

GET1024 / GEC1036 Lecture 19

# Applications of Science, Arts & Research

A Natural Nuclear Reactor?

Neutron Activation Analysis

Radioactive Dating

Carbon Dating – including  
bomb pulse dating and some  
examples

Potassium-Argon and Argon-  
Argon Dating – Extinction of  
Dinosaurs

Lead-Lead Dating – Age of  
Earth (briefly)

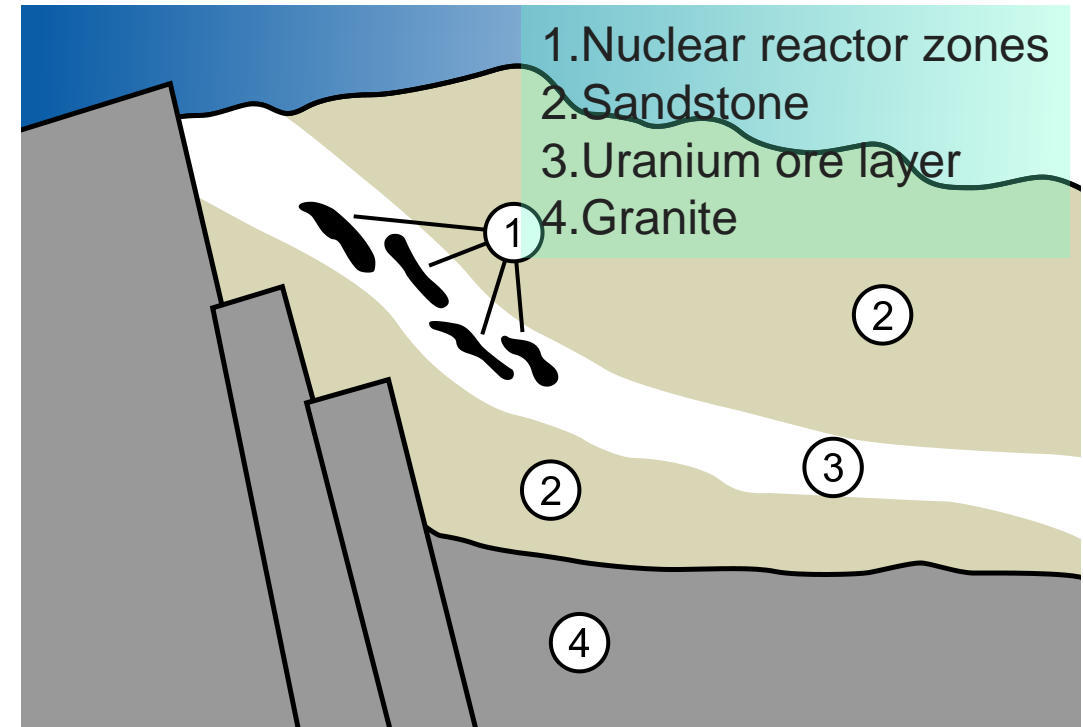
Cultural Heritage Preservation

Some Other Applications in  
Research

Concluding Remarks

# A Natural Nuclear Reactor

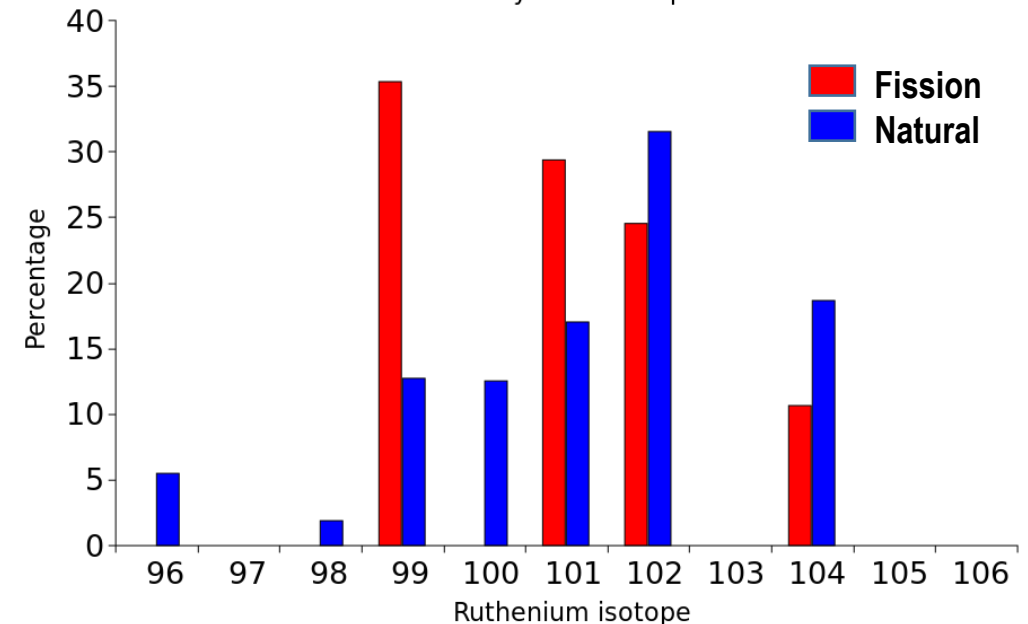
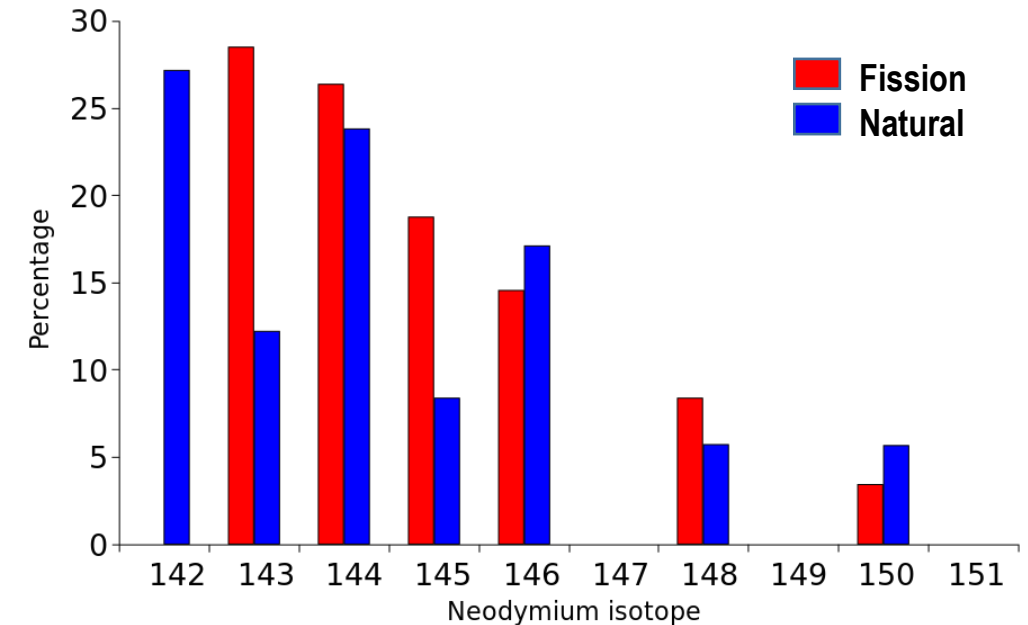
- 1972 – Oklo in Gabon, Africa. Uranium mine: Ore contains 0.60% U-235 instead of 0.72%. 16 sites. Some even as low as 0.44%.
- About 2 billions years ago, concentration of U-235 constitutes about 3 – 4%
- Uranium ore layer filled with groundwater – acted as a neutron moderator – nuclear chain reaction took place.
- This lasted for about 30 minutes. The heat generated from the nuclear fission caused the groundwater to boil away, which slowed or stopped the reaction.
- After cooling of the mineral deposit, the water returned and the reaction restarted, completing a full cycle every 3-hours.



- The fission reaction cycles continued for hundreds of thousands of years and ended when the ever-decreasing fissile materials no longer could sustain a chain reaction (probably less than 100 kW)

# Evidence of Chain Reaction

- Evidence of fission products were found at the sites. For example, the isotopic compositions of neodymium and ruthenium in the area were very different from what is usually found on Earth as seen on the right. The isotopic composition matched that produced by the fission of U-235.
- Fission of uranium normally produces five known isotopes of the fission-product gas xenon; all five have been found trapped in the remnants of the natural reactor, in varying concentrations.
- The concentrations of xenon isotopes, found trapped in mineral formations 2 billion years later, make it possible to calculate the specific time intervals of reactor operation: approximately 30 minutes of criticality followed by 2 hours and 30 minutes of cooling down to complete a 3-hour cycle.



# A Natural Nuclear Reactor

- The Oklo uranium ore deposits are the only known sites in which natural nuclear reactors existed. Other rich uranium ore bodies would also have had sufficient uranium to support nuclear reactions at that time, but the combination of uranium, water and physical conditions needed to support the chain reaction was unique, as far as is currently known, to the Oklo ore bodies.
- It is estimated that nuclear reactions in the uranium in centimeter- to meter-sized veins consumed about five tons of  $^{235}\text{U}$  and elevated temperatures to a few hundred degrees Celsius. Most of the non-volatile fission products and actinides have only moved centimeters in the veins during the last 2 billion years. Studies have suggested this as a useful natural analogue for nuclear waste disposal.

# Neutron Activation Analysis (NAA)

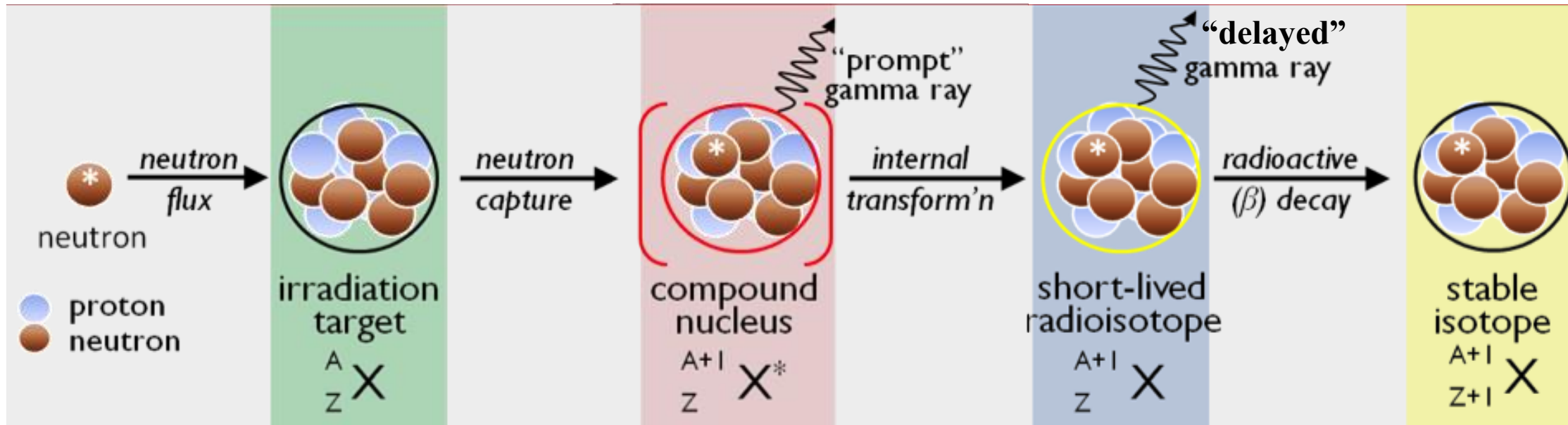
- Sample is bombarded with neutrons, causing some elements to form radioactive isotopes. From gamma emission of these isotopes, can determine concentrations of these elements within it.
- Does not destroy sample physically or chemically – suitable for analysis of works of art and historical artifacts.
- Sensitive: detection limits range from 0.03 ng to 4 µg. Most elements can be analyzed to 1 ppm and many can be analyzed many orders of magnitude below that.
- Focuses solely on its nucleus – disregards chemical form of sample.

Neutron activation analysis being performed on replicas of ancient Mochica pottery. (Photo: Instituto Peruano de Energía Nuclear, Peru – from <https://www.iaea.org/newscenter/news/application-of-large-sample-neutron-activation-analysis-techniques-for-inhomogeneous-bulk-archaeological-samples-and-large-objects-f23027>)



# Neutron Activation Analysis (NAA)

- After capturing a neutron, the compound nucleus is unstable and will emit one or more gamma rays (prompt – emitted and measured while sample is irradiated)
- The new nucleus may also undergo a beta decay with gamma rays emitted during the process (delayed – depending on the half-life)
- Both these gamma rays – prompt gamma-rays (PGNAA) and delayed gamma-rays (DGNAA) – can be used to identify the elements.





# Neutron Activation Analysis (NAA)

## ➤ Possible Neutron Sources:

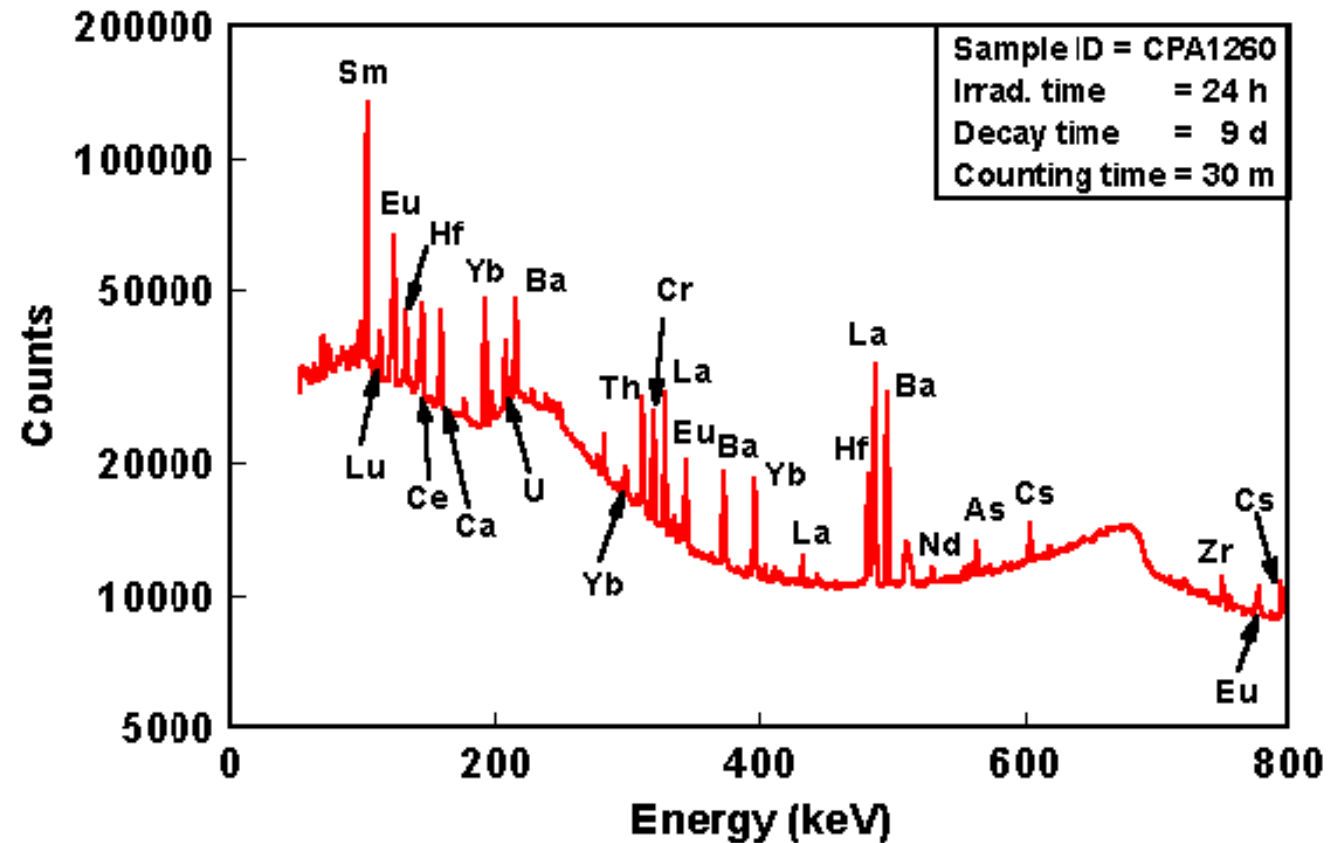
- Nuclear reactors
- Actinides such as californium which emits neutrons through spontaneous fission
- Alpha sources such as radium or americium, mixed with beryllium

## ➤ Detector:

- High Performance Germanium detector (HPGe)
- Sodium Iodide (NaI) detector

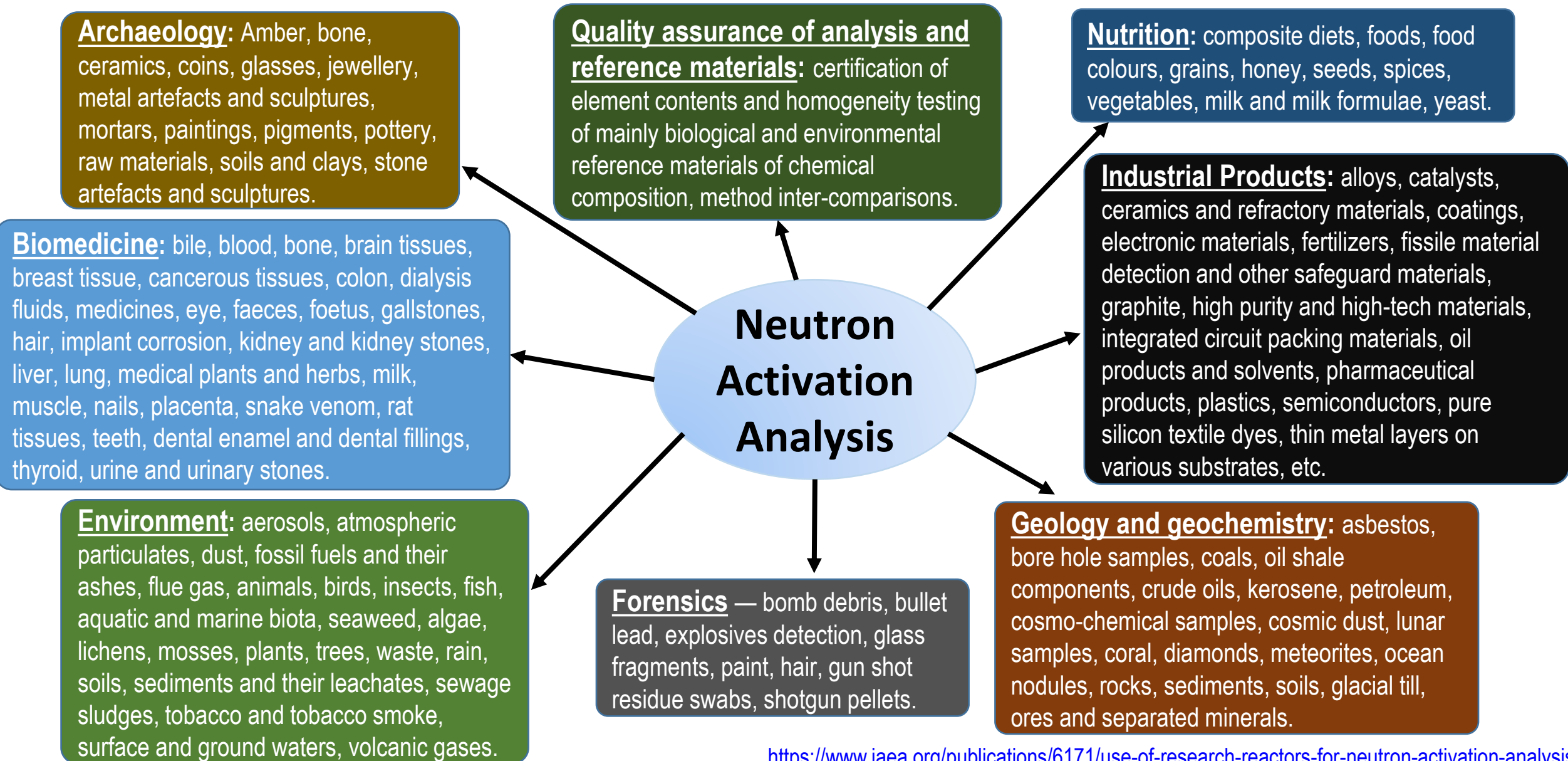
## ➤ Sensitivity

- Very sensitive – better than parts per million level for more than 25 elements



Gamma-ray spectrum from 0 to 800 keV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 hours, decayed for 9 days, and counted for 30 minutes on an HPGe detector.

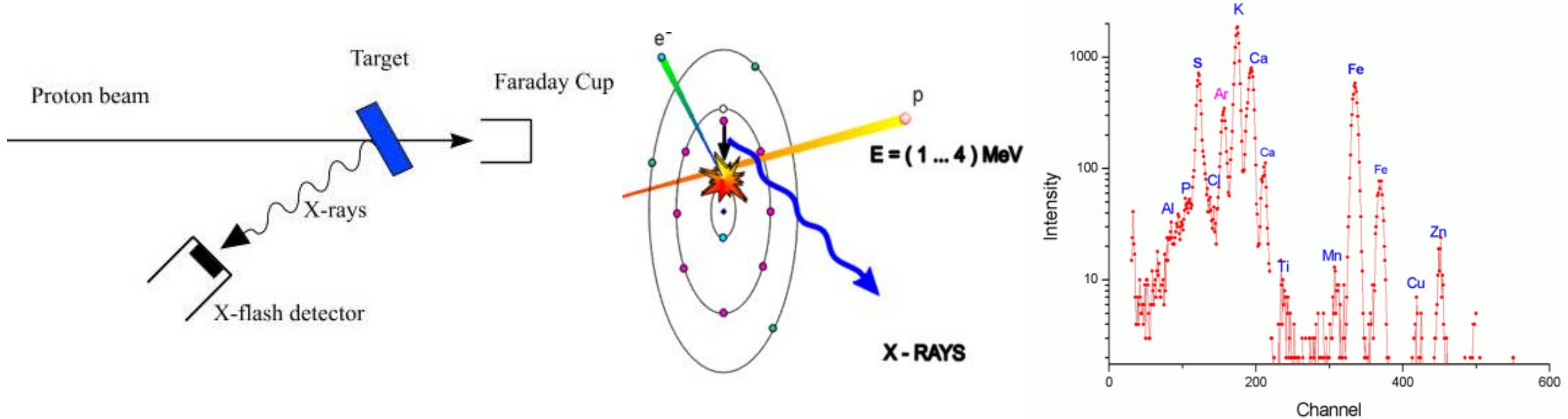
# Applications of Neutron Activation Analysis (NAA)





# Particle (or Proton) Induced X-ray Emission (PIXE)

- Non-destructive technique used in the determining of the elemental make-up of a material or sample. Used routinely by geologists, archaeologists, art conservators and others to help answer questions of provenance, dating and authenticity.
- Accelerated particles (to MeV) knocked **off the electrons from inner shells** – de-excitation of the atoms results in emission of characteristic x-rays which may be used to identify the atoms present.



- Can be focused even tighter in microPIXE – used to scan through different parts of a cell or tissue.

[https://en.wikipedia.org/wiki/Particle-induced\\_X-ray\\_emission](https://en.wikipedia.org/wiki/Particle-induced_X-ray_emission)

# Radioactive Dating

- **Radioactive dating** or radiometric dating is a technique which is used to date materials such as rocks or carbon, in which trace radioactive impurities were selectively incorporated when they were formed. The method compares the abundance of a naturally occurring radioactive isotope within the material to the abundance of its decay products.

$$N(t) = N_0 e^{-\lambda t}$$

$$D^* = D_0 + N(t) (e^{\lambda t} - 1)$$

$t$  is age of the sample,

$N(t)$  is number of atoms of the parent isotope in the sample at time  $t$

$D^*$  is number of atoms of the radiogenic daughter isotope in the sample

$D_0$  is number of atoms of the daughter isotope in the initial composition

- Radiometric dating is also used to date archaeological materials, including ancient artifacts.
- Among the best-known techniques are radiocarbon dating, potassium–argon dating and uranium–lead dating. By allowing the establishment of geological timescales, it provides a significant source of information about the ages of fossils and the deduced rates of evolutionary change.

Dating Method	Parent and Daughter Nuclides
Carbon Dating	$^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^0_{-1}\text{e}^- + \bar{\nu}_e$ ( $T_{1/2} = 5,730$ yrs – archaeology)
Potassium-Argon Dating	$^{40}_{19}\text{K} + ^0_{-1}\text{e}^- \rightarrow ^{40}_{18}\text{Ar} + \nu_e$ ( $T_{1/2} = 1.25$ billion yrs – rocks)
Lead-Lead Dating	$^{238}_{92}\text{U} \rightarrow \dots \rightarrow ^{206}_{82}\text{Pb}$ (4.46B yrs) $^{235}_{92}\text{U} \rightarrow \dots \rightarrow ^{207}_{82}\text{Pb}$ (704M yrs) (Meteorites – age of Earth)

# Carbon Dating

- $^{14}\text{C}$  is a radioactive isotope of carbon ( $\beta^-$  emitter), with a half life of 5730 years.



- $^{14}\text{C}$  is made in the upper atmosphere by high energy cosmic ray collisions,  $^{14}\text{N} + n \rightarrow ^{14}\text{C} + p$  and forms carbon dioxide ( $^{14}\text{CO}_2$ ).
- At any one time in the atmosphere, the ratio  $^{14}\text{C}$  to  $^{12}\text{C}$  in the carbon dioxide molecules is approximately  **$1.3 \times 10^{-12}$**  (see later slide).
- Living organisms take in carbon dioxide from the atmosphere (plants/animals) in a continuous process, and so in general while the plant/animal is alive it will also have the ratio of  $1.3 \times 10^{-12}$  for  $^{14}\text{C} / ^{12}\text{C}$
- At death, the  $^{14}\text{C}$  clock starts ticking, as it no longer exchanges carbon dioxide from the atmosphere, and therefore the  $^{14}\text{C}$  in the organism starts to decay according to the radioactive decay laws. The level of  $^{12}\text{C}$  however remains the same ( $^{12}\text{C}$  does not decay).
- By measuring the current activity of the  $^{14}\text{C}$  in a dead organism ( $R$ ), and comparing it with the activity at the time of its death ( $R_0$ ), we can calculate  $t$  (the time since death) from the equation

$$R = R_0 e^{-\lambda t}$$

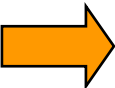
# Carbon Dating

A 25-gm piece of charcoal is found in the ruins of an ancient city. The sample is measured for  $^{14}\text{C}$  activity and shows 250 decays per minute. How long has the tree from which the charcoal came from been dead?

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

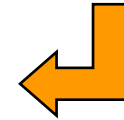


$$\lambda = \frac{\ln 2}{5730 \times 365 \times 24 \times 3600} = 3.84 \times 10^{-12} \text{ s}^{-1}$$

Using  $-\frac{dN(t)}{dt} = \lambda N(t)$    $\frac{250}{60} = 3.84 \times 10^{-12} N(t)$

Number of  $^{14}\text{C}$  atoms now:

$N(t) = 1.09 \times 10^{12} \text{ atoms}$




# Carbon Dating

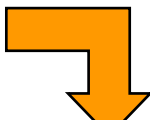
Number of  $^{12}\text{C}$  atoms in 25 g (assuming all  $^{12}\text{C}$  atoms, actually 99%, 1%  $^{13}\text{C}$ ) is:

$$N_0(^{12}\text{C}) = \frac{25}{12} \times N_A = \frac{25}{12} \times 6.02 \times 10^{23} = 1.25 \times 10^{24}$$

Ratio of  $^{14}\text{C}$  atoms to  $^{12}\text{C}$  atoms when tree just died ( $t = 0$ ) is:


$$\frac{N_0(^{14}\text{C})}{N_0(^{12}\text{C})} = 1.3 \times 10^{-12}$$
$$N_0(^{14}\text{C}) = 1.3 \times 10^{-12} \times 1.25 \times 10^{24} = 1.63 \times 10^{12}$$

But:  $N(t) = N_0 e^{-\lambda t} \quad \Rightarrow \quad \lambda t = \ln \frac{N_0}{N(t)}$



$$t = \frac{1}{3.84 \times 10^{-12}} \ln \frac{1.63 \times 10^{12}}{1.09 \times 10^{12}} = 1.05 \times 10^{11} \text{ s} = \boxed{3300 \text{ years}}$$



# Real Examples



## Dead Sea scrolls

Believed to be ancient Jewish religious manuscripts found in the Qumran Caves near the Dead Sea.

Carbon dating: 200 BC to 68 AD.

[https://en.wikipedia.org/wiki/Shroud\\_of\\_Turin](https://en.wikipedia.org/wiki/Shroud_of_Turin)  
[https://en.wikipedia.org/wiki/Dead\\_Sea\\_Scrolls](https://en.wikipedia.org/wiki/Dead_Sea_Scrolls)

## Shroud of Turin

Believed by some to be the burial shroud Jesus Christ was wrapped in when he was buried after crucifixion.

Carbon dating tests performed in 1988

Arizona –  $646 \pm 31$  years

Oxford –  $750 \pm 30$  years

Zurich –  $676 \pm 24$  years

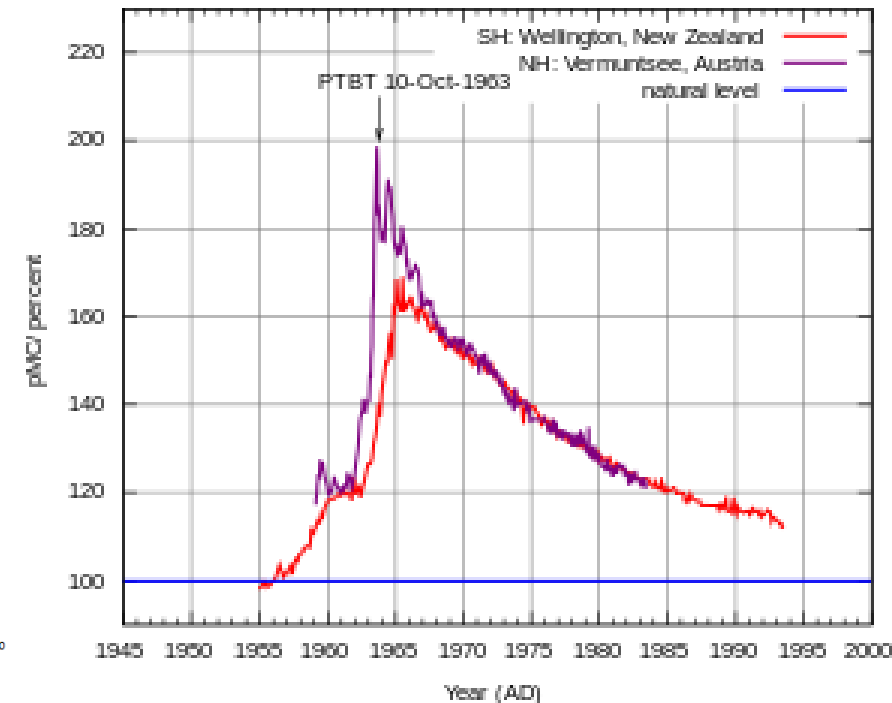
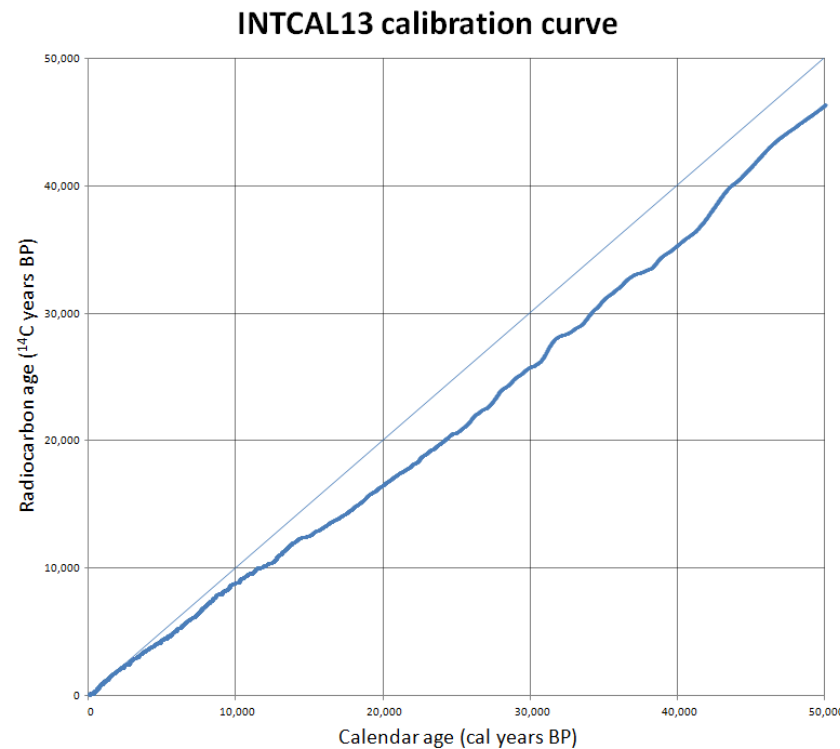
⇒ **1260 to 1390 AD**





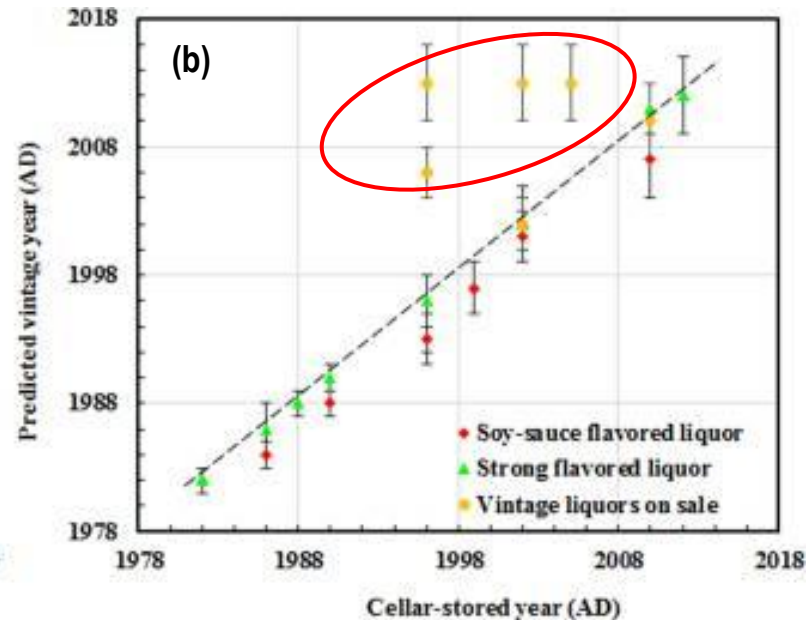
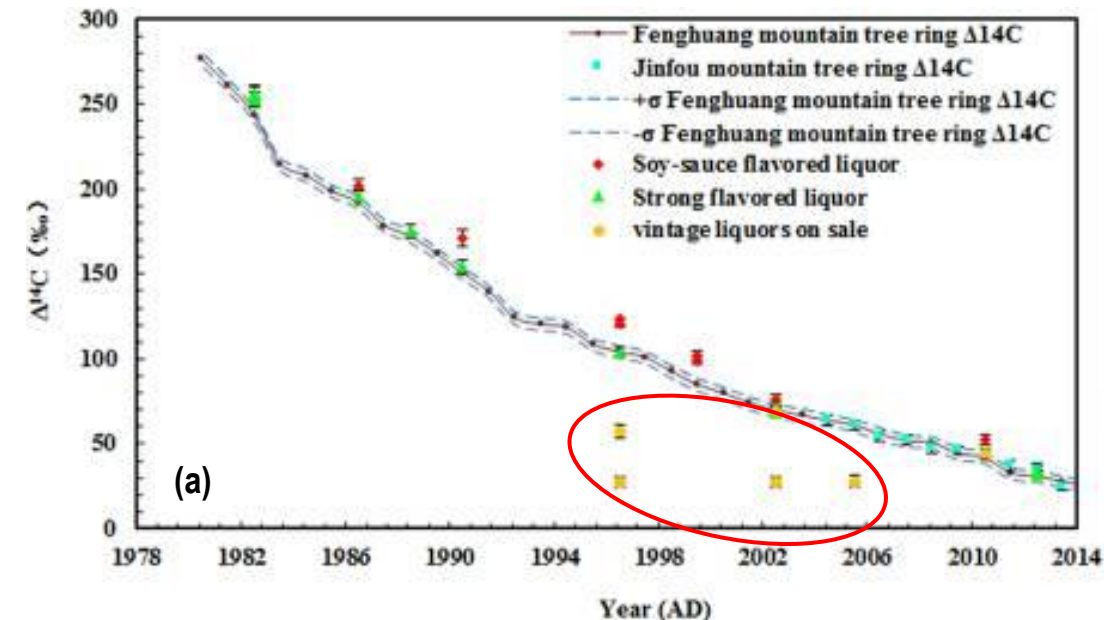
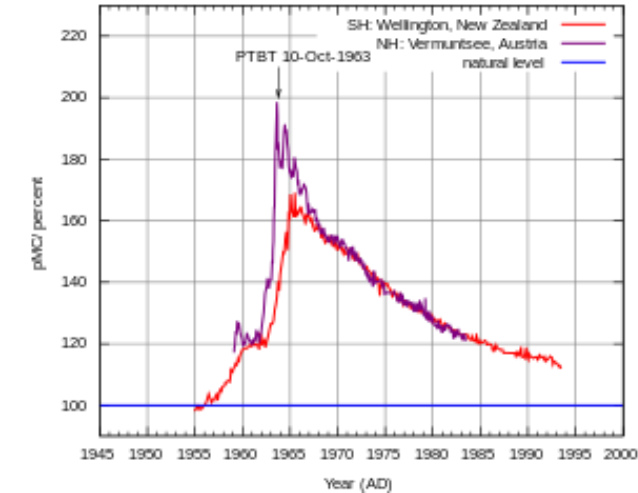
# Variation of Ratio of $^{14}\text{C}/^{12}\text{C}$

- Use of coal and oil since 19<sup>th</sup> century – which are mainly depleted of  $^{14}\text{C}$ . So, any measurement of recent artefacts will contain less  $^{14}\text{C}$  and thus appear older (if not corrected).
- Similarly, for those near built-up areas – lower  $^{14}\text{C}$  concentration.
- Variation over the years. From studies of tree-rings. Each ring is a record of  $^{14}\text{C}/^{12}\text{C}$  for the year the ring was formed as  $^{14}\text{C}$  was no longer replenished.
- Atmospheric atomic tests before 1965 as discussed earlier – added a few %.
- Variation over location. Lower  $^{14}\text{C}/^{12}\text{C}$  in southern atmosphere – ocean effect.
- Volcanic eruptions, contamination, etc. also contribute to variation.



# Bomb Pulse Dating – for Wine Vintage Verification

- In fact, the variation of  $^{14}\text{C}/^{12}\text{C}$  ratio due to the atomic tests is also used for dating – known as bomb pulse dating! For example:
  - Validate tree ring ages and to date recent trees that have no annual growth rings
  - Forensics, e.g., assisted in identification of victims of the Southeast Asian tsunami 2004 by examining  $^{14}\text{C}$  their teeth enamel to determine when the victims were born (good to  $\pm 1.6$  yrs)
- Interesting Application: Detecting fake wine vintage



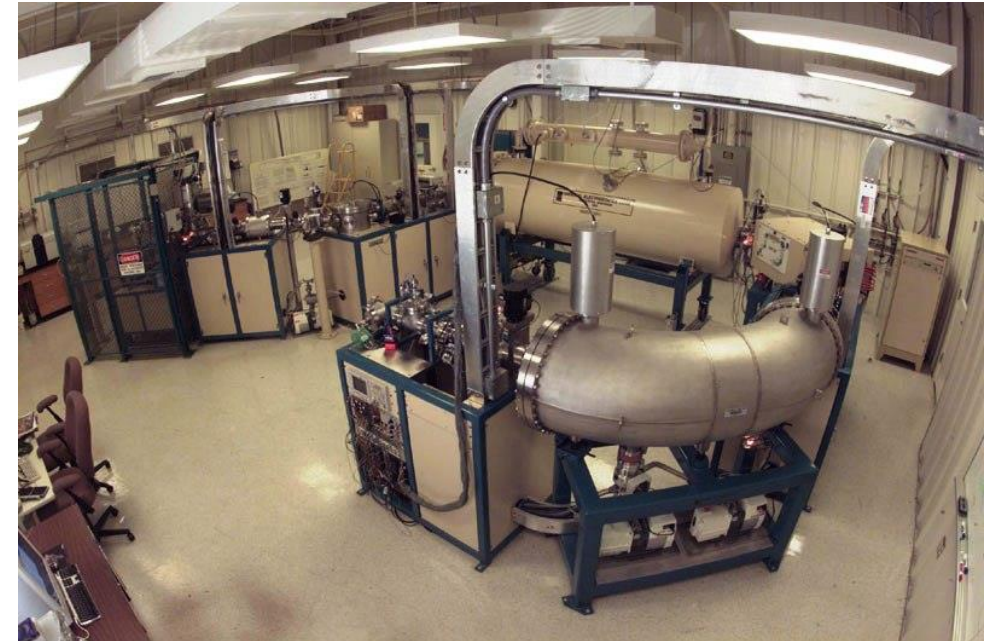
- (a) Comparison of  $\Delta^{14}\text{C}$  (‰) in Chinese liquor with local atmospheric  $\Delta^{14}\text{C}$  (‰) from tree rings;
- (b) the relationship of cellar-stored year and predicted vintage year.

<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5138620/>

[https://en.wikipedia.org/wiki/Bomb\\_pulse](https://en.wikipedia.org/wiki/Bomb_pulse)

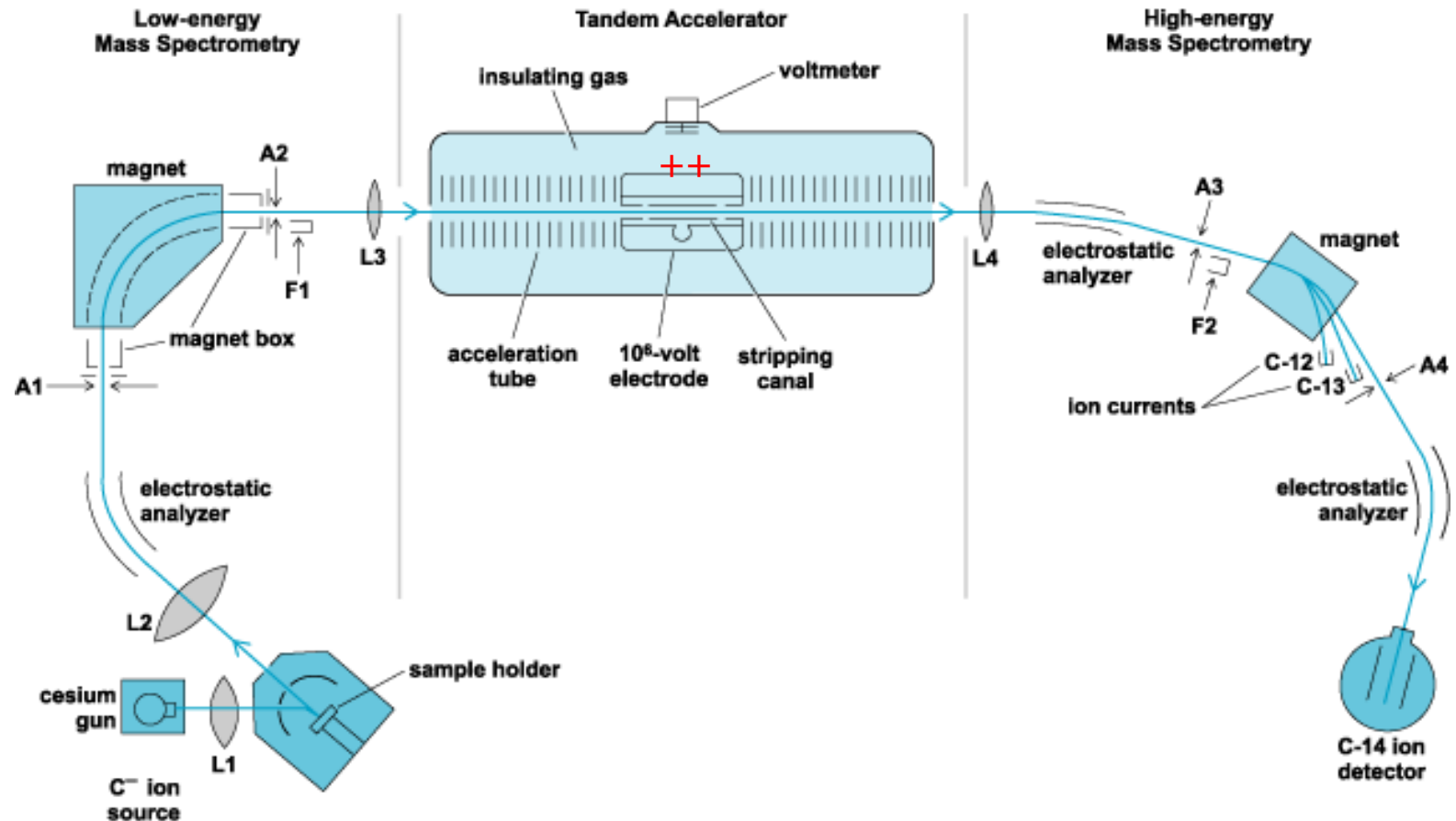
# Accelerator Mass Spectrometry (AMS)

- Radiometric method for  $^{14}\text{C}$  – Counting of beta particles (Geiger counter, liquid scintillation, etc.) – usually a very slow process and could take days to get good results.
- Accelerated Mass Spectroscopy (AMS) - Developed by Willard Libby in the late 1940s – awarded 1960 Nobel Prize in Chemistry. Used extensively from 1970s
- Some advantages.
  - Need very small sample (20 – 500 milligram) – blood, grain, seed, etc.
  - Extremely sensitive – can measure very minute amount of  $^{14}\text{C}$  (isotopic abundance to as low as  $10^{-18}$ ) – possible to measure much older artefacts.
  - Fast – 1% accuracy within minutes.
- Disadvantages: Expensive and require careful handling since any contamination of minute sample results in large errors.



# Accelerator Mass Spectrometry (AMS)

- Prepared sample – sputtered by cesium gun – negative ions of  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$ , etc.
- The first low-energy mass spectrometer can select ions with specific atomic mass, e.g., 14.
- Noted that these include  $^{14}\text{C}$ , and also molecular  $^{13}\text{C}^1\text{H}$  and  $^{12}\text{C}^1\text{H}_2$  but not  $^{14}\text{N}$  (no stable negative nitrogen ion)
- Accelerated through the tandem accelerator towards positive electrode.
- Stripping canal removed electrons and ions become positively charged.
- Electrons that binds the molecule are also stripped – all molecules destroyed.
- Final spectrometer selects only  $^{14}\text{C}$  and counted in ion detector.



# Potassium-Argon Dating

- Potassium-argon dating is a radiometric dating method used in geochronology and archaeology.
- Three natural isotopes of potassium:  $^{39}\text{K}$  (93.2581%, stable),  $^{40}\text{K}$  (0.0117%,  $t_{1/2} = 1.25 \times 10^9$  years),  $^{41}\text{K}$  (6.7302%, stable). The long half-life of  $^{40}\text{K}$  allows the method to date rocks beyond 100,000 years.
- $^{40}_{19}\text{K}$  has two main modes of decay:
  - $^{40}_{19}\text{K} \rightarrow ^{40}_{20}\text{Ca} + ^{-1}_0 e^- + \bar{\nu}_e$  (89.3%, beta decay, max. energy = 1.33 MeV)
  - $^{40}_{19}\text{K} + ^{-1}_0 e^- \rightarrow ^{40}_{18}\text{Ar} + \nu_e$  (10.7%, electron capture, with gamma emission of 1.46 MeV)
- Measure ratio of  $^{40}\text{Ar}/^{40}\text{K}$  to determine age of rocks. (Note:  $^{40}\text{Ca}$  is seldom used for measurement as natural calcium is one of the most common elements found in rocks.  $^{40}\text{Ar}$  is often trapped in rocks)

No of original  $^{40}\text{K}$  atoms

No of  $^{40}\text{K}$  atoms:  $N_K = N_0 e^{-\lambda t}$

No of  $^{40}\text{Ar}$  atoms:  $N_{Ar} = N_0(1 - e^{-\lambda t}) \times 0.107$

Dividing:  $\frac{N_{Ar}}{N_K} = \frac{(1 - e^{-\lambda t}) \times 0.107}{e^{-\lambda t}}$

$= (e^{\lambda t} - 1) \times 0.107$

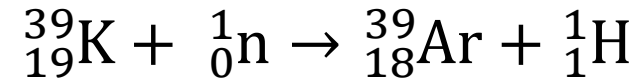
$e^{\lambda t} - 1 = \frac{N_{Ar}}{0.107 N_K}$   
 $\hookrightarrow e^{\lambda t} = \frac{N_{Ar}}{0.107 N_K} + 1$

$t = \frac{t_{1/2}}{\ln(2)} \ln\left(\frac{N_{Ar}}{0.107 N_K} + 1\right)$



# Argon-Argon Dating

- Potassium-argon dating involves measurement of two very different elements, argon and potassium, and is thus increases the uncertainty.
- Alternatively, we can use the number of  $^{39}\text{K}$  nuclides to determine that of  $^{40}\text{K}$  (the ratio of  $^{40}\text{K}/^{39}\text{K}$  is assumed to be known and constant).
- When  $^{39}\text{K}$  is irradiated with neutrons, e.g., in a reactor, some  $^{39}\text{K}$  nuclides transmute to  $^{39}\text{Ar}$  through:



- Note that  $^{39}\text{Ar}$  is radioactive with half-life of 269 years. It is not expected to be present in the rock before the measurement and number will not change significantly during measurement.
- Simultaneous measurement of  $^{39}\text{Ar}$  and  $^{40}\text{Ar}$  is easier as both are noble gases and can be measured in mass spectroscopy together. The measurement of the ratio of  $^{39}\text{Ar}/^{40}\text{Ar}$  is known as the argon-argon dating and has superseded the potassium-argon for most applications.
- Note that there may be complications of argon from the air or additional argon isotopes produced during the irradiation process but these can be measured or corrected.



# Example: Measuring When the Dinosaurs Became Extinct



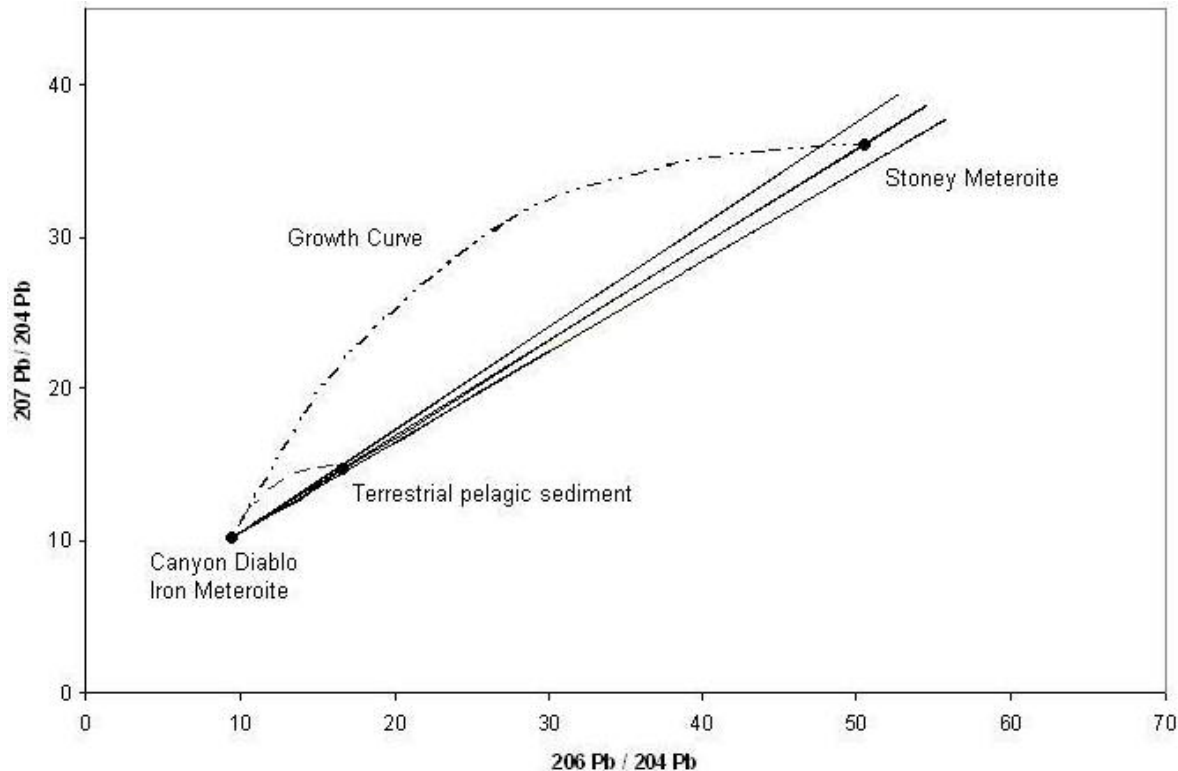
- It is believed that about 66 million years ago, a massive comet or asteroid of about 10 km in diameter hit Earth (in the Mexico Gulf).  $\frac{3}{4}$  of the Earth's species, including dinosaurs, became extinct in the lingering winters due to the materials ejected to the atmosphere from the impact including iridium from the asteroid which forms a iridium-rich layer around the Earth.
- In 2102, an international team of scientists collected volcanic ash from the Hell Creek Formation in Montana - the source of many dinosaur fossils and one of the best sites to study the change in fossils from before and after the extinction.
- Using argon-argon dating, they obtained the most precise date of the event:  $(66,038,000 \pm 11,000)$  years ago!

[http://images.nationalgeographic.com/wpf/media-live/photos/000/010/cache/mass-extinction\\_1077\\_600x450.jpg](http://images.nationalgeographic.com/wpf/media-live/photos/000/010/cache/mass-extinction_1077_600x450.jpg)

<http://www.bbc.com/news/uk-scotland-glasgow-west-21379024>

# Lead-Lead Dating – Determining Age of Earth

- Another important radiometric dating method is lead-lead dating. It is based on two lead isotopes  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$  in rock samples which are the final stable nuclides from the decay series of  $^{235}\text{U}$  and  $^{238}\text{U}$  respectively.
- By comparing the ratio of these isotopes with another non-radiogenic lead isotope  $^{204}\text{Pb}$  in iron and stony meteorites, scientists can calculate quite accurately and consistently the age of Earth which was determined to be **(4.550 ± 0.070) billion years old**.



Iron meteorite from  
Canyon Diablo



[https://en.wikipedia.org/wiki/Lead%E2%80%93lead\\_dating](https://en.wikipedia.org/wiki/Lead%E2%80%93lead_dating)

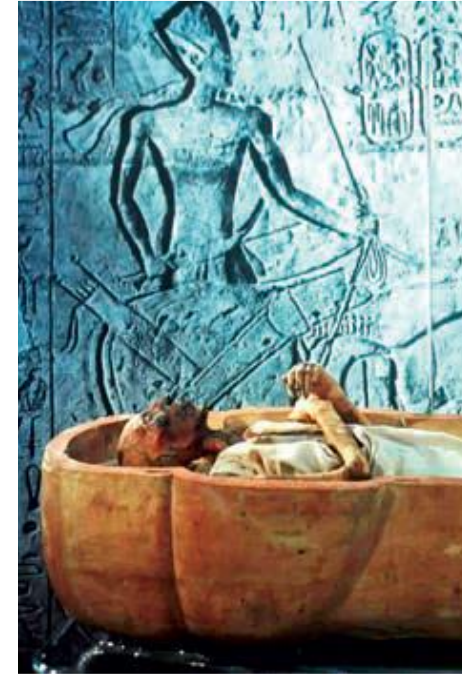


# Applications in Preservation of Physical Cultural Artefacts

- Radiation technology has been successfully used in recent years, with participation of museums and libraries, for preservation and consolidation of cultural heritage artefacts.
- Physical cultural heritage includes works of art, books, manuscripts, drawings, archive documents, musical instruments, ethnographic objects, archaeological findings, natural history collections, historical buildings and historical places, monuments and industrial heritage objects.

- **Biodegradation Agents**

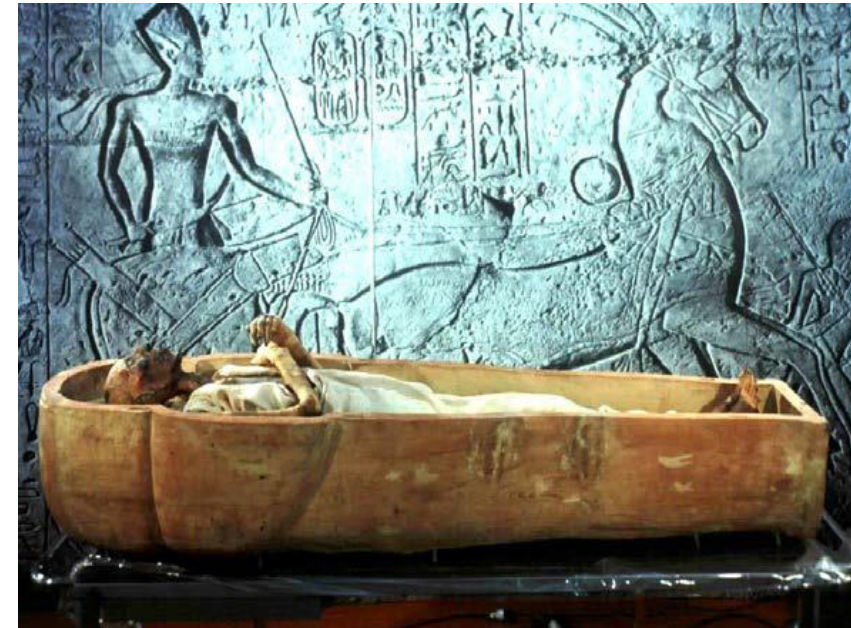
- Micro-organisms such as fungi, bacteria, actinomycetes, yeasts, algae and lichens – enzymes, organic acids and other reactive metabolites released breaking down structural biopolymers.
- Insects, e.g., coleoptera (beetles, weevils) in temperate regions, termites in tropical regions.
- Act on books, leather, wood, textiles.



<https://www.iaea.org/publications/10937/uses-of-ionizing-radiation-for-tangible-cultural-heritage-conservation>

# Example: Disinfection of the Mummy of Ramses II

- When the mummy of Ramses II was received at the “Musée de l’Homme”, a French museum, to be treated, it was infested with larvae and fungi. Having been damaged in the past by insect larvae, the mummy was also found to be infested by a dense population of various types of fungi.
- Irradiated at Commissariat à l’Energie Atomique (CEA) in Saclay, which had an irradiator capable of getting the pharaoh rid of his pests. On May 8, 1977, the mummy was given a dose of 18,000 Grays (Gy) in two sessions of 6 hours, without having to leave his sarcophagus.
- With gamma-ray from Cobalt-60 source with radiation activity of  $5.92 \times 10^{15}$  Bq (160 kCi).
- Success of irradiation – excellent conditions of mummy of Ramses II displayed in sealed transparent Plexiglas cover in sterilized atmosphere for 40 years.

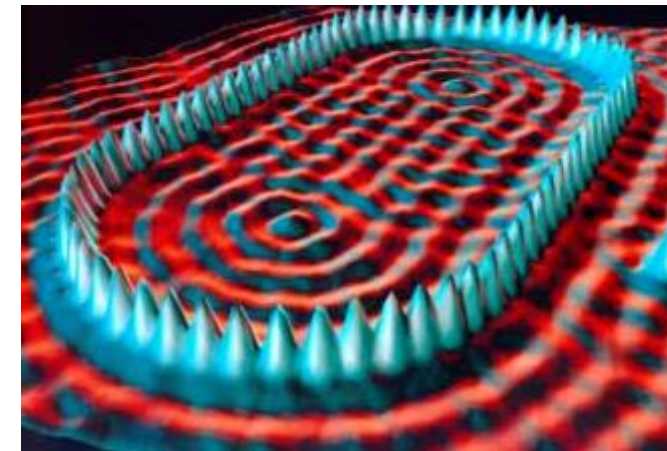
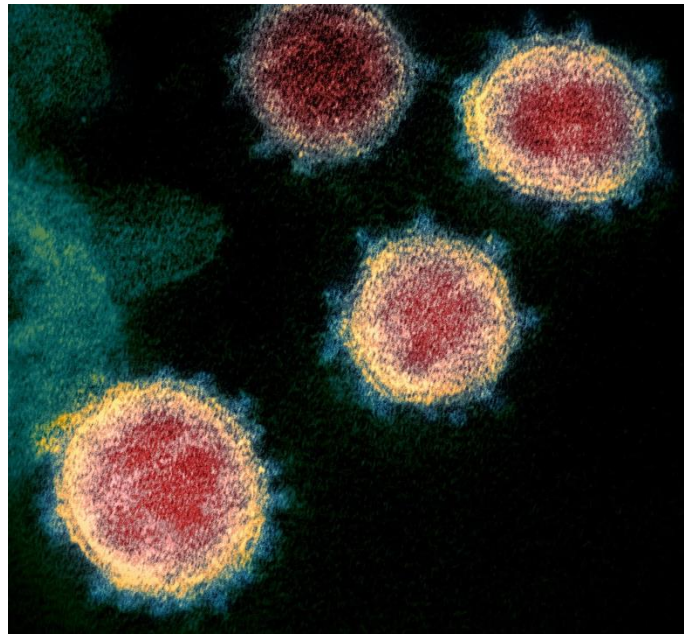




# Some Applications in Research

- Ionization radiation (x-rays, gamma-rays, charged particles and neutrons) are used in many techniques to study matter and develop new materials.
- Imaging - much higher resolution than optical means due to the much shorter wavelengths of x-rays, gamma rays and energetic charged particles.

Transmission electron microscope (TEM) image showing the virus that causes COVID-19—isolated from a patient in the U.S. Virus particles are shown emerging from the surface of cells cultured in the lab. The spikes on the outer edge of the virus particles give coronaviruses their name, crown-like from [https://en.wikipedia.org/wiki/Coronavirus\\_disease\\_2019#/media/File:Novel\\_Coronavirus\\_SARS-CoV-2.jpg](https://en.wikipedia.org/wiki/Coronavirus_disease_2019#/media/File:Novel_Coronavirus_SARS-CoV-2.jpg)

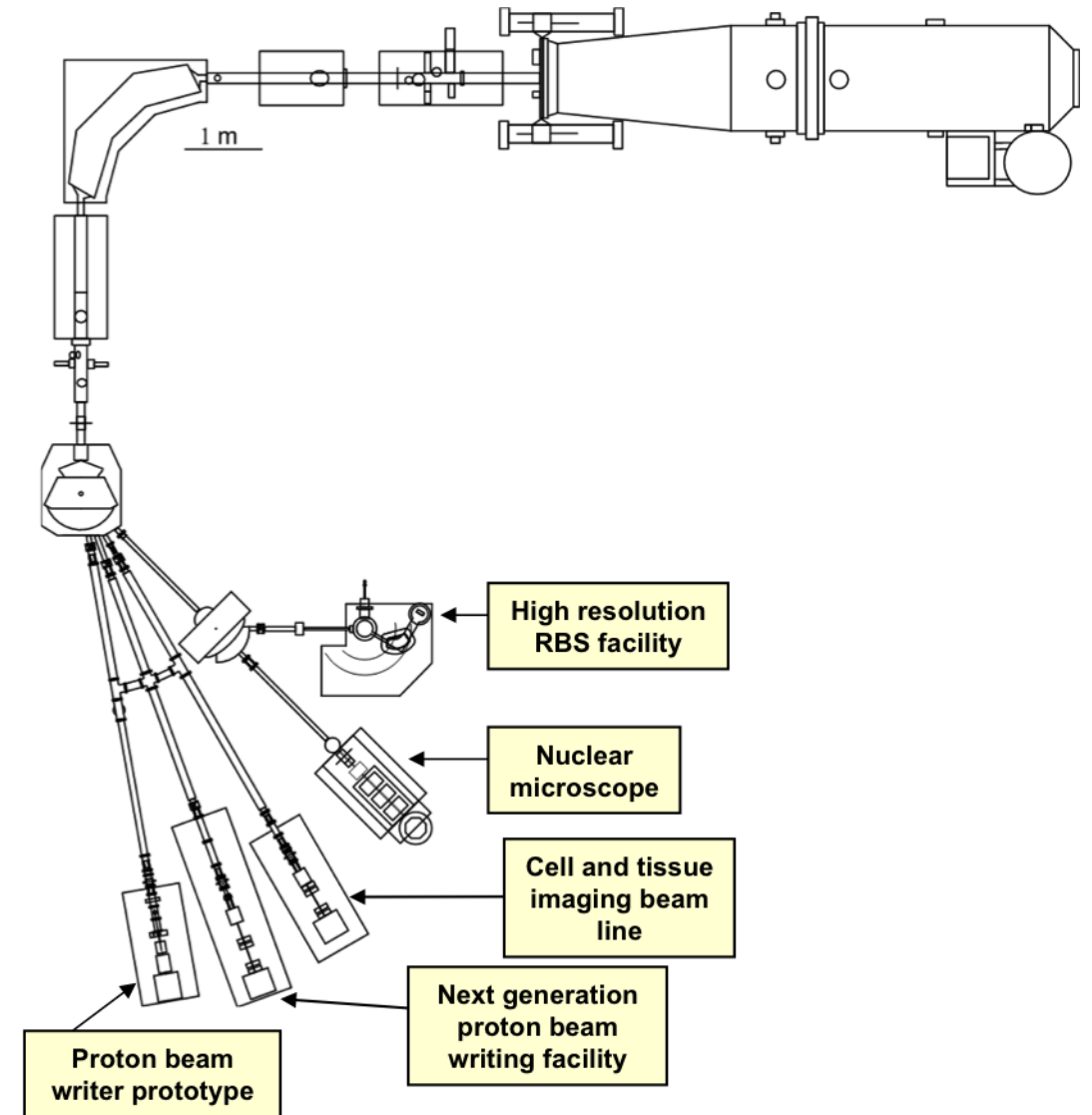


STM (Scanning Tunneling Microscope) image of iron atoms on copper surface from <http://researcher.watson.ibm.com/researcher/files/us-flinte/stm15.jpg>

- Analysis of materials – composition, concentration, structure, etc.
- Fabrication – Nano-structures, change of properties, e.g., in polymers and semiconductors, etc.

# Ion Beam Applications

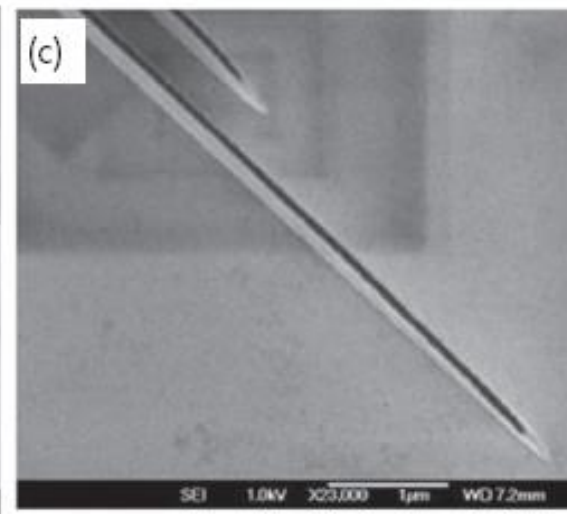
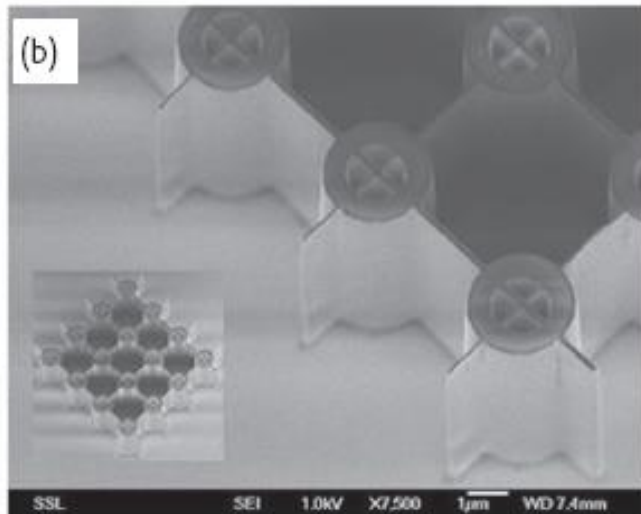
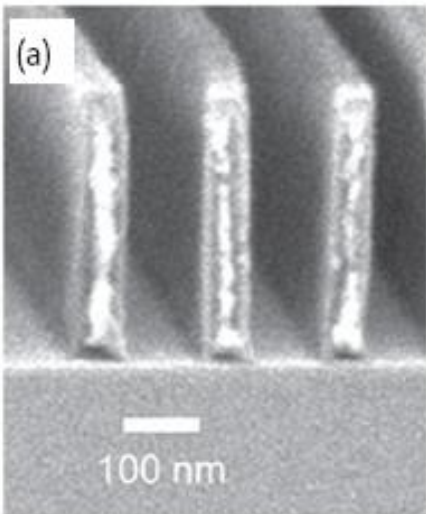
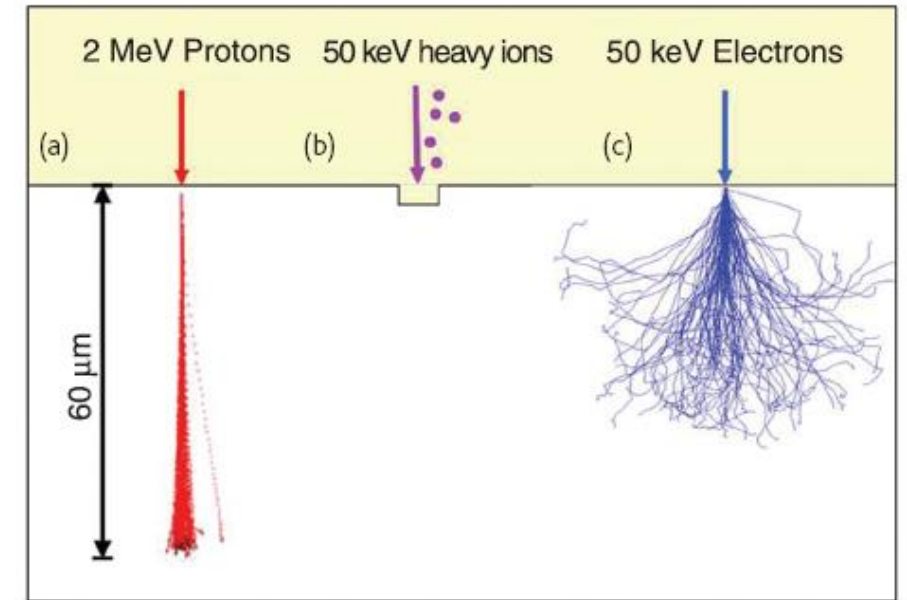
- Ions may be accelerated and used for a variety of applications including 3-D nano-structure fabrication, nuclear microscopy, tissue/cell imaging and micro-analysis, etc.
- Ions such as protons may be accelerated to a few MeV. Multiple beamlines, each designed for a particular purpose.





# Proton Beam Writing

- Uses a focused beam of MeV protons to pattern resist material at nanometers scale.
- The proton beam travels in a straight line apart from a small amount of end-of-range broadening
- The penetration depth of the proton beam is well defined and can be varied by changing the proton beam energy.



SEM images of some of the structures fabricated with MeV proton beam

# Concluding Remarks

- We have presented many useful applications of radiation and nuclear technologies. These include power generation, medical diagnosis and treatment, agriculture and food, industries, science, arts, research, etc.
- There are risks associated with radiation which we must be aware of and take necessary precautions to prevent over-exposure especially if one works with equipment or materials that can deliver a high dose.
- In financial terms, it has been estimated that the direct annual contributions to the economy in advanced countries are in the orders of tens to hundred of billions of US\$ as shown below for US and Japan for the year 1997<sup>1</sup>.

	US (US\$B)	Japan (US\$B)
Radiation Technologies	119	52
Nuclear Power	39	47
<b>Total</b>	<b>158</b>	<b>99</b>
<b>% of GDP</b>	<b>1.9</b>	<b>2.3</b>

It was also estimated that the actual impact on the economy is about 2.5 times that of the direct contribution.

<sup>1</sup> <http://www.laradioactivite.com/site/pages/RadioPDF/Waltar.pdf>