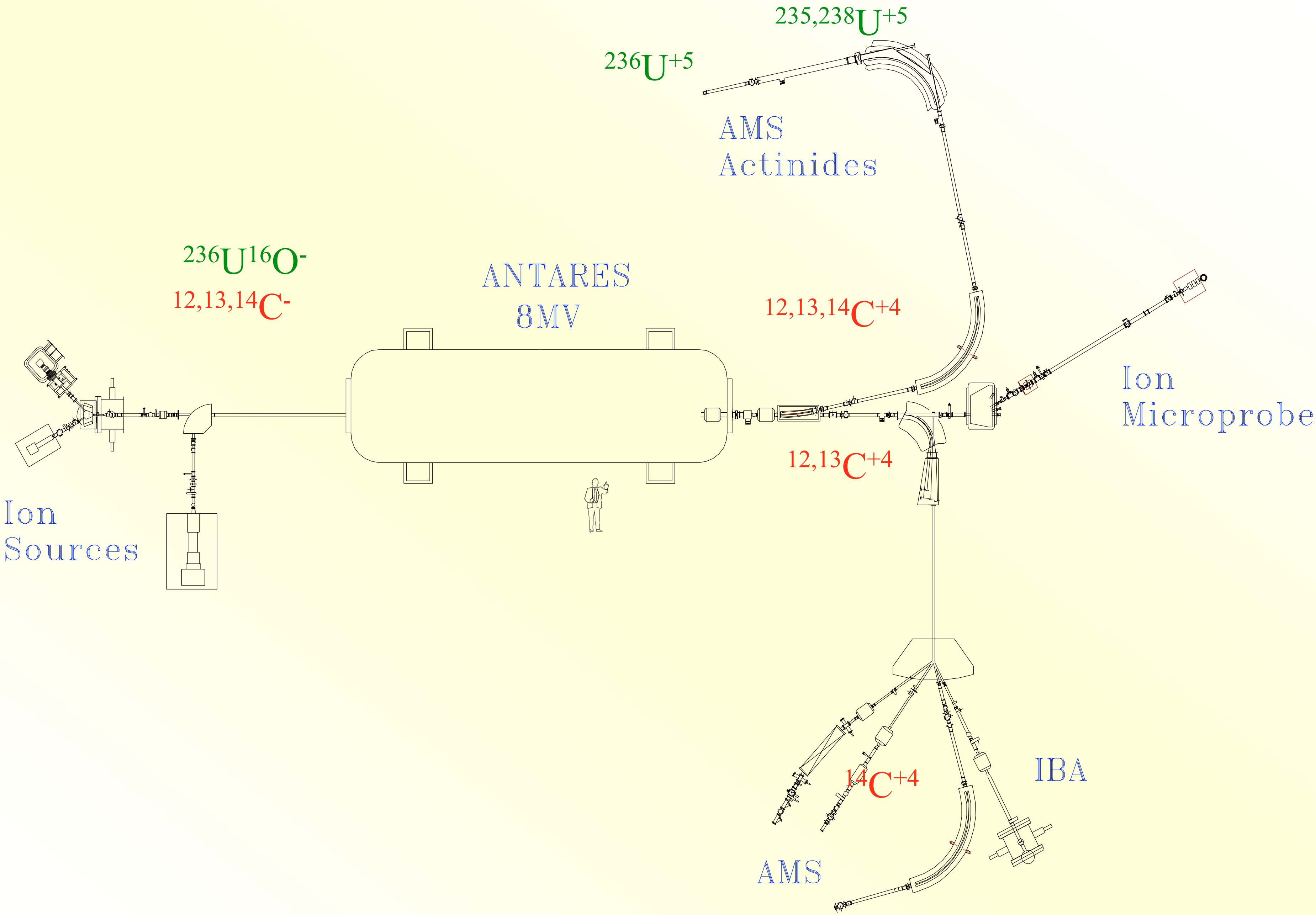
Equilibrium charge state



Equilibrium charge state distribution



- Velocity dependence of charge state probability ⟶ machine induced fractionation ⟶ normalization to a standard with known isotopic ratio
- Dissociation of molecules by Coulomb explosion for $q \geq 3$
  - High TV (>5 MV) accelerators adapted from nuclear physics facilities ▶
  - Dedicated low TV (2-3 MV) systems ▶
- Collisional dissociation of molecules for $q = 1$ in large thickness strippers
  - Compact and table top systems ▶



ANTARES – ANSTO, Sidney

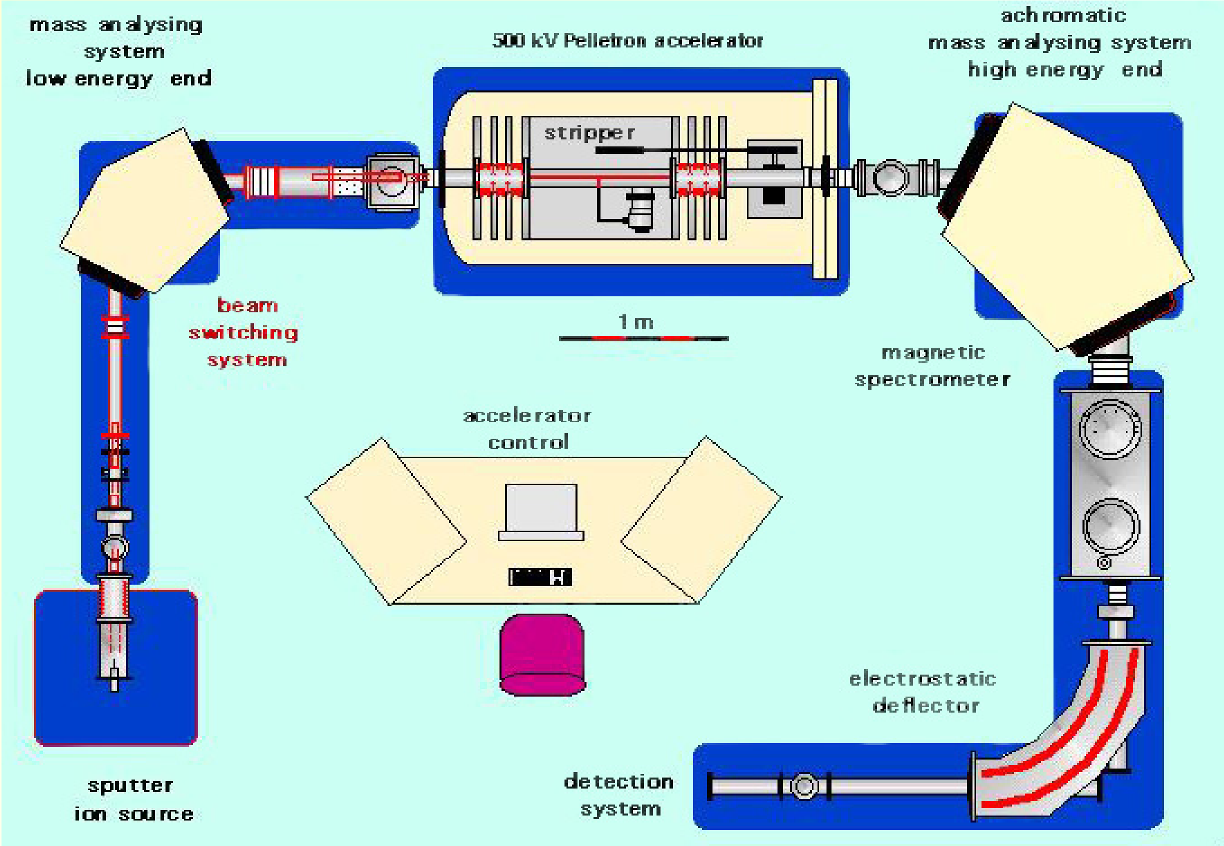
The AMS system in Caserta (3 MV)

Center for **I**sotopic **R**esearch on **C**ultural and **E**nvironmental heritage

aserta

INNOVA
CENTRO REGIONALE DI COMPETENZA
PER LO SVILUPPO ED IL TRASFERIMENTO
DELL'INNOVAZIONE APPLICATA AI
BENI CULTURALI E AMBIENTALI

DSA-SUN

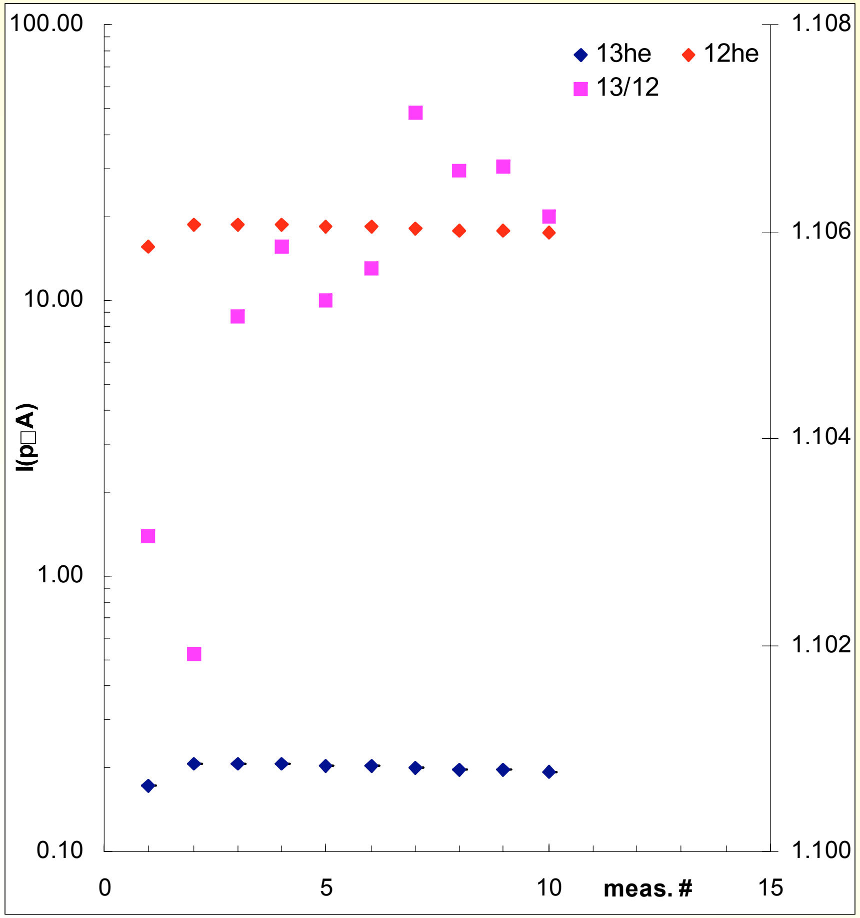


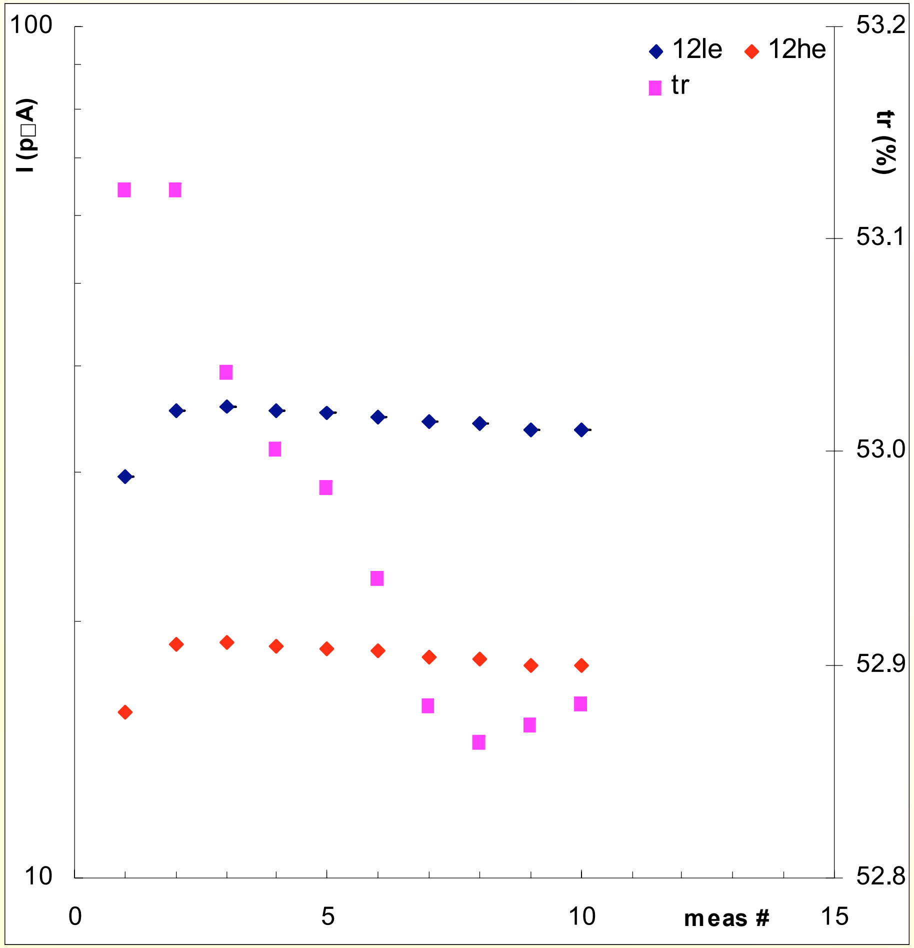
Compact AMS system (Zurich) ….. mini

Displacement in focal plane:

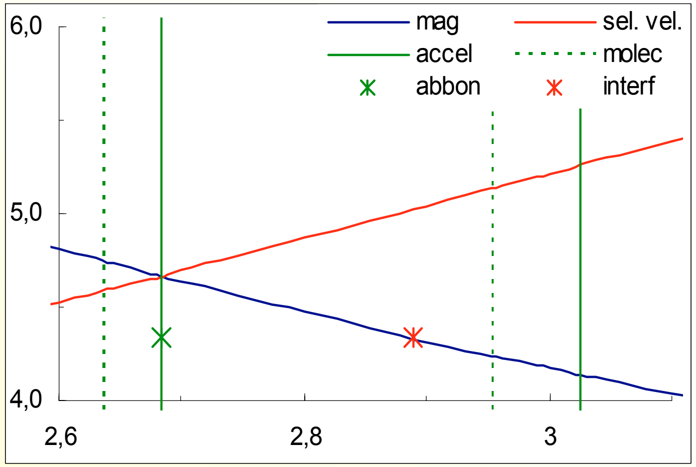
$D = 4\,\rho\,\Delta p/p = 2\,\rho\,\Delta M/M\ (\phi = 90°)$

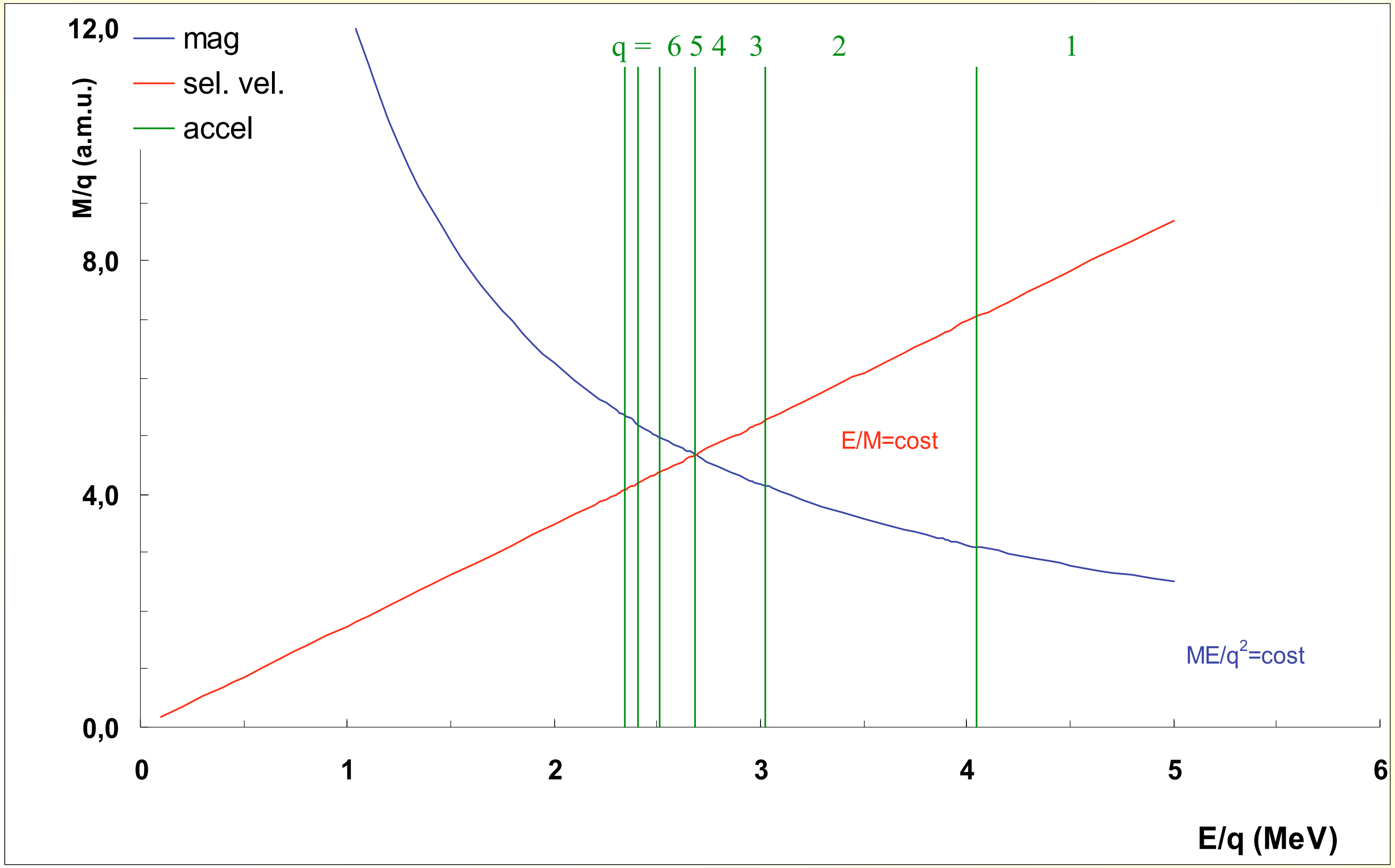
13/12 isotopic ratio



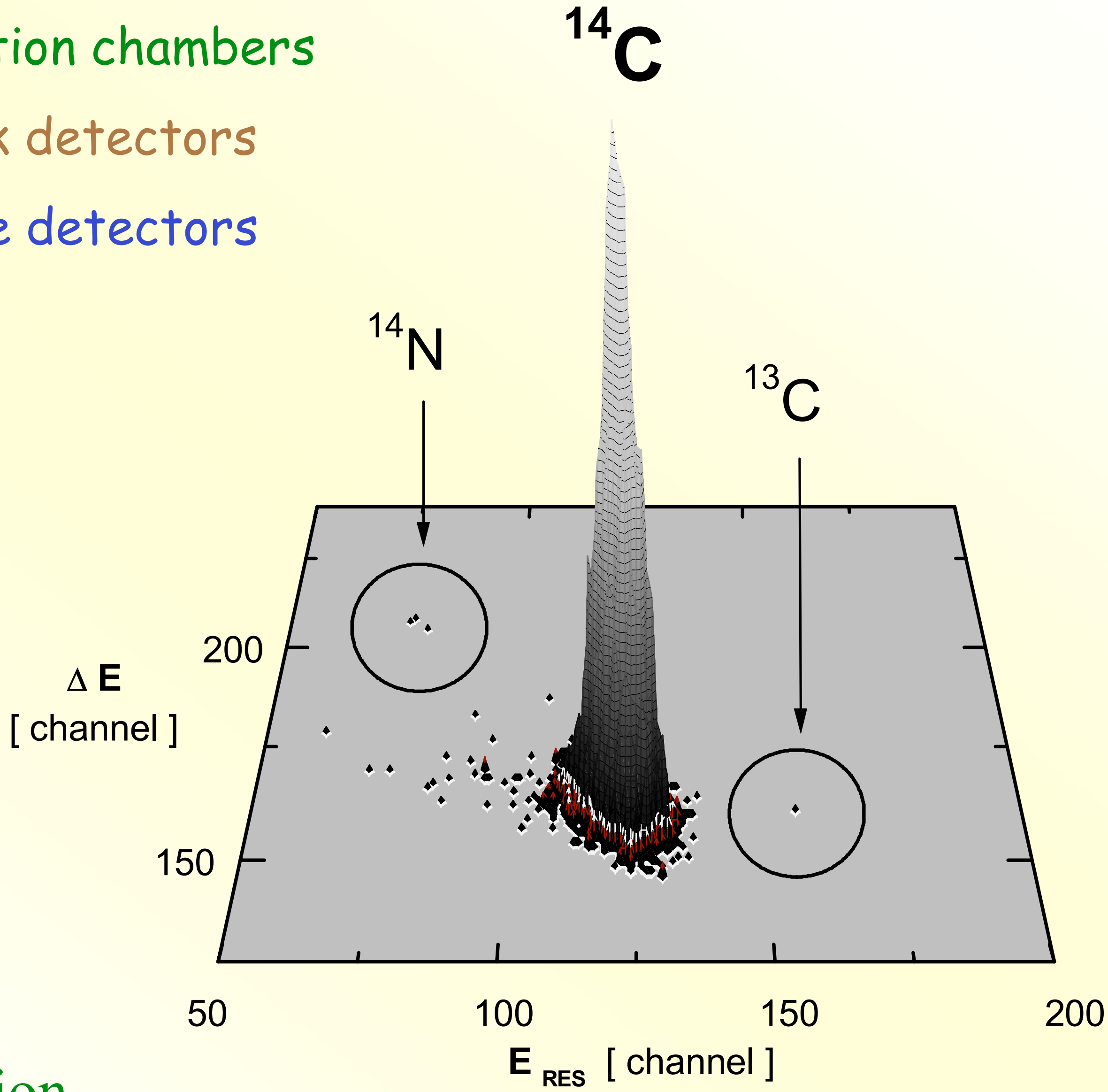


le - he transmission

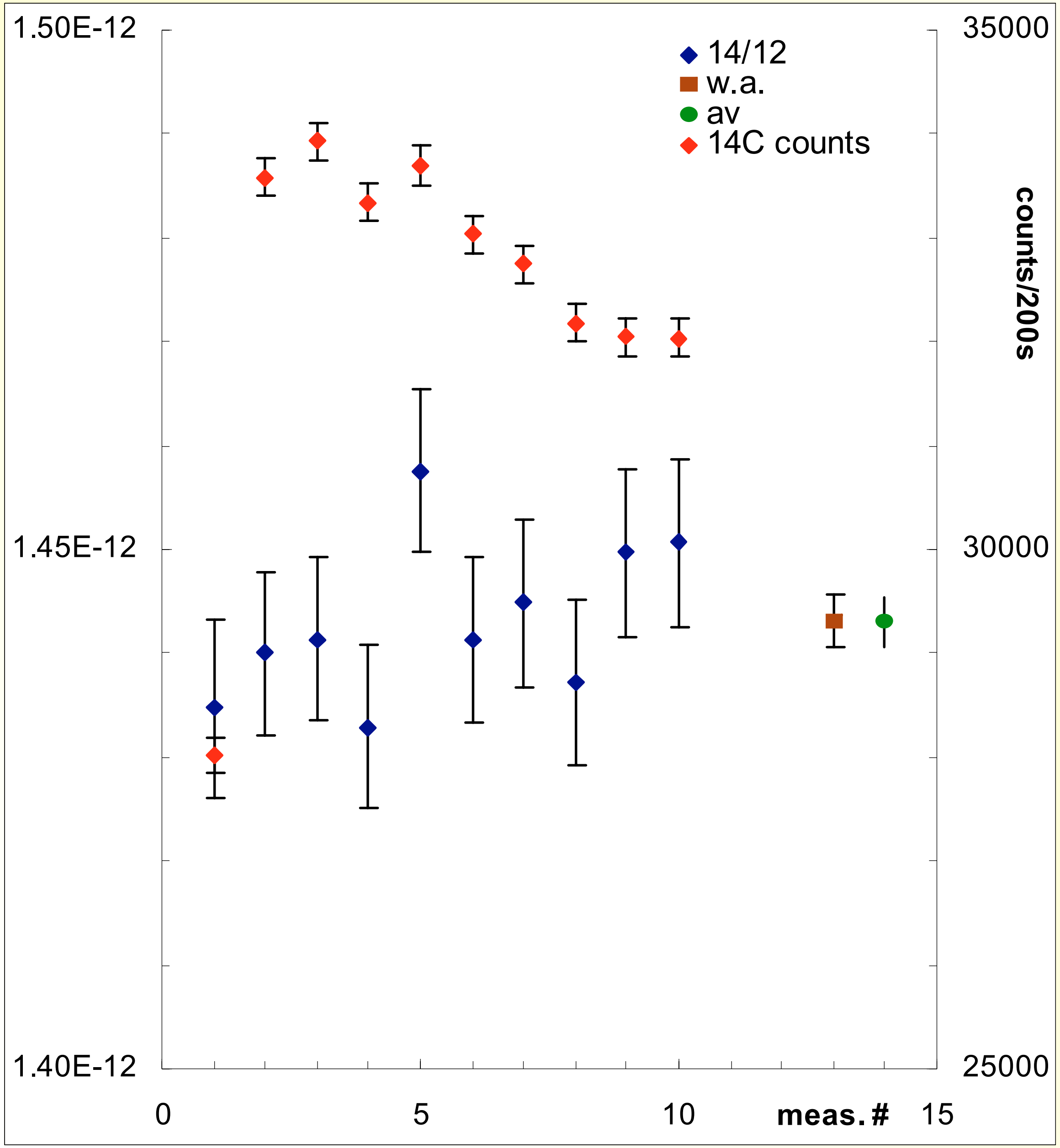

6,0
5,0
4,0
2,6
2,8
3
mag
sel. vel.
accel
molec
abbon
interf


12,0
8,0
4,0
0,0
mag
sel. vel.
accel
M/q (a.m.u.)
q = 6 5 4 3 2 1
E/M=cost
ME/q²=cost
0
1
2
3
4
5
6
E/q (MeV)

- Gas ionization chambers
- Bragg peak detectors
- Solid state detectors



Identification matrix



14/12 isotopic ratio

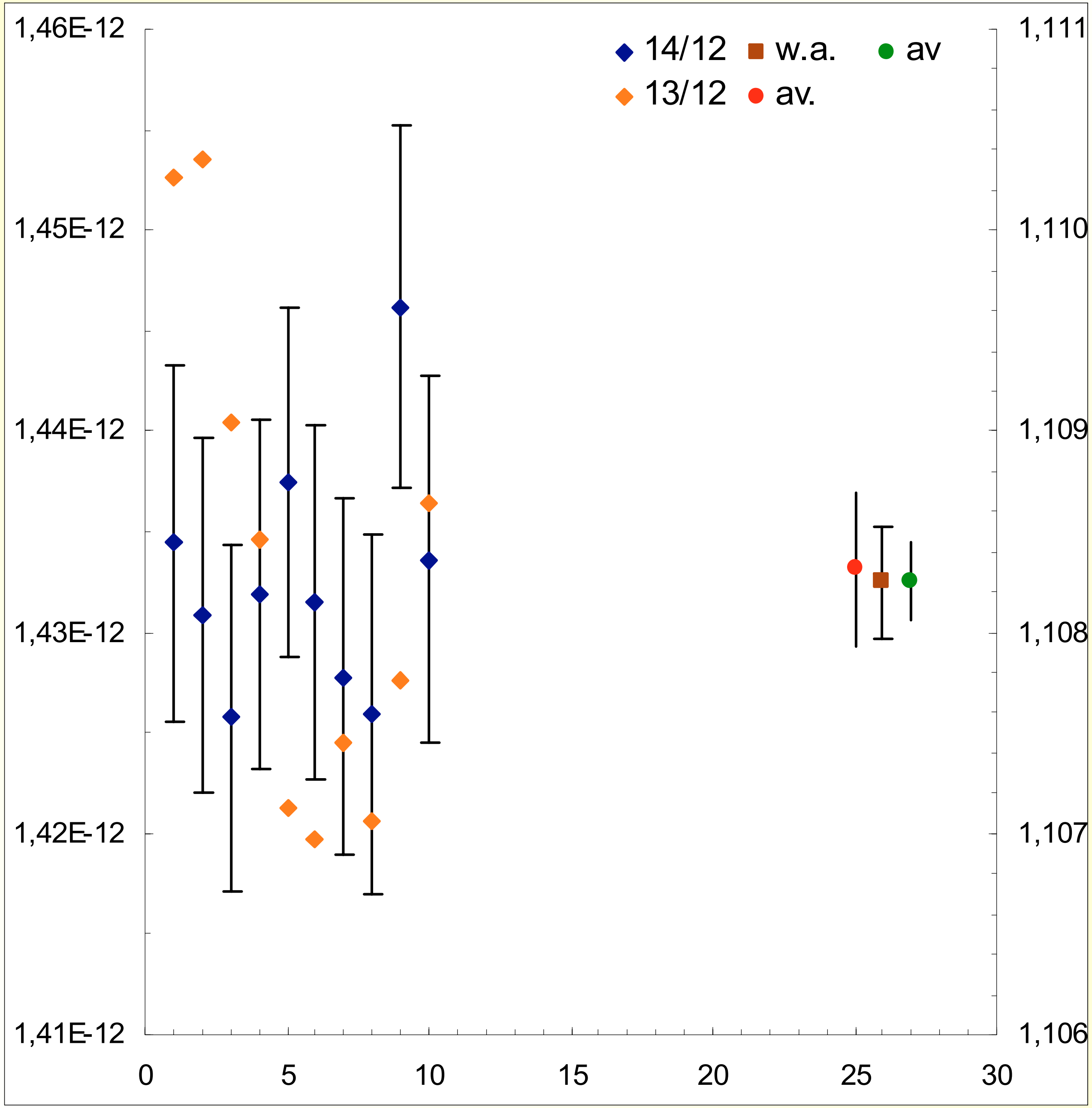
Internal error:

$[\Sigma_i(1/\sigma^2_i]^{-1/2}$

External error:

sdom

F test for consistency

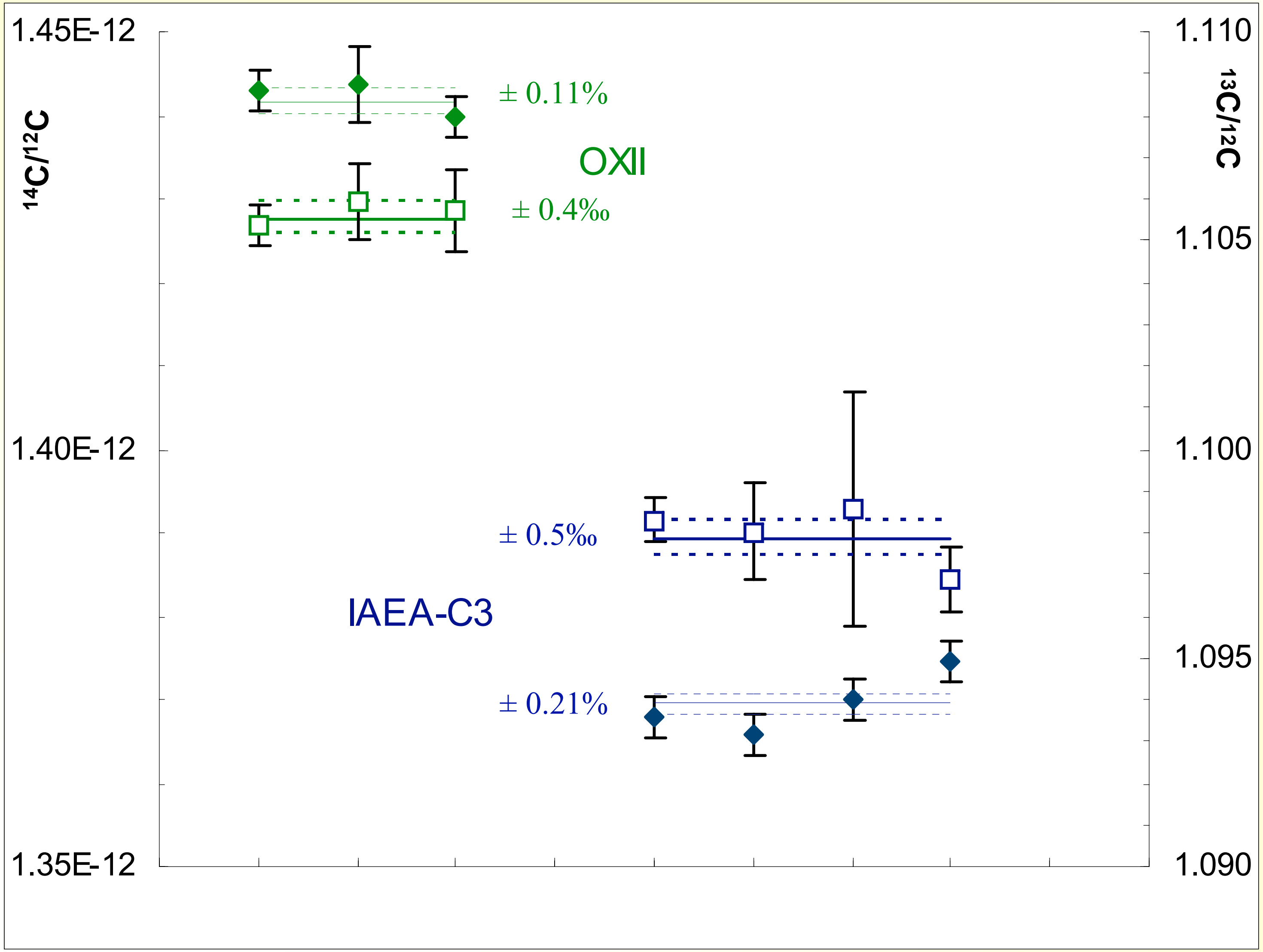


pos/type
22
OXII
name
OXII
2
summary
6
oxII
runs
10
$^{14}C/^{12}C$
1,4325E-12
0,20%
1,4325E-12
0,13%
89%
$^{14}C/^{13}C$
1,2925E-10
0,20%
1,2925E-10
0,14%
86%
$^{13}C/^{12}C$
1,1083
0,03%
14,72

… summarizing

-Sample is placed in the ion source
- First ion mass selection is performed before injection
- Ions are accelerated up to ≈ 1 MeV/A
- Rare isotope A and q are selected by magnetic and electrostatic analysis
- Rare isotope ions are Z-identified and counted in the final detector
- The ratio to the integrated charge of abundant isotope accelerated with similar transmission is measured
- Isotopic abundance is obtained by comparison with a standard

Normalization to a standard



CONTAMINATION

1. Sample contamination during C uptake (incorporation of older organic matter, reservoir effect)
2. Contamination during found burial
    - Humic infiltration
    - Roots penetration
    - Mixing with spurious material
3. Contamination during sample treatment: blank background subtraction.

SAMPLE TREATMENT (solid samples)

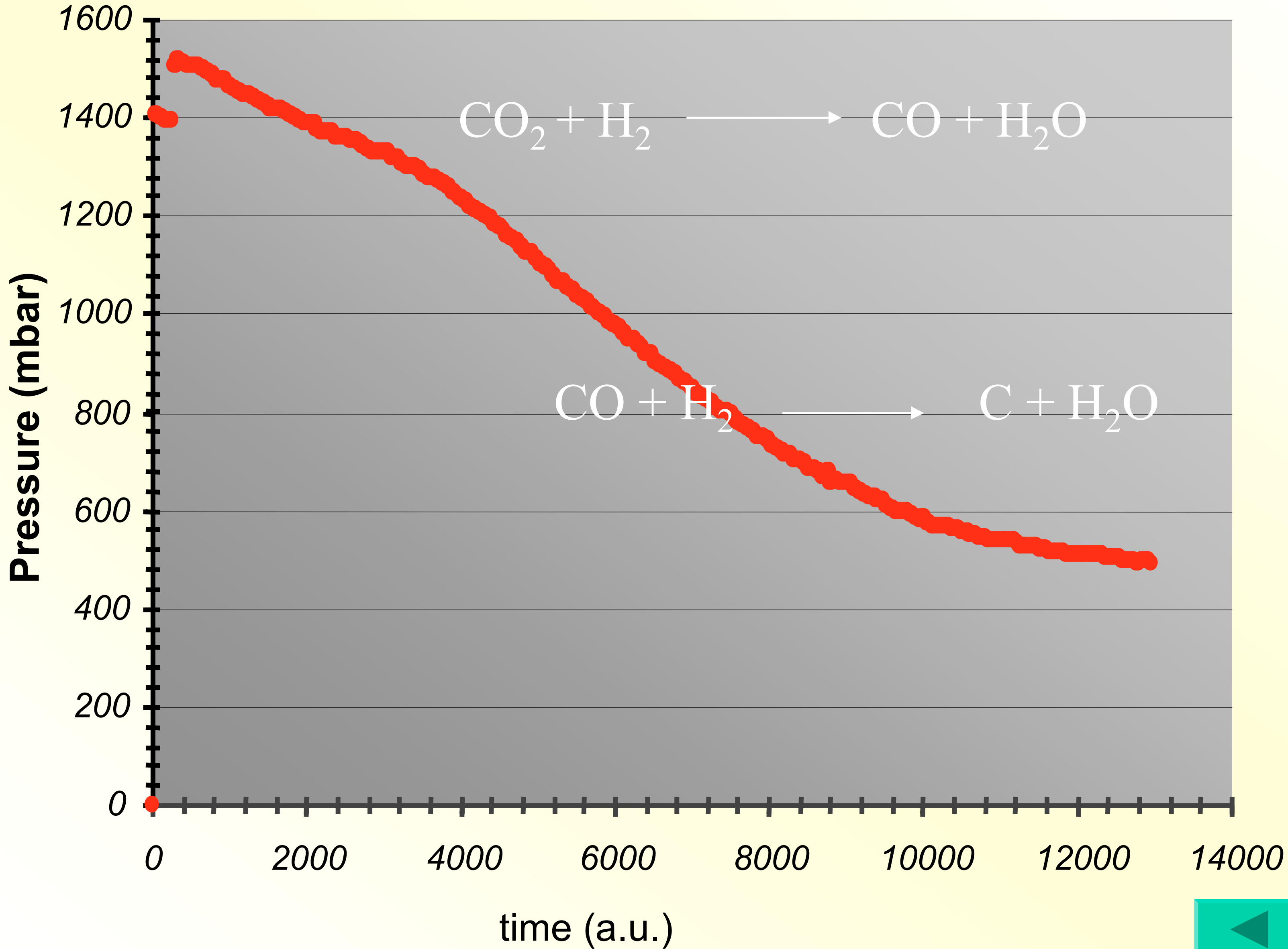
Removal of extraneous material and reduction to elementary carbon.

1. Physical and chemical pretreatment
   - AAA (carbonates and humics removal)
   - Collagen gelatine extraction (bones)
   - Carbonate hydrolysis with H_3PO_4
   - …………
2. Oxidization to CO_2
   - Combustion with CuO at 900 °C
   - Combustion in furnace with elemental analyzers

SAMPLE TREATMENT (cont)

3. Graphitization
   - Reduction by H_2 (Fe or Co catalyzed) (slow process)
   - Zn reduction with TiH_2

Incorporation of modern atmospheric $^{14}CO_2$



Pressure (mbar)
1600
1400
1200
1000
800
600
400
200
0
$CO_2 + H_2 \rightarrow CO + H_2O$
$CO + H_2 \rightarrow C + H_2O$
0
2000
4000
6000
8000
10000
12000
14000
time (a.u.)

BACKGROUND SUBTRACTION

	or. mat.		cont.		meas. (*)
Sample	R_c	+	R_{con}	→	$\frac{R_c + a_c R_{con}}{(1+a_c)}$
Standard	R_s	+	R_{con}	→	$\frac{R_s + a_s R_{con}}{(1+a_s)}$
Blank	$R_b = 0$	+	R_{con}	→	$\frac{R_b + a_b R_{con}}{(1+a_b)}$

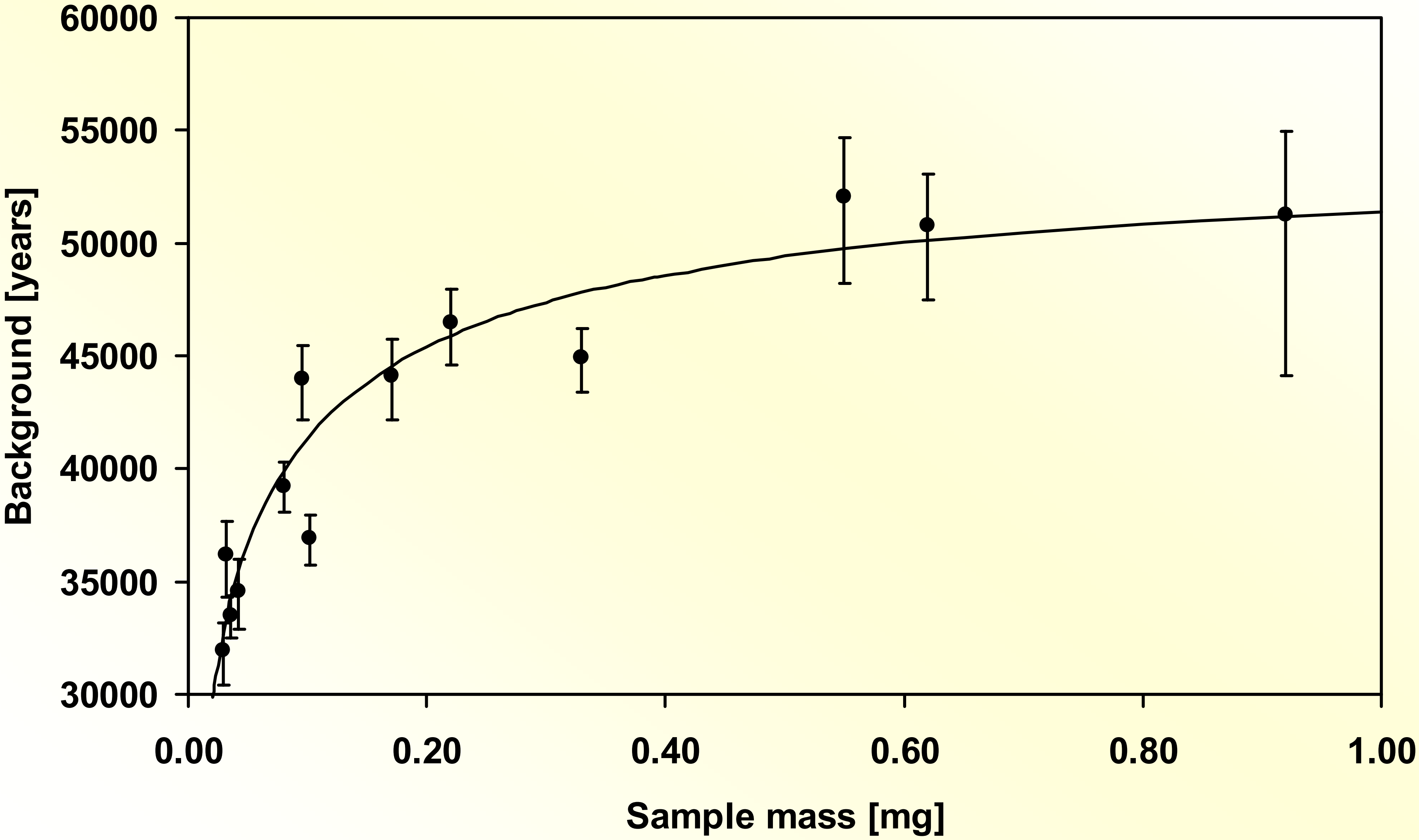
def: $f_c^* = R_c^*/R_s^*$; $f_b^* = R_b^*/R_s^*$; if $a_c \sim a_b$ ($\sim a_s$) → $f_c = R_c/R_s = (f_c^* - f_b^*)/(1-f_b^*)$

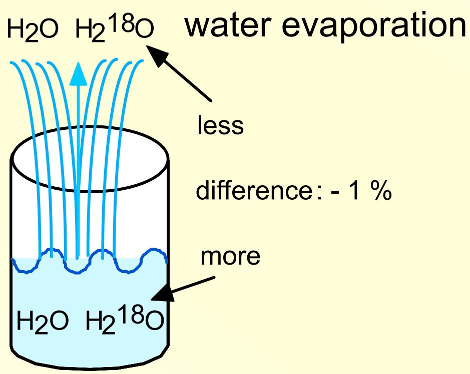
$$\sigma_{fc}/f_c = [(\sigma_{Rs}/(R_s^* - R_b^*))^2 + (\sigma_{Rc}/(R_c^* - R_b^*))^2 + (\sigma_{Rb}(R_c^* - R_s^*)/(R_s^* - R_b^*)(R_c^* - R_b^*))^2]^{1/2}$$

↓

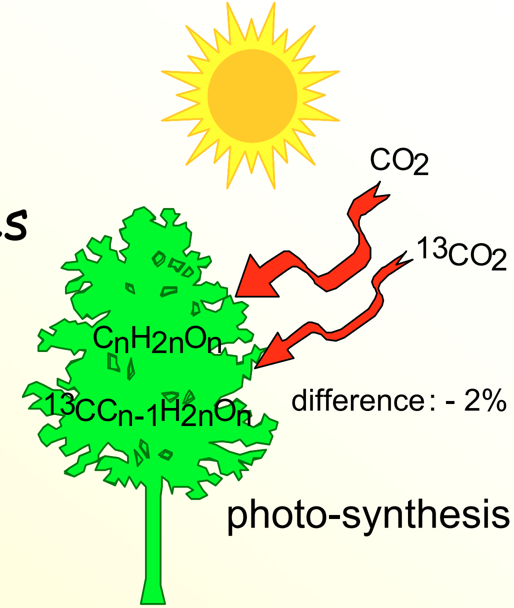
Datable age

Micro samples: background
ANSTO data





Due to the mass dependence of molecular mobility and binding energy, physico-chemical processes alter the isotopic composition of different phases or compounds



Mass dependent fractionation

$^{13}C/^{12}C$ $\quad$ $^{14}C/^{12}C$ $\quad$ A (atmosphere)

↓ $\quad$ ↓

$\alpha\ ^{13}C/^{12}C$ $\quad$ $\alpha^2\ ^{14}C/^{12}C$ $\quad$ B (vegetation)

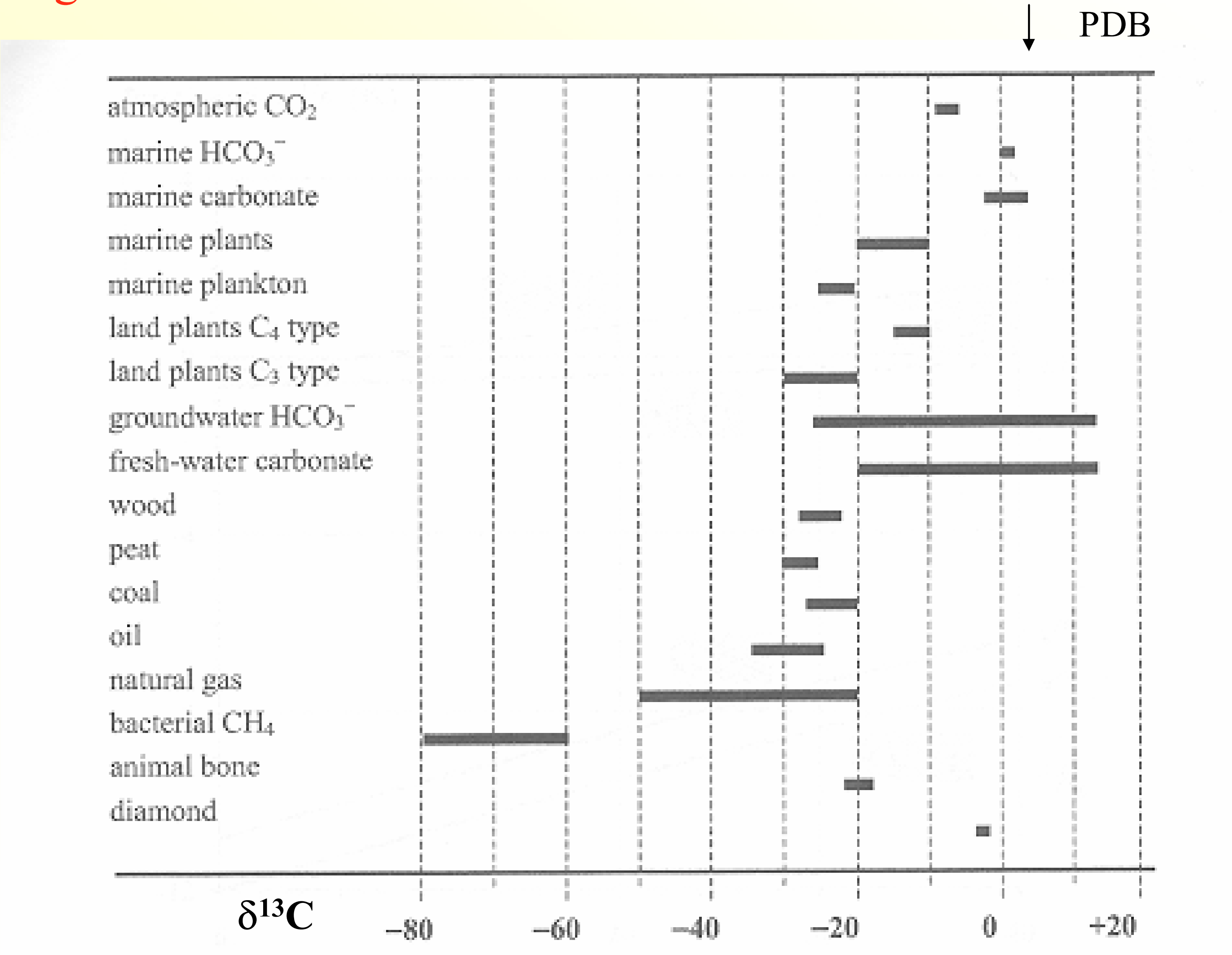
$$\varepsilon_{B/A}\ (‰) = 1 - \alpha$$

$$(^{14}C/^{12}C)_v / (^{14}C/^{12}C)_a = [(^{13}C/^{12}C)_v / (^{13}C/^{12}C)_a]^2$$

δ notation : $(\delta^{13}C)_{c/ref} = (13/12)_c / (13/12)_{ref} - 1$ expressed in ‰ ;

$(\delta^{13}C)_B \approx (\delta^{13}C)_A + \varepsilon_{B/A}$

Average natural ^{13}C fractionations



Conventional average wood: -25 ‰

Isotopic ratios normalized to the working standard and corrected for fractionation

$$f_{c[-25]}=f_c[(1-25‰)/(1+\delta^{13}C_c)]^2/[(1+\delta^{13}C_{s[ref]})/(1+\delta^{13}C_s]^2$$

STD	(pMC)ref	err	$\delta^{13}C$	err	$\delta^{13}C_{ref}$
	%	%	‰	‰	‰
IAEA-C1	0.00	0.02	2.42	0.33	-25
IAEA-C2	41.14	0.03	-8.25	0.31	-25
IAEA-C3	129.41	0.06	-24.9	0.49	-25
IAEA-C4	0.2	0.44	-24	0.62	-25
IAEA-C5	23.05	0.2	-25.5	0.72	-25
IAEA-C6	150.61	0.11	-10.8	0.47	-25
IAEA-C7	49.54	0.13	-14.5	0.13	-25
IAEA-C8	15.03	0.18	-18.3	0.23	-25
ANU	150.81	0.2	-10.8	0.1	-25
OxI	105.26		-19.3		-19
OxII	134.07	0.04	-17.8		-25

Normalization to the international absolute standard and radiocarbon age determination

$$A_{abs} = 0.95\ A_{OXI[-19]} = 0.7459\ A_{OXII[-25]}$$

"modern" = 1950 AD

Fraction of modern of secondary standard $F_{s[ref]}$ in 1950 AD

$$F_{c[ref]} = f_{c[ref]}\ F_{s[ref]};\ t_{RC} = -\ \tau\ \ln(F_c);\ \sigma_t/\tau = \sigma_{Fc}/F_{c[ref]}$$

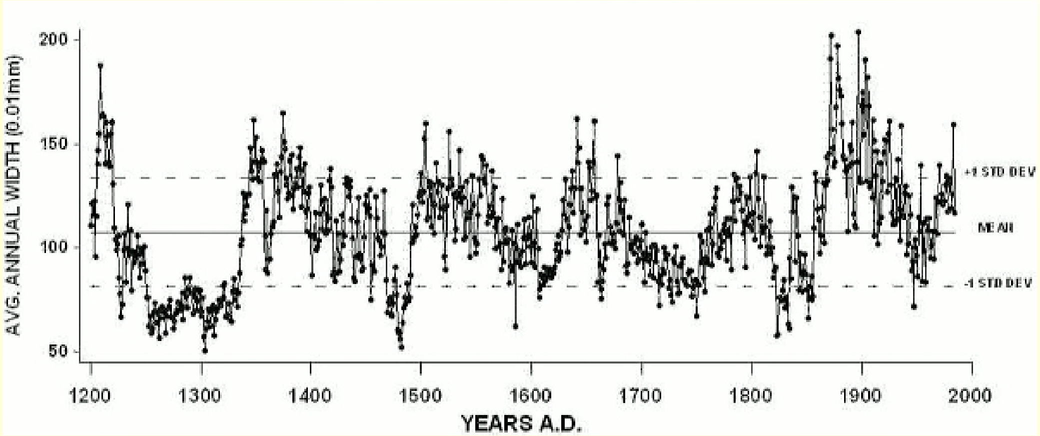
↓

"Libby half life" (8033 a) +

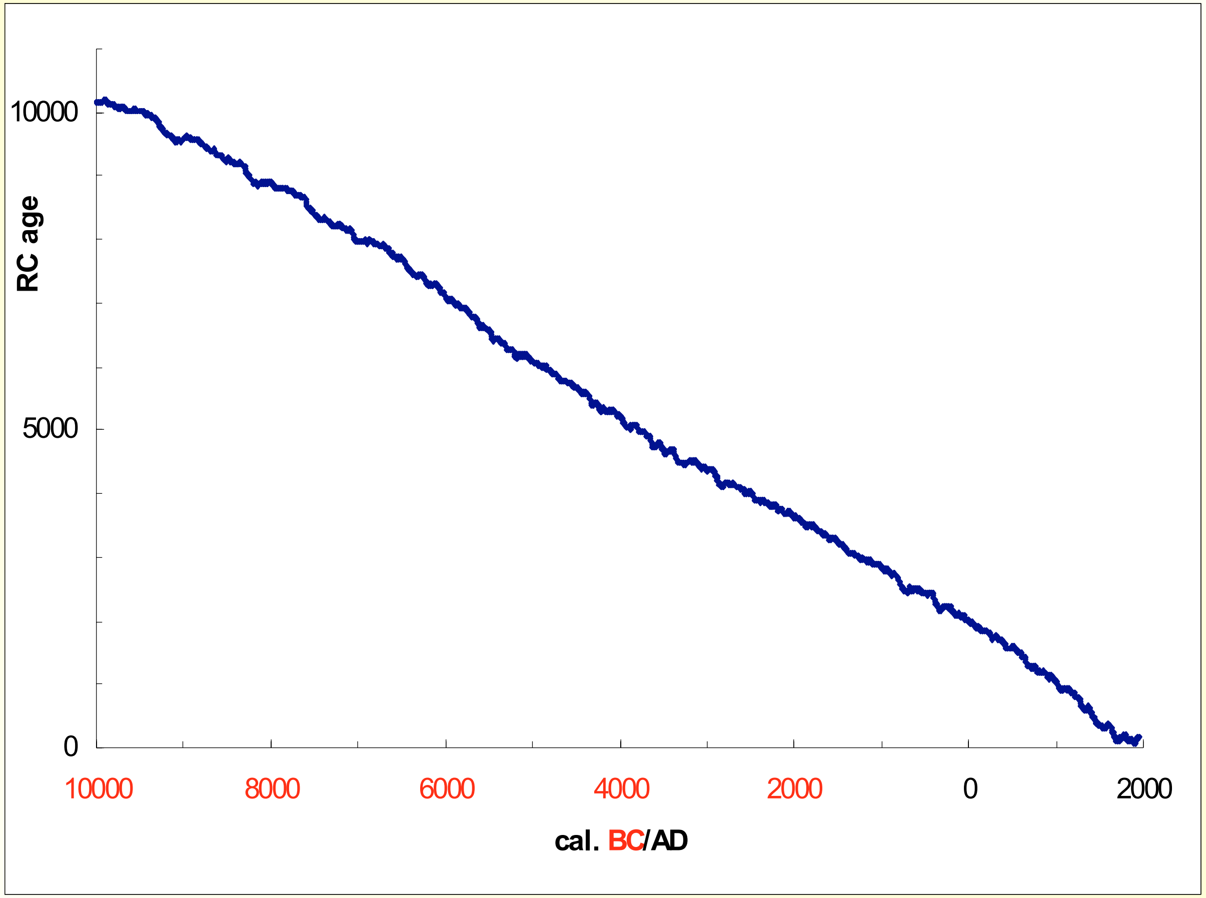
non constant isotopic composition of the atmosphere

CALIBRATION

For the last 12400 a dendrochronologically dated tree-ring series are used



From 12,4 to 26 cal. ka b.p. reservoir-corrected marine data (from corals and foraminifera)



Calibration curve as conventional RC age (a bp) vs calendar age for terrestrial samples (INTCAL04)

Tree-ring data for the calibration of RC age

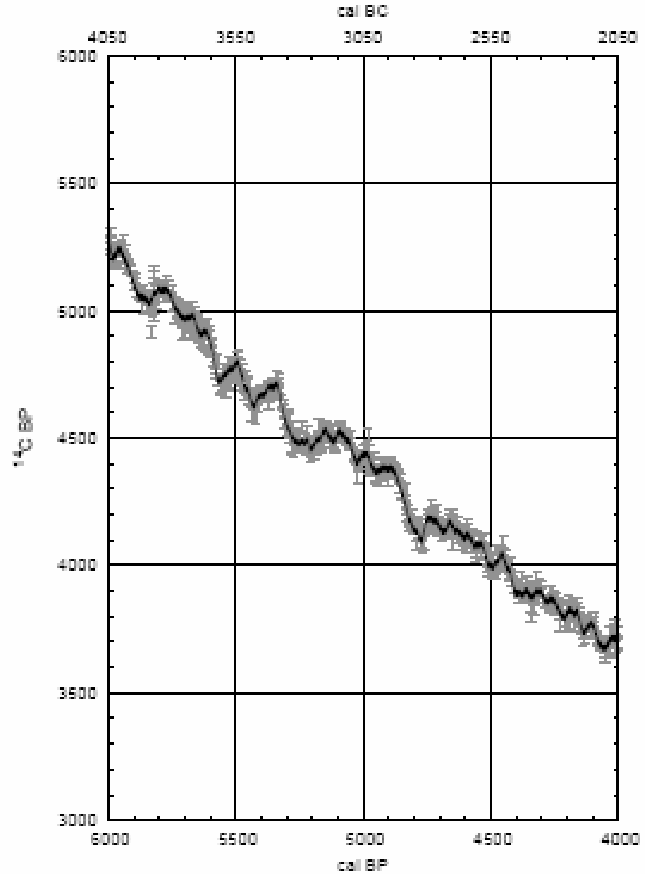
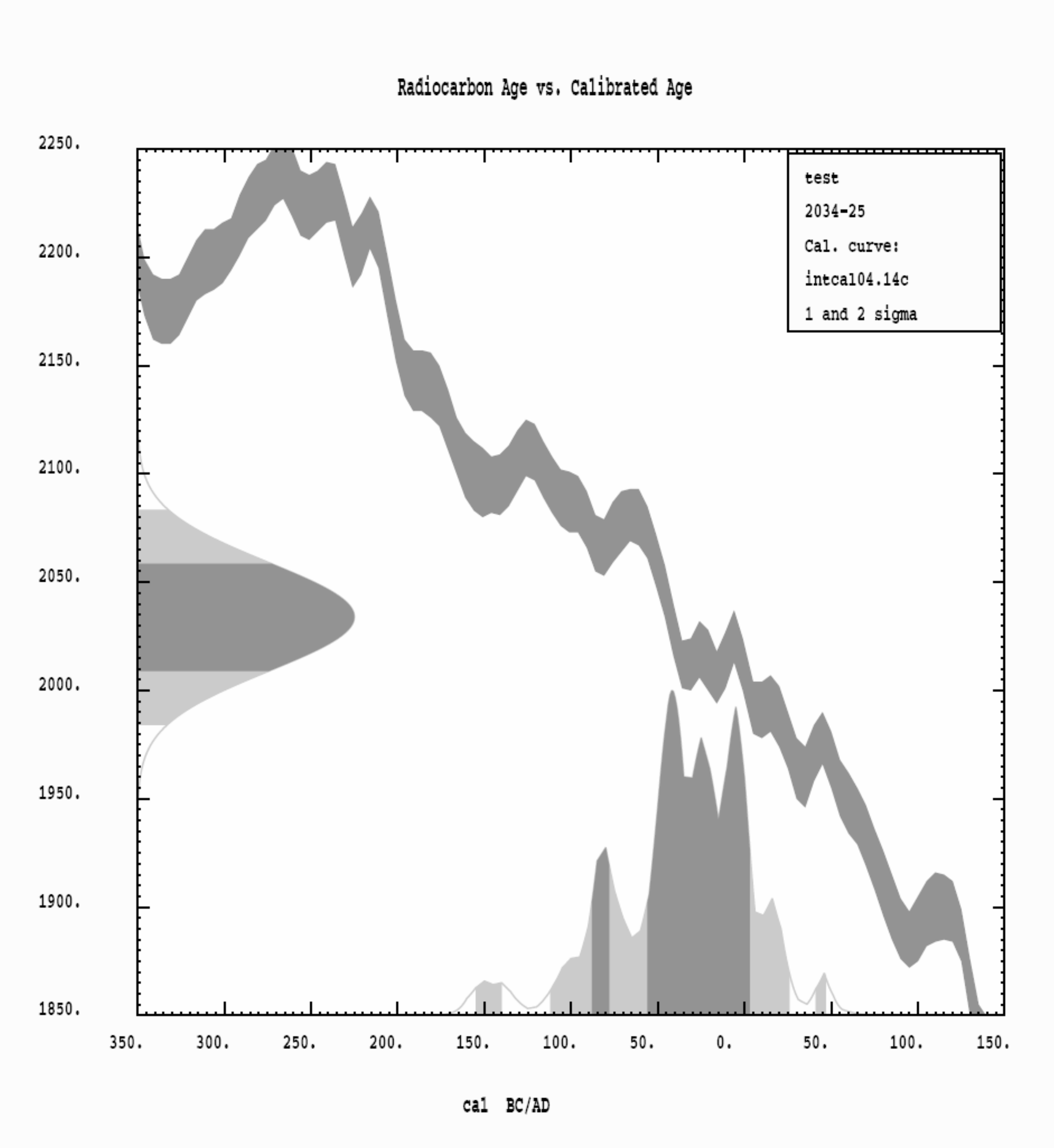
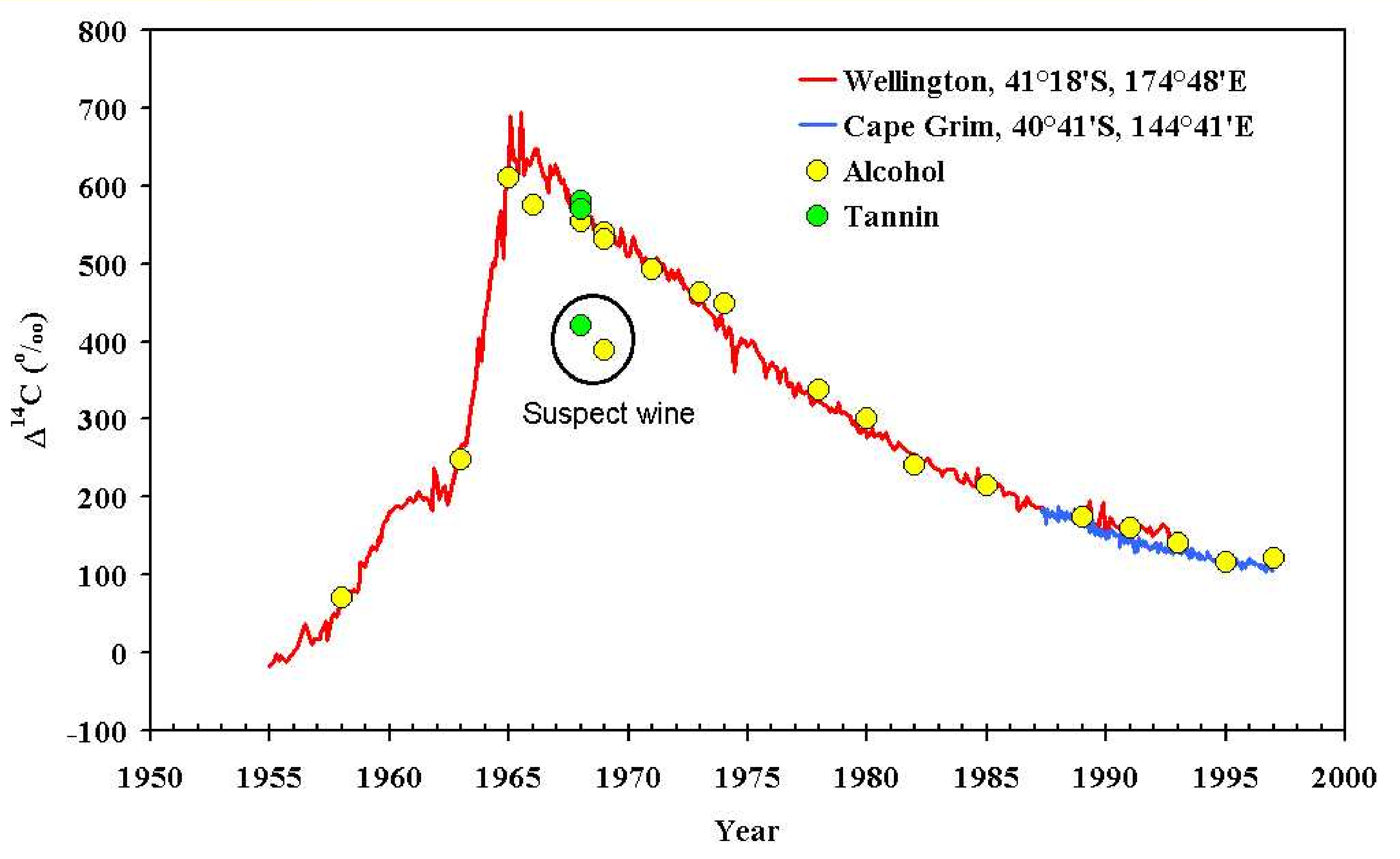


Figure A11 The IntCal04 terrestrial calibration curve (1-standard deviation envelope) and data with 1-standard deviation error bars in ^{14}C increased by the laboratory error multipliers described in the text. The uncertainty in the calendar ages is not shown, but is taken into account in the random walk model.



Projection of the results of an RC age measurement with 1σ and 2σ confidence intervals onto the calendar age axis

"Bomb carbon" dating



AMS and Nuclear Astrophysics

- Off line measurement of very low reaction cross sections
- AMS equipment and know how has lead to the development of Recoil Mass Separators, a very selective and efficient tool for the on-line measurement of very low reaction cross sections of astrophysical interest

Stellar nucleosynthesis

Nuclear inputs to evolutionary models:

Energetics of reaction

Reaction rates:

$R_{ij}(T) = (n_i\, n_j / (1+\delta_{ij})) < \sigma_{ij}\, v_{rel} >$

Boltzmann distribution

Exponential behaviour

$$<\sigma v> = (8/\pi\mu)^{1/2}\,(1/kT)^{3/2} \int_0^{\infty} \sigma(E)\, E\, \exp(-E/kT)\, dE$$

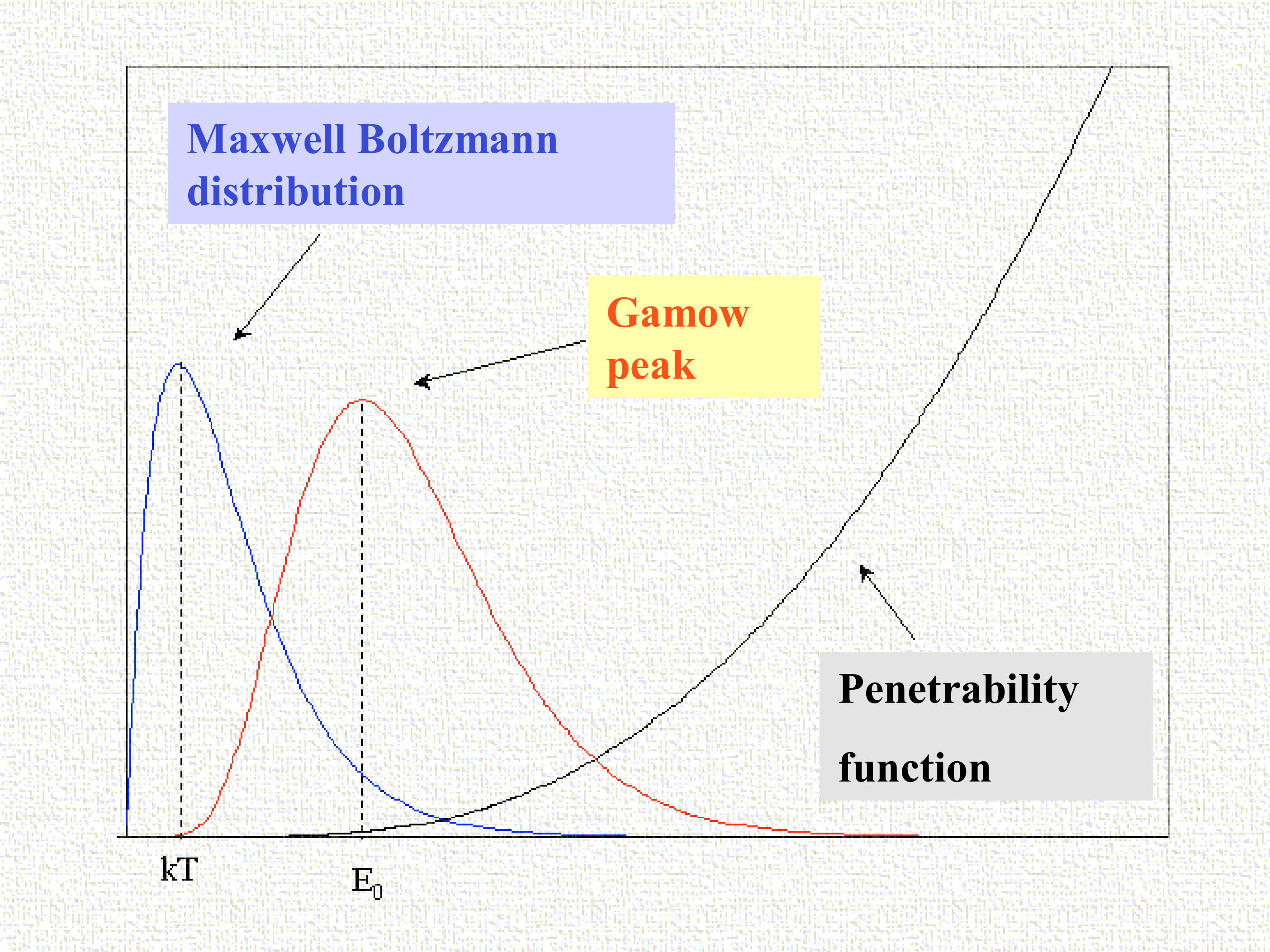
$\tau_{ij}(T) = 1/(n_j\, < \sigma_{ij}\, v_{rel} >)$

Astrophysical S-factor:

$S(E) = \sigma(E)\, E\, \exp(2\pi\eta);\ \eta = Z_1 Z_2 e^2/hv$

Case of charged particle induced non resonant reactions: Gamow peak

$$< \sigma v > = \left(\frac{8}{\pi\mu}\right)^{1/2} \frac{1}{(kT)^{3/2}} \int_0^\infty S(E) \exp\left[-\frac{E}{kT} - \frac{b}{E^{1/2}}\right] dE$$



If $S(E) \sim$ const :

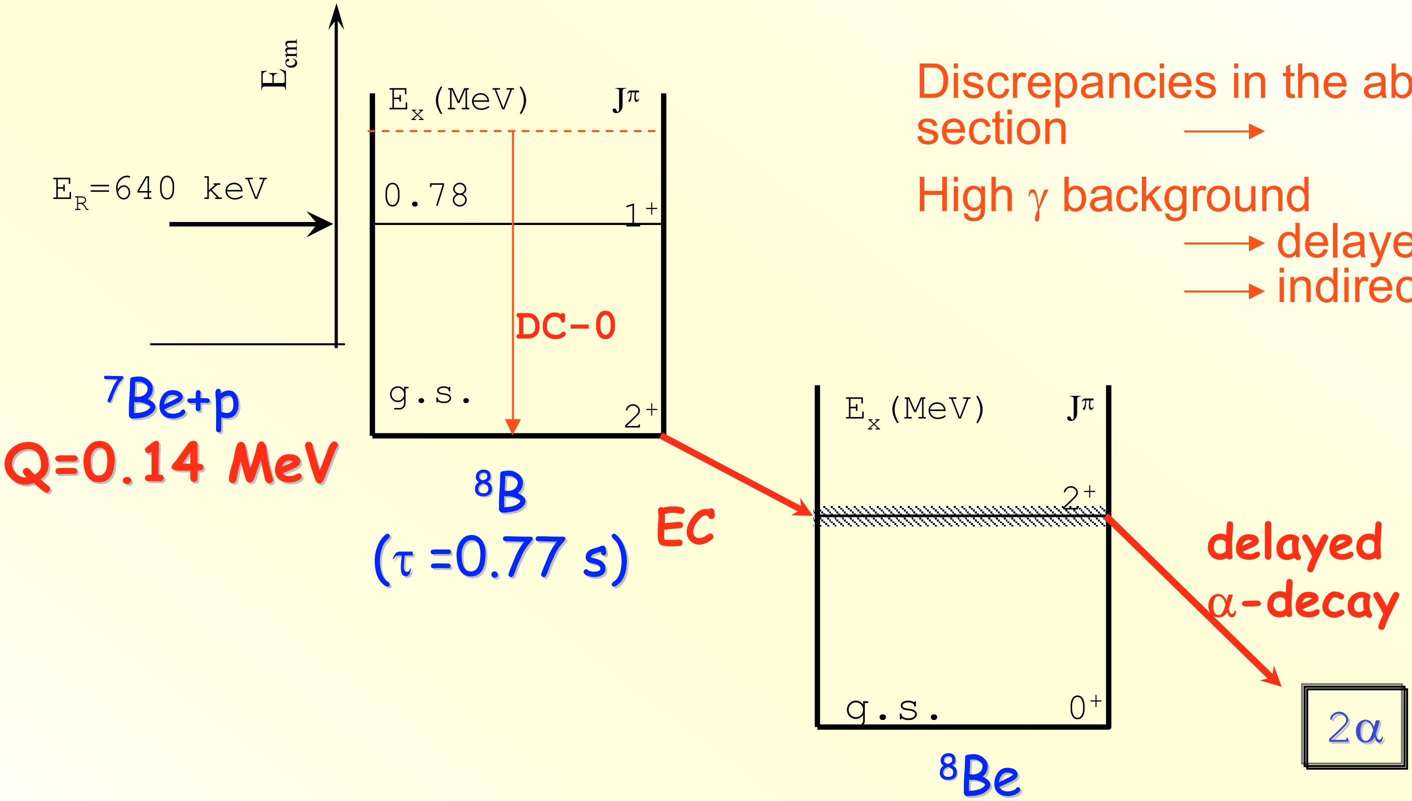
$<\sigma v> \propto S(E_0)\,(E_0\,kT)^{1/2}$

$\exp(-3E_0/kT)$

With $E_0 = (b\,kT/2)^{2/3}$;

$b = 0.989\, Z_1 Z_2 \mu^{1/2}$

The $^{7}Be(p,\gamma)^{8}B$ reaction



Discrepancies in the absolute cross section →

High γ background

→ delayed α detection;

→ indirect methods (CB)

INVERSE KINEMATICS REACTION:

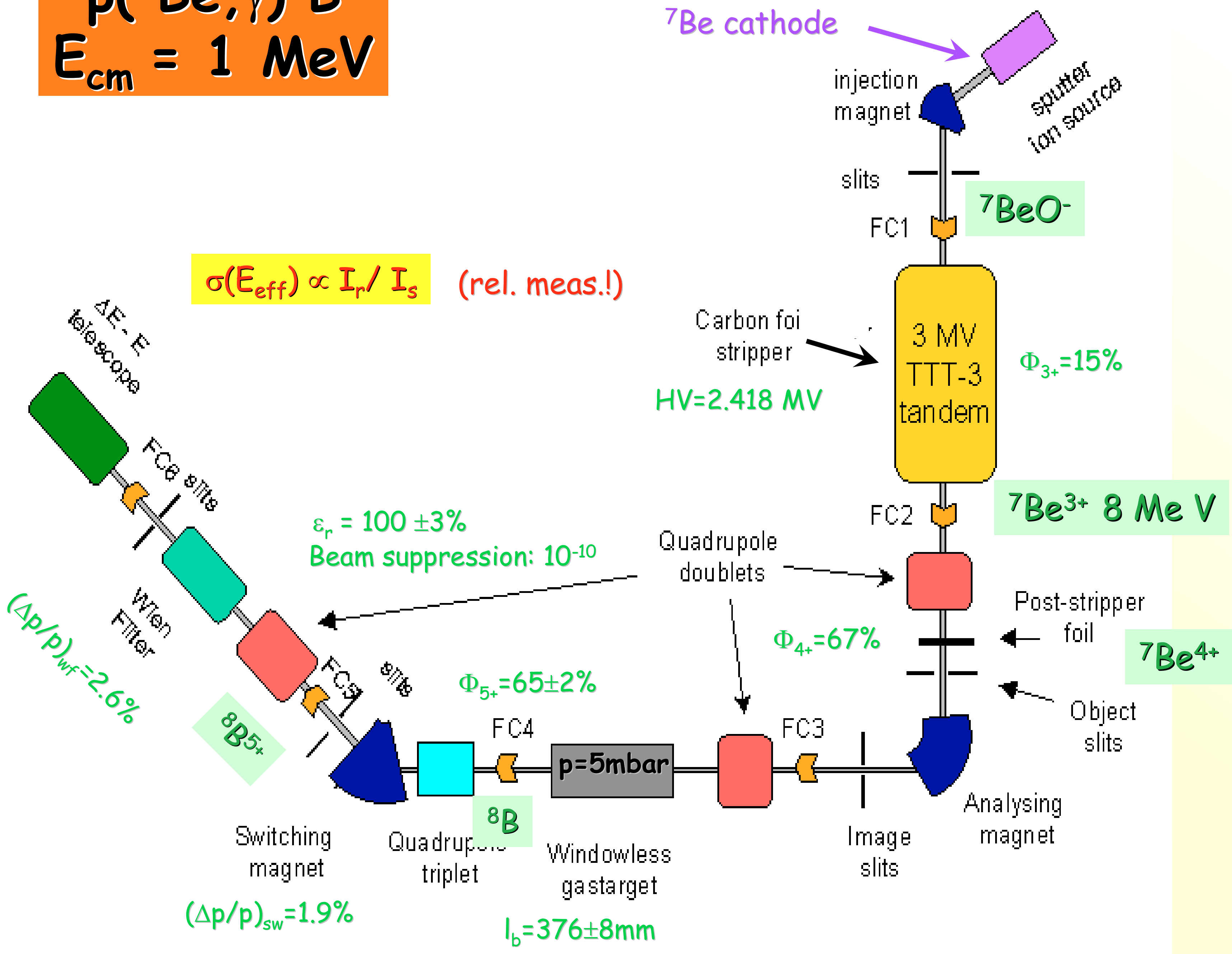
$^{1}H\ (\,^{7}Be, \gamma)\ ^{8}B$

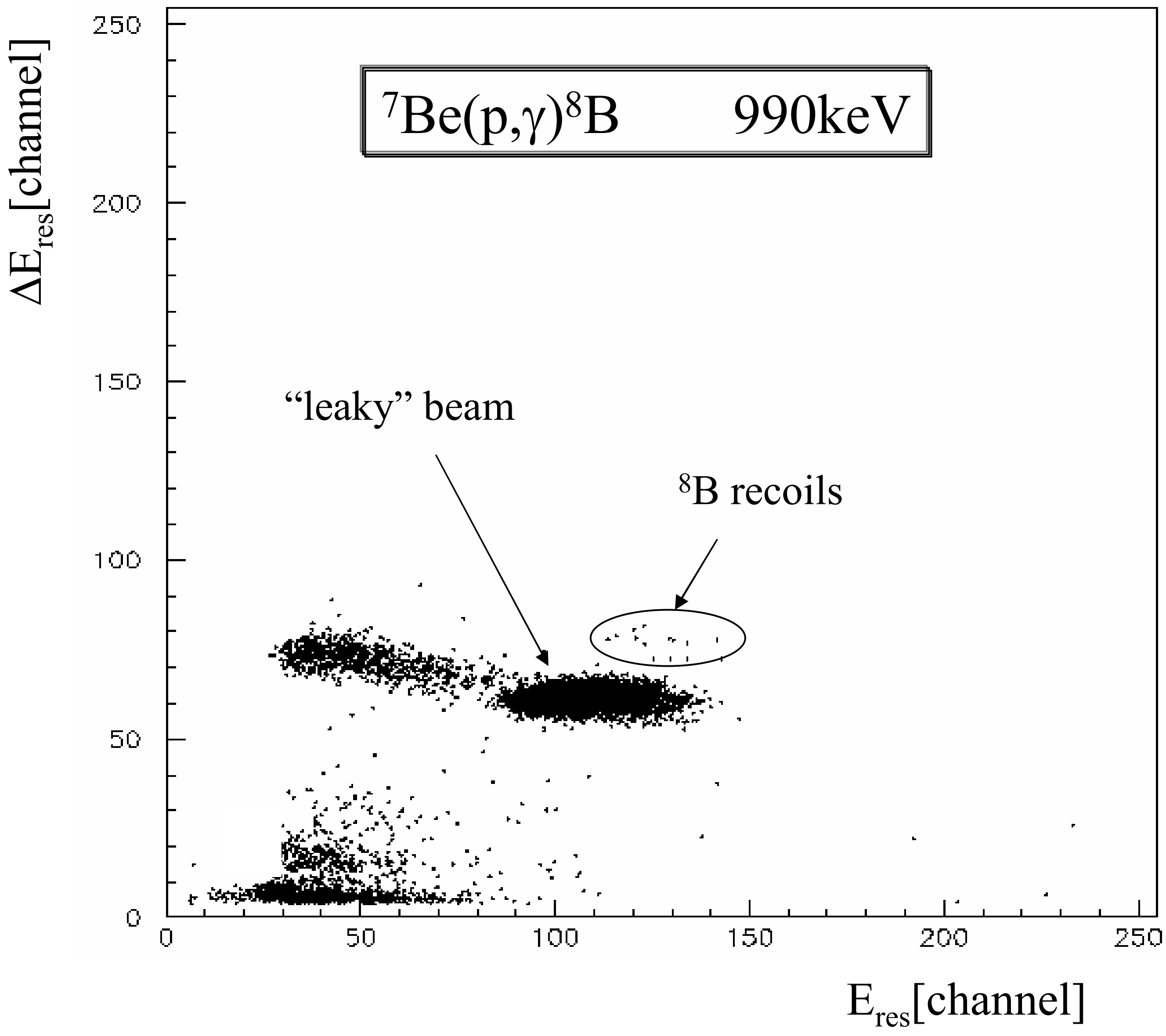
^{8}B → Recoil Mass Spectrometer

^{7}Be → RIB

^{1}H → gas target

$p(^7Be,\gamma)^8B$
E_{cm} = 1 MeV

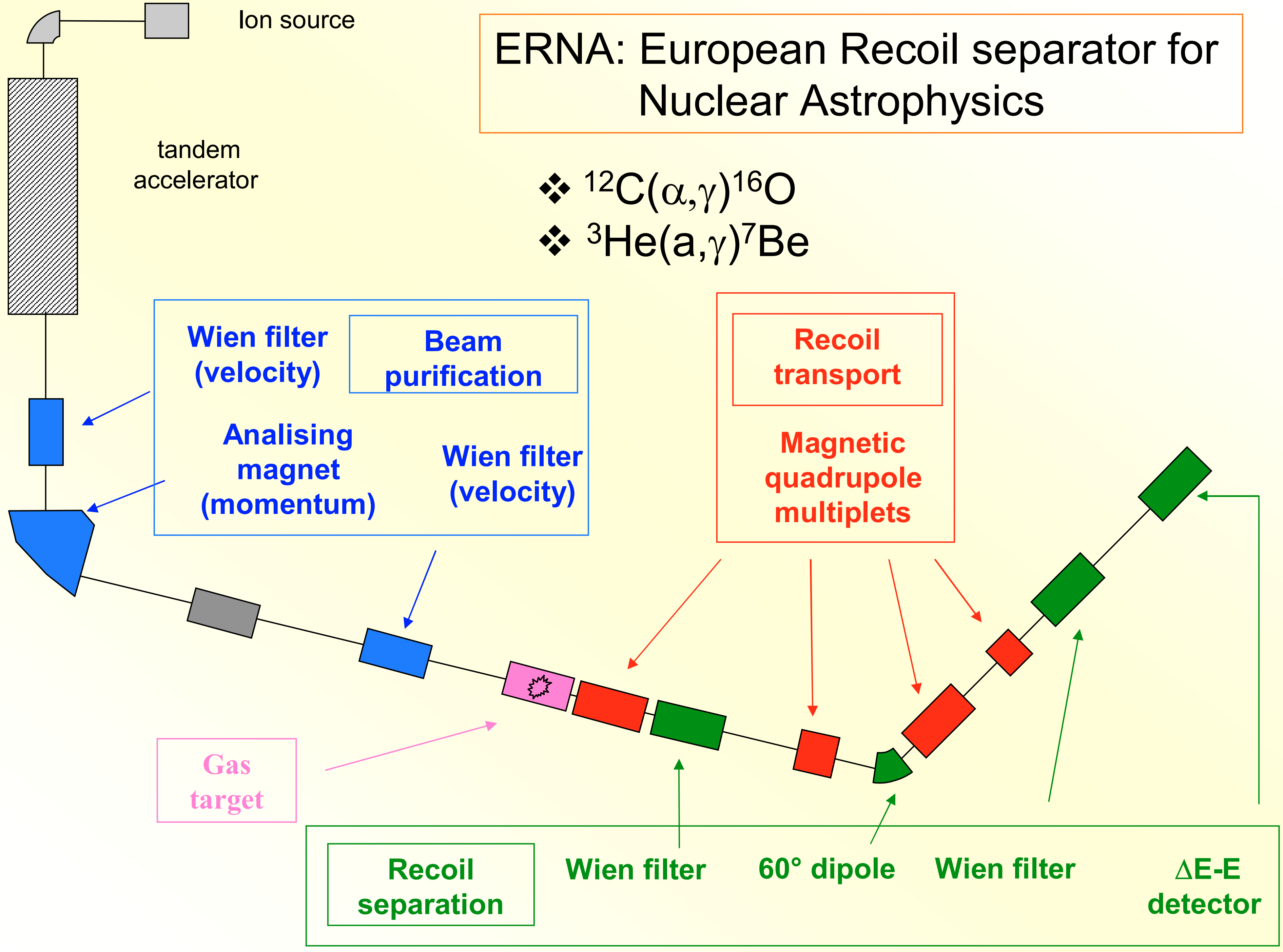




7Be(p,γ)8B 990keV
"leaky" beam
8B recoils
ΔEres[channel]
Eres[channel]
0
50
100
150
200
250

ERNA: European Recoil separator for Nuclear Astrophysics

- $^{12}C(\alpha,\gamma)^{16}O$
- $^{3}He(a,\gamma)^{7}Be$



SUMMARY

- AMS is an ultrasensitive analytical technique allowing precise and accurate measurements of the abundance of rare isotopes in the 10^{-16} – 10^{-12} range in samples containing few hundred thousands atoms
- ^{14}C AMS is widely used to date sub-milligram founds of organic origin with ages up to 50 ka with a precision of ±25 a
- After 30 years of applications and refinements the techniquehas been proven to be reliable and accurate in spite of its complexity and sophistication, both instrumental and methodological