

- Energy
- renewable energy
- nuclear energy
- Radioactivity in the industrial production process
- Radioactivity in the art market
- Radioactivity and medical applications
- Radioactivity and homeland security
- Radioactivity in war
- Radioactivity and fear

## Visible Energy Consumption of Mankind



ի՞նչ է տալիս մեզ էներգիան: Human Development Index: 0.78 81 out of 189 countries

Կրթություն Չարստություն Առողջություն Անվտանգություն





Figure 1.6 Relationship between human development index (HDI) and per capita electricity consumption, 2003 – 2004

Note: World average HDI equals 0.741. World average per capita annual electricity consumption, at 2,490 kWh per person.year, translates to approximately 9 gigajoules (GJ)/person.year [10,000











### **ARMENIA ENERGY MIX**

### Total Primary Energy Supply (TPES)



Oil

Natural gas

- Hydro
- Wind, solar PV and solar thermal
- Biofuels
- Nuclear

Electricity





Source: Global Carbon Project

## Climate Change for Armenia: Very Strong







## **Metsamor 2 to operate until 2026** 17 November 2021

### Armenia is constantly monitoring

## Radioactivity





## More than 2000 Nuclear Weapons Tests 1945-1999, with major emission of radioactivity into the atmosphere













Each fission releases more than 1 neutron

.



Nuclei weigh less than the sum of the masses of their protons and neutrons

Energy and mass are related



Nuclear binding energy

$$(2m_p + 2m_n) > m(^4He)$$

 $BE = (2m_p + 2m_n) - m({}^4He)$ 



## Յայաստանը և ԱՄՆ

# SMALL MODULAR REACTORS





## Accelerating advanced reactor demonstration & deployment





### **Nuclear Medicine**





18 MeV Cyclotron Proton Beams

<sup>64</sup>Cu <sup>68</sup>Ga <sup>99</sup>Mo





## **Experimental hall: External Beam line + data acquisition and analysis rooms**



#### Two similar ones in the world

- University Hospital of Bern
- University of Seville

Research: Fundamental Nuclear Science Fundamental Nuclear Astrophysics Research in the development of new Isotopes Material Science Many other possibilities... Cultural Heritage Manusrcipts/artifact Testing electronics

### AANL enabled the operation of the cyclotron located at the lsotope production center



#### Life Sciences

#### Medical Diagnostics, Drug Testing

Medical Therapy
Radiobiology
Biomedical tracers

### 18 MeV Cyclotron from IBA

### **Isotope Production**

Creation and development of accelerator based methods of isotopes production, <sup>99m</sup>Tc, <sup>67</sup>Ga, <sup>64</sup>Cu and others.

First Beam June 12, 2019 !!! <sup>18</sup>F Isotopes (9 Ci) produced July 3, 2019 Several Experiments in 2020! *Diagnostic Tool during COVID-19 pandemic* 

### Radioisotopes in Medicine (Updated May 2020)

### <sup>99m</sup>Tc : SPECT

**Traditionally Produced from Fission** 

•Nuclear medicine uses radiation to provide diagnostic information about the functioning of a person's specific organs, or to treat them. Diagnostic procedures using radioisotopes are now routine.

•Radiotherapy can be used to treat some medical conditions, especially cancer, using radiation to weaken or destroy particular targeted cells.

•Over 40 million nuclear medicine procedures are performed each year, and demand for radioisotopes is increasing at up to 5% annually.

Diagnostic radiopharmaceuticals can be used to examine blood flow to the brain, functioning of the liver, lungs, heart, or kidneys, to assess bone growth, and to confirm other diagnostic procedures. Another important use is to predict the effects of surgery and assess changes since treatment. For PET imaging, the main radiopharmaceutical is fluoro-deoxy glucose (FDG) incorporating F-18 – with a half-life of just under two hours – as a tracer. The FDG is readily incorporated into the cell without being broken down, and is a good indicator of cell metabolism.

In diagnostic medicine, there is a strong trend towards using more **cyclotron-produced isotopes such as F-18,** as PET and CT/PET become more widely available.

Positron Emission Tomography 1 in Armenia that began in June 2020



## **Beyond Diagnostics**, isotopes for Targeted therapeutic use in cancer treatments

Armenian Isotope Production Presently: Diagnostic Radioisotopes

Future: Targeted Therapeutic ones as well Over 10,000 hospitals worldwide use radioisotopes in medicine, and about 90% of the procedures are for diagnosis. The most common radioisotope used in diagnosis is **technetium-99 (Tc-99)**, with some 40 million procedures per year, accounting for about 80% of all nuclear medicine procedures and 85% of diagnostic scans in nuclear medicine worldwide. SPECT stands for single-photon emission computerized tomography. It use

SPECT stands for single-photon emission computerized tomography. It uses a radioactive substance and a special gamma camera to create 3-D pictures of your organs at different angles.

Technetium-99m<sup>99m</sup>Tc (T<sub>1/2</sub>= 6h; Eγ~140 keV) Emission of a gamma-ray



#### WHAT IS SPECT?

SINGLE >

Unlike PET, which uses dual annihilation photons for image creation, SPECT uses **single photons**.

**EMISSION** *→ emission imaging* 

(NOT Transmission imaging like X-ray or Reflection-based imaging like Ultrasound)

**COMPUTED** → uses algorithms (NOT Geometric Tomography)

**TOMOGRAPHY** → *produces 3D imaging* (NOT planar)

Canadian Model: cyclotrons located In geographically centralized areas with accessibility for the population of CANADA.

Extracting <sup>99m</sup>Tc from Mo/Tc generators irradiated material during 6-7 days using centrifuge extractor one can "milk" total up to 2-3 Ci of activity.

Armenia: There are 5 clinics in Armenia having SPECT scanners –

Oncocenter, Cardiocenter Center of radiology and burns, Erebuny clinic and Radioisotopes Production Center.

All 5 are located in Yerevan. Before COVID-19 Mo/Tc generators were purchased and delivered


## Alternative Production Methods for <sup>99m</sup>Tc using cyclotron 99Mo + 0 P 100 MOLE PROPERTY 100 Mo(p,2n)99m Tc 100Mo 99mTc + 0 + 0ISSNOLD 211 Safe Incident proton Stable target 140 keV nucleus photon for imaging Technique demonstrated to work with natural Mo by group of 999**Tc** Dr. Avetisyan at AANL. Next steps with separated isotope of <sup>100</sup>Mo

## **Therapeutic Isotopes: Big Advance in Cancer Treatments**

- Targeted Radioisotope Therapy
- $\beta^{-}$ , alpha, and Auger electrons

Isotopes that decay by the emission of  $\beta$ -, alpha, and Auger electrons can be used to kill/damage tumor cells

Challenge is in the delivery of the radioisotope Must be highly selective and targeting the tumor (antibodies) Examples: <sup>90</sup>Y or <sup>131</sup>I do not need targeting since they naturally accumulate

## **Theranostic Approach**



The theranostic approach in nuclear medicine couples diagnostic imaging and therapy using the same molecule or at least very similar molecules, which are either radiolabeled differently or given in different dosages.

Example 1: iodine-131 and lutetium-177 are gamma and beta emitters; thus, these agents can be used for both imaging and therapy.
Example 2: iodine-123 (gamma emitter) and iodine-131 (gamma and beta emitters)
Example 3: yttrium-86/yttrium-90
Example 4: terbium isotopes (Tb): <sup>152</sup>Tb (beta plus emitter), <sup>155</sup>Tb (gamma emitter), <sup>149</sup>Tb (alpha emitter), and <sup>161</sup>Tb (beta minus particle).

## Dr. Aboian Radionuclide as a Therapeutic





## Radioisotope implanted **porous silicon nanoparticles** for theranostic applications

## THERAPEUTIC USE OF RADIOACTIVE ISOTOPES

In December, researchers from <u>ISOLDE-CERN</u>, the <u>Paul Scherrer Institute</u> (PSI) and the <u>Institut</u> <u>Laue-Langevin</u> (ILL) published the results of an *in vivo* study which successfully proved the effectiveness of four terbium isotopes for diagnosing and treating cancerous tumors.

Tb 149		Tb 152	
4.2 m	4.1 h	4.2 m	17.5 h
ε	ε	ly 283;	ε
β*	α.3.97	160	β* 2.8
α 3.99	β*1.8	ε; β*	γ 344;
γ 796;	γ 352;	γ 344;	586;
165	165	411	271
Tb 155		Tb 161	
5.32 d		6.90 d	
ε γ 87; 105; 180, 262		β <sup>.</sup> 0.5; 0.6 γ 26; 49; 75 e <sup>.</sup>	

## -ves -ves collaboration with Materials Science to deliver the radioisotor Collaboration with Pharmaceutical developments in Armenia Scoper 68Ga PETI 67Ga Auger therapy Collaborations with Biologists for in-vivo testing 99mTc SPECT/ 94mTc PET 119Sb Auger/118Sb PET/117Sb SPECT 124| PETI 125| Auger therapy 149Tb Alpha therapy/ 161Tb B- therapy 203Pb/ 212Pb Alpha therapy 213Bi Alpha therapy 223,224Ra Alpha therapy 225Ac Alpha therapy 227 228 Th Alpha therapy



## **Cyclotron: New Directions**

# Cultural Heritage New Beginning in Armeni





## **PIXE: Proton Induced X-ray Emission**

## Material analysis with radiation

The analysis and imaging of material can be done by particle induced x-ray emission (PIXE) or x-ray fluorescence (XRF) or neutron activation techniques (NAA). These techniques allow punctual analysis or also the development of images for specific material components.

Particle induced X-ray/ $\gamma$  emission (PIXE/PIGE)



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



## PIXE and XRF



Aι

## Art Analysis





Energy - keV

PbCO<sub>3</sub> (lead-white) white pigment for preparing the backing (canvas, wood) and for highlighting bright areas, today TiO (titanium oxide)  $C_xH_y$ + FeO + CaCO<sub>3</sub>) (calcinated Van Dyke Brown) – a local product from the region near Cologne, which was used for the toning of darker brownish areas.  $(Fe_4[Fe(CN)_6])_3$ (Prussian Blue, based on Fe)- was used for the blue tones of broche – no Cu (Azurite) was observed. CoAlO<sub>4</sub> (Cobalt Blue or Smalt ) was used for sleeve.  $C_xH_y$ + FeO + CaCO<sub>3</sub>) (calcinated Van Dyke Brown) – a local product from the region near Cologne, which was used for the toning of darker brownish areas.

## XRF for consumer goods

Easy approach for quick analysis of elemental composition of materials



## Neutron Activation Analysis (NAA)

Expose material to high neutron flux and add neutrons to nuclei to produce a radioactive isotope with subsequent analysis of elemental components



## Prompt Neutron Activation Analysis with Am-Be neutron sources

Sorting of security issues at airports



 $^{14}$ N(n, $\gamma$ ) $^{15}$ N ejecting prompt 10.8 MeV  $\gamma$ -rays



Sorting of waste components by activity analysis



<sup>37</sup>Cl(n, $\gamma$ )<sup>38</sup>Cl ejecting prompt 5.6 and 6.11 MeV  $\gamma$ -rays.

![](_page_50_Figure_8.jpeg)

## **Nuclear Batteries**

![](_page_51_Picture_1.jpeg)

Nuclear batteries get their energy from the decay of radioactive material. The lifetime of a battery is associated with the lifetime  $\tau$  or the half life  $T_{1/2}$  of its radioactive fuel:

$$\tau = \frac{1}{\lambda} = \frac{T_{1/2}}{\ln 2} = 1.44 \cdot T_{1/2}$$

Example: radioactive fuel <sup>3</sup>H:  $\tau$  = 17.8 y, <sup>63</sup>Ni:  $\tau$  = 144 y, <sup>210</sup>Po:  $\tau$  = 200d.

The power *P* (Watt=Joule/s) generated by the battery depends on the decay energy *Q* and the activity *A* of the radioactive fuel at any given time *t*:

$$P = Q \cdot A = Q \cdot \lambda \cdot N(t) = Q \cdot \frac{N(t)}{\tau} = Q \cdot \frac{N_0 \cdot e^{-\lambda \cdot t}}{\tau}$$

Example: energy release <sup>3</sup>H: Q=5.7 keV, <sup>63</sup>Ni: Q = 66.9 keV, <sup>210</sup>Po: Q = 5304 keV.

$$A = \frac{P}{Q} \qquad 1 \, eV = 1.6022 \cdot 10^{-19} \, J$$

Example: activity of a 12W battery <sup>3</sup>H: **A=**1.3·10<sup>16</sup>Bq, <sup>63</sup>Ni: **A=**1.1·10<sup>15</sup>Bq, <sup>210</sup>Po: **A=**1.4·10<sup>13</sup>Bq. The use is pretty much restricted to micro-batteries with nano-Watt or micro-Watt power output with Giga- to Mega-Becquerel activities (Micro-electronic-mechanical systems MEMS)

**Beta-voltaics** 

![](_page_52_Picture_1.jpeg)

Micro-batteries use electric diode techniques to convert the nuclear decay energy into electrical energies for micro-electronic devices. Small scale nuclear batteries expand the longevity compared to micro-batteries based on electro-chemical processes. Batteries powered by nuclear decay have a lifespan of decades and are up to 200 times more efficient

 $\beta$  articles (electrons) from decay of a radioactive sample generate electron-hole pair in semi-conductor material generating voltage between the electrodes.

Radioactive samples should be free from  $\gamma$  radiation to avoid external activity.

Used up-batteries are considered nuclear waste!

![](_page_52_Figure_6.jpeg)

Applications for electronic units in long-term space missions, nuclear powered pacemakers. The nuclear-powered laptop battery Xcell-N has a 150-day life-time!

Future Applications: car batteries, deep-sea water probes, and long-term sensors

## Radioisotope Thermoelectric Generator (RTG)

A RTG is an instrument that uses an array of thermocouples to convert the heat released by the decay of a suitable radioactive material into electrical voltage.

Thermocouples consist of two wire legs made from different metals. The wires legs are welded together at one end, creating a junction. This junction is where the temperature is measured. When the junction experiences a change in temperature, a voltage is created that generates an electrical current.

![](_page_53_Figure_3.jpeg)

# Space craft applications

The Multi-Mission RTG (MMRTG) contains a total of **10.6 pounds (4.8 kilograms) of plutonium dioxide** (including Pu-238) that initially provides approximately 2,000 watts of thermal power and 110 watts of electrical power when exposed to deep space environments. The thermoelectric materials (PbSnTe, TAGS, and PbTe) have extended lifetime and performance capabilities. The MMRTG generator is about 25 inches (64 centimeters) in diameter (fin-tip to fin-tip) by 26 i ches (66 centimeters) tall and weighs about 94 pounds (45 kilograms).

![](_page_54_Picture_2.jpeg)

A plutonium oxide pellet  $(^{238}Pu^{16}O_2)$ , glowing from its own heat, generated by the energy release of 5.6 MeV in the  $\alpha$  decay. One-gram  $^{238}Pu$  generates thermal power of approximately 0.5 W.

![](_page_54_Figure_4.jpeg)

![](_page_54_Picture_5.jpeg)

Nuclear battery efficiencies

![](_page_55_Figure_1.jpeg)

## Radiation and microelectronics

- Radiation damage on chips and/or microelectronics in integrated circuits
- Affects as Single Event Effect SEE
- Satellite and airplane control
- Computer and cell phone operation
- Remote and computer controlled car and other traffic units

Everything is computer controlled. Through the miniaturization of electronics, everything is vulnerable!

![](_page_56_Picture_7.jpeg)

## Single Event Effect, SEE

![](_page_57_Figure_1.jpeg)

SEE effects are statistical; damage and response of an electronic unit are difficult to predict, because of the complexity of damage. But the higher radiation level, the higher the likelihood of electronic failure; space exploration units and airplane control electronic are particularly susceptible to damage due to the combination of high radiation environment and microelectronic complexity. But a single hit can also do substantial damage to ground-based electronic units, doing local damage in chip structure and performance, flipping bits, damaging memory and control.

## Endangered electronic systems

Malfunctions in integrated circuits (IC) due to radiation effects from high energy neutrons or alpha particles at ground level are now becoming a major concern; especially for life-critical and safety-critical applications such as aviation, industrial automation, medical devices, automotive electronics and for high-availability, revenue-critical applications such as communication infrastructure.

![](_page_58_Picture_2.jpeg)

![](_page_59_Picture_0.jpeg)

# Modern Tools for Ancient Art

Modern art analysis techniques rely on the quantum nature of matter to determine providence, age, techniques, and forgeries.

The most frequently used methods are x-ray analysis such as PIXE and XRF, coupled with atomic analysis techniques such as Raman spectroscopy, and nuclear physics techniques such as Neutron activation analysis. This is complemented by radioactive dating taking the half-life as time scale.

![](_page_59_Picture_5.jpeg)

![](_page_59_Picture_6.jpeg)

## The origin of materials

XRF analysis with portable instrumentation

The "Relics of the three Magi", came from Milan, Italy to Cologne, Germany in 1162. The shrine was made in 1180-1225 AD. Where did jewels, gems, and other precious materials come from?

## X-ray Analysis by XRF and PIXE

![](_page_61_Figure_1.jpeg)

Each element emits its own characteristic line due to the quantum transition of electrons to lower excited orbits in the atomic shell.

![](_page_61_Figure_3.jpeg)

![](_page_61_Figure_4.jpeg)

$$E_{x} = (Z-1)^{2} \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^{2}}\right)$$
  
for S: Z = 16;  $E_{x} = (15)^{2} \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^{2}}\right) = 2.29 [eV]$   
for Ca: Z = 20;  $E_{x} = (19)^{2} \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^{2}}\right) = 3.68 [eV]$   
for Ti: Z = 22;  $E_{x} = (21)^{2} \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^{2}}\right) = 4.50 [eV]$   
for Fe: Z = 26;  $E_{x} = (25)^{2} \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^{2}}\right) = 6.37 [eV]$   
for Zn: Z = 30;  $E_{x} = (29)^{2} \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^{2}}\right) = 8.58 [eV]$ 

![](_page_62_Picture_0.jpeg)

## Analysis of paint pigments

Pre 1800 oil paintings contained specific pigments prepared from naturally available materials to achieve color effects. After 1850 these pigments were gradually replaced by organic (Carbon based) pigments provided by the chemical industry.

#### White pigments

Antimony white Lithopone Permanent white Titanium white White lead Zinc white Zirconium oxide

Chalk Gypsum

### Yellow pigments

Auripigmentum Cadmium yellow Chrome yellow Cobalt yellow Lead-tin yellow Massicot Naples yellow Strontium yellow Titanium yellow Yellow ochre Zinc yellow

### Red pigments

Cadmium red Cadmium vermilion Chrome red Molybdate red Realgar Red lead Red ochre Vermilion  $Sb_2O_3$   $ZnO + BaSO_4$   $BaSO_4$   $TiO_2$   $2PbCO_3 \cdot Pb(OH)_2$  ZnO  $ZrO_2$   $CaCO_3$  $CaSO_4 \cdot 2H_2O$ 

 $\begin{array}{l} As_2S_3\\ CdS\\ 2PbSO_4 \cdot PbCrO_4\\ K_3[Co(NO_2)_6] \cdot 1.5H_2O\\ Pb_2SnO_4 / PbSn_2SiO_7\\ PbO\\ Pb(SbO_3)_2 / Pb_3(SbO_4)_2\\ SrCrO_4\\ NiO \cdot Sb_2O_3 \cdot 20TiO_2\\ Fe_2O_3 \cdot nH_2O (20-70\%)\\ K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O \end{array}$ 

 $\begin{array}{l} CdS + CdSe\\ CdS + HgS\\ PbO\cdotPbCrO_4\\ 7PbCrO_4\cdot 2PbSO_4\cdot PbMoO_4\\ As_2S_3\\ Pb_3O_4\\ Fe_2O_3 \ (up \ to \ 90\%)\\ HgS \end{array}$ 

### Green pigments

Basic copper sulfate Chromium oxide Chrysocolla Cobalt green Emerald green Guignent green Malachite Verdigris

### Blue pigments

Azurite Cerulean blue Cobalt blue Cobalt violet Egyptian blue Manganese blue Prussian blue Smalt Ultramarine

### Black pigments

Antimony black Black iron oxide Carbon or charcoal black Cobalt black Ivory black Manganese oxide  $\begin{array}{l} Cu_{x}(SO_{4})_{y}(OH)_{z} \\ Cr_{2}O_{3} \\ CuSiO_{3}\cdot nH_{2}O \\ CoO\cdot5ZnO \\ Cu(CH_{3}COO)_{2}\cdot 3Cu(AsO_{2})_{2} \\ Cr_{2}O_{3}\cdot nH_{2}O + H_{3}BO_{3} \\ CuCO_{3}\cdot Cu(OH)_{2} \\ Cu(CH_{3}COO)_{2}\cdot nCu(OH)_{2} \end{array}$ 

 $\begin{array}{l} 2CuCO_{3}\cdot Cu(OH)_{2}\\ CoO\cdot nSnO_{2}\\ CoO\cdot AI_{2}O_{3}\\ Co_{3}(PO_{4})_{2}\\ CaO\cdot CuO\cdot 4SiO_{2}\\ BaSO_{4}\cdot Ba_{3}(MnO_{4})_{2}\\ Fe_{4}[Fe(CN)_{6}]_{3}\\ Co-glass~(K_{2}O+SiO_{2}+CoO)\\ Na_{8-10}AI_{6}Si_{6}O_{24}S_{2-4}\\ \end{array}$ 

 $\begin{array}{l} Sb_2O_3 \\ FeO\cdot Fe_2O_3 \\ C \ (95\%) \\ CoO \\ C+Ca_3(PO_4)_2 \\ Mno+Mn_2O_3 \end{array}$ 

## Pigments available until 1800 AD

Paint is composed of a colored pigment and a binder substance

Pigment: colored powdered substance grinded from minerals salts, or dyes

Binder: Material that evenly disperses the pigment, applied and then dries.

Paints are throughout uniform homogeneous mixtures.

![](_page_63_Figure_5.jpeg)

## X-Ray Fluorescence of Manuscripts

Analysis of Ink and ink composition which can be used as tracer to identify the origin of manuscripts

![](_page_64_Picture_2.jpeg)

## Painting techniques on the example of Pollock

### Jackson Pollock's Number 1A (1948)

![](_page_65_Picture_2.jpeg)

XRF spectra for different color combinations

![](_page_66_Figure_1.jpeg)

Signature spectra for the twelve components (11 paints and canvas) identifying the characteristic x-ray *lines* for the elements present.

## XRF analysis of use of overlaying colors

Overlapped distribution maps of the *white, red* and *yellow* paints for area (1) and image of that area. The sequence in which they were applied can be established by examining how the paints overlap: *white, red, yellow* and *white* again. Overlapped distribution maps of the *white, glossy* and *matte black* paints for a section in area (1) showing that the gray paint was made by mixing the *white* paint and the *black glossy* paint and not the *matte black* 

![](_page_67_Picture_3.jpeg)

Pollock mostly applied each paint straight out of the tube or can, and with a specific gesture, brushstroke (matte black and white), dripping (cream, glossy black and silver gray), thrusting (turquoise, matte black and white), squeezing the tube (red and yellow) or splattering (cream and silver gray), and using a specific tool, brush or stick. Some of the paints were applied wet on wet like the thinner cream and glossy black house paints creating a marbling look by overlapping the corresponding distribution maps for the area. He used his hands to apply the red brick and matte black paints leaving clear handprints, or creating large stains by dragging his hands or pressing his palms against the canvas.

# Identification of Art Forgeries

Science techniques are an emerging tool for:

- Forgery analysis by nuclear forensic techniques in a competitive art market (Vermeer, Van Gogh, Modigliani, Rothko, etc)
- e.g. Vermeer forgeries by Hans van Meegeren Van Gogh forgeries by Otto Wacker >1000 Modigliani fakes by Elmyr de Hory New York galleries sold Mark Rothko, Jackson Pollock and Willem de Kooning forgeries; damage unknown Recent forgeries by Wolfgang Beltracchi of German expressionists such as Heinrich Campendonk and Max Ernst caused a major art scandal in Europe.

![](_page_68_Picture_4.jpeg)

## Proton Induced X-ray Emission (PIXE)

![](_page_69_Picture_1.jpeg)

Accelerated particles like protons penetrate deeper into material, which reduces distorting surface effects that handicap XRF analysis. Depending on energy the composition of deeper material layers can be explored. That provides an additional insight in chemical decomposition processes important for restoration procedures.

![](_page_69_Figure_3.jpeg)

# Tracing Material Origins

The red stone eyes of the statue of the Parthian goddess of love Ishtar were originally thought by Louvre curators to be made of colored glass

![](_page_70_Figure_2.jpeg)

PIXE analysis showed that the inlays were rubies.  $AL_2 SIO_4 (F,OH)_2+(Cr,Fe rich)$ 

![](_page_70_Picture_4.jpeg)

## **Provenance**, or where did the rubies come from?

The trace element content provides the fingerprint of provenance in archaeology

Comparison of Fe versus Cr content in the Ishtar rubies found in Mesopotamia with rubies from various provenances shows strong indication that rubies did originate from Burma. Ancient trade connections (silk road) between near and far east empires!

![](_page_71_Picture_3.jpeg)

![](_page_71_Figure_4.jpeg)


# PIXE and Dürer travels







Albrecht Dürer silverpoint drawings





# Testing ink pigments of medieval monastery handwriting of letter $\Re$

Lead white:  $k=1050 \text{ cm}^{-1} (PbCO_3)$ Malachite:  $(Cu^{2+}_2(CO_3)(OH)_2)$ Azurite:  $(Cu^{2+}_3(CO_3)_2(OH)_2)$ Vermillion:  $k=253 \text{ cm}^{-1} 285 \text{ cm}^{-1}$ , 343 cm<sup>-1</sup> (HgS) (cinnabar) Minium:  $k=226 \text{ cm}^{-1}$ , 313 cm<sup>-1</sup>, 390 cm<sup>-1</sup>, 549 cm<sup>-1</sup> (Pb<sub>2</sub>O<sub>3</sub>)



Best et al. Endeavour, New Series 16 (1992) 66-73

1500 1000 500 Wavenumber / cm<sup>-1</sup>

Malachite

## Frescoes in Herod's Tomb in Jericho

Roman fresco technique: lime wash, followed by pigment application



Analysis of fragments with Raman spectroscopy





Cinnabar (Persian Dragon's blood): HgS (vermilion)



1064 nm excitation

Provenance of HgS pigment (Pliny & Vitruvius claim Spain)



H. G. M. Edwards et al. J. Raman Spectrosc. 30 (1999) 361-377

# Neutron Activation (NA)

Expose material to high neutron flux and add neutrons to nuclei to produce an radioactive isotope with subsequent analysis of its characteristic

radioactive decay pattern.



### Timescale and Radiation Sensitivity

Signatures are either characteristic radiation or characteristic decay time, which is different for

each radioactive isotope



Taking advantage of radioactive decay

1200 - 12000 - 1200 - 1200 - 12000 - 12000 - 12000 - 12000 - 12000 - 12000 - 12000 - 12000 - 12000 - 12000 - 12000				
Chemical element	emical Associated du ment pigment ar		Time period after activation during which best images in autoradiographs are produced	
manganese	umber, dark ocher	Mn <sup>56</sup> , 2.6 hours	0-24 hours	
copper	malachite, azurite, verdigris	Cu <sup>66</sup> , 5.1 minutes Cu <sup>64</sup> , 12.8 hours	0-20 minutes 1-3 days 1-3 days	
sodium	glue, medium, canvas, ultramarine	Na <sup>24</sup> , 15.0 hours		
arsenic	smalt, glass	As <sup>76</sup> , 26.5 hours	2-8 days	
phosphorus	bone black	P <sup>32</sup> , 14.3 days	8-30 days	
mercury	vermilion	Hg <sup>203</sup> , 48 days	more than 25 days	
cobalt	smalt, glass	Co <sup>60</sup> , 5.3 years	more than 25 days	

Table 1. Chemical elements and associated pigments most frequently observed in autoradiography of seventeenth-century Dutch and Flemish paintings.

The following pigments generally do not cause distinct images in autoradiographs: chalk, lead white, ocher, lead-tin yellow, lakes, madders, and indigo.

# The Man with the Gold Helmet

t van Rijn?

# Was Napoleon murdered by the British?

Neutron activation comes handy



# Napoleon's Death,

#### poisoned by Arsenic?????



<sup>75</sup>As is the only stable isotope of Arsenic



The Emperor's hair had an average arsenic level of around 10-15 ppm, whereas the arsenic level in the hair samples from currently living persons is around 0.1 ppm. But surviving relatives had similar levels!

### May 5 1821



Napoleon has declared in his will that 'I die before my time, murdered by the English oligarchy and its hired assassin'.

### Stable Isotope Analysis (SIA), the King of Stonehenge at 2300 BC

Chemophysical fractionation of isotopes cause local changes in abundance ratio. Climate and rain pattern influence the <sup>18</sup>O to <sup>16</sup>O isotope ratio from sea to land.







The Daily Express expressed the opinion "This is as shocking as the discovery that the first cricket players wore leather pants and ate Bratwurst with their tea".

# Archaeological Dating the past

"Everything which has come down to us from heathendom is wrapped in a thick fog; it belongs to a space of time we cannot measure. We know that it is older than Christendom, but whether by a couple of years or a couple of centuries, or even by more than a millennium, we can do no more than guess"

Rasmus Nyerup, 1802

### Archaeological clocks





105<sub>F</sub>

COUNTS



AMS: counting the radioactive <sup>14</sup>C particles with accelerators: Accelerator Mass Spectrometry

TOTAL ENERGY ET

# Dating Mummies

'My name is Ozymandias, king of kings: Look on my works, ye Mighty, and despair!'



The mummy of Ramses II was one of the first samples tested by the new <sup>14</sup>C radiocarbon method to check the reliability of Egyptian dynasty counting versus biblical counting.







Thames & Hudson



## Conserved by ice - Oetzi, the iceman



3100

🔲 1σ 🔲 2σ

3100

# Murder 5000 years ago





# The big business with (false) artifacts

Police raid of an art dealer in Karachi, Pakistan in October 2000 found a mummy, supposedly the daughter of Cyrus the Great (576-530 BC). The asking price of the dealer was US \$ 11 Million.



AMS analysis determined a large  $^{14}$ C amount in the mummy and dated her death to ~1993 !

# Tracking Illegal Ivory Trade



Increasing slaughter of elephants since 1970 with increased use of automatic weapons.

Ivory trade ban in 1989 to protect elephants from becoming extinct

 Growth in poaching and smuggle leading to local decline of elephant population as high as 90%

# Fernand Léger purchased by Guggenheim Collections



Contraste de formes, Fernand Léger (?) Peggy Guggenheim Collection, Venice



Detail of the canvas sample



Contraste de formes, Fernand Léger (1881-1955), 1913, Solomon G. Guggenheim Foundation, New York







Aerial view: section of the loop, displaying hovering over the vegetation.

Aerial view: Loop smoothly continuing inside second floor of the proposed cafe building.





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### Phasing







Landscape

Renovating Buildings + Loop

New Buildings

## Renewable Energies

- Fossil fuel is bad (CO<sub>2</sub> emission, climate change)
- Nuclear fuel is bad (radioactivity)
- Are Renewable energy sources th solution?



## Rare Earth Metal Needed

Atomic	Element	Symbol		
Number				
21	Scandium**	Sc		
39	Yttrium	Y		
57	Lanthanum	La		
58	Cerium	Ce		
59	Praseodymium	Pr		
60	Neodymium	Nd		
61	Promethium*	Pm		
62	Samarium	Sm		
63	Europium	Eu		
64	Gadolinium	Gd		
65	Terbium	Tb		
66	Dysprosium	Dy		
67	Holmium	Ho		
68	Erbium	Er		
69	Thulium	Tm		
70	Ytterbium	Yb		
71	Lutetium	Lu		







CERIUM

THULIUM



LUTETIUM



lanthanum or cerium are formed from 17 chemically

similar elements and are extremely rare. Because of their strong magnetic properties and high electrical conductivity,

they are light in weight and efficient, making them critical to the clean energy industry.

Wind turbines, energy-efficient light bulbs, electric car batteries, and efficiency motors or generators all depend on dysprosium, neodymium etc to generate the magnets that make them work. No substitute has been found that can match rare earths in weight and efficiency.

YTTERBIUM

## Magnetic Materials

	Magnetic	Resistance to	Energy	Temperature Range		-
Magnet	field (T)	demagnetize (kA/m)	Density (kJ/m³)	(°C)	(°F)	
Nd <sub>2</sub> Fe <sub>14</sub> B (sintered)	1.0–1.4	750–2000	200–440	310–400	590–752	
Nd <sub>2</sub> Fe <sub>14</sub> B (bonded)	0.6–0.7	600–1200	60–100	310–400	590–752	
SmCo₅ (sintered)	0.8–1.1	600–2000	120–200	720	1328	
Sm(Co, Fe, Cu, Zr) <sub>7</sub> (sintered)	0.9–1.15	450–1300	150–240	800	1472	
Alnico (sintered)	0.6–1.4	275	10-88	700–860	1292–1580	
Sr-ferrite (sintered)	0.2–0.78	100–300	10–40	450	842	A

Multiple applications of Rare Earth based materials in computer, information, transportation and energy industries.

## Rare Earth Economy

In 2000 China's low prices forced US producers out of business; 2013 China dominated the production with 90%. With increase in prices and demands US and other countries created new mining initiatives!



World Mine Production and Reserves (2015 Estimates)

Country	Production (Metric Ton)	Reserves (Metric Ton)	
United States	4,100	1,800,000	
Australia	10,000	3,200,000	
Brazil		22,000,000	
China	105,000	55,000,000	
India		3,100,000	Clo
Russia	2,500	?	lar
Thailand	2,100	not available	sa
World total (rounded)	110,000	140,000,000	



Clockwise from top center: praseodymium, cerium, lanthanum, neodymium, samarium, and gadolinium.

## Rare Earth Element

#### Harvesting Rare earths are often located within minerals such as Bastnaesite, Monazite, Xenotime, and Thorite



The four Rare Earth containing minerals, Bastnaesite, Monazite, Xenotime, and Thorite, require special chemical treatment with acids to dissolve, extract and separate their basic elements.

### Biggest (and only) US Rare Earth Mining Facility



## Magnetic Separation



Magnetic ore (rare earth particles) stick to drum, and are separated into an extra container, the non-magnetic tailings are being removed. This can be a multi-step process with increasing purity

### Beaches of Brazil



Monazite enriched black sand washed down from the mountains along the shore lines contains significant amounts of Thorium! The reading is  $\mu$ Sv/h.



The locals believe in the healing powers of the Monazite black sands!



### The radioactive foot print of windmills

A 2 megawatt (MW) wind turbine contains about 800 pounds of neodymium and

130 pounds of dysprosium, which is mostly harvested and processed in China.

- The mining of one ton of rare earth minerals produces about one ton of radioactive waste.
- Each year, the U.S. adds a record 10 15 GW of wind generating capacity.
- That translates to about 5 million pounds of rare earths in newly installed wind turbines.
- Consequently 5 million pounds of radioactive waste were created in the harvesting process.
- In comparison, America's nuclear industry produces around 5 million pounds of spent nuclear fuel each year.
- Nuclear energy provides about 20% of America's energy needs, wind accounts for just 4%.



# Solar Energy



Solar thermals systems: Solar photovoltaic systems: convert sunlight into heat convert sunlight into electricity

## Power production by solar energy



High power generation requires large areas; 1 GW of total irradiance requires an area 732,000m<sup>2</sup> or 0.73 km<sup>2</sup> if all the sunlight is converted to energy. Irradiance in the US is typically near 50-60% of total irradiance. The photovoltaic efficiency of conversion is 20%. This ten folds the required area to 7.3 km<sup>2</sup> or 3 square-mile, an order of magnitude improvement over wind power.





### The photovoltaic effect

A photovoltaic (PV) cell corresponds to two semi-conductor materials n (negative) and p (positive type are sandwiched together. The photovoltaic effect occurs when photons release electrons near the np-junction from the valence band to the conducting band in the lattice of a semi-conductor material Si, Ge, GaAs, etc. The electric charges are moved by an internal electrical potential at the semi-conductor junction, creating an electric current that is proportional to the amount of absorbed light energy. An individual PV cell is usually small, typically producing about 1 or 2 watts of power. For producing energy for a 60 W light bulb, about 100 PV cells need to be matched together.



 Table II. Confirmed terrestrial module efficiencies measured under the global AM1.5 spectrum (1000 W/m<sup>2</sup>) at a cell temperature of 25 °C (IEC 60904-3: 2008, ASTM G-173-03 global).

Classification	Effic. (%)	Area (cm <sup>2</sup> )	$V_{\rm oc}~(V)$	$I_{\rm sc}\left(A\right)$	FF (%)	Test centre (date)	Description
Si (crystalline)	$22.9 \pm 0.6$	778 (da)	5.60	3.97	80.3	Sandia (9/96) <sup>a</sup>	UNSW/Gochermann [32]
Si (large crystalline)	$22.4 \pm 0.6$	15 775 (ap)	69.57	6.341 <sup>b</sup>	80.1	NREL (8/12)	SunPower [33]
Si (multicrystalline)	$18.5 \pm 0.4$	14 661 (ap)	38.97	9.149 <sup>c</sup>	76.2	FhG-ISE (1/12)	Q-Cells (60 serial cells) [34]
GaAs (thin film)	$24.1 \pm 1.0$	858.5 (ap)	10.89	2.255 <sup>d</sup>	84.2	NREL (11/12)	Alta Devices [35]


## Ion Implantation

The ion beam is produced in an ion source by plasma ionization of sputtering, extracted and separated by mass and charge in a magnetic field, accelerated and implanted in Si wafers. This approach is not for mass production!





#### Neutron activation of rare isotope components with subsequent decay to doping material

 ${}^{30}Si(n,\gamma){}^{31}Si(\beta^{-}){}^{31}P \quad {}^{30}Si: 3.1\%$ Similar neutron activation processes at other semiconductor materials Reaction probability or cross section requires thermal neutron energies! c30 c (Si):(Si :(Si) (Si):(Si):(Si):(Si): :(Si):(Si) (Si):(Si)

<sup>30</sup>Si isotope in Si lattice is converted to <sup>31</sup>P

(Si)



Utilization of Nuclear Reactors for efficient production of Solar Energy

Reactor	Thermal power	Irradiation rig	Neutron flux [cm <sup>-2</sup> s <sup>-1</sup> ]	Gamma ray heating or temperature
MARIA in Poland	30 MW		2.1×10 <sup>13</sup> , (thermal), Fast (>1 MeV)/thermal=0.02	0.5 W/g
BR2 in Belgium	56 MW (Nominal: 85 MW)		1.74×10 <sup>14</sup> (thermal), 1.9×10 <sup>13</sup> (fast),	< 200°C Si core temp.
SAFARI-1 in South Africa	20 MW	4 inch SILIRAD	2.5×10 <sup>13</sup> -8×10 <sup>13</sup> (thermal)	Measured temperature at Si: ~80°C
FRM II in Germany	20 MW	8 inch	1.6×10 <sup>13</sup> (thermal) Thermal/fast=1700	Max. temp.: 110°C (Si core temp.) [44]
OPAL in Australia	20 MW	5, 6, 8 inch	$2.5 \times 10^{12} - 1.5 \times 10^{13}$ (thermal) Thermal/fast=900	•
HANARO in the Republic of Korea	30 MW	5,6 inch NTD2	Thermal/fast=400 Cd ratio for gold: 16~22	0.2–0.9 W/cm <sup>3</sup>

Smaller scale reactors (TRIGA type) that don't generate much energy, but a relatively high neutron flux between  $10^{12}$  and  $10^{14}$  neutrons/cm<sup>2</sup>/s!







### **Nuclear Energy Production**



The energy release per atomic mass unit is 0.7MeV for fission and 6.2MeV for fusion, fusion is the more effective nuclear reaction!

Fusion occurs by the nuclear reaction between two light hydrogen isotopes, such as  $d+d(^{2}H+^{2}H)$ , or  $d+t(^{2}H+^{3}H)$ , while fission is the neutron induced splitting of  $^{235}U$  or  $^{239}Pu$  into two lower mass isotopes between mass 100 and mass 130.

## **Confinement of hot Plasmas**



Nature's approach

human approach

# Plasma fusion

through magnetic confinement

A major advantage of fusion reactors is the small if not negligible amount long-lived radioactive decay products! Light radioactive isotopes are short-lived and produce additional energy through the decay heat.



Plasma has to have temperatures of ten times the temperature in the core of the sun to generate the required energy output. The plasma is contained by magnetic fields 10,000 times that of the Earth's field. The shape of the fusion plasma is dictated by the magnetic field generation. These provides enormous technical challenges that have not been achieved yet. The main project towards the goal is the international ITER project in France, but there are still a number of smaller projects in the US, CHINA, and Germany.

## Laser Induced Fusion

#### through inertial confinement

195 Peta-Watt Lasers aiming at one spot generating an implosion of capsule reaching temperatures and densities close or superseding solar values.





Shot physics is not fully understood yet. Rapid convective processes seems to inhibit the production and release of positive net energy. A problem is the limited frequency or shot-rate, three shots/day, desired rate is 100 shots/second, a three million times improvement is necessary!



 $M_{impl}$ ~6×10<sup>-6</sup>g

## Time-line 30-50 years



The general statement is that it takes 30-50 years towards reliable energy production by fusion, but the world cannot wait, the energy demand is growing exponentially! Nuclear fission is one of the existing options for bridging the time until a reliable fusion concept is developed!



#### Present concepts: ITER

LIFE



The assembly of fuel and moderator elements is an engineering problem towards optimized operation, safety, assembly, and disassembly for storage and recycling.

# Alternative fission reactions Nuclear Fuel Breeder



a neutron.

Breeding reaction converts U-238 to fissionable plutonium  $B^{e^-}$ 

Fissionable

 $n \equiv n$ 



### **Fission Process**



Fission product yields by mass for thermal neutron fission of <sup>235</sup>U, <sup>239</sup>Pu, a combination of the two typical of current nuclear power reactors, and <sup>233</sup>U used in the thorium cycle. The fission products are very neutron-rich and therefore highly radioactive and decay by  $\beta$  decay back to stability. Long-lived isotopes in the <sup>233</sup>U decay chains are: <sup>93</sup>Zr T<sub>1/2</sub>=1.5·10<sup>6</sup> y, <sup>137</sup>Cs T<sub>1/2</sub>=30 y;



Unit:	(a)	(%)	(keV)	
<sup>155</sup> Eu	4.76	0.0803	252	βγ
<sup>85</sup> Kr	10.76	0.2180	687	βγ
<sup>113m</sup> Cd	14.1	0.0008	316	β
<sup>90</sup> Sr	28.9	4.505	2826	β
<sup>137</sup> Cs	30.23	6.337	1176	βγ
<sup>121m</sup> Sn	43.9	0.00005	390	βγ
<sup>151</sup> Sm	96.6	0.5314	77	β
	Onit:     155Eu     85Kr     113mCd     90Sr     137Cs     121mSn     151Sm	Onit: (a)   155Eu 4.76   85Kr 10.76   113mCd 14.1   90Sr 28.9   137Cs 30.23   121mSn 43.9   151Sm 96.6	Onit:(a)(%)155Eu4.760.080385Kr10.760.2180113mCd14.10.000890Sr28.94.505137Cs30.236.337121mSn43.90.00005151Sm96.60.5314	Onit:(a)(%)(keV)155Eu4.760.080325285Kr10.760.2180687113mCd14.10.000831690Sr28.94.5052826137Cs30.236.3371176121mSn43.90.00005390151Sm96.60.531477

Heat

βν

Uranium fission and possible fission products in subsequent  $\beta^{-}$  decay processes along the isobaric lines towards stability. These decay chains originate from the primary fission product distribution.

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Long-lived fission products								
Prop: Unit:	t <sub>½</sub> (Ma)	Yield (%)	<b>Heat</b> (keV)	βγ				
<sup>99</sup> Tc	0.211	6.1385	294	β				
<sup>126</sup> Sn	0.230	0.1084	4050	βγ				
<sup>79</sup> Se	0.327	0.0447	151	β				
<u><sup>93</sup>Zr</u>	1.53	5.4575	91	βγ				
<sup>135</sup> Cs	2.3	6.9110	269	β				
<sup>107</sup> Pd	6.5	1.2499	33	β				
129	15.7	0.8410	194	β				

## The basic technical

### principles







The cooling water that also functions as moderator for neutrons circulates through the reactor core and carries the heat that is generated by the fission process away in a closed water cycle, heating water in a secondary cycle. The water in the first cycle is radioactive from fission products the water in the second cycle should not be radioactive unless a leak has occurred. The hot water or steam in the second cycle drives the turbine. The control rods are made of Boron containing material since Boron has a large cross section for neutron capture. If in place the released fission neutrons are absorbed and the chain fission reactions stops. But there is still substantial decay heat being released, which requires continuous cooling!

## **Reactor Generations**

Technical developments and safety concerns – sometimes even new physics results - drive the change in the different reactor generations from the early prototypes such as the pile to latest generation of reactors with high neutron flux to high energy out-put. A reactor life-time is 40-50 years, Public and political concerns often lead to administrative delays forcing the lifetime extension with consequences in aging and safety reduction.





#### The pressurized light water reactor



The PLWR is the present is the most used reactor type, developed at Oak Ridge and utilized for the nuclear submarine development under Admiral Rickover.



The <u>Light Water Reactor (LWR)</u> concept of water cooling seemed the obvious choice since water was available in large abundance. However, Rickover was also charged with the development of reactor types for peaceful applications (Atoms for Peace) and he continued with the same type despite the fact that it had more risk factors than other versions developed at Oak Ridge. The industrial military complex had started, since military requirements dictated the direction of civilian developments.

# Other reactor types with potentially far advanced features

- **Boron Reactor**: a-neutronic fusion reactor device based on the <sup>11</sup>B(p,2 $\alpha$ )<sup>4</sup>He reaction with little radioactive output from isotopic impurity <sup>10</sup>B(p, $\alpha$ )<sup>7</sup>Be(e<sup>-</sup> $\nu$ )<sup>7</sup>Li (T<sub>1/2</sub>=53 d). High intensity proton beam injected into a hot boron plasma in the magnetic confinement chamber
- Liquid Metal Reactor (LMR): uses liquid sodium of lithium as coolant and uranium and/or thorium as fuel elements with a different distribution of fission products. Production of radioactive <sup>24</sup>Na occurs by neutron capture, but <sup>24</sup>Na has only 15 h half life. No stable <sup>8</sup>Li!
- Molten Salt Reactor (MSR): the uranium fuel is dissolved in the sodium fluoride salt coolant which circulates through graphite core channels to achieve some moderation. Fission products are removed continuously and the actinides are fully recycled. A secondary coolant system is used for electricity generation.





Liquid Metal cooled Fast Breeder Reactors (LMFBR)



# **Thorium Reactor**

Special version of Molten Salt Reactor (MSR)

The thorium reactor uses <sup>232</sup>Th as fuel converting it by neutron capture to <sup>233</sup>U, <sup>232</sup>Th( $n,\gamma$ ) <sup>233</sup>Pr( $\beta$ - $\nu$ )233U which a fissile material. It removes the costs for the production and possible enrichment of <sup>235</sup>U as fission source.

The salts concerned as primary coolant, mostly lithium-beryllium fluoride and lithium fluoride, remain liquid without pressurization from about 500°C up to about 1400°C, in marked contrast to a PWR which operates at about 315°C under 150 atmospheres pressure.

The main MSR concept is to have the fuel dissolved in the coolant as fuel salt, and ultimately to reprocess that online. Thorium, uranium, and plutonium all form suitable fluoride salts that readily dissolve in the LiF-BeF2 (FLiBe) mixture, and thorium and uranium can be easily separated from one another in fluoride form. Batch reprocessing is likely in the short term, and fuel life is quoted at 4-7 years, with high burn-up. Intermediate designs and the AHTR have fuel particles in solid graphite and have less potential for thorium use

## **Most Valuable Resource**

# Շևորիակալություն