XXXI Giornate di Studio sui Rivelatori
Cogne, 26-30 giugno 2023

Small electrostatic accelerators for Cultural Heritage

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INFN CHNet

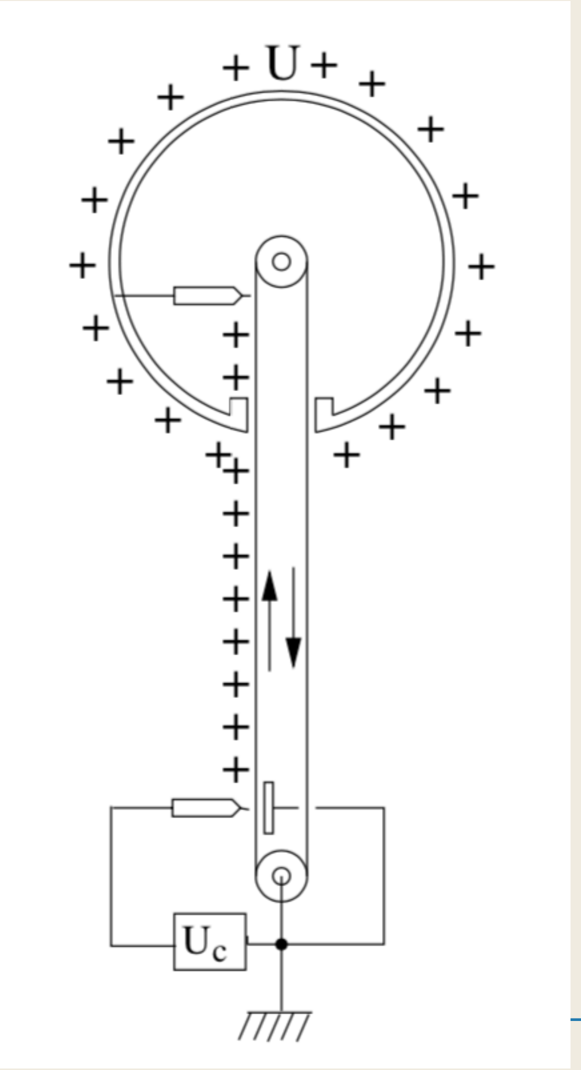
Small: the keyword of this lecture

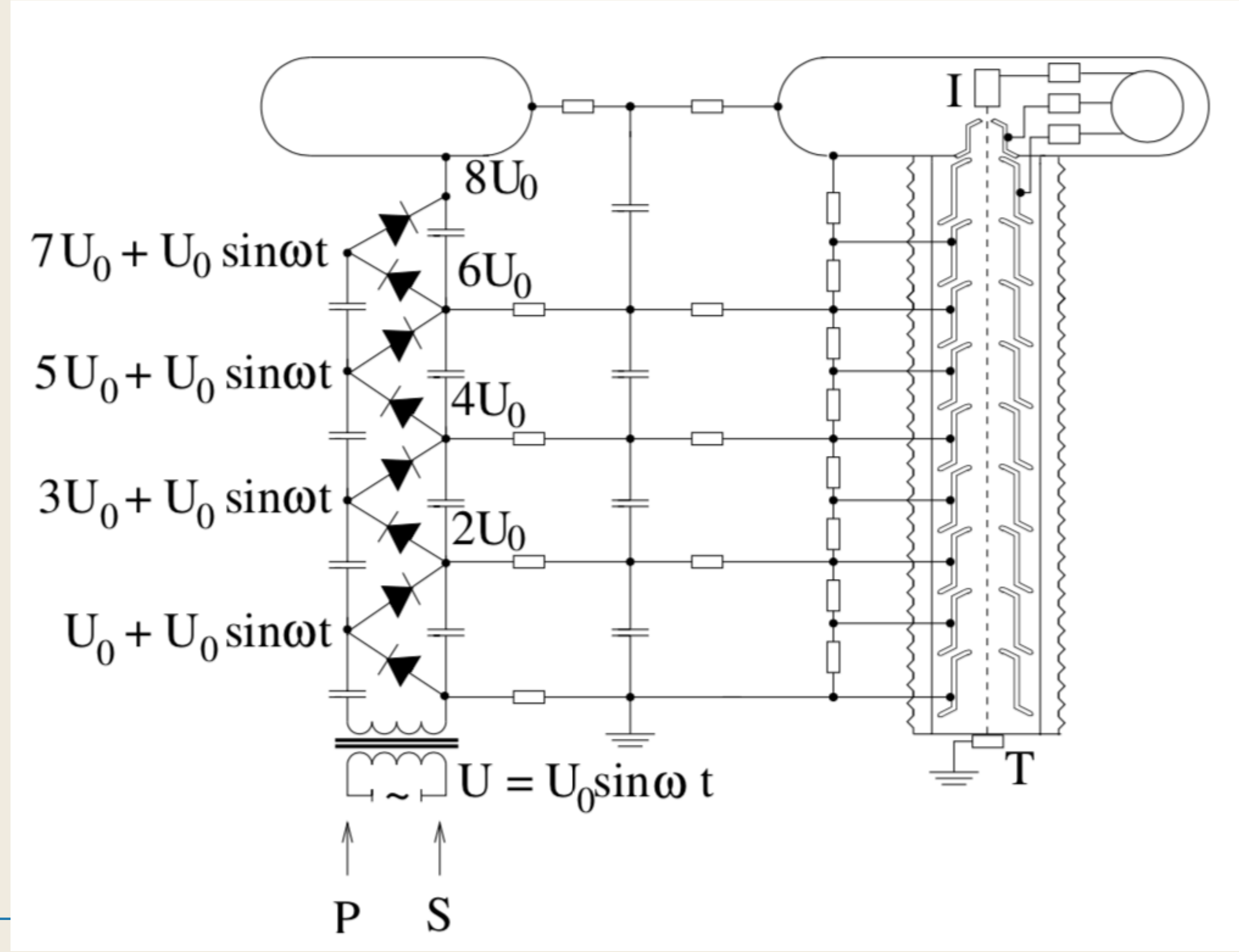
- I will focus my attention on **small** electrostatic accelerators, especially tandem
- This kind of accelerators began to be "old" in the 1970s when the interest in fundamental physics began to move towards higher energies

"Small" can be also considered as the keyword to explore the up-to-date research in the field

Electrostatic accelerators

- Ions are accelerated through an electrostatic field by applying a voltage which does not change with time
- The high voltage can be established by different mechanisms that are basically based on:
  - either a Van de Graaff generator
  - or a Cockroft-Walton generator

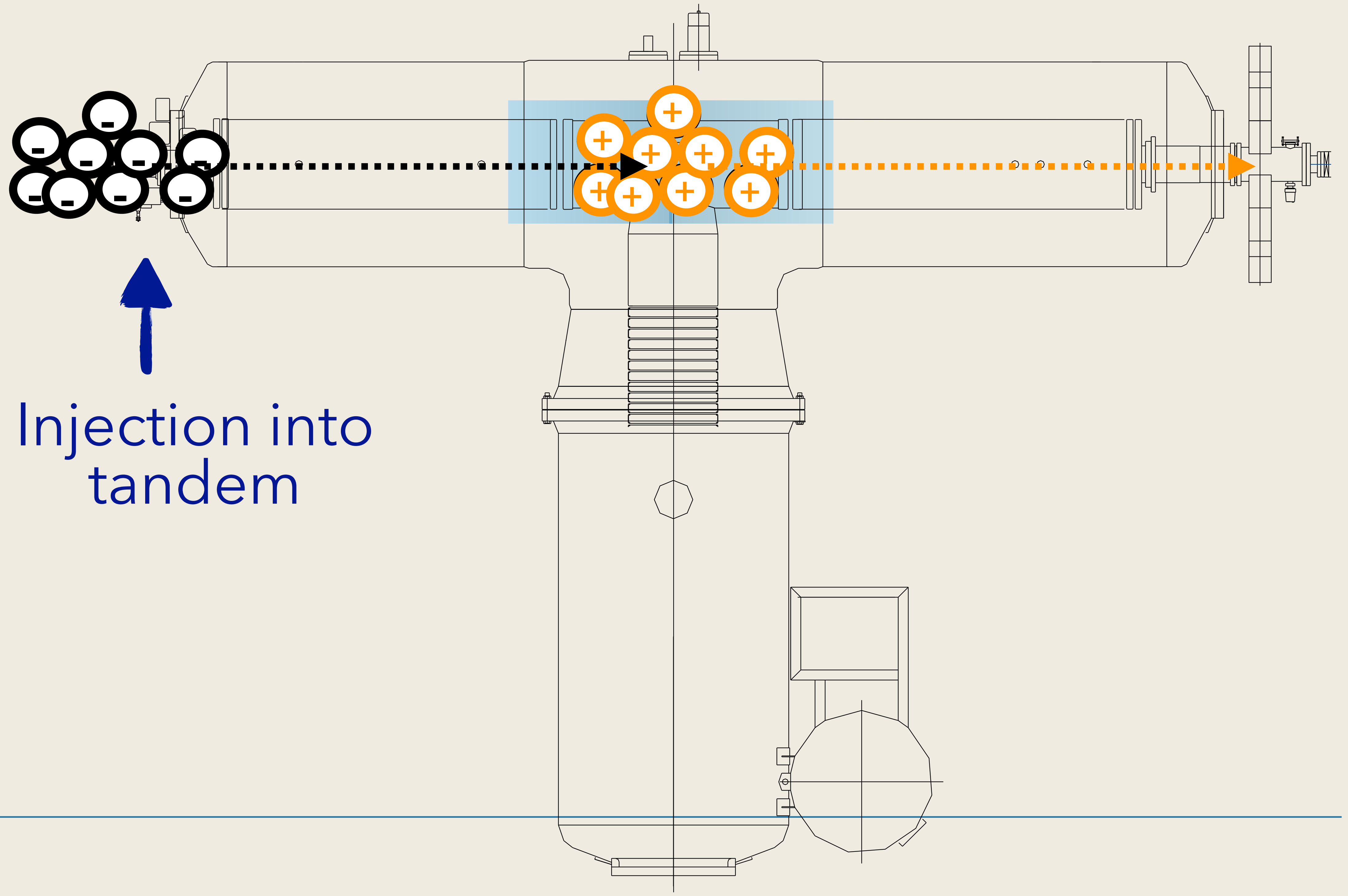




A type of electrostatic accelerators: the tandem

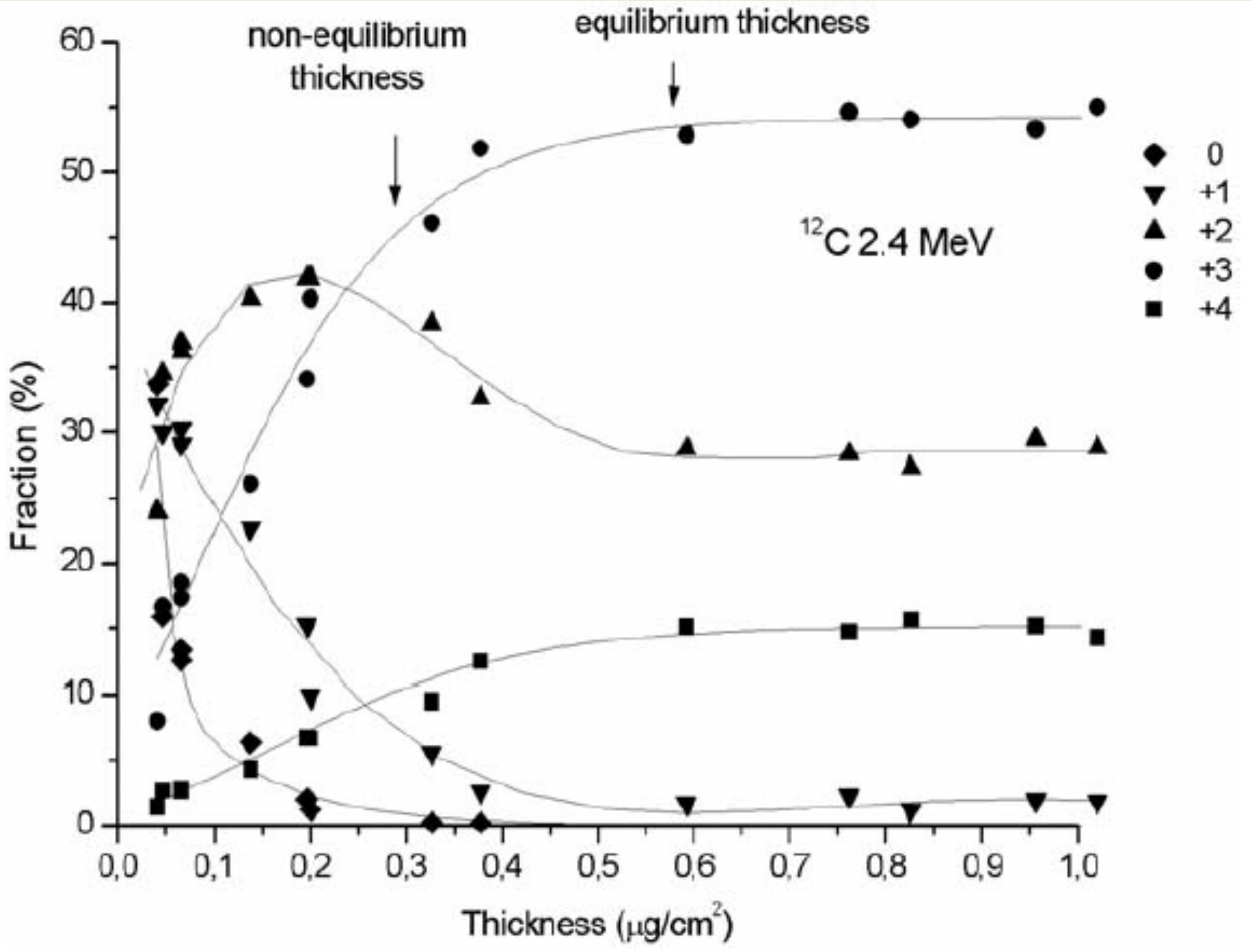
- The high voltage terminal is in the middle of ions path
- Ions undergo two following acceleration steps, thanks to the stripping process at the terminal

$$E_{fin} = E_{inj} + q_1 \Delta V + q_2 \Delta V$$



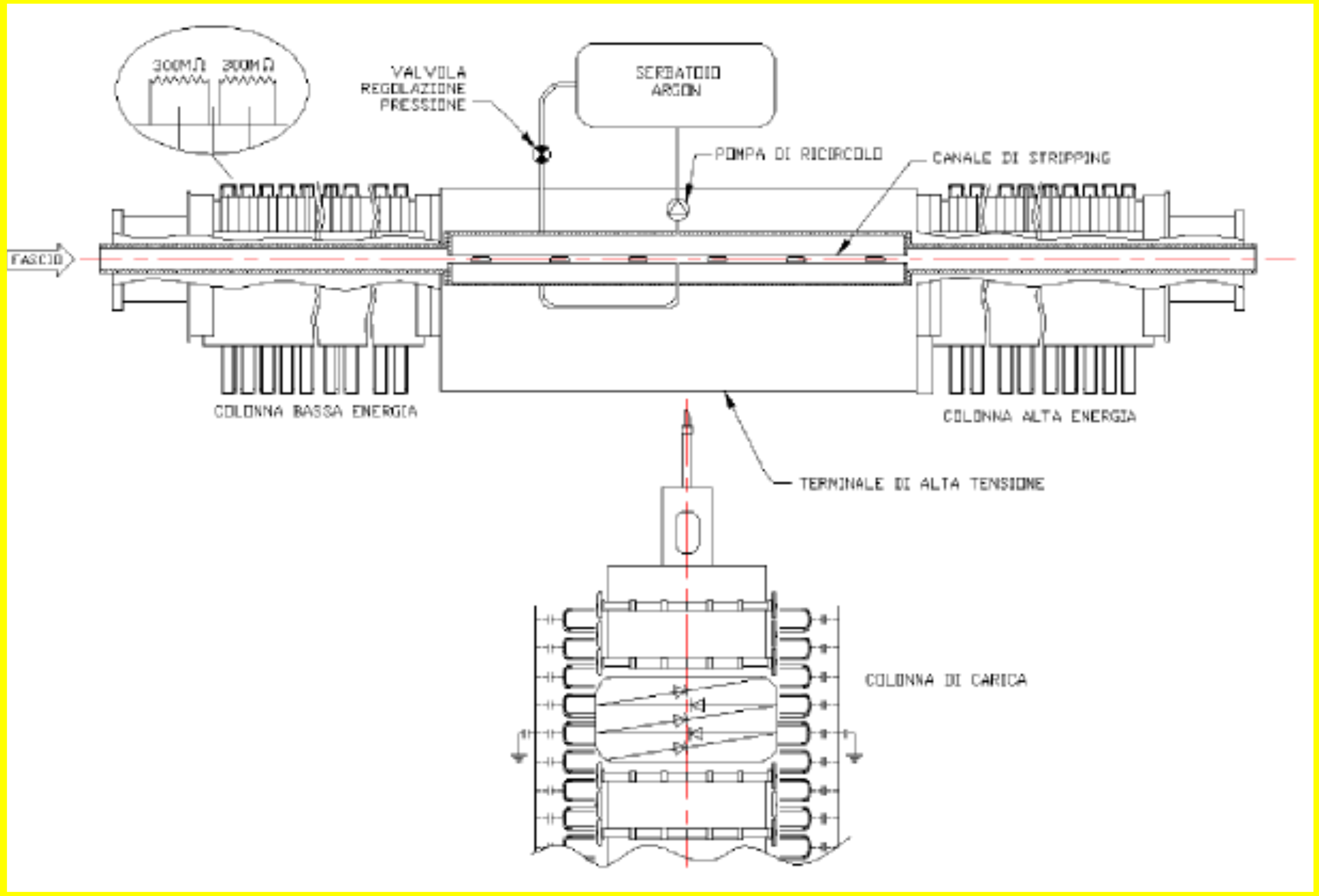
The stripping process

- When a swift ion penetrates a target medium, it undergoes a large series of ion–electron collisions ➜ electron loss and/or electron capture ➜ charge-exchange at the high voltage terminal
- Distribution of charge state after stripping depends on stripper thickness and incident ion velocity



3 MV tandem accelerator at INFN-LABEC, Florence

The high voltage terminal



Why accelerators and Cultural Heritage?

- Is it possible to give information on the chronology?
- Which are the used materials?
- Is it possible to identify successive interventions on the artwork (like e.g. a restoration)?

Let's start from tandem and the issue of chronology

tected ions, drawn as contour lines, plotted against ΔE and E_T. These data were collected over a 7-hour period. We established the identities of the peaks in Fig. 1, using the measured magnetic rigidity, total energy, and ΔE values. The analyzing magnet would allow only the ions with the specific charge states and masses shown in Fig. 1 to pass given their measured values. Comparison of the measured ΔE values for these ions with calculated values showed that all agreed within the expected experimental uncertainty except for those of the boron isotopes. It is not known whether this difference is due to error in the experiment or in the calculation.

The peak due to ^{14}C stands out clearly and contains about 800 counts. We would have expected about five times this number of counts from wood of this age if we had been able to use the precision energy stabilization system. However, the value is approximately that expected when the less precise direct stabilization system is used.

Unfortunately, we did not have an appropriate carbon sample of sufficient age to be able to measure the system background. However, one can estimate the background by examining the spectrum on all sides of the ^{14}C peak. Such an analysis predicts that less than 1 count in the ^{14}C peak is due to background. This is equivalent to the count rate expected for a sample age of 50,000 to 60,000 years. This result suggests that, with development, the technique will be capable of extending the age limit for ^{14}C dat-

an isotope rati[...] quite independent of the system eff[...]ncy but will also allow the beam ene[...] to be precisely stabilized by use [...] ^{12}C beam. Ion-

pointing out the usefulness of a negative ion source. Funding was supplied by Imperial Oil Limited and the National Research Council of Canada.

29 June 1977; revised 15 September 1977

Radiocarbon Dating Using Electrostatic Accelerators: Negative Ions Provide the Key

Abstract. *Mass spectrometric methods have long been suggested as ways of measuring $^{14}C/^{12}C$ ratios for carbon dating. One problem has been to distinguish between ^{14}N and ^{14}C. With negative ions and a tandem electrostatic accelerator, the ^{14}N background is virtually absent and fewer than three ^{14}C atoms in 10^{16} atoms of ^{12}C have been easily measured.*

It has been recognized for some time (*1*) that one can achieve great improvements in the sensitivity of radioisotope dating by counting directly the number of radioactive atoms that are present in a sample rather than waiting for their decay and measuring the resultant radiation. More recently, Muller (*2*) discussed one possible way for making such direct measurements, using a cyclotron with a positive ion source as an extremely sensitive mass spectrometer. If such direct methods of measurement become possible for ^{14}C they could considerably increase the accuracy of ^{14}C dating and make possible new understanding of cosmic-ray fluctuations over many millennia.

In carbon from contemporary biological samples the ratio of ^{14}C to ^{12}C is approximately 1.2×10^{-12}. This ratio decreases by a factor of 2 for each 5730 years after the sample's death. If dating is to be done for samples having an age greater than 70,000 years, it is necessary to detect less than three atoms of ^{14}C in a sea of 10^{16} stable ^{12}C and ^{13}C atoms. The formidable problems expected in counting with such sensitivity, in the presence of ^{14}N contamination, have so far discouraged attempts to do it. The mass of the ^{14}N atom differs by only one part in 10^5 from that of the ^{14}C atom; thus in any mass spectroscopic method these atoms are virtually indistinguishable. Muller (*2*) suggested several ways of reducing the ^{14}N background, but all of these are difficult to apply in light of the fact that $^{14}N^+$ is an almost inevitable contaminant from positive ion sources and can be expected with appreciable intensities (~ 10^{10} sec^{-1}).

Our earlier measurements (*3*) showed that the negative nitrogen ion is so fragile

REVUE DE PHYSIQUE APPLIQUÉE TOME 12, OCTOBRE 1977, PAGE 1487

AN ATTEMPT TO DETECT STABLE N⁻ IONS FROM A SPUTTER ION SOURCE AND SOME IMPLICATIONS OF THE RESULTS FOR THE DESIGN OF TANDEMS FOR ULTRA-SENSITIVE CARBON ANALYSIS

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Résumé. — Dans cette communication on discute d'une expérience où l'on fait une recherche d'ions $^{14}N^-$ en présence d'un faisceau intense de carbone. On utilise une source d'ions Middleton à *sputtering*. Malgré un champ accélérateur de 1,5 MV/m nous n'avons pas trouvé d'ions azote négatifs avec des intensités détectables. La publication indique aussi les conditions que doivent remplir l'accélérateur si on veut bénéficier pleinement de ce résultat négatif afin de faire des mesures avec des faisceaux très faibles de ^{14}C.

Abstract. — The present paper discusses an experiment, using a Middleton sputter ion source, where a sensitive search was made for $^{14}N^-$ ions in the presence of an intense carbon beam. It was found that negative nitrogen ions, capable of withstanding acceleration fields of 1.5 MV/m, were not produced in detectable intensities. The paper also points out some design requirements of tandem facilities that must be satisfied if full advantage is to be taken of this negative result to permit the measurement of very weak ^{14}C beams.

ARTICLE

Radioisotope Dating with a Cyclotron: The sensitivity of radioisotope dating is improved by counting atoms rather than decays.

RICHARD A. MULLER

SCIENCE • 29 Apr 1977 • Vol 196, Issue 4289 • pp. 489-494 • DOI: 10.1126/science.196.4289.489

^{14}C

- ^{14}C is one of the carbon isotopes which is naturally occurring on Earth (in addition to ^{12}C and ^{13}C)
- It is **radioactive ➜** it decays through **β-** mechanism to ^{14}N

Half life $t_{1/2} = 5700 \pm 30$ yrs

Mean life $\tau = \frac{t_{1/2}}{ln2} \simeq 8220 yrs$

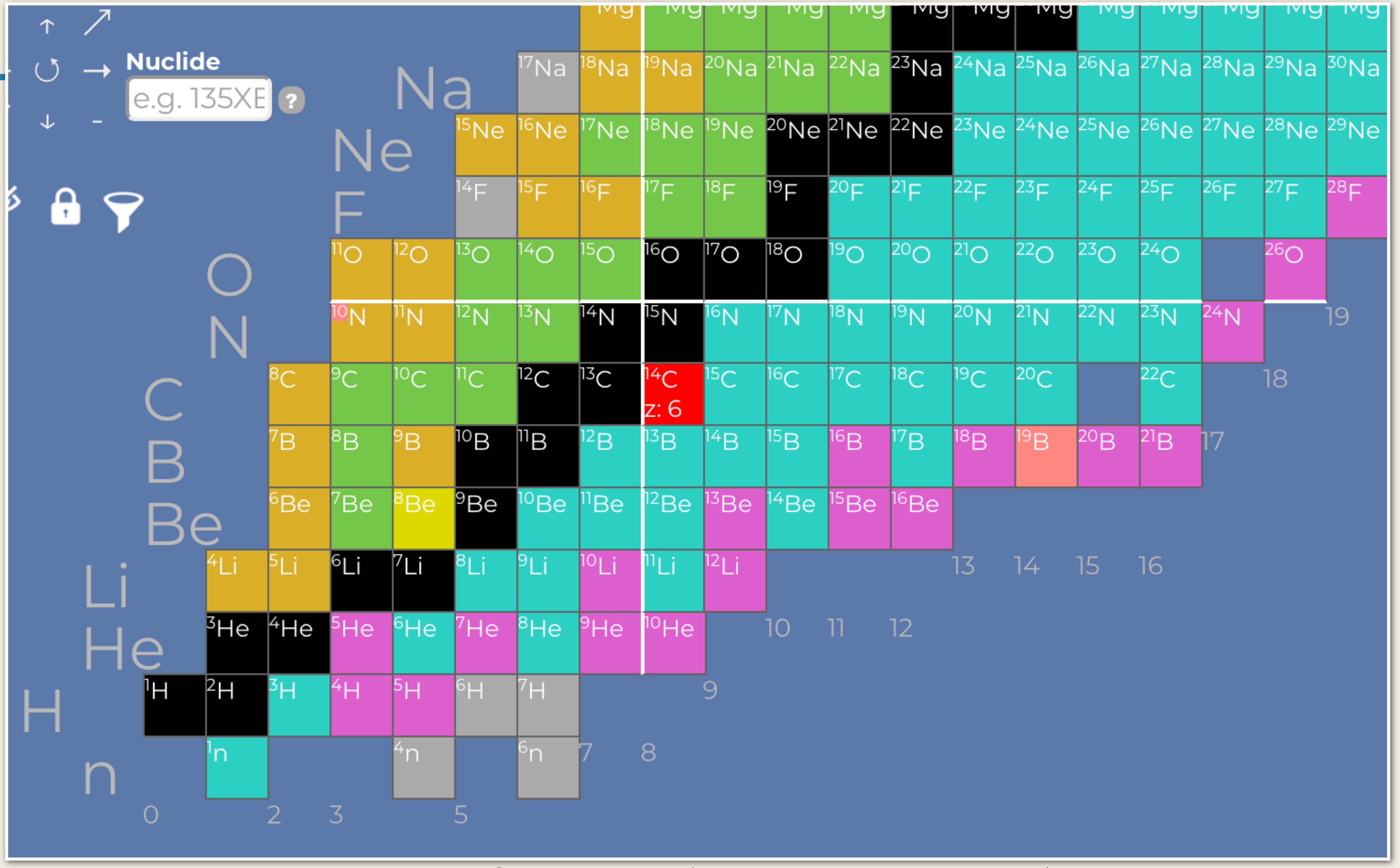
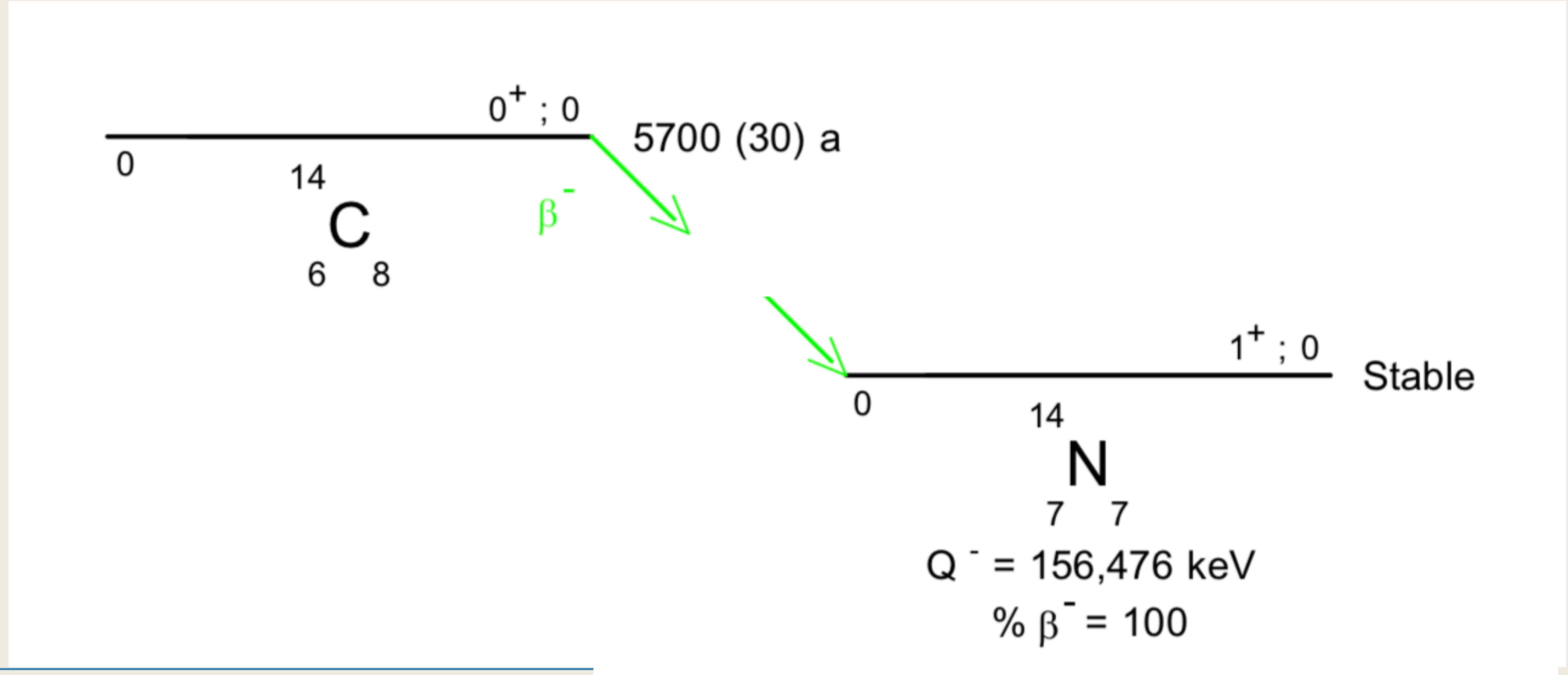


Table of nuclides (www-nds.iaea.org)

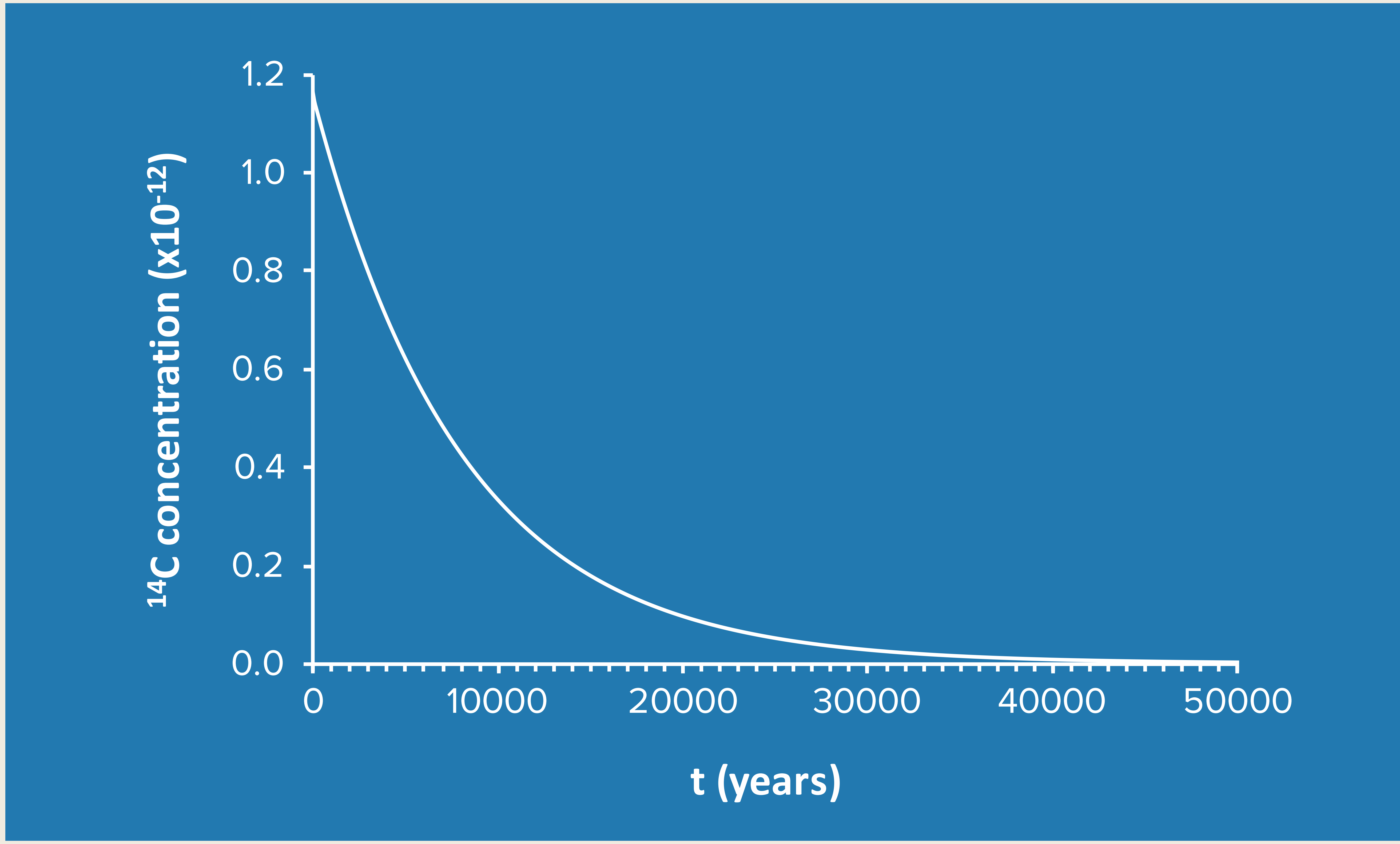


Radioactive decay

- In a **closed** system:

$$\frac{dN}{dt} = -\lambda N = -\frac{1}{\tau}N$$

$$N(t) = N_0\, e^{-\frac{t}{\tau}}$$



→ How can we measure a natural abundance of ^{14}C here on Earth?

^{14}C: the production mechanism

$^{14}N\left(n,p\right)^{14}C$

^{14}C average production rate ~ 2.2 nuclei $cm^{-2}\ s^{-1}$

Production happens in the upper atmosphere and it is negligible at ground level

It is ~5 times higher at the Poles than at Equator

^{14}C: natural abundance

- In atmosphere (and, consequently, in all the organisms and systems that exchange with the atmosphere itself), we can consider an equilibrium between the continuous production and the decay

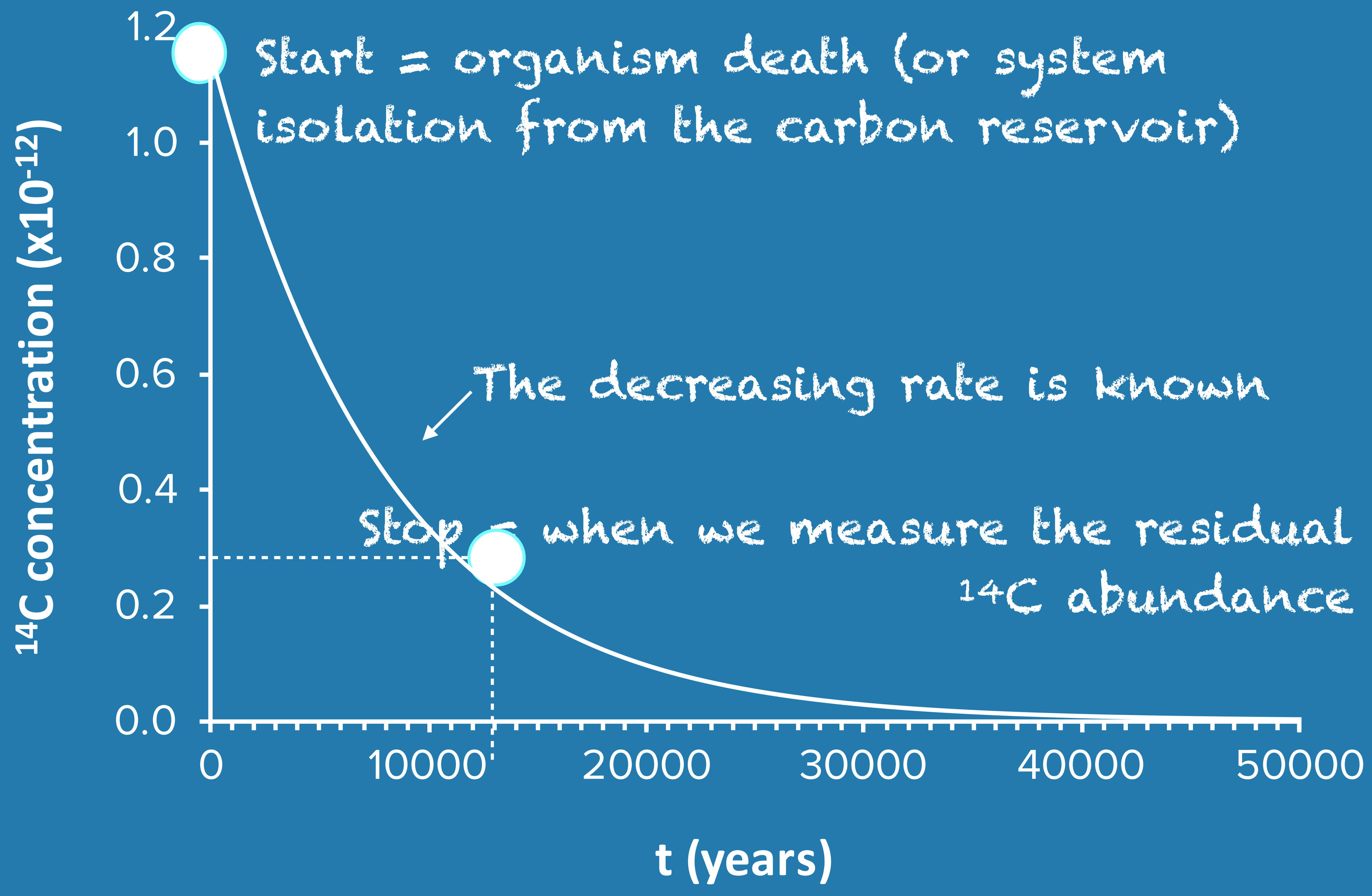
^{12}C: ~99%

^{14}C: ~1.2 E-12

^{13}C: ~1%

Basics of radiocarbon dating

- Every organism in the biosphere is in equilibrium with the atmosphere until its death (*or a system continuously exchanging carbon with the atmosphere is in equilibrium until those exchanges cease*): its radiocarbon concentration is - **basically** - equal to the concentration in atmosphere
- Since the death (*or since the end of the exchanges*), the mechanism of continuous production/uptake of radiocarbon stops
- If we can consider the system as closed (➜ contaminations), the ^{14}C balance starts to decrease according to the radioactive exponential law



$$^{14}R(t) = \frac{^{14}C}{C_{tot}} \approx \frac{^{14}C}{^{12}C} = {^{14}R_0}\, e^{-\frac{t}{\tau}} \quad \rightarrow \quad t = \tau \, ln\left(\frac{^{14}R_0}{^{14}R(t)}\right)$$

$$t = \tau \, ln\left(\frac{^{14}R_0}{^{14}R\,(t)}\right)$$

- Of course, the above equation can be solved only if we know $\boldsymbol{\tau}$ and $^{14}R_0$
- But… experimental estimates of $\boldsymbol{\tau}$ can be updated when measuring techniques improve and $^{14}R_0$ has not been always constant during the times
- We can define t as the **conventional radiocarbon age** if:
    - $\boldsymbol{\tau}$ is chosen as 8033 yrs (Libby mean life)
    - $^{14}R_0$ is chosen as the radiocarbon concentration in a reference year, i.e. 1950
- The conventional radiocarbon age is measured in years BP, *Before Present*

Pay attention!

- The dating measurement is not over once the conventional radiocarbon age has been determined

- Experimental data has to be converted to “calendar ages” ➜ calibration of the measured age through one of the internationally agreed calibration curve (*IntCal20, Marine20, SHCal20, Bomb21NH1, …*) is mandatory ➜ the result is expressed as a distribution of probability for which we can evaluate time intervals associated to fixed level of confidence

- *Pay attention to other natural processes that can influence the radiocarbon concentration in living organisms: reservoir effect and isotopic fractionation*

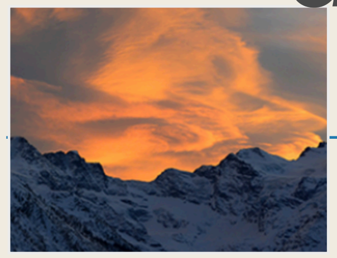
- *Many discussions can be also dedicated to the issues of possible contaminations, to selection of either samples or the subfraction of samples to be collected*

Some key points to choose the most appropriate measurement technique

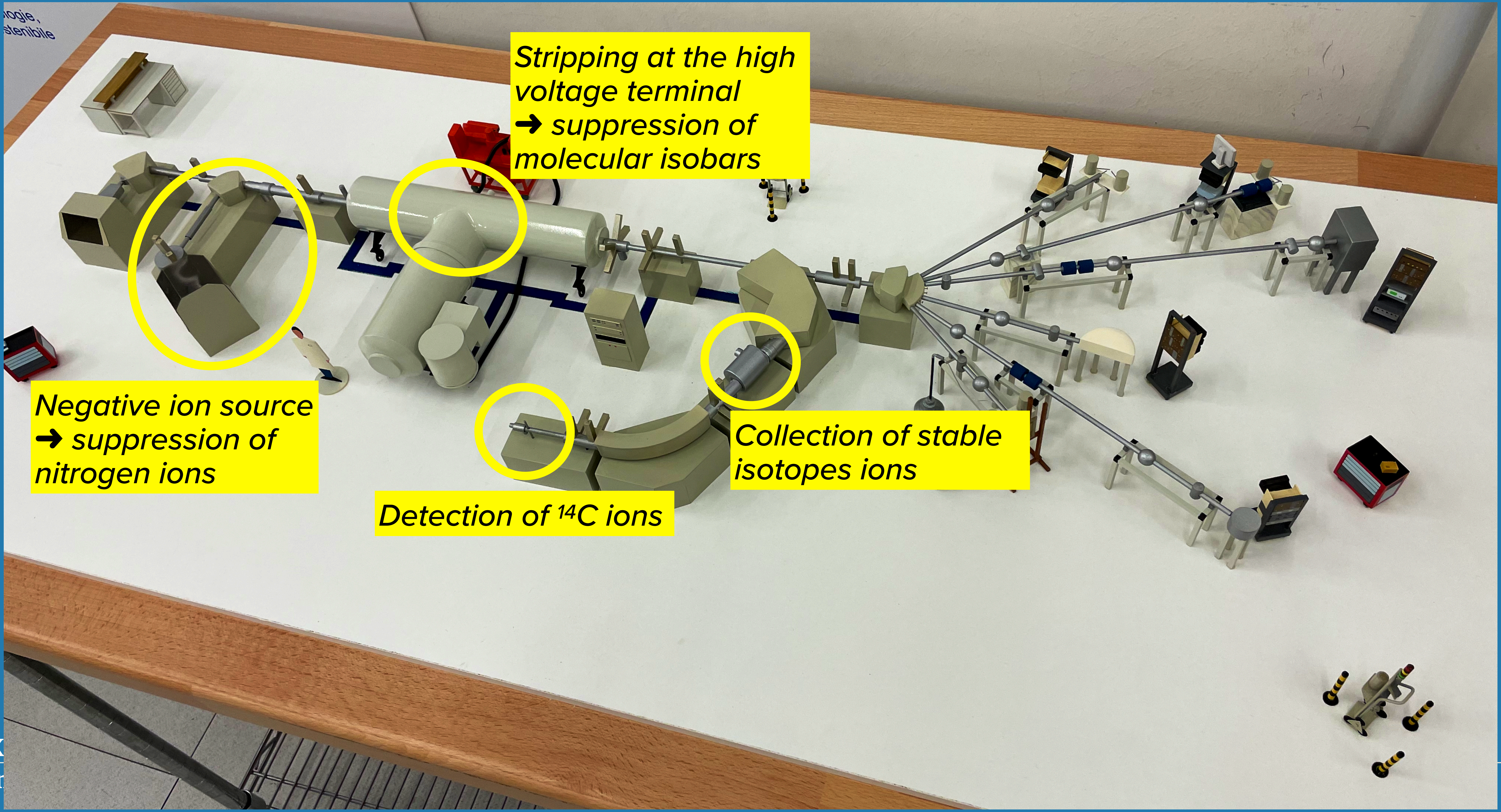
- The measurement of radiocarbon concentration is invasive: a sample is needed
  ➜ *a technique that allows us to collect a sample as smallest as possible is clearly preferable*

- The natural radiocarbon abundance is very low and it decreases as time passes by
  ➜ *the measurement technique has to be very efficient and sensitive (the higher is the sensitivity the older are the possible datable ages)*

- ^{14}C has interfering isobars that are more abundant in nature (^{14}N, $^{12}CH_2$, ^{13}CH)
  ➜ *the measurement technique has to suppress these interferences without decreasing the radiocarbon count rate*

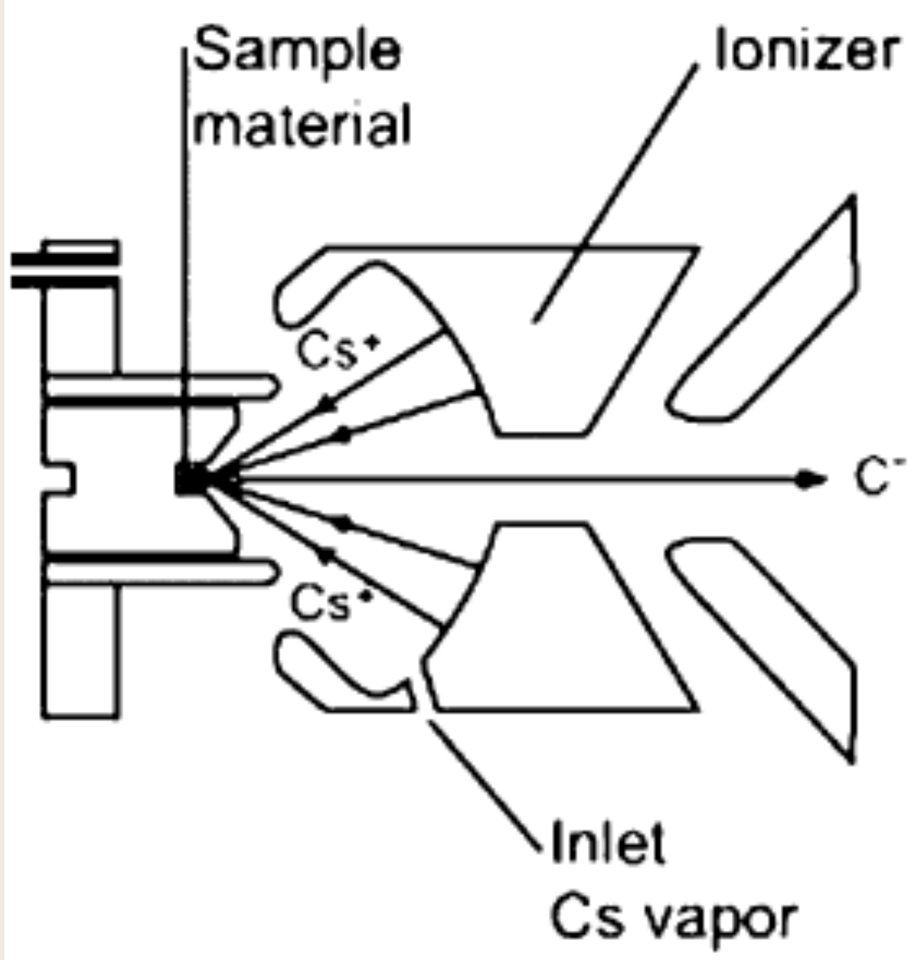


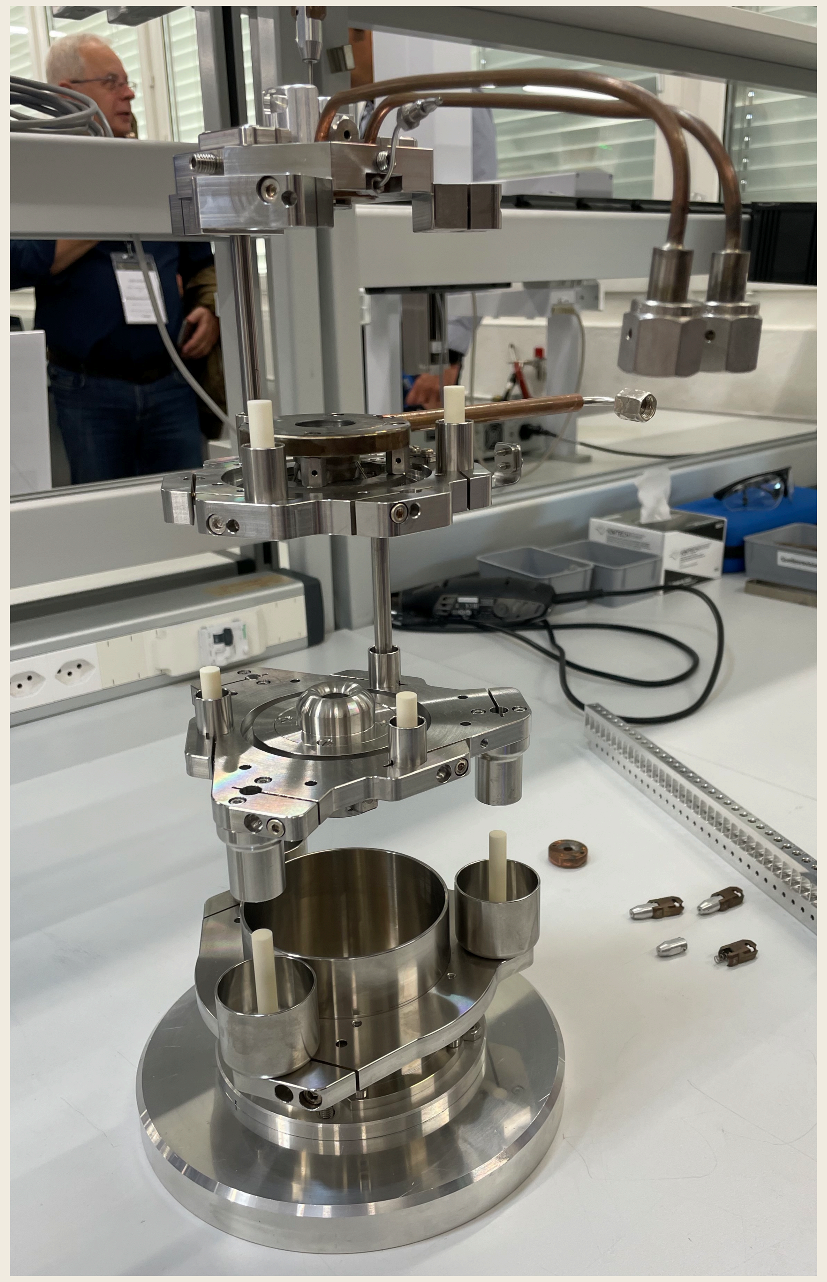
… and we can now go back to tandem accelerators and to Accelerator Mass Spectrometry (AMS)



About the negative ions source

- It is based on sputtering by Cs+ ions
- Negative ions (elemental, molecular, cluster…) are extracted through a voltage of few tens of keV
- Not all the elements can be extracted as negative ions
- In a ^{14}C-AMS measurement, -1-charged ions are extracted and analyzed from the source





Cs sputtering ion source by IonPlus

Ionization Potentials and Electron Affinities of the Elements

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
$_{1}$**H** 13.59 0.754	Ionization Potential Electron Affinity						$_{2}$**He** 24.48 0.078*
$_{3}$**Li** 5.39 0.618	$_{4}$**Be** 9.32 0.195*	$_{5}$**B** 8.30 0.277	$_{6}$**C** 11.26 1.263	$_{7}$**N** 14.53 -0.07	$_{8}$**O** 13.61 1.461	$_{9}$**F** 17.42 3.399	$_{10}$**Ne** 21.56 < 0
$_{11}$**Na** 5.14 0.548	$_{12}$**Mg** 7.64 < 0	$_{13}$**Al** 5.98 0.441	$_{14}$**Si** 8.15 1.385	$_{15}$**P** 10.48 0.747	$_{16}$**S** 10.36 2.077	$_{17}$**Cl** 13.01 3.617	$_{18}$**Ar** 15.76 < 0
$_{19}$**K** 4.34 0.501	$_{20}$**Ca** 6.11 0.043	$_{31}$**Ga** 6.00 0.30	$_{32}$**Ge** 7.90 1.2	$_{33}$**As** 9.81 0.81	$_{34}$**Se** 9.75 2.021	$_{35}$**Br** 11.81 3.365	$_{36}$**Kr** 14.00 < 0
$_{37}$**Rb** 4.18 0.486	$_{39}$**Sr** 5.70 < 0	$_{49}$**In** 5.79 0.3	$_{50}$**Sn** 7.34 1.2	$_{51}$**Sb** 8.64 1.07	$_{52}$**Te** 9.01 1.971	$_{53}$**I** 10.45 3.059	$_{54}$**Xe** 12.13 < 0
$_{55}$**Cs** 3.89 0.472	$_{56}$**Ba** 5.21 < 0	$_{81}$**Tl** 6.11 0.2	$_{82}$**Pb** 7.42 0.364	$_{83}$**Bi** 7.29 0.946	$_{84}$**Po** 8.42 1.9	$_{85}$**At** 9.5 2.8	$_{86}$**Rn** 10.75 < 0

*Metastable

R. Middleton, A negative-ion cookbook (www.pelletron.com/cookbook.pdf)

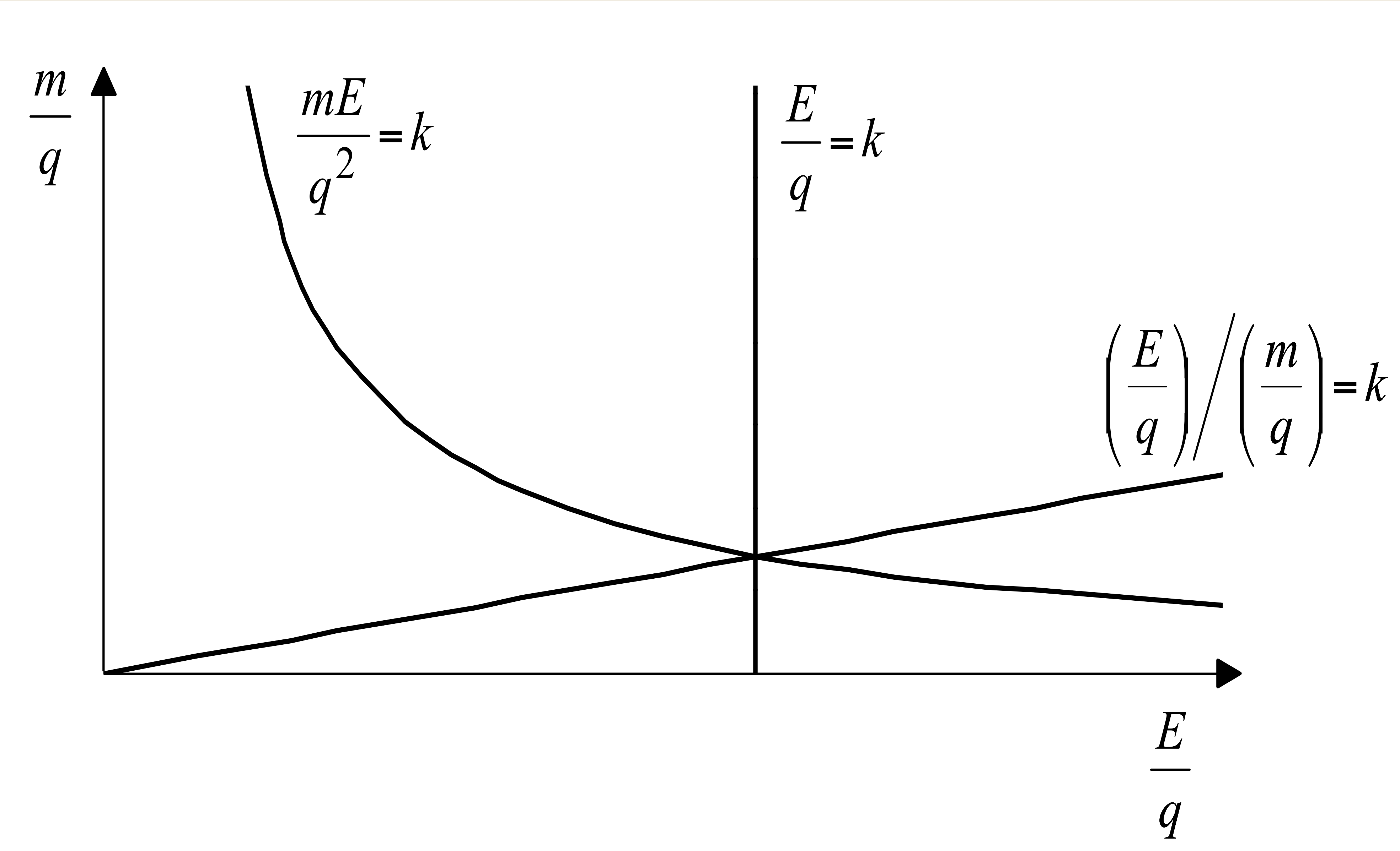
Beam analysis

ESA by IonPlus

- Electrostatic analyser: this is basically an electrostatic capacitor with parallel plates and r as bend radius
- Magnetic analyser: this is basically a region with a magnetic field whose direction is orthogonal to the plane where the particles move
- Velocity filter (Wien filter): this is basically a region where there are both an electric field (in the plane where the particles move) and a magnetic field whose direction is orthogonal to that plane) –> only those particles for whom the result of the two forces is zero can be transmitted beyond the filter

Why just an analyser is not enough

- Each of the analyzing elements identifies a locus of points



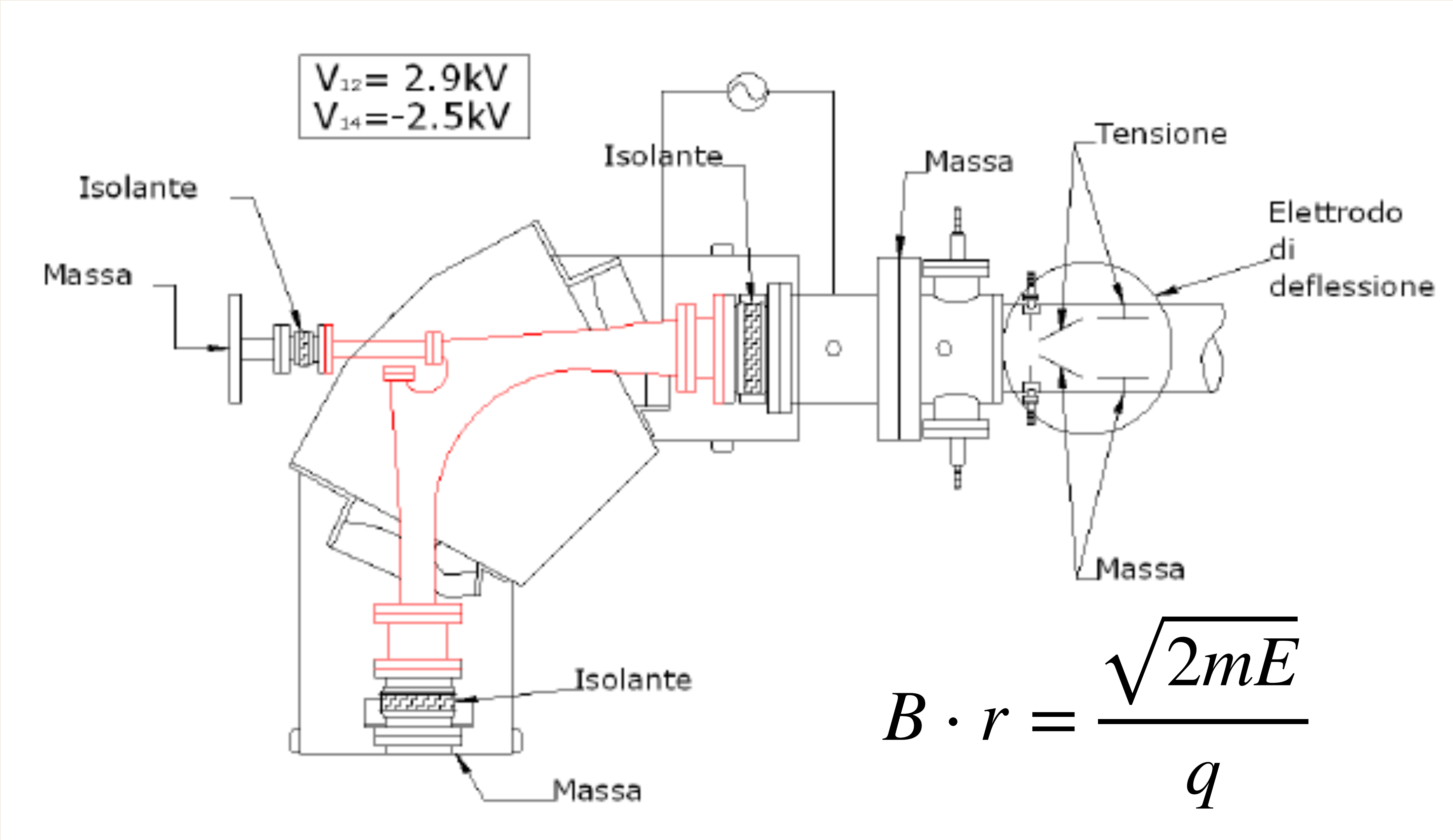
In AMS our goal is however to transmit, accelerate and count not only ^{14}C ions, but also ^{12}C and ^{13}C

^{12}C –> to estimate the total amount of carbon

^{13}C –> to correct for isotopic fractionation

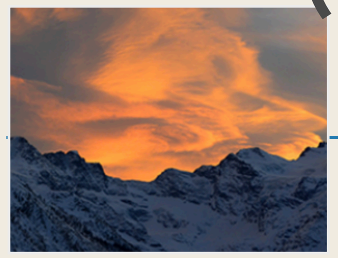
How to switch mass?

- Using a magnetic analyser



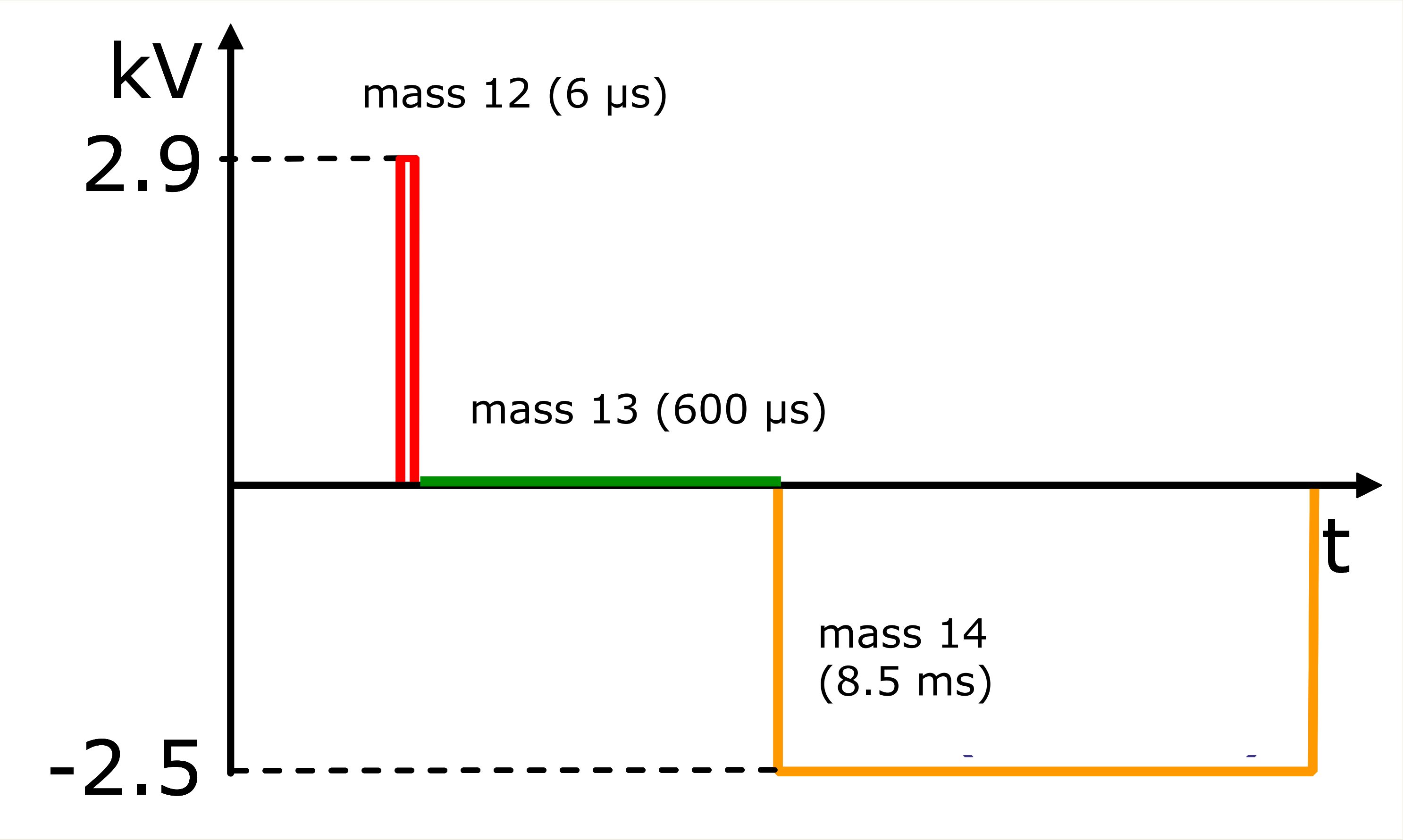
$$B \cdot r = \frac{\sqrt{2mE}}{q}$$

- But changing currents to change magnetic field is not fast (consider hysteresis)



Bouncing injection

- Magnet tuned to transmit mass 13
- Different voltages are applied to the magnet chamber so that masses other than 13 can acquire a different energy and can be thus transmitted

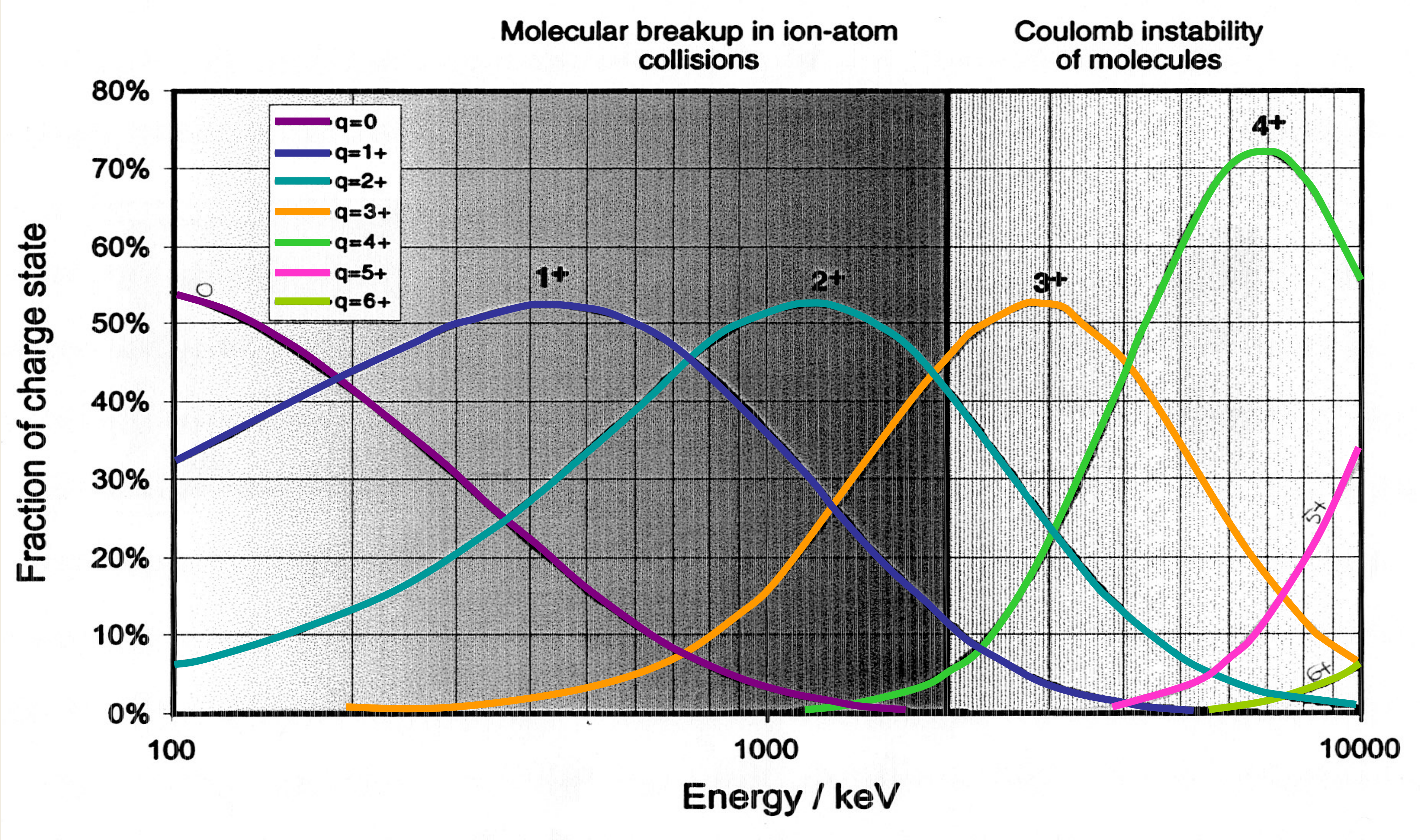


Injection times adjustable according to the average currents we would like to measure on the high energy side

Pay attention to molecular isobars!

Acceleration and stripping

- In a ^{14}C-AMS measurement*, the terminal voltage is kept at 2.5 MV



$$E_{fin} = (0.035 + 2.5 + 3 \cdot 2.5) MeV$$

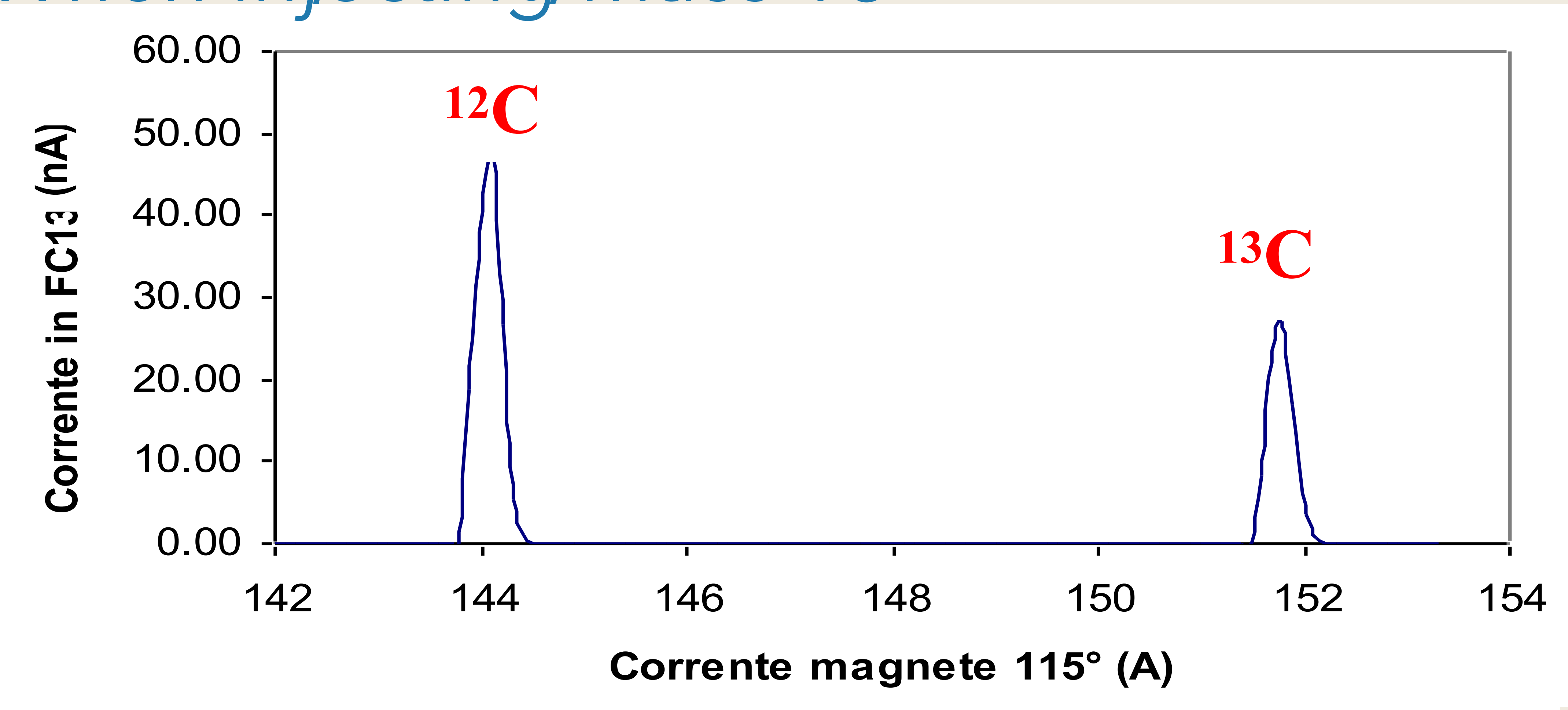
*at our tandem in Florence

What happens to molecular isobars

- After stripping, the probability to find molecules characterized by a high charge state is low (*Coulomb explosion*) ➜ the capability to suppress isobars is due to the combination of terminal voltage, stripper thickness and charge state that is analyzed on the high energy side

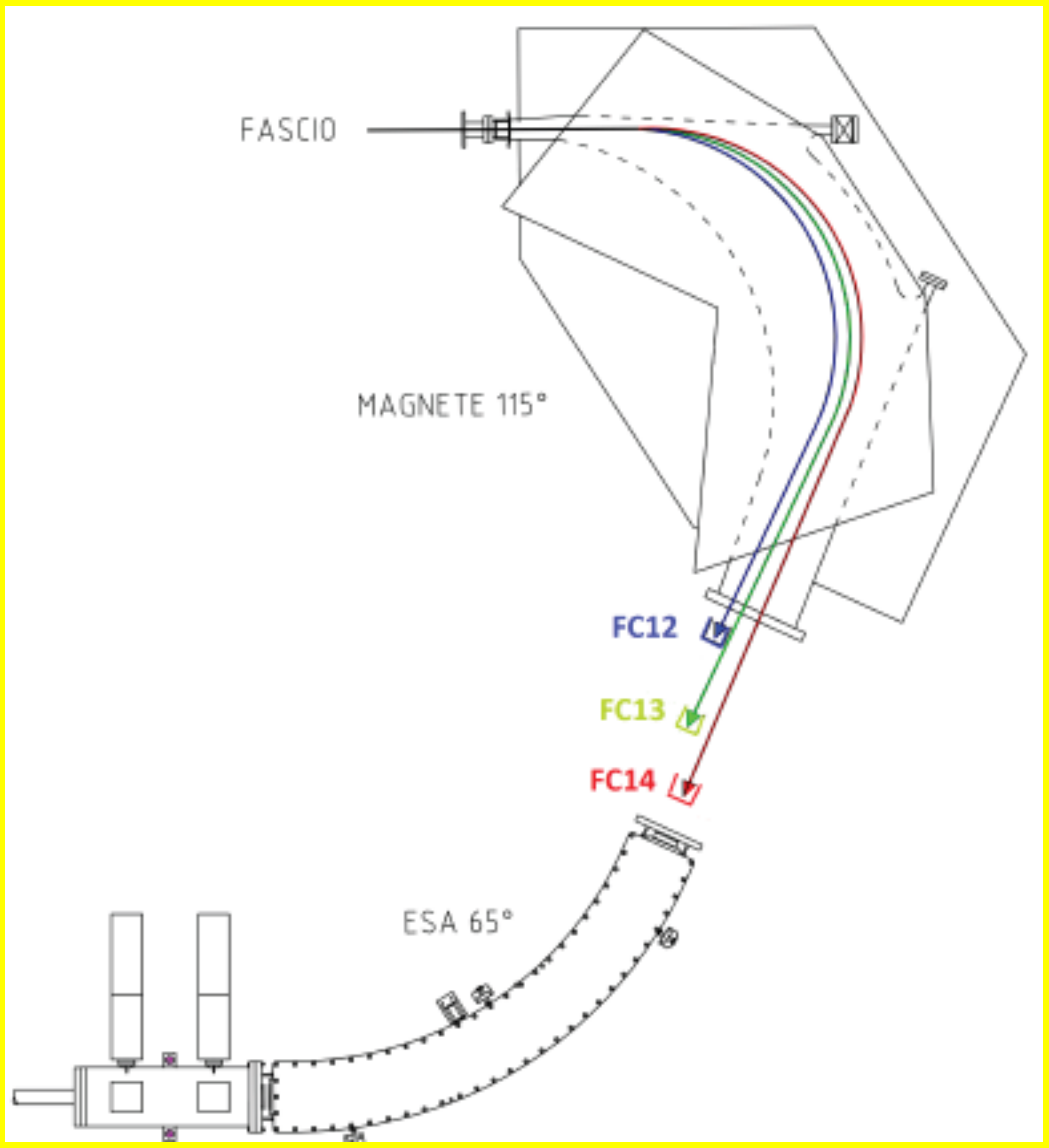
When injecting mass 14

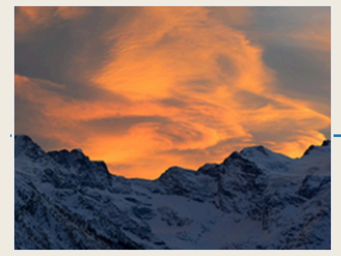
Scan of the analysing magnet on the high energy side



Analysis on the high energy side

- Analysing magnet ➜ to identify ions with mass 14, charge 3+ and energy 10 MeV
  - At the exit of the magnet, stable isotopes ^{12}C and ^{13}C abundances are measured by off-set Faraday cups
  - Faraday cup for ^{13}C: also mechanism to stabilize terminal voltage
- Electrostatic analyser ➜ to suppress further possible interferences

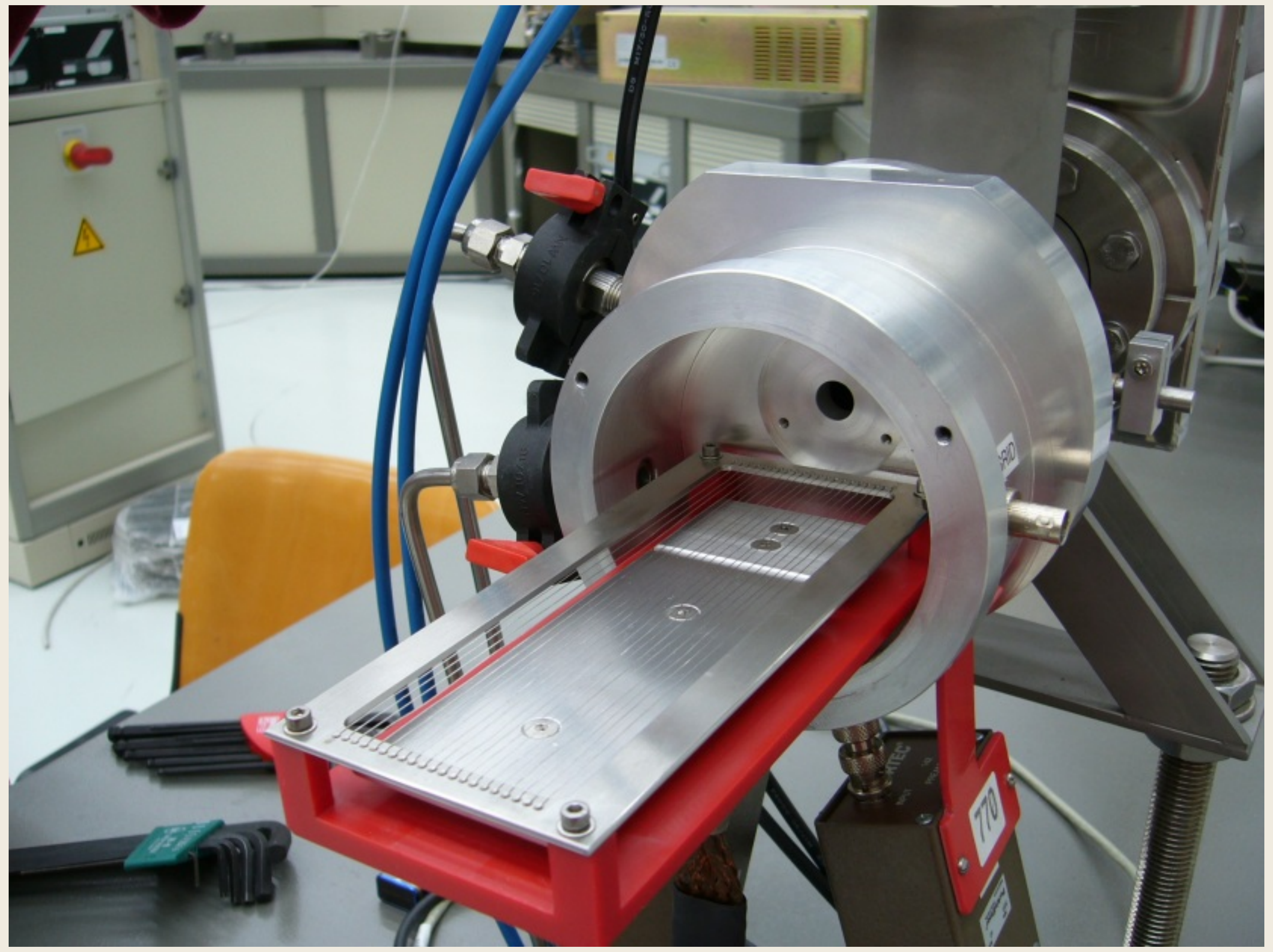




About the rare isotope detector

- We can choose to use the detector as a further element to discriminate the beam particles, thus supporting in better identifying ^{14}C ions or as a simple counter

Ionization chamber



Solid state detector

The use of a silicon diode is only possible thanks to the very low counting rates

<20Hz for modern samples!

The present challenges of ^{14}C and AMS

- Dating campaigns often require many samples to be measured
  ➜ experimental set-ups should be highly reliable and as much simple as possible
  (this is true not only for Cultural Heritage and archaeology, but also for environmental applications)

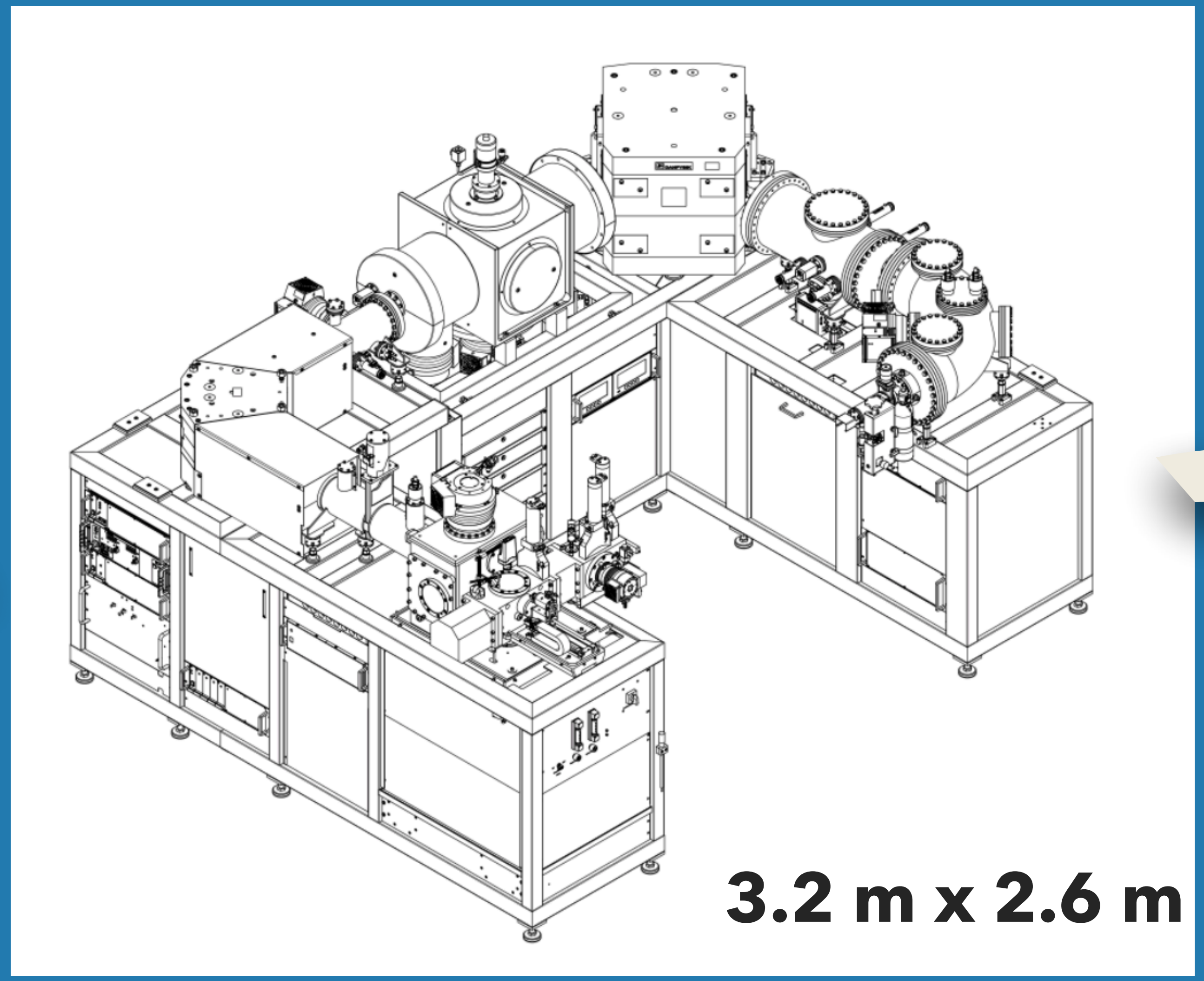
- Some materials can have a very complex matrix
  ➜ the "right" carbon has to be extracted and cleaned from all the possible contaminations

SMALL

Towards smaller AMS machines

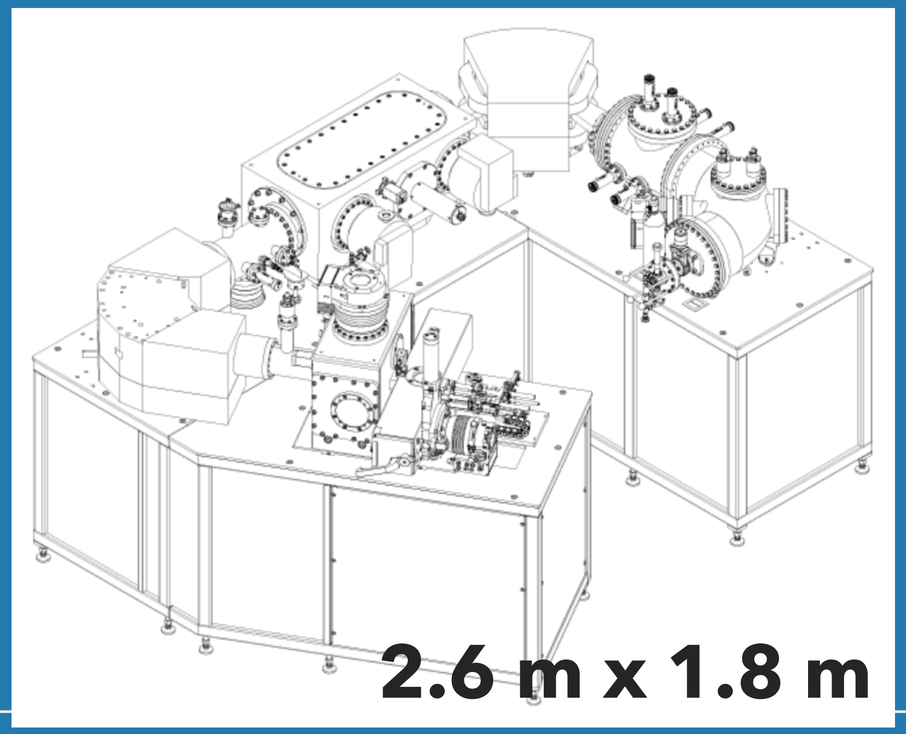
Low-voltage tandem machines: from research at ETH to commercial set-ups

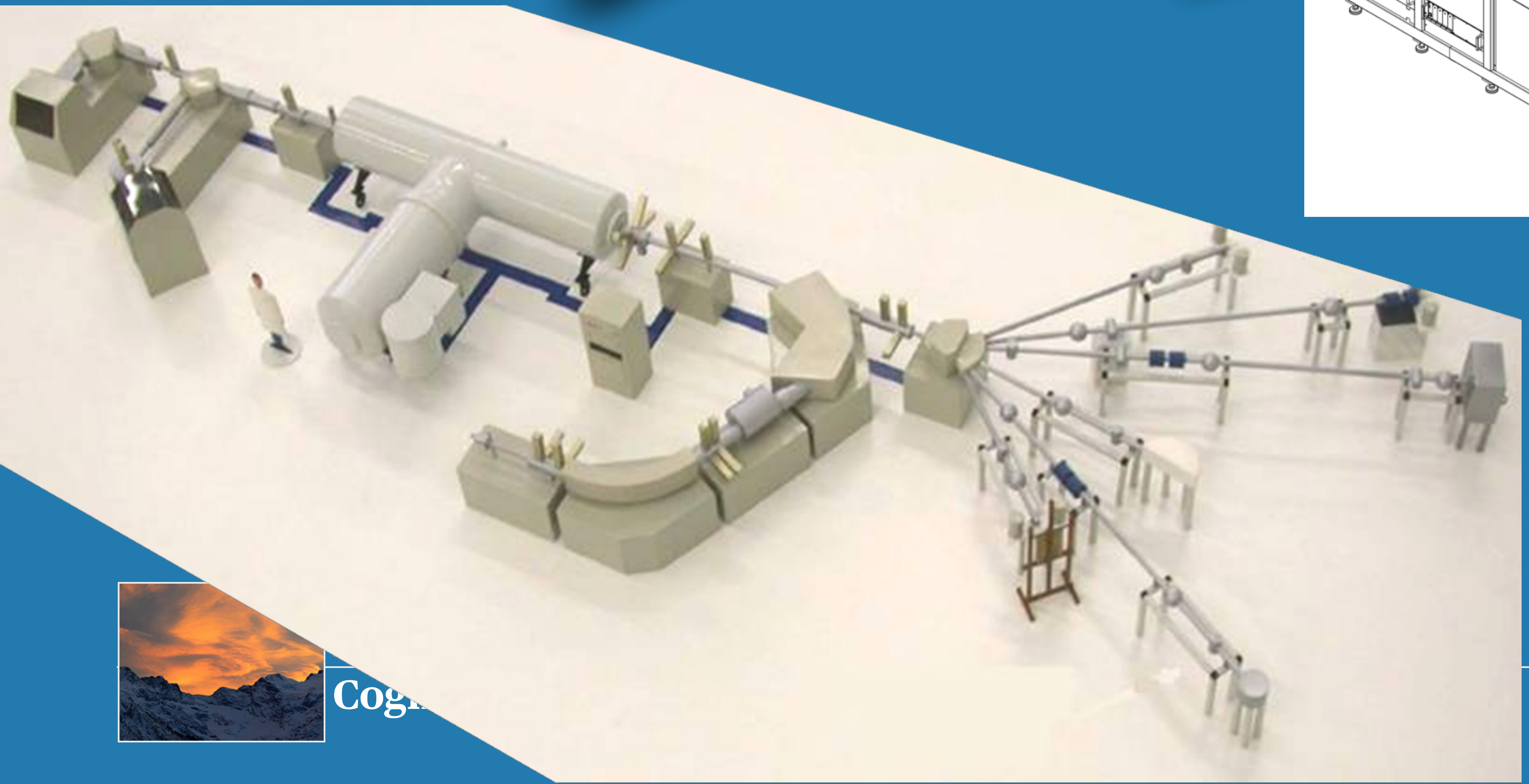
MICADAS



Lower costs; easier mainteinance

LEA



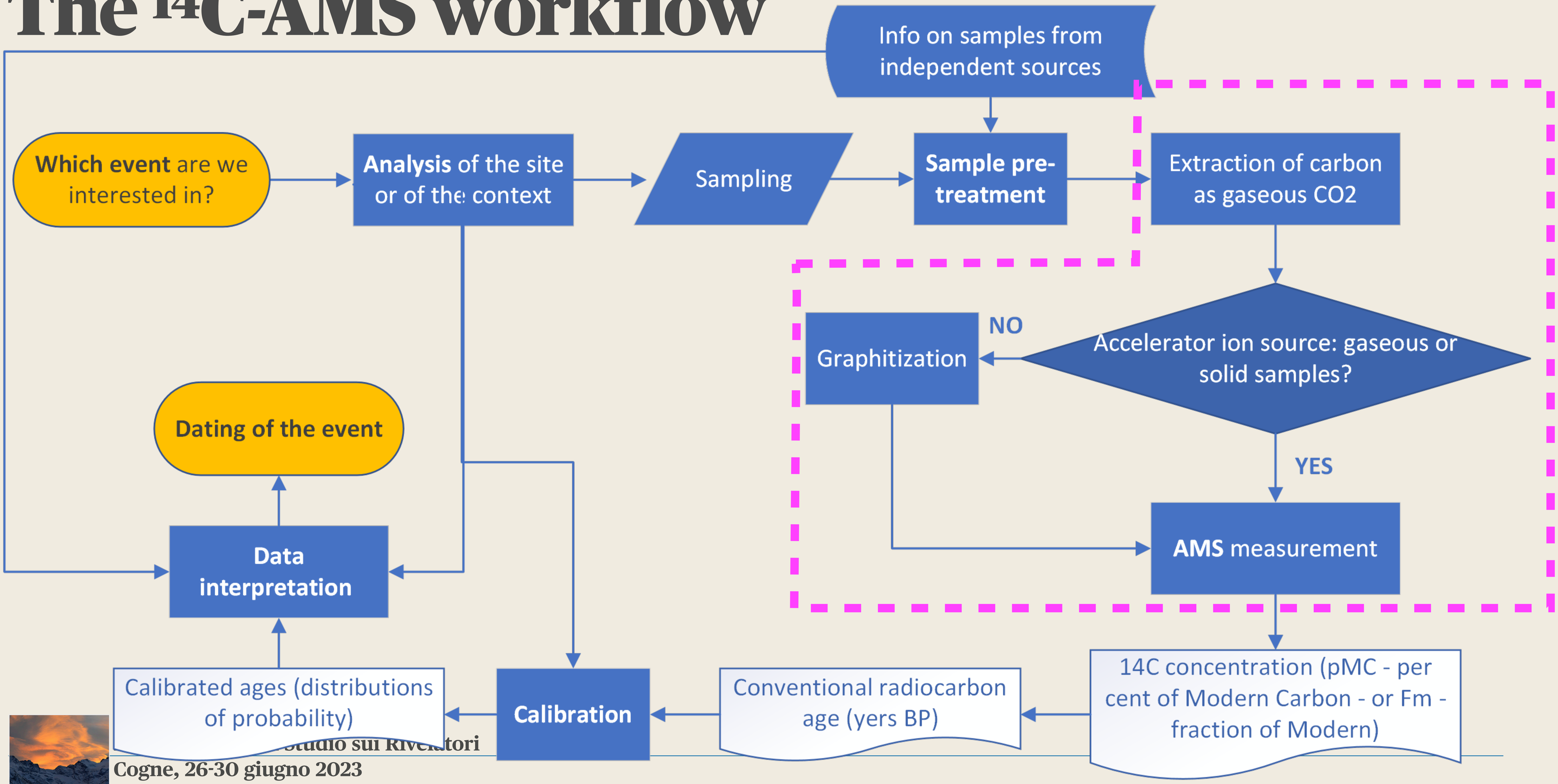


Towards smaller samples

At INFN-CHNet in Florence, we have developed a graphitization line designed for very small samples (mass of about 50 µg of carbon - while our standard samples are of about 700 µg of carbon)

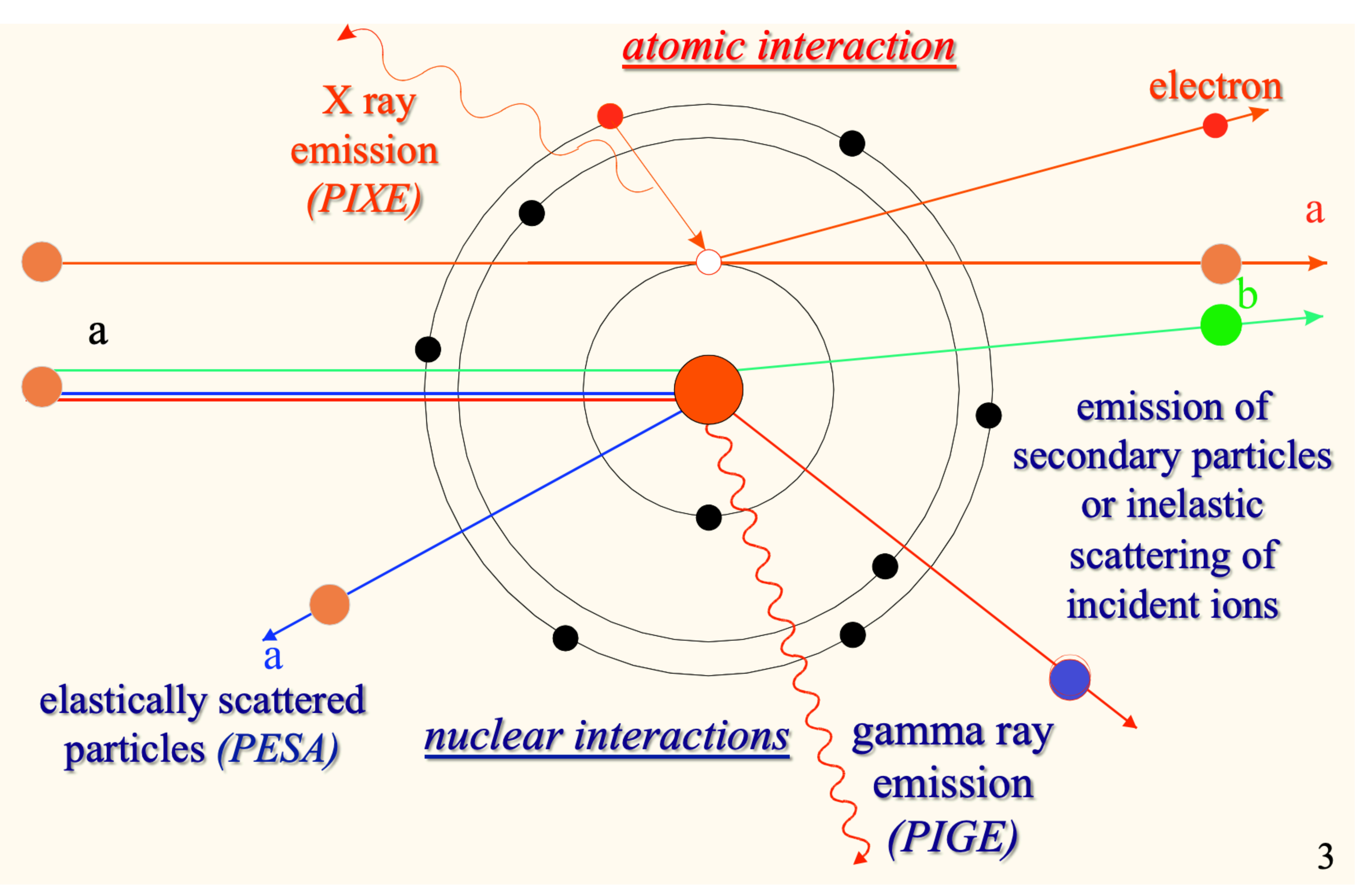
M. Fedi et al., Towards micro-samples radiocarbon dating at INFN-LABEC, Florence, NIM B 465 (2020), 19

The ^{14}C-AMS workflow



… and what about the composition of the artworks?

The world of Ion Beam Analysis (IBA)



A MeV particle beam (typically proton) impinging on target

➜ collection and identification of the different products of interaction, i.e.

- X-rays (PIXE)
- gamma-rays (PIGE)
- backscattered particles (BS)
- …

Particle Induced X-ray Emission

Some milestones in its history

1912: Chadwick shows that alpha-particles emitted from a radioactive source induce X-ray emission

In 1950s, accelerators began to be widely exploited to investigated X-ray emission cross sections

In the 1960s, first experiments, e.g. at Livermore, show that X-ray produced due to proton irradiation can be used for analytical purposes

The first Si(Li) are introduced, improving the attainable energy resolution in X-rays detection

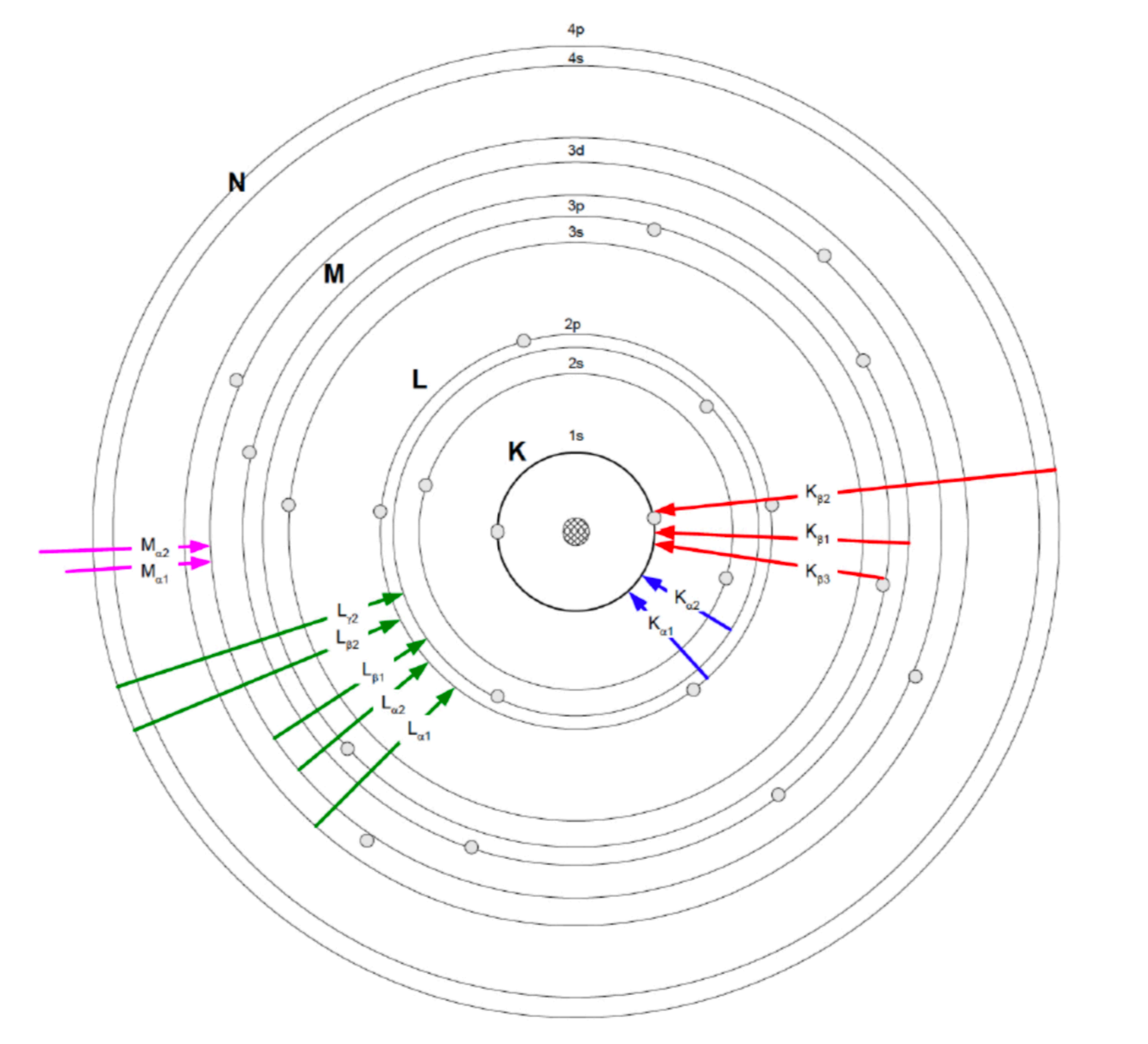
In 1970, Johansson et al demonstrate the multielementarity of PIXE by 2 MeV protons

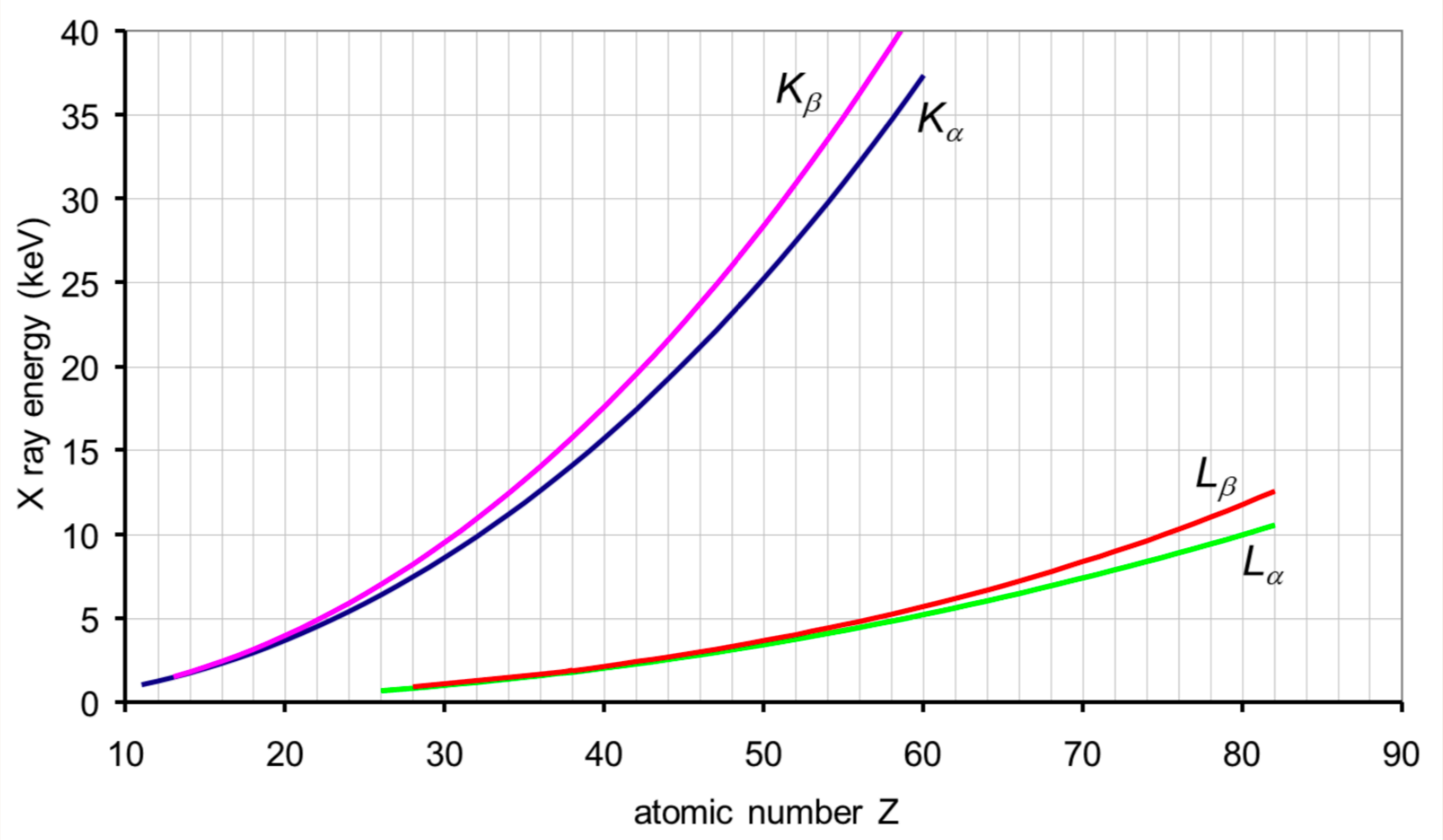
Introduction of the first external beam set-ups

Introduction of strong focusing and microbeams

Introduction of Silicon Drift Detectors

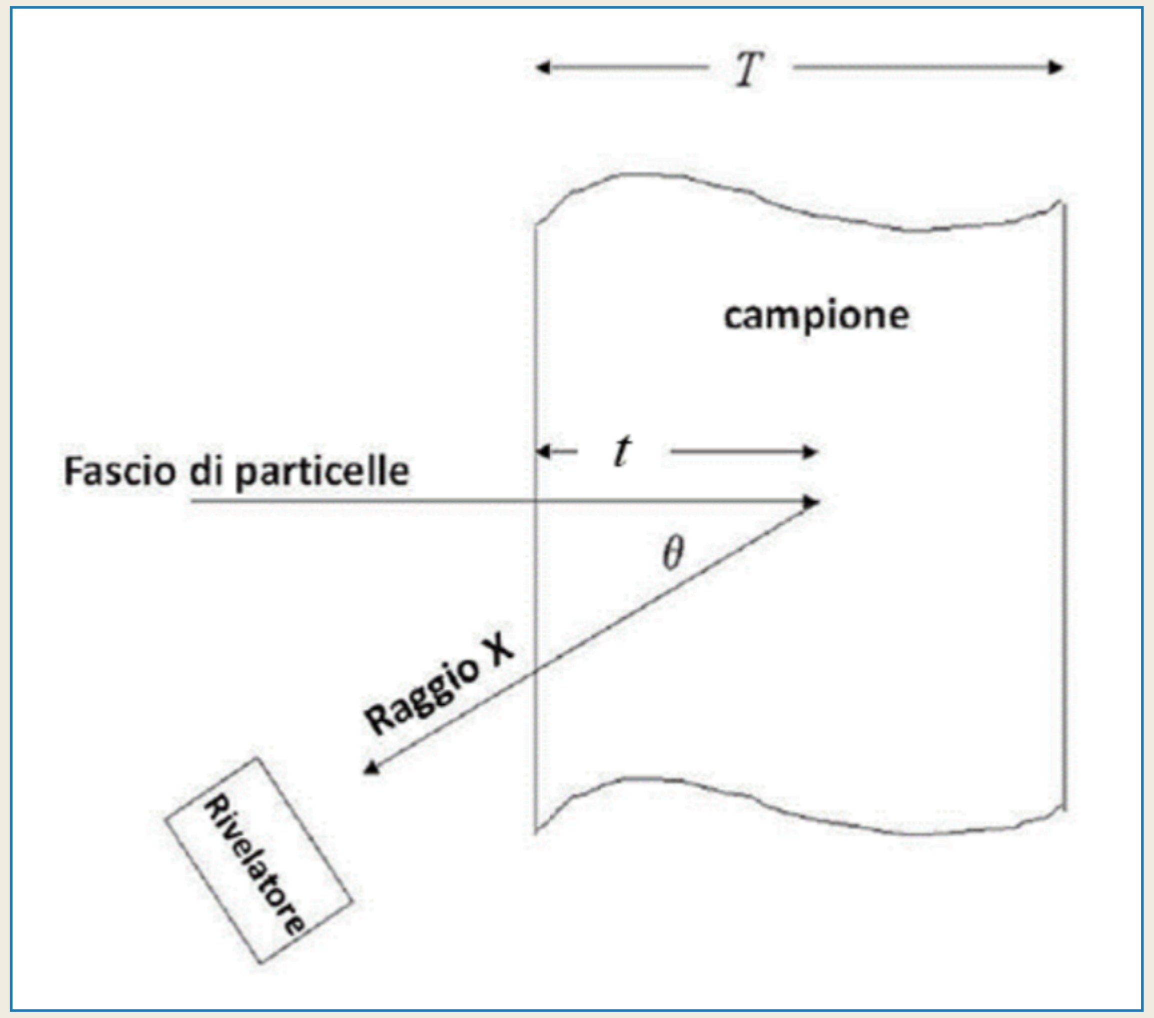
Features of X-rays





In a PIXE measurement, collection of X-rays allows us to identify the Z of the element present in the investigated object

Quantitative analysis by PIXE



Thin target approximation

$$Y_{X_j}(Z) = \sigma_{X_j} \cdot \frac{Q}{e} \cdot \frac{N_{Av}\rho_Z t}{A} \cdot \frac{\Omega}{4\pi} \varepsilon_{int} a_Z$$

Infinite thickness target approximation

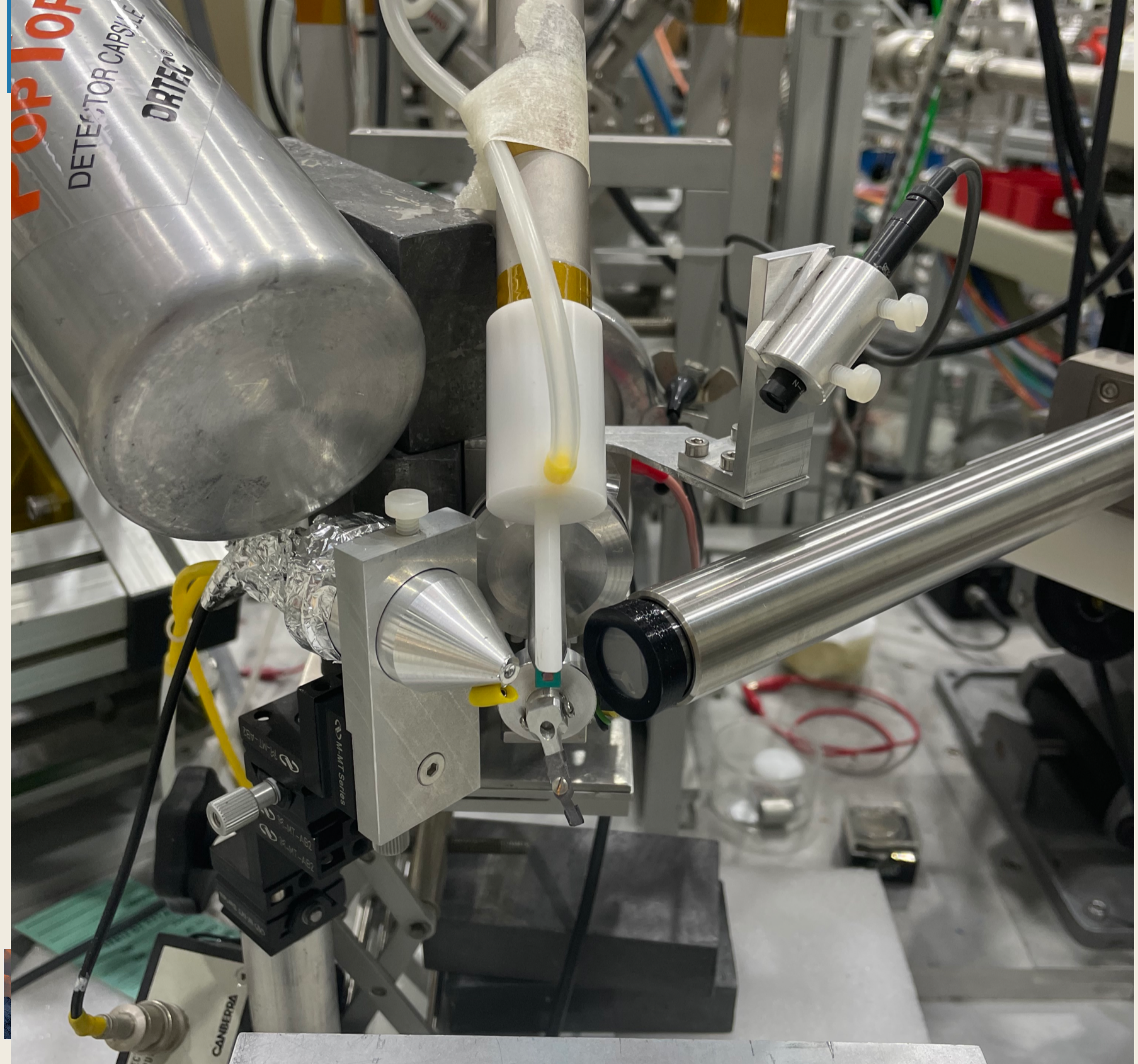
$$Y_{X_j}(Z) = \frac{Q}{e} \cdot \frac{N_{Av}}{A} \cdot \frac{\Omega}{4\pi} \varepsilon_{int} a_Z \cdot \frac{\rho_Z}{\rho} \cdot \int_{E_0}^{0} \sigma_{X_j}(E) \cdot e^{-\frac{\mu\, t(E)}{\cos\theta}} \cdot \frac{dE}{S(E)}$$

In a PIXE measurement, the integrated number of X-rays emitted by a defined element allows us to estimate the abundance of that element in the investigated object

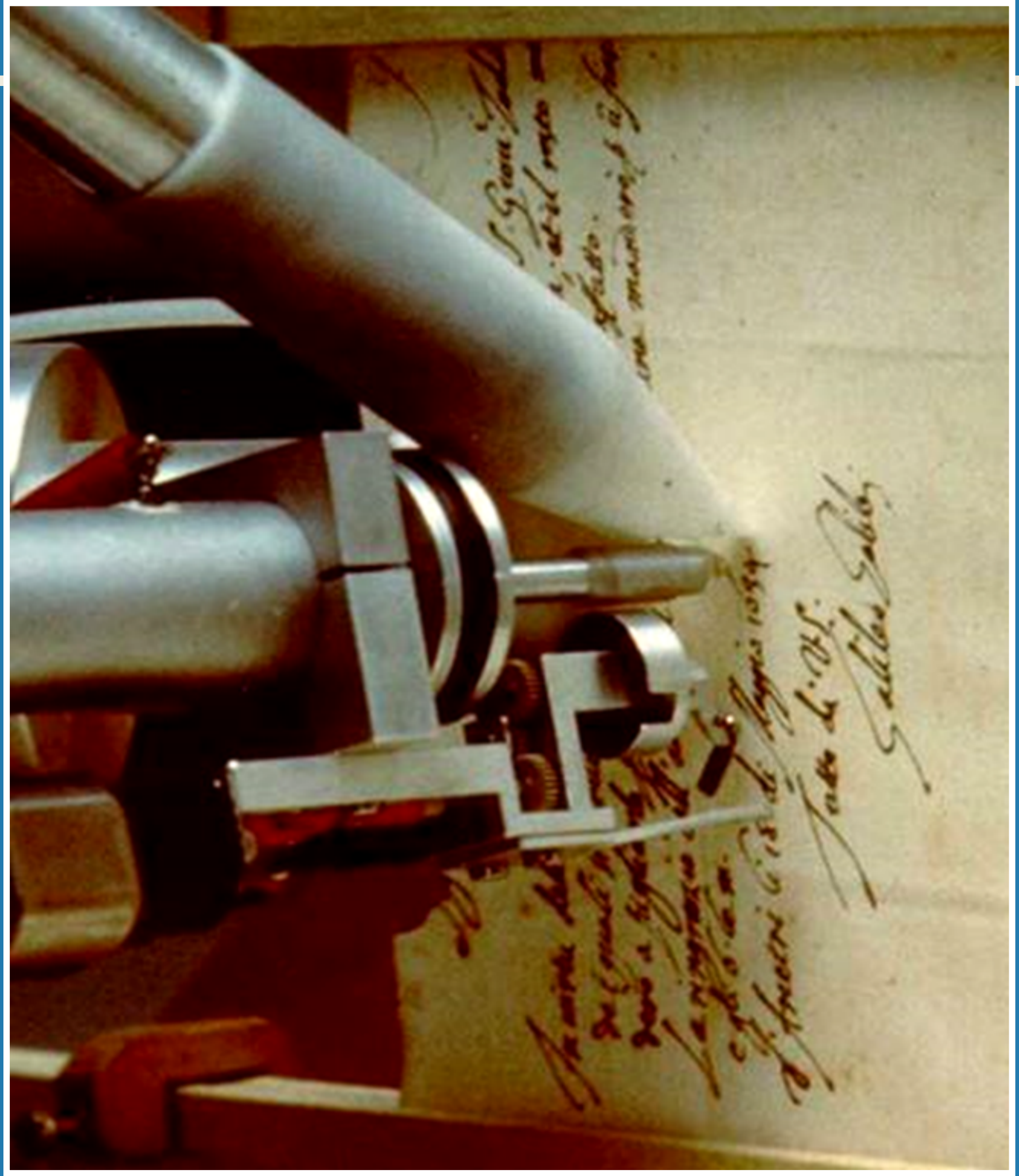
The big revolution in PIXE: external beam

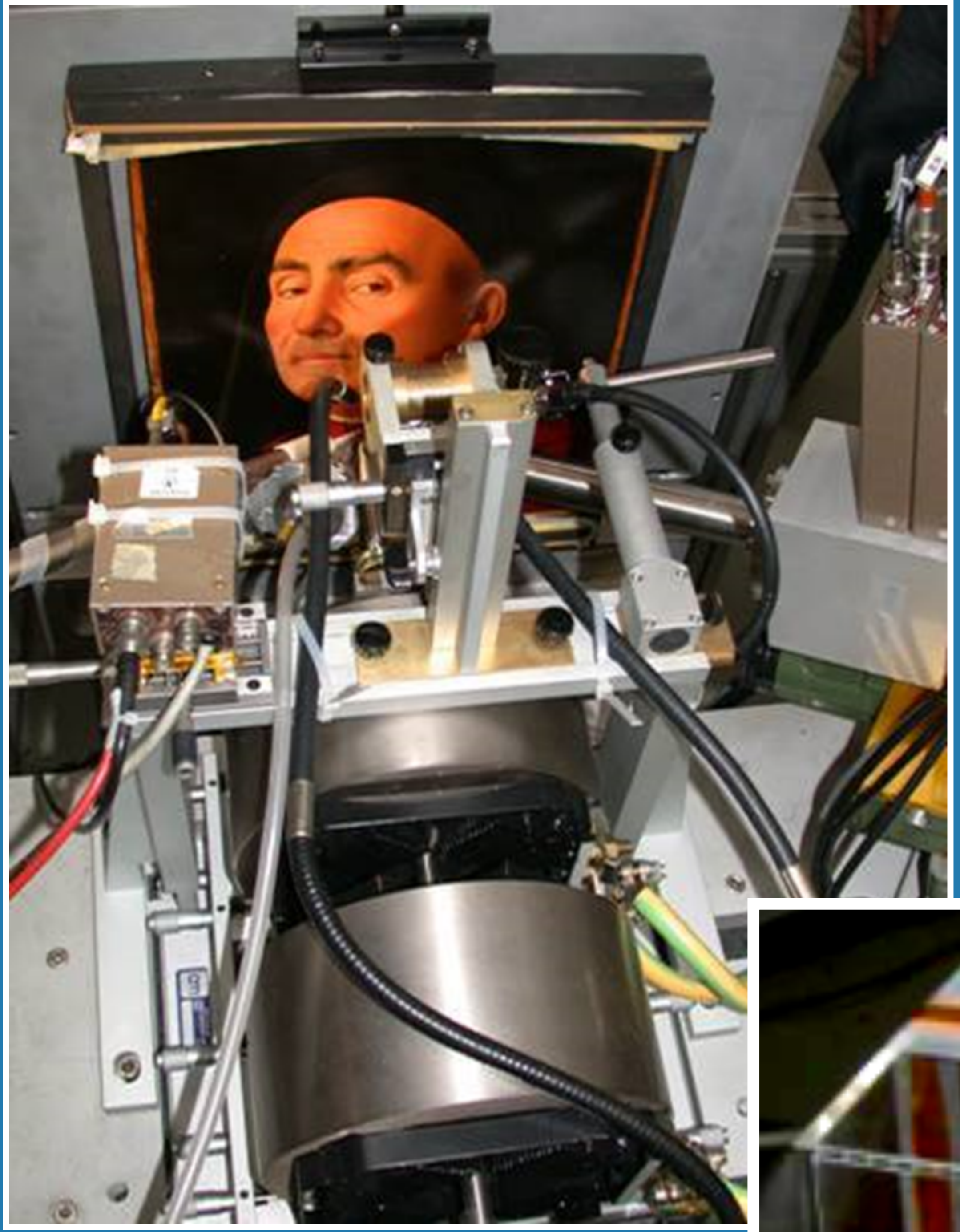
➜ *no need to collect samples from the object to be investigated* ➜ *non invasive and non destructive measurements*

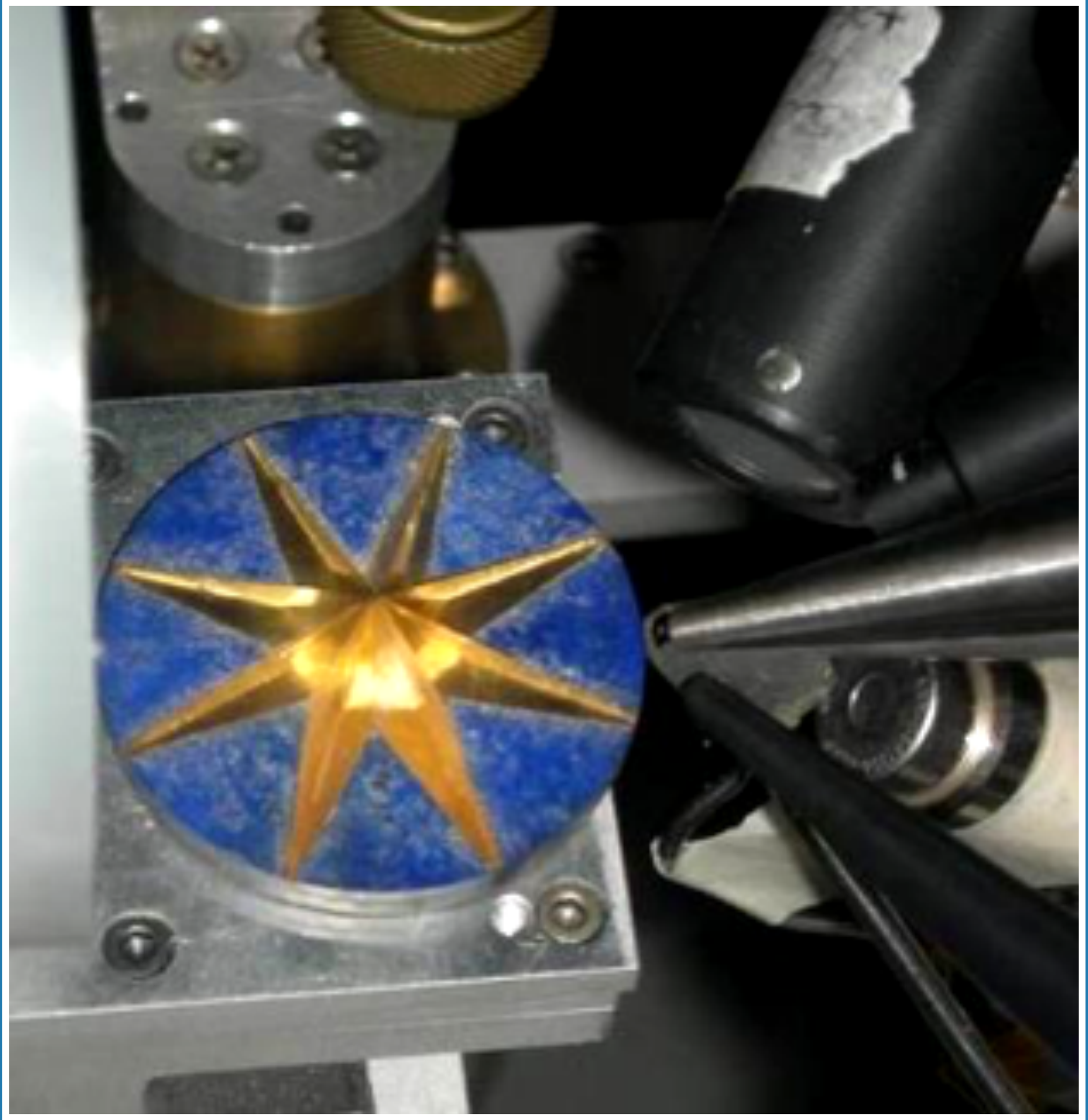
➜ *some limitations on the elements that can be detected and the artefacts that can be analysed*

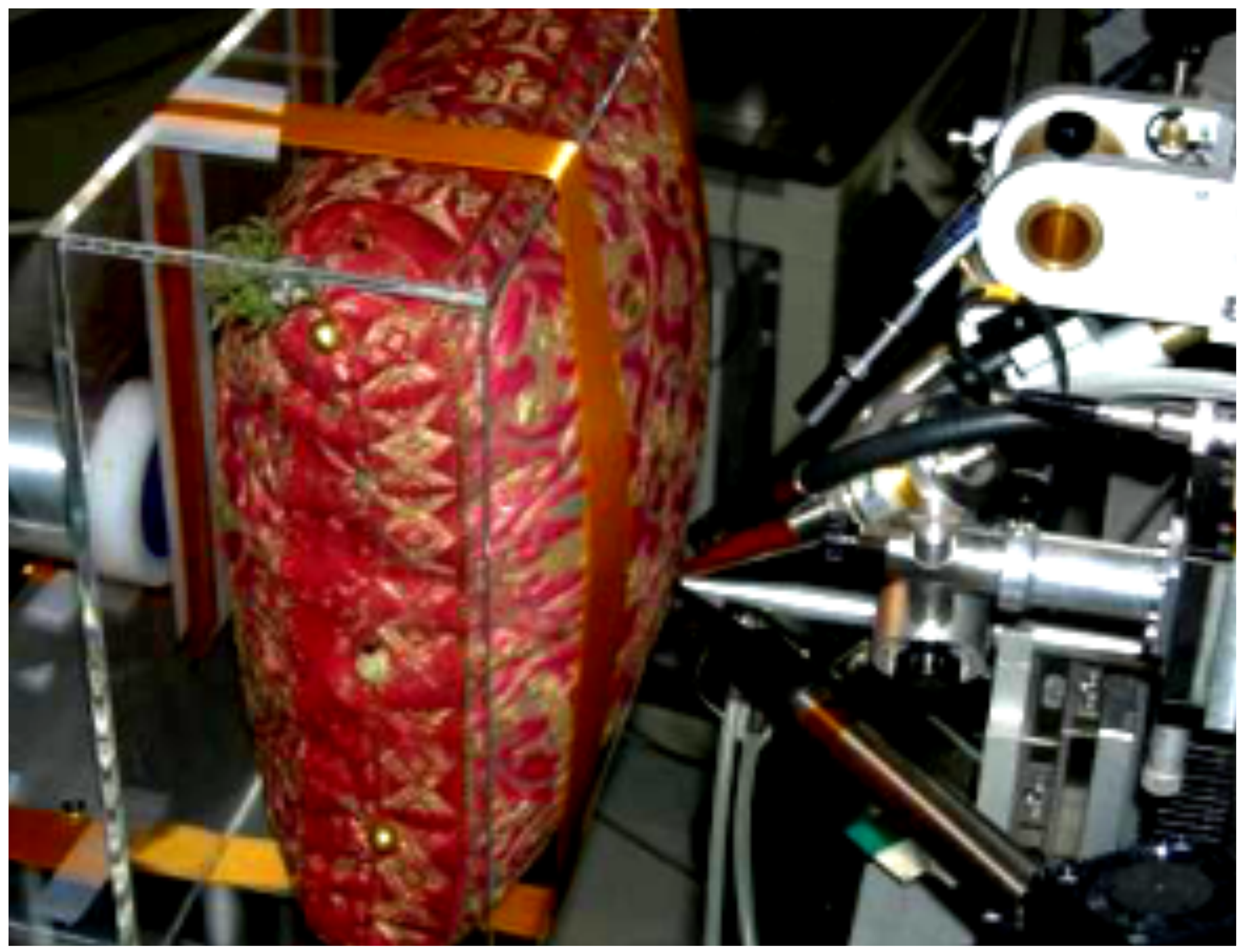


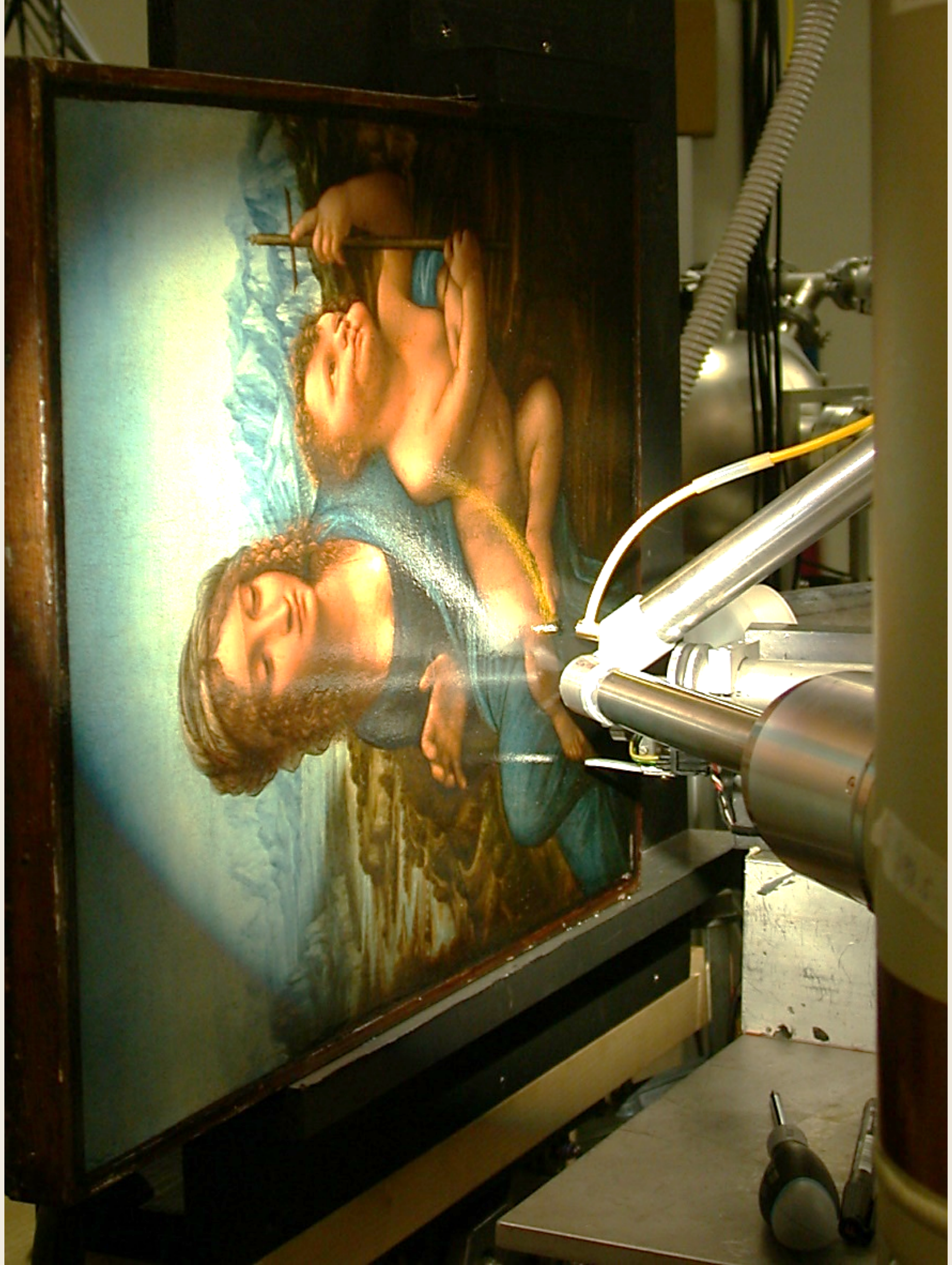
The external beam set-up for Cultural Heritage at LABEC (*Laboratorio di tecniche Nucleari per l'Ambiente e i Beni Culturali*) - Florence









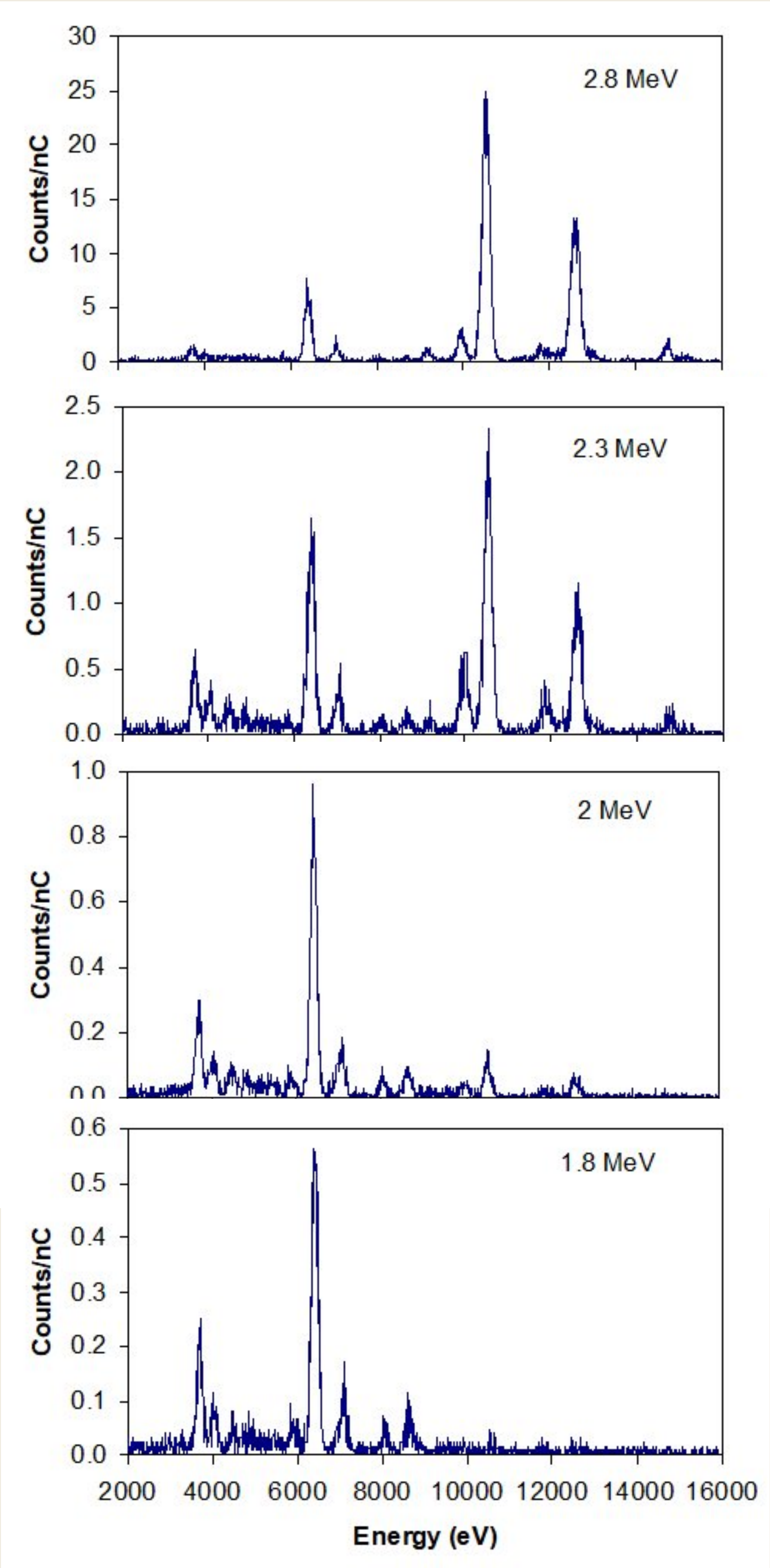


Leonardo

Madonna dei Fusi (versione Reford)

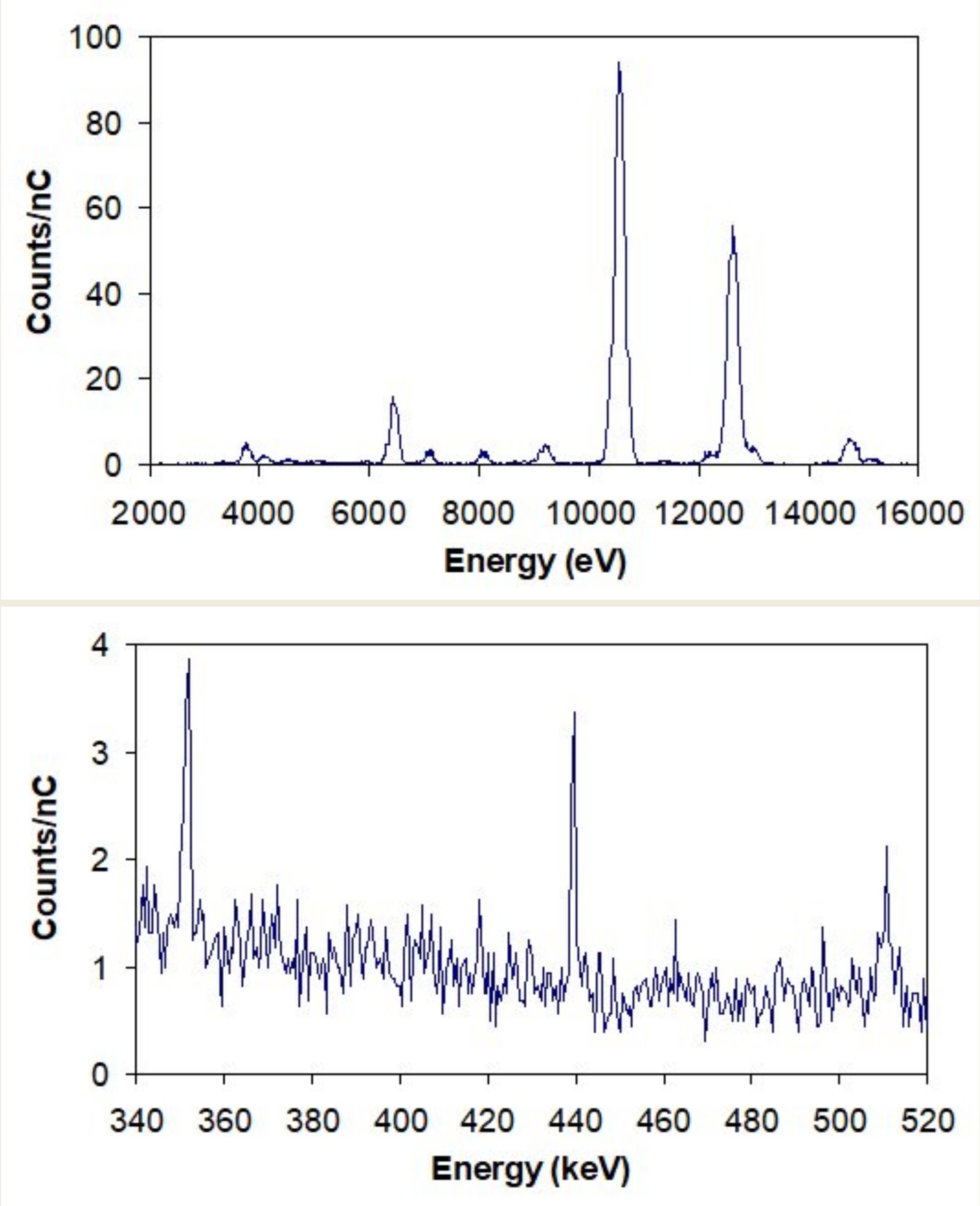
Differential PIXE

➜ study of the technique: use of several very thin superimposed layers



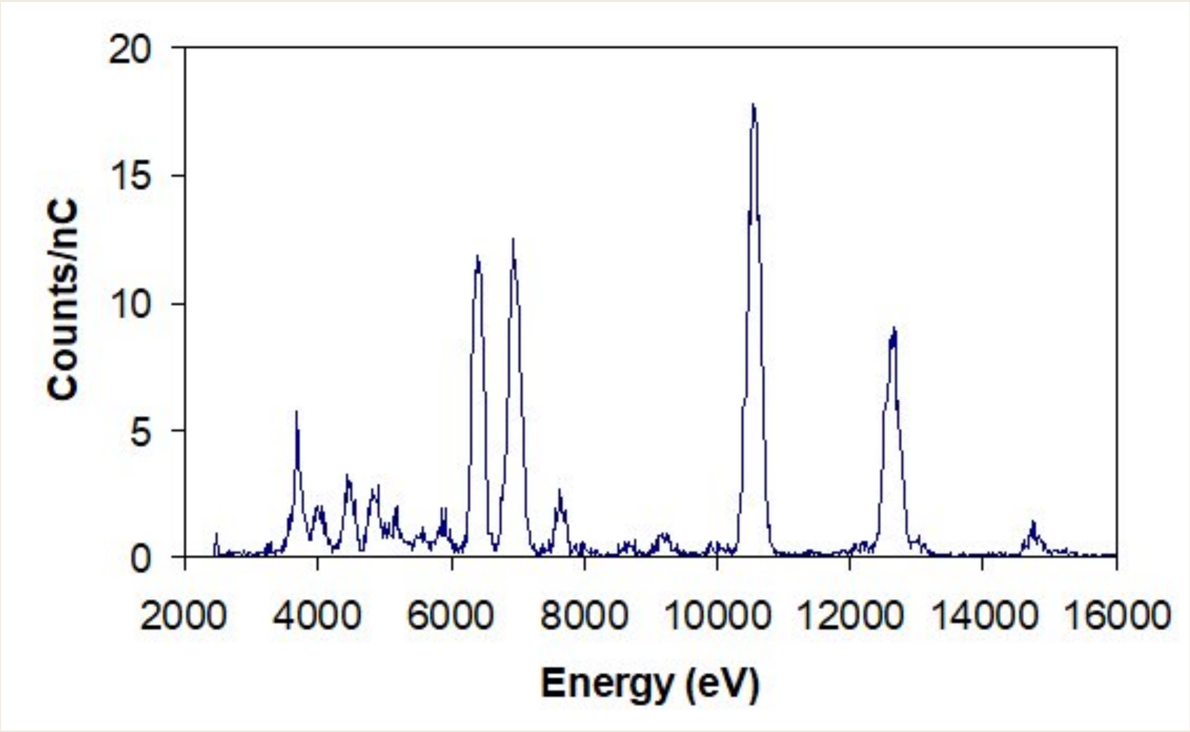
PIGE

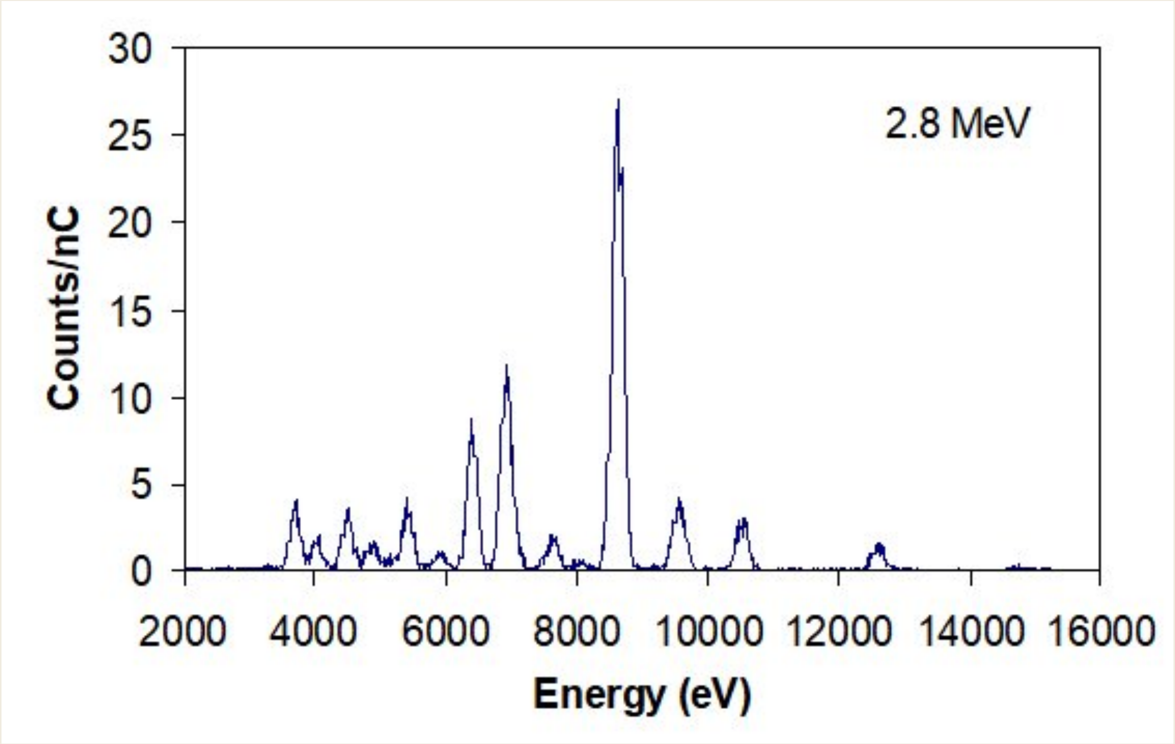
➜ identification of lapis lazuli



Detection of an anachronistic pigments

➜ identification of restorations





P.A: Mandò et al., Differential PIXE for investigating the layer structure of paintings, NIM B 239 (2005), 71

N. Grassi et al., Identification of lapis-lazuli pigments in paint layers by PIGE measurements, NIM B 219-220 (2004), 48

What's for the next?

- Each of the IBA techniques has its own limitations
  ➜ smaller detectors allow integrating different techniques in the same experimental set-ups
  ➜ improvement of the detector sensitivity to optimize measurement times to scan over larger and larger surfaces

- Is it possible to overcome the limitations due to the non-portability?
  ➜ we can use complementary techniques, such as XRF (X-ray fluorescence) or…

MACHINA *(Movable Accelerator for Cultural Heritage In-situ non-Destructive Analysis)*

At present, under development by INFN and CERN KT

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Zio Paperone e Battista e l'Organipotogramma (Topolino, 2016)

Thanks to all the colleagues at LABEC (and INFN-CHNet)

Thanks to the organizers

Thank you for your attention!

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