Introduction to Radiochemistry

Special Topics

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Introduction

- Nuclear Dating Methods
- Accelerator Mass Spectrometry
- Archaeology Application: The Thera Eruption
- Cultural Heritage Applications
- Application: Paintings Analysis
- Ion Beam Analysis
  - PIXE
- Radiotracers
  - Medical Applications

Nuclear Dating Methods

The basic principle:

If at some time in the past t1 a radionuclide was present in an amount N1 and at the present time t2 the amount is N2 we have:

$$N_2 = N_1 e^{-\lambda(t_2 - t_1)}$$

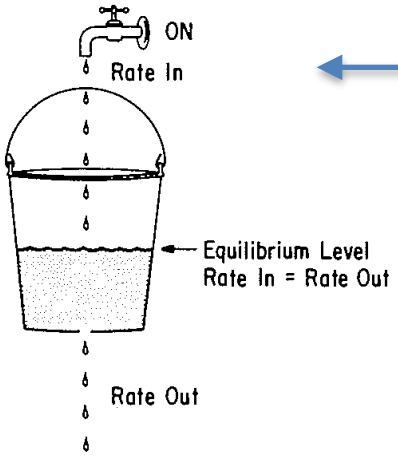
Solving for the time interval:

$$t_2 - t_1 = \frac{1}{\lambda} \ln \frac{N_1}{N_2}$$

If the two amounts and the decay constant are known, we can obtain the time interval. The real problem in the procedure is to know the original amount of the radionuclide. There are two basic procedures for that:

1) The Equilibrium Clock
2) The Accumulation Clock

The "Bucket Analogy"

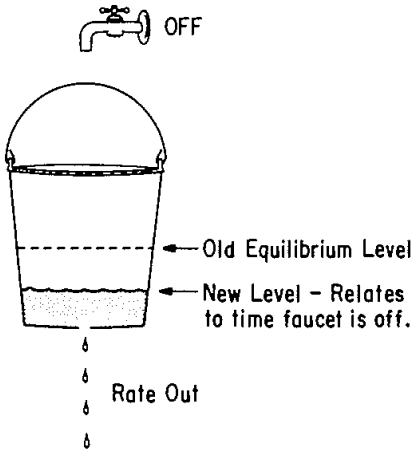


Equilibrium Decay

After closing the faucet:

t = (1/R)(Eq. amount water - Residual amount)

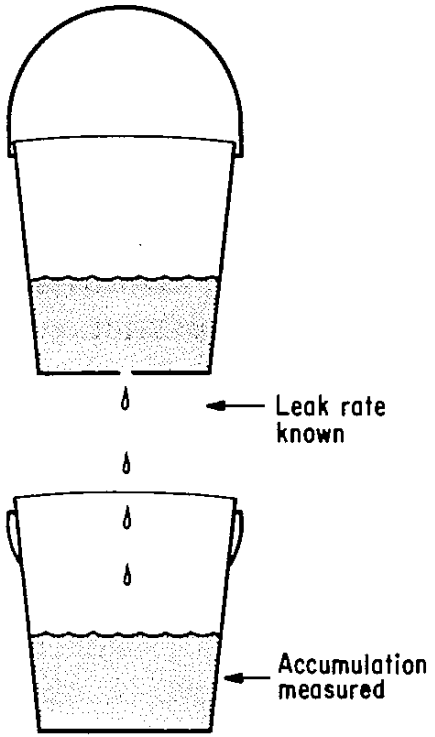
Examples: ^{14}C, ^{3}H dating methods



Accumulation

t = (Accumulation in lower bucket/leak rate)

Examples: K-Ar, U-Pb, Rb-Sr dating methods for closed chemical systems.



Radiocarbon Dating Method (1)

Developed by **W.F. Libby** (1908-1980), J.R. Arnold and collaborators at University of Chicago.
Libby won the Nobel Prize in Chemistry in 1960.
The method is based on the ^{14}C nuclide.

Carbon 14: Primary cosmic rays (mainly protons) produce in the atmosphere a variety of nuclear fragments, including neutrons.
Since the main component of the atmosphere is Nitrogen the following neutron-induce reaction can happen:

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

Since the cosmic-ray flux on earth is quite constant since at least 70000 years, the rate of production of ^{14}C has been also constant. The half-life of ^{14}C is 5730y. The formation and decay created an equilibrium concentration level in the atmosphere. The newly created carbon isotopes quickly react with oxygen giving rise to carbon dioxide $^{14}CO_2$.

Radiocarbon Dating Method (2)

Following the equilibrium decay clock principle, living beings metabolizing CO_2 are constantly acquiring and expelling it thus keeping a constant concentration inside them.

For example, in plants there is a **specific activity (SA)** of about 15 disintegrations per minute per gram due to ^{14}C decays.

When the living being dies, the equilibrium is broken, since there is not new ^{14}C introduced and what is left just decays.
Following the known decay law we have:

$$SA_{now} = SA_{eq} e^{-\lambda t}$$

and the time interval can be estimated.
Due to ^{14}C lifetime, times of the order of 70000 years can be estimated.
Before that time, the counting statistics is too low and overwhelmed by backgrounds.

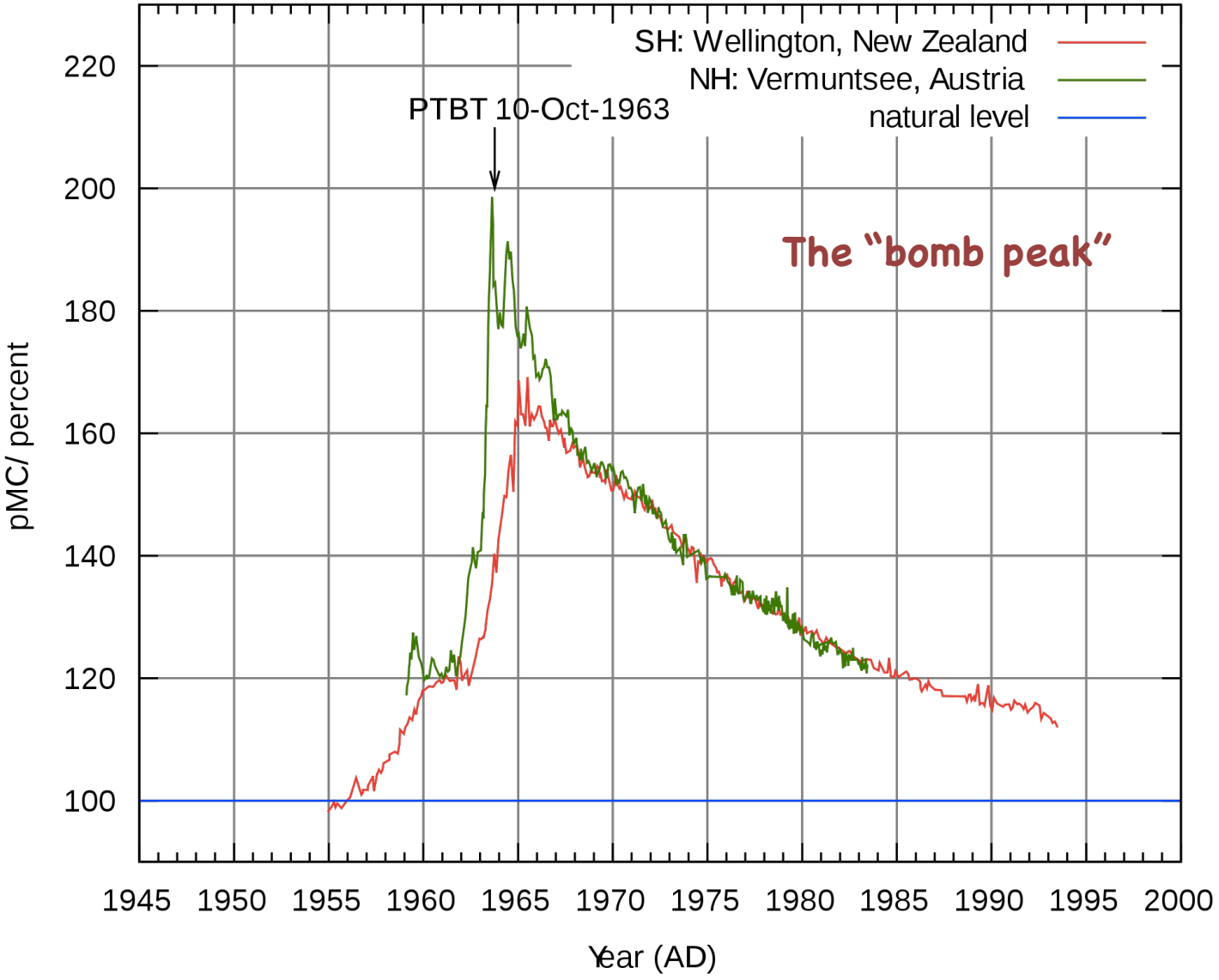
Radiocarbon Dating Method (3)

Radiocarbon dating looks straightforward, but there are a number of problems which cannot be overlooked for a reliable time estimation.

1) The **cosmic-ray flux** is not really constant in time and we have to account for this effect. This happens because of differences in the solar activity, changes in the earth's magnetic field and other changes to the equilibrium of ^{14}C in the atmosphere.
2) **Suess Effect**: H.Suess observed in 1955 that after the industrial revolution the burning of huge amounts of coal and petroleum delivered a high quantity of carbon to the atmosphere. This resulted in a decreased ^{14}C specific activity in the atmosphere.
3) **Nuclear Tests**: After the WW2, many atmospheric nuclear tests were done for the development of atomic and H-bombs. This raised the ^{14}C specific activity in the atmosphere.

All these effects should be taken into account for correcting the time estimates by activity measurements.

Radiocarbon Dating Method (4)



Radiocarbon Dating Method (5)

Calibration:

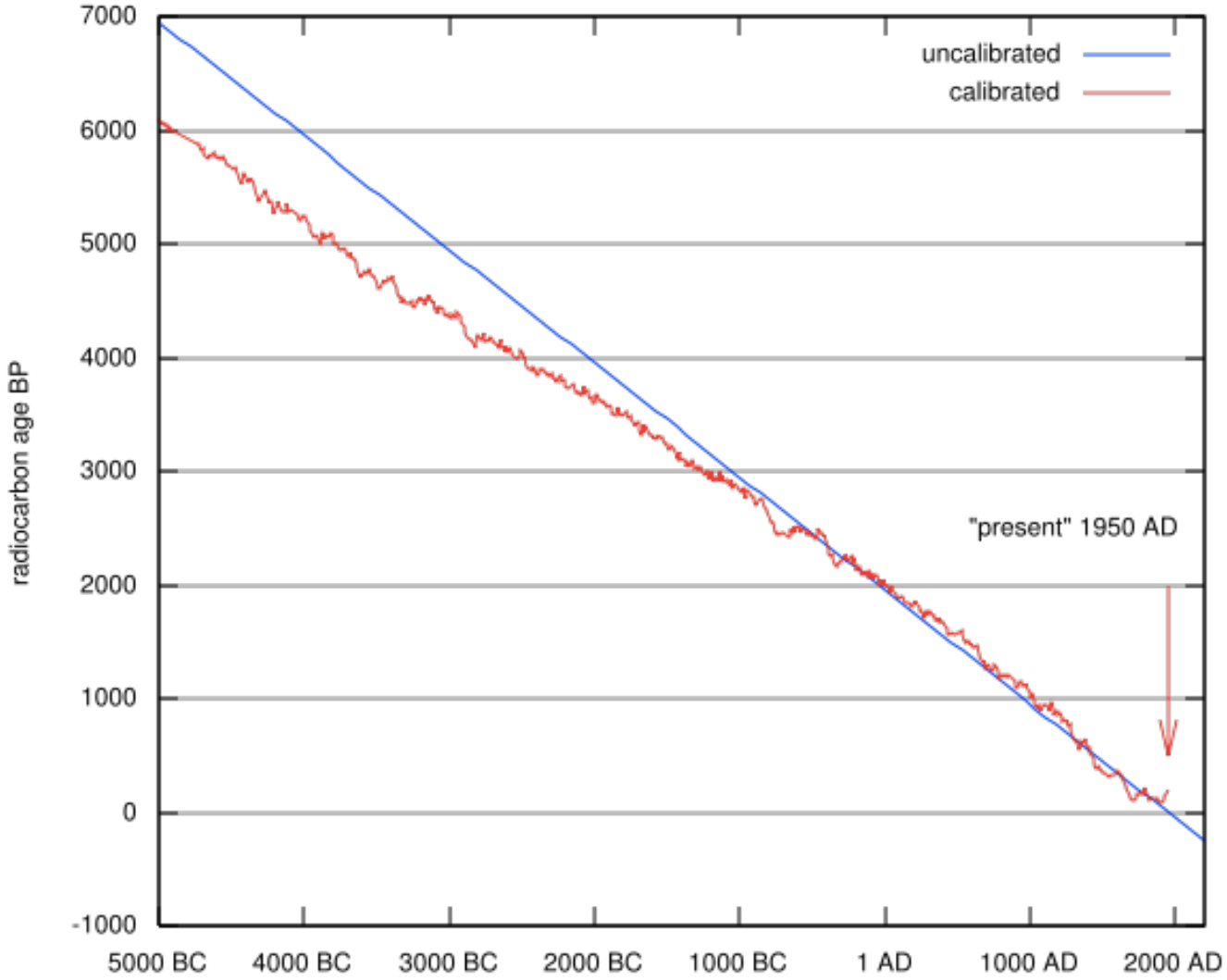
The central problem is to convert activities in times and it involves a careful calibration which takes into account all the effects discussed before.

For avoiding issues connected with 2) and 3), we have to calibrate our measurements with samples which are not recent or that at least do not overlap with nuclear tests and the industrial revolution times.

The problem posed by 1) is more difficult and one main tool to tackle it is **dendrochronology**.
Only the outer shell of wood trees is in ^{14}C equilibrium with the atmosphere while the inner rings (one for each consecutive year) are not accumulating it anymore. The analysis of old tree rings of known age gives an important information for calibrating the dating process.

Old organic sediments in glaciers or lakes of known geological age can extend the calibration further in the past.

Radiocarbon Dating Method (6)



Accelerator Mass Spectrometry (1)

At the beginning, the radiocarbon analysis was relying on chemical CO_2 extraction from a sample and precipitation as $BaCO_3$ in a solution.
The solid precipitate was then measured by a thin-window gas counter.

The energy of the emitted electron is very small: 157keV and absorption in the sample itself was very likely.

A better approach is to convert the organic matter chemically into gases like C_2H_2 or CH_4. In this way electron absorption is much less given the lower density of a gas.

The latter methods require a significant amount of matter and have limited sensitivity for very old samples. These problems are solved by **AMS: accelerator mass spectrometry**. This method:

- **needs very small sample quantities**
- **has very high sensitivity**

Accelerator Mass Spectrometry (2)

The challenge of radiocarbon dating is to measure tiny concentrations which in living organisms are of the order of 10^{-12}. After a ^{14}C half life (~5700y) the concentrations drop tp 10^{-15} and therefore a very good sensitivity is required.

We have seen that the time can be estimated with $t = \tau \ln \frac{C(0)}{C(t)}$

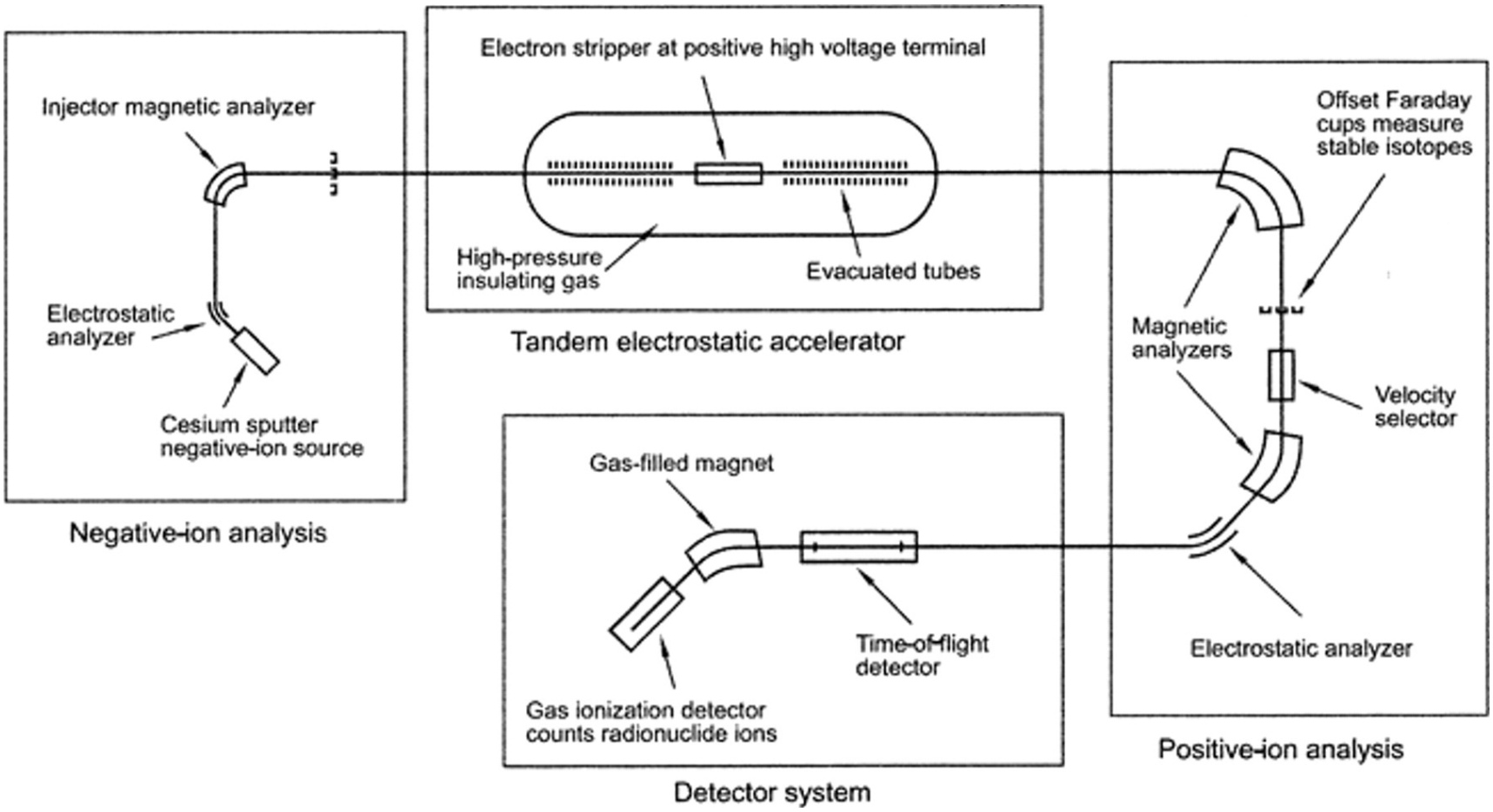
where C(t) is the concentration of ^{14}C at time t and C(0) the concentration when the organism was still living. A simple error propagation gives:

$$\delta t = \tau \frac{\delta C(t)}{C(t)}$$

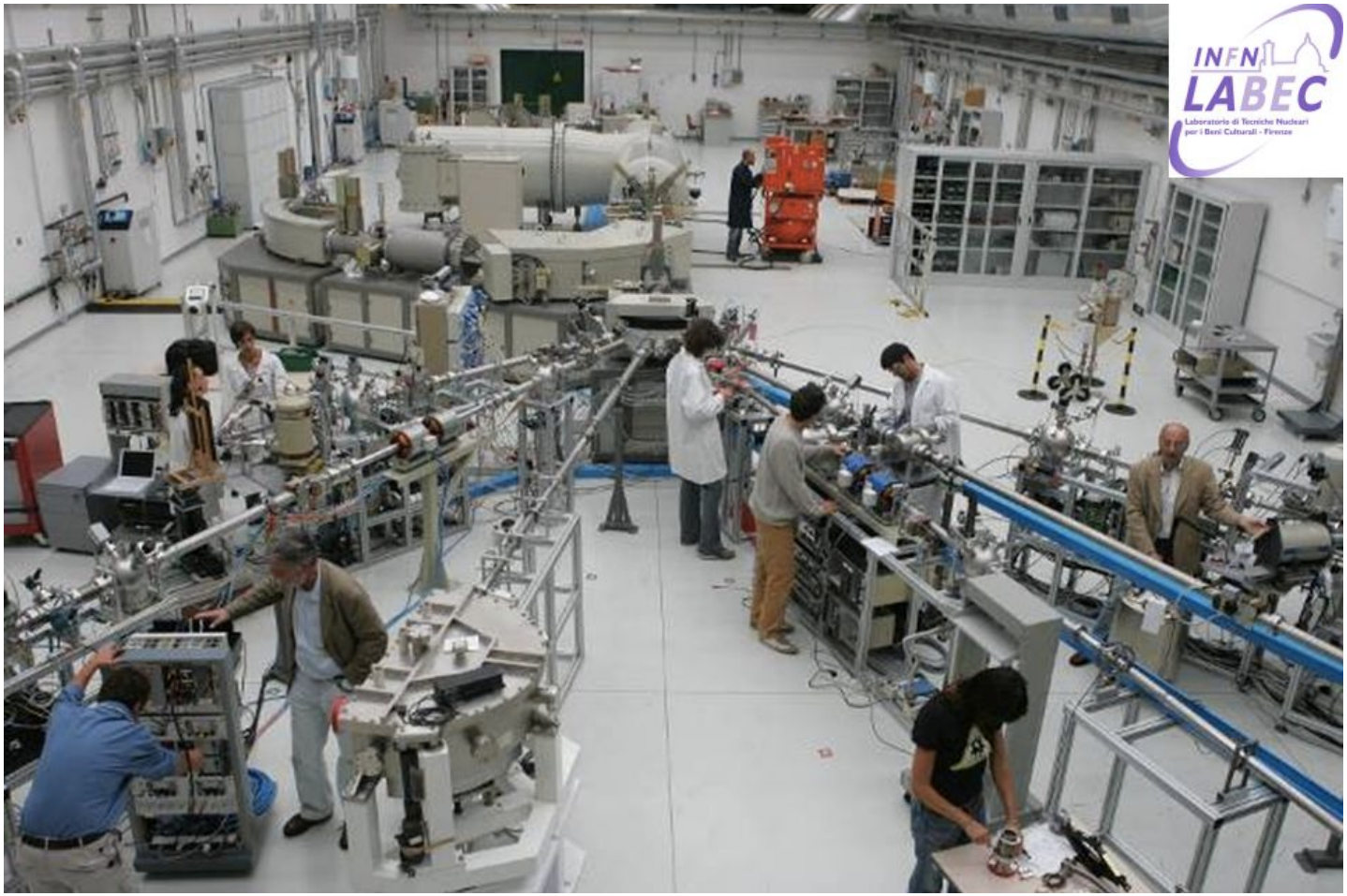
This means that if we measure C(t) with a +/-1% error, this translates in +/-80 years error on the date estimate.

Clearly, we do not need only sensitivity but also precision.

Accelerator Mass Spectrometry (3)



Accelerator Mass Spectrometry (4)



Accelerator Hall of the LABEC Laboratories in Florence, Italy

Accelerator Mass Spectrometry (5)

The most important point in AMS is the almost complete suppression of the molecular isobars $^{12}CH_2$ and ^{13}CH which are destroyed during electron stripping in the Tandem accelerator.

Just few mg of material are needed for AMS. An analysis lasts about 30min and counts of the order of 10.000 can be achieved.

Given the high sensitivity and small material needed, AMS can:

- Extend more in the past the dating
- Analyze samples from objects we cannot destroy (archeology/art)
- Overall, AMS is still the best tool for radio-dating.

Case Study: The Thera Eruption

About 1600 years B.C the vulcano on the Thera (aka Santorini) Island in Greece erupted with such power that consequences of the explosion were felt worldwide.

Today, the shape of Thera marks the contour of the ancient vulcano.

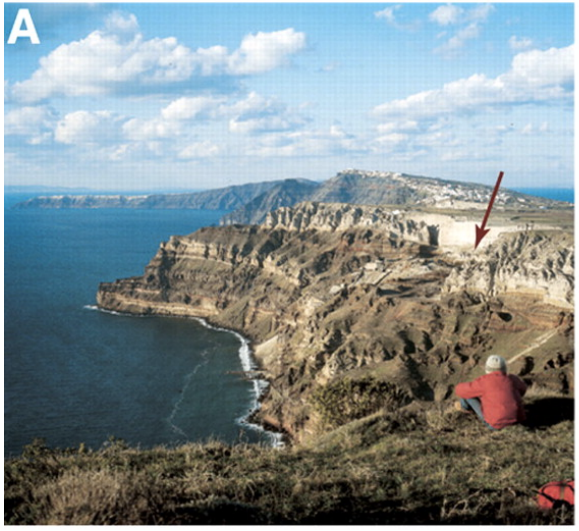
Case Study: The Thera Eruption

About 1600 years BC, the eruption of Thera (Santorini) in Greece devastated the island spreading volcanic ashes over the east mediterranean basin.
Traces of the catastrophic event can be found also in the ice of Greenland and climatic changes in the same period due to sunlight screening.
The explosion ejected about 4 times more material than the Krakatoa one in 1883

The time corresponds to the Bronze Age and the explosion wiped out important human settlements in the area connected to the Minoic civilization.

There are speculations about the end of the Minoic civilization due to this event which should have also generated extremely high waves which affected the nearby island of Crete.
The matter is not fully settled.

A central historical problem is the precise date of this important event.



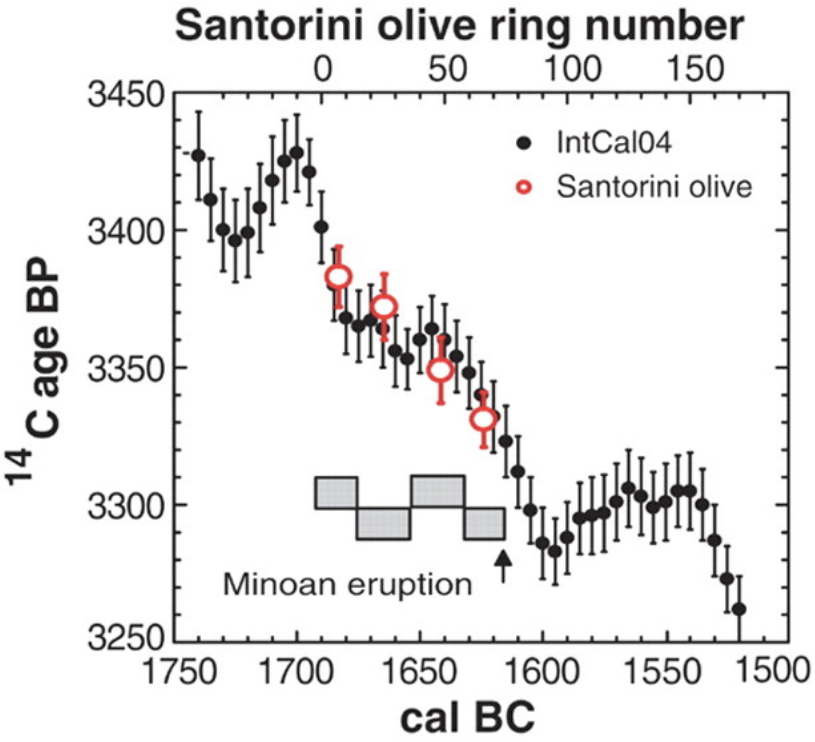
Case Study: The Thera Eruption

A olive tree branch was found on Thera buried into tephra.
There are important features of the finding which lead to the conclusion that the branch was buried alive by the volcanic ashes.
This finding is extremely remarkable:

- It dates to the time of the explosion
- It contains tree rings —> **wiggle matching**

Wiggle-Match Dating (WMD) is the matching of more consecutive dates (e.g. from tree rings) to the calibration curve, greatly enhancing the dating precision.

In this case, the 72 rings (identified by X-ray tomography) where divided in four bunches and carbon-dated. In the plot, it is shown how the 4 consecutive points match the calibration curve.



Case Study: The Thera Eruption

Conclusion:

Some historians were estimating as eruption date around 1520 B.C on the basis of correlations with Egyptian cultures. This date was already in conflict with other carbon dating results.

The study using the olive branch and WMD gives as eruption date:

1621-1605 BC (1-sigma, 68% conf.)

1627-1600 BC (2-sigma, 95% conf.)

The eruption took place about 100 years earlier than what was estimated by historians and the result is extremely robust. Even assuming a 50% error on the count of the rings (due e.g. to growth irregularities), the date varies only by 1 decade.

The result stirred new debates among historians and added an important piece of information to our knowledge of the past. **The controversy is not over!!**

Tritium Dating

This is another method based on the existence of an equilibrium concentration. As ^{14}C:

- Originally proposed by Libby and collaborators
- tritium is a beta- emitter (with a half-life of 12.3y)
- it is created constantly by cosmic rays
- Due to nuclear tests, the tritium concentration varied in time.

TU = Tritium Units = 1 tritium atom per 10^{18} hydrogen atoms.

The normal content of sea water is 1TU which is ~10^3 after nuclear tests.

Water removed from contact with atmosphere will start loosing tritium via radioactive decay —> **dating method**.

Libby originally calibrated the method using old French wine bottles!

U-Pb / Th-Pb Dating

These are **accumulation** methods, sometimes called **Plumbology** (based on Pb).

The method is able to date samples few billions of years old.

Lead is the end-point of the radioactive decay chains of ^{235}U, ^{238}U and ^{232}Th. In particular, ^{206}Pb, ^{207}Pb and ^{208}Pb are formed.

During the decay chains, He is also formed via alpha-decay.
He content can also be used for dating purposes.

These methods are useful in geological dating problems, in particular for determining the solidification date of rocks.

The original amount of U or Th is equal to the remaining atoms, plus the Pb daughter atoms.

Ion Beam Analysis (IBA)

IBA is an analytic technique based on the bombardment of the sample with a particle beam.

Beams are typically protons or alpha particles provided by a particle accelerator.

Information on the composition of the target is obtained from the spectroscopy of the particle-induced radiation emitted by:

- the atoms (X-rays)
- the nuclei (gamma rays or other particles)

There are many variants of the IBA technique, among them:

- **PIXE** (Particle induced X-ray emission)
- **LIBS** (Laser induced Breakdown spectroscopy)
- **LIPS** (Laser induced plasma spectroscopy)

A technique competitive with IBA is **XRF** (X-Ray Fluorescence).

Ion Beam Analysis (IBA)

IBA is:

- **Very sensitive (~ ppm level)**
- **Quantitative**
- **Non-invasive**
- **Non-damaging**
- **With adequate tools, sensitive to all elements of the Periodic Table**

Given the above qualities, this kind of techniques are very well suited for the analysis of Cultural Heritage works of art (statues, paintings, …).

PIXE

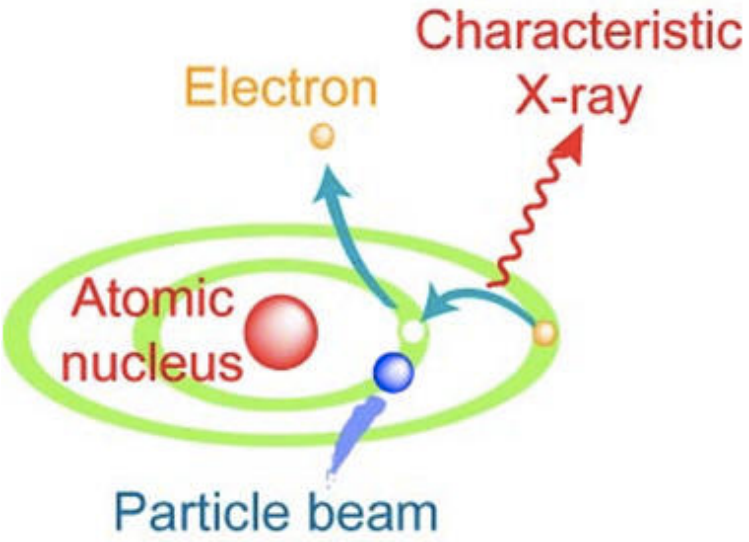
Particle Induced X-ray Emission:

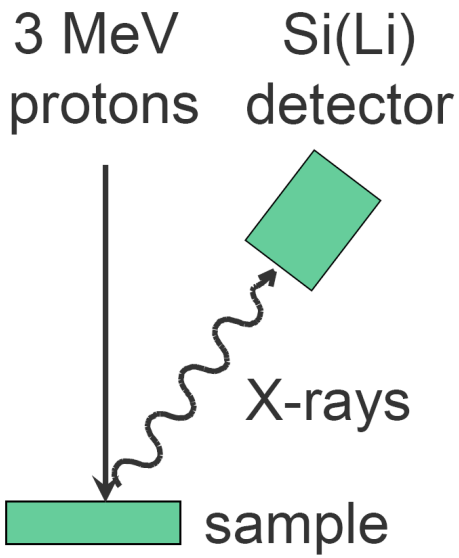
Covers with very good efficiency all the Z>10 elements (Z=11 is Na).

The target can even stay in air (no vacuum needed): "external beam setup".

X-rays from Z<11 are too low energy to be detected and are absorbed by other materials.

With the addition of gamma ray detectors, a PIXE setup can be sensitive also to low-Z materials making PIXE available for essentially the whole Periodic Table elements.

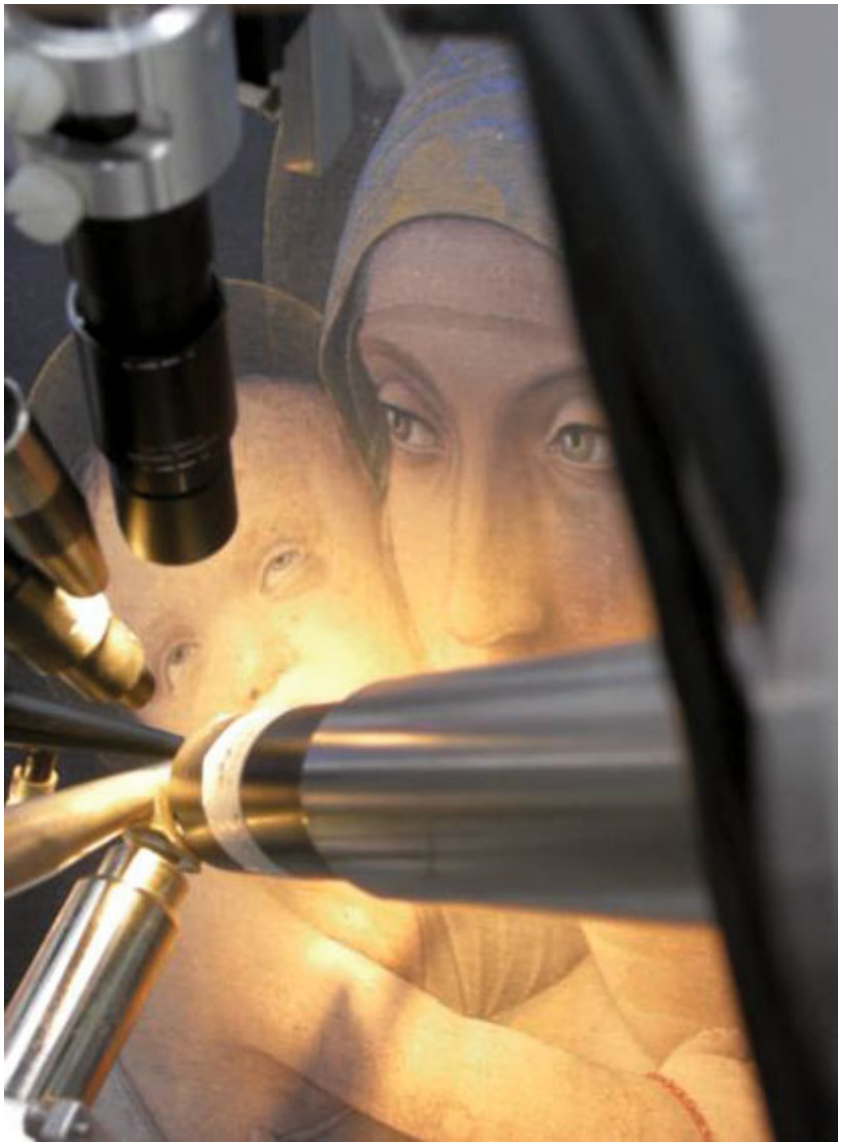


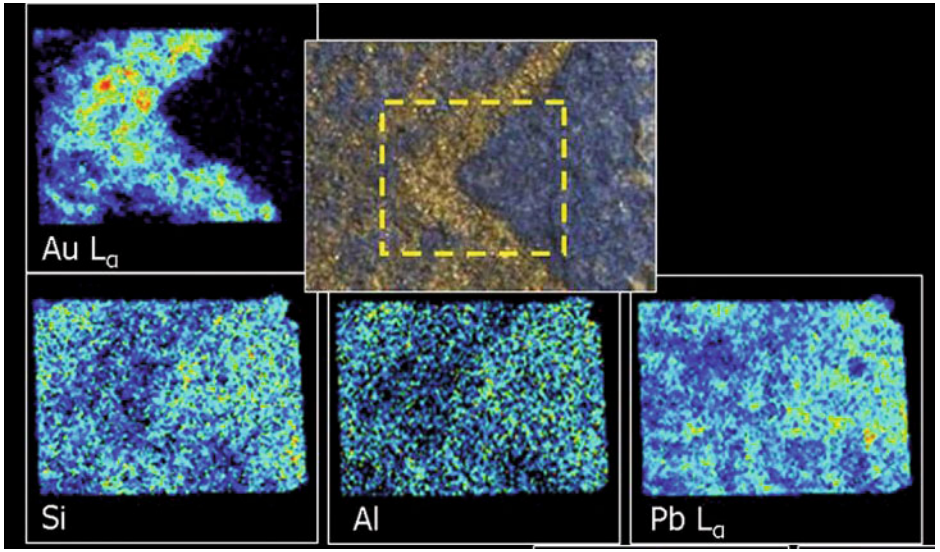


Analysis of Paintings with PIXE

Mantegna's Madonna col Bambino
(oil on canvas, 1460)

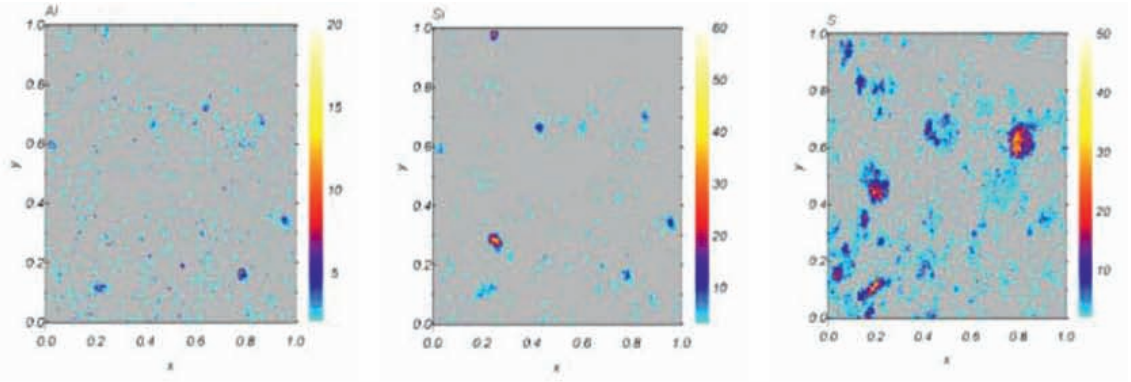
The painting in the figure is under analysis in the INFN-LABEC laboratories in Florence.
A 2D scan permits the reconstruction of the location of various elements.

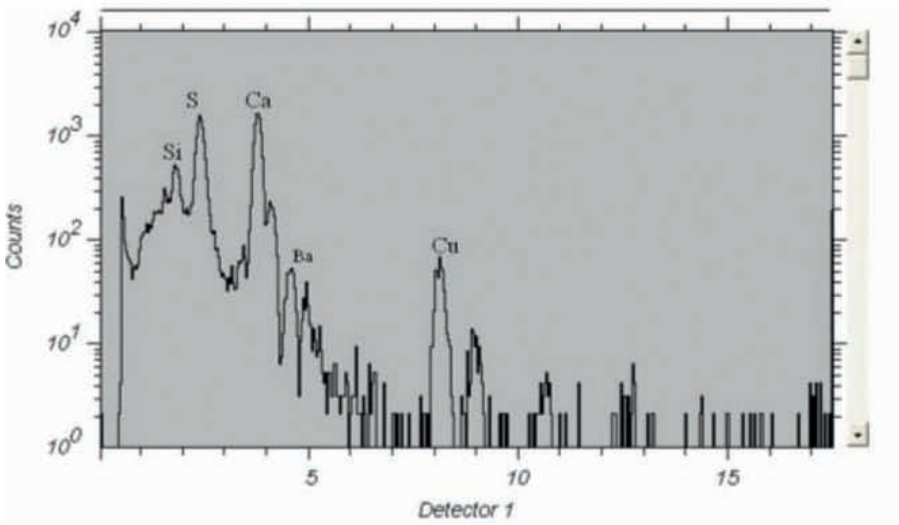


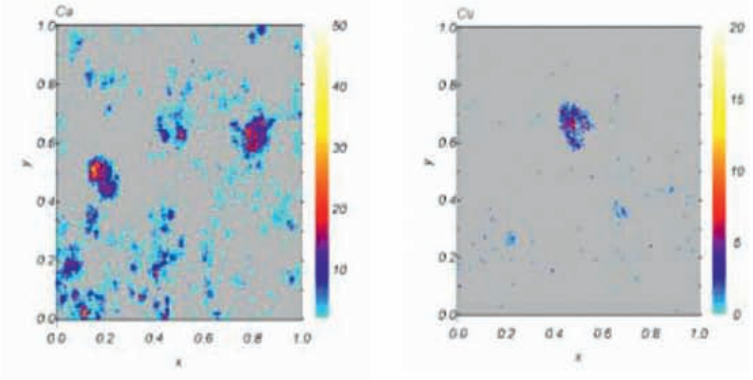


Analysis of Paintings with PIXE

Another PIXE example.







Analysis of Paintings with PIXE

Example of color-element association in a PIXE analysis

White:

— Lead white ($2PbCO_3 \cdot Pb(OH)_2$);
— Gypsum ($CaSO_4 \cdot 2H_2O$);
— Barium white ($BaSO_4$) (nineteenth century).

Red:

— Cinnabar (HgS);
— Red ochre ($Fe_2O_3 \times nH_2O$);
— Bolus ($Al_2O_3 \times SiO_2 + Fe_2O_3$);
— Organic red;
— Alizarin ($Al(OH)_2$);
— Minium (Pb_3O_4).

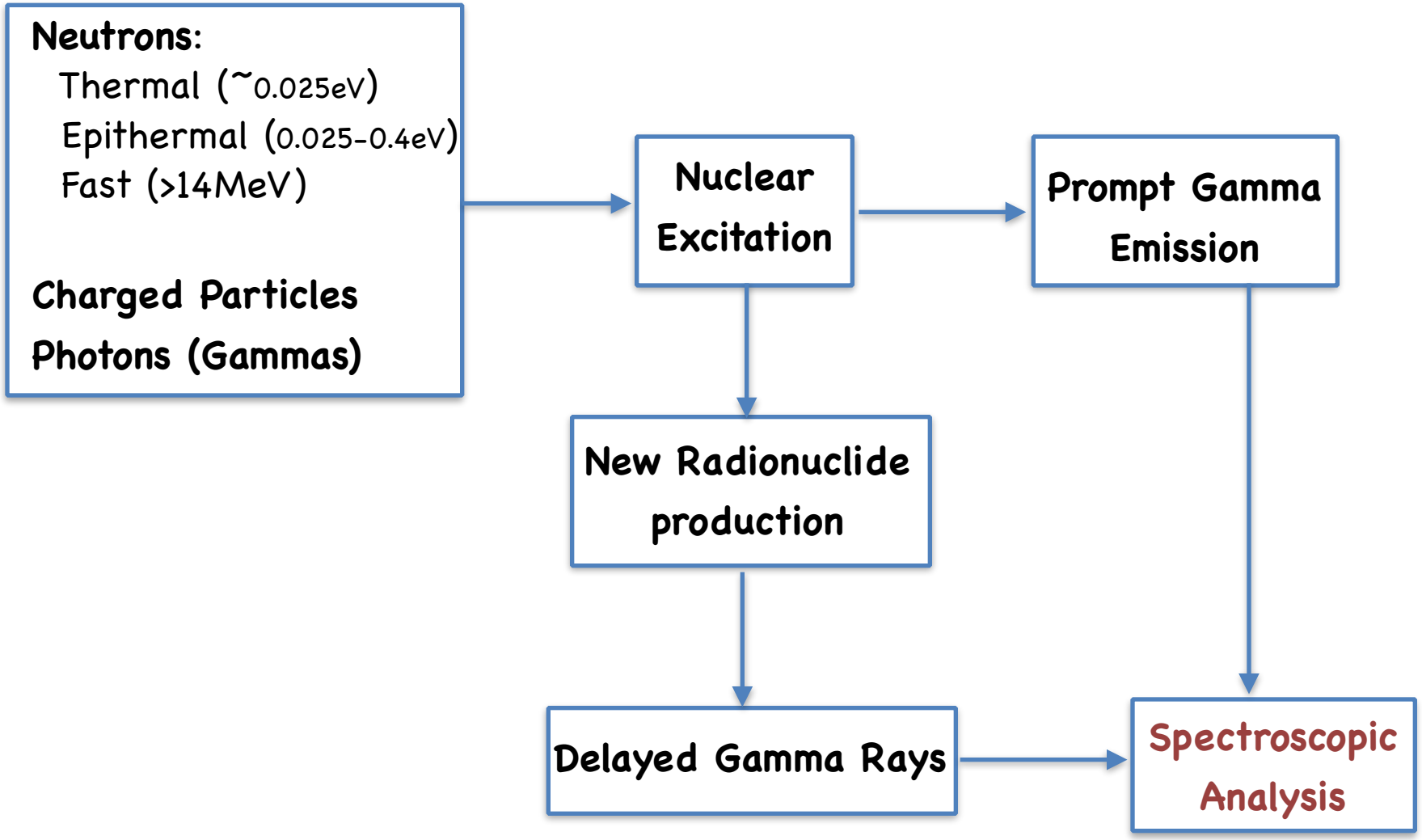
Blue:

— Azurite ($2CuCO_3 \times Cu(OH)_2$) – ($CaCuSi_4O_{10}$) (cuprorivaite?);
— Ultramarine ($2Na_2Al_2Si_2O_6 \times NaS_2$).

Brown and yellow:

— Iron oxide (brown and yellow ochre).

Nuclear Activation Analysis



Analysis of Paintings with Neutrons

Example of **Nuclear Activation Analysis**

Neutron bombardment can create radioactive isotopes in the sample.

Gamma-ray spectroscopy can give important information about the original colours used. This is very important for restorers and art historians.

In the table: induced radioactive characteristics of common pigments:

Element	Pigment	Radionuclide (n, γ)	$T_{1/2}$ (half-life)	$E_{av,\beta}$ (average beta energy)
Manganese	Umber, dark ocher	Mn-56	2.6 h	1.84 MeV
Copper	Malachite, azurite	Cu-64	12.8 h	0.57 MeV
Potassium	Smalt, glue	K-42	12.5 h	3.27 MeV
Sodium	Glue, medium canvas, ultramarine	Na-24	15 h	1.39 MeV
Arsenic	Smalt, realgar, auripigment	As-76	26.5 h	2.55 MeV
Antimony	Naples yellow	Sb-122 Sb-124	2.8 d 60 d	1.5 MeV 1.02 MeV
Mercury	Vermilion	Hg-203	47 d	0.21 MeV
Cobalt	Smalt, glass	Co-60	5.26 a	0.31 MeV

Radiotracer Methods

Very wide application range:

- **Chemical**
- **Analytical**
- **Medical**
- **Biological**
- **Industry**

Radiotracers are chemical species containing a radionuclide. The activity of the nuclide is monitored to follow the process under investigation.

The radio tracer must blend perfectly with the environment without disturbing chemically or its radiation the process under study.

Radiotracers: Medical Applications

Radionuclide	Chemical Form	Use
^{99m}Tc	Sodium pertechnetate	Brain, thyroid, salivary gland, and blood pool imaging; placenta localization
^{99m}Tc	Albumin colloid	Liver, spleen, and bone marrow imaging
^{99m}Tc	Etidrontate (EHDP)	Bone imaging
^{99m}Tc	Pentetate (DTPA)	Brain imaging, renal perfusion, kidney renograms, lung inhalation imaging
^{99m}Tc	Pyrophosphate (PPi)	Bone imaging, infarction avid imaging
^{131}I	Sodium iodide	Thyroid function diagnosis, thyroid imaging
^{125}I	Albumin	Blood and plasma volume determination, turnover studies
^{123}I	Sodium iodide	Thyroid function diagnosis, thyroid imaging
^{201}Tl	Thallous chloride	Myocardial infarction imaging
^{133}Xe	Gas	Pulmonary inhalation imaging, cerebral blood flow studies
^{67}Ga	Gallium citrate	Tumor imaging

Radiotracers: Medical Applications

Technetium 99 (^{99m}Tc):

- The most used radio tracer in nuclear medicine

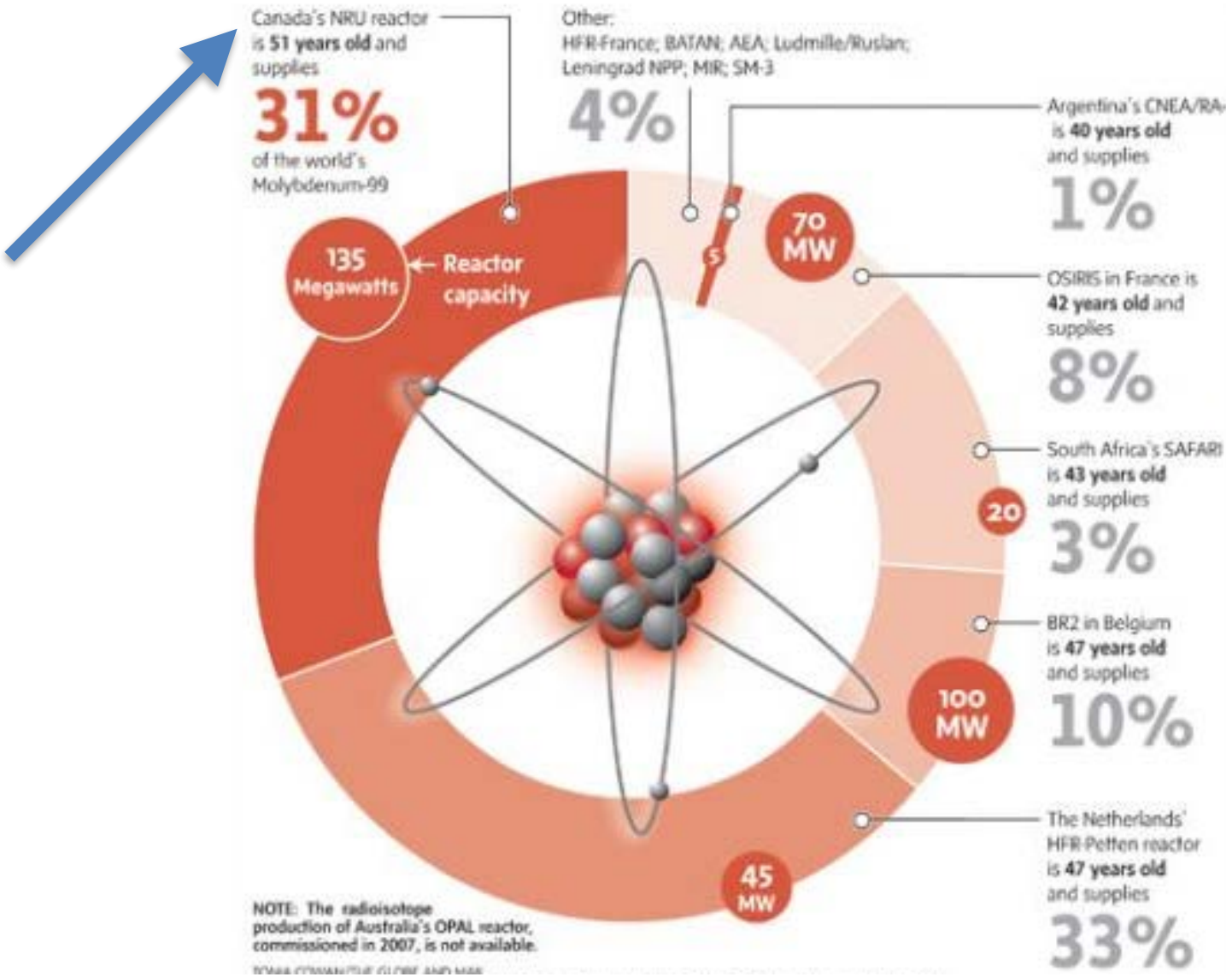
- Why:
  1. Short lifetime (but not too short): 6.01h (—> low dose)
  2. 142.7keV gamma decay: low energy but enough to escape from tissues.
  3. Versatile chemistry

Can be obtained by Molibdenum irradiation. Formation and decay are:

$$^{98}Mo(n,gamma)^{99}Mo \xrightarrow{e^-} {}^{99m}Tc \xrightarrow{142.7keV} {}^{99g}Tc$$

Tc was discovered in 1937 with the first cyclotrons irradiating Molibdenum.

Radiotracers: Medical Applications



Radiotracers: Medical Applications

In recent years, due to the shutdown of nuclear reactors, the world experienced a shortage of Tc for medical applications.
The main method for Tc production is via nuclear reactors.

Are there alternative methods?

TRIUMF scientists in Vancouver proposed an alternative method based on accelerators for the production of Tc for medical uses.

The technique is under development and it is extremely promising.

Radiotracers: Medical Applications

Production Methods:

Neutron-based (mostly nuclear reactors)

$^{235}U(n,F)^{99}Mo$

$^{98}Mo(n,gamma)^{99}Mo$

Photon-based

$^{238}U(gamma,F)^{99}Mo$

$^{100}Mo(gamma,n)^{99}Mo$

Proton-based (—> CYCLOTRONS ~20MeV proton beam range)

$^{100}Mo(p,2n)^{99m}Tc$

Other Radiotracers

Iodine: $^{130}Te(n,gamma)^{131}Te \xrightarrow{beta-} {}^{131}I \xrightarrow{beta-,gamma} {}^{131}Xe$

Often used for thyroid exams.
Te is a fission byproduct in reactors.
Iodine is less used than Tc since it has 8d half-life and gamma+beta decay.

Thallium: $203Tl(p,3n)201Pb \xrightarrow{beta+} 201Tl \xrightarrow{EC} 201Hg$

Thallium is chemically similar to K and it is useful for heart imaging

Xenon: ^{133}Xe

It is a fission byproduct and being a gas can be inhaled: lung imaging.

Gallium: $^{67}Ga \xrightarrow{EC} {}^{67}Zn$

Chemically similar to Al. Used for soft-tissues imaging.