DE LA RECHERCHE À L'INDUSTRIE

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Plutonium chemistry and other actinides in aqueous solutions

Part 1

Actinide Familly

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FROM RESEARCH TO INDUSTRY

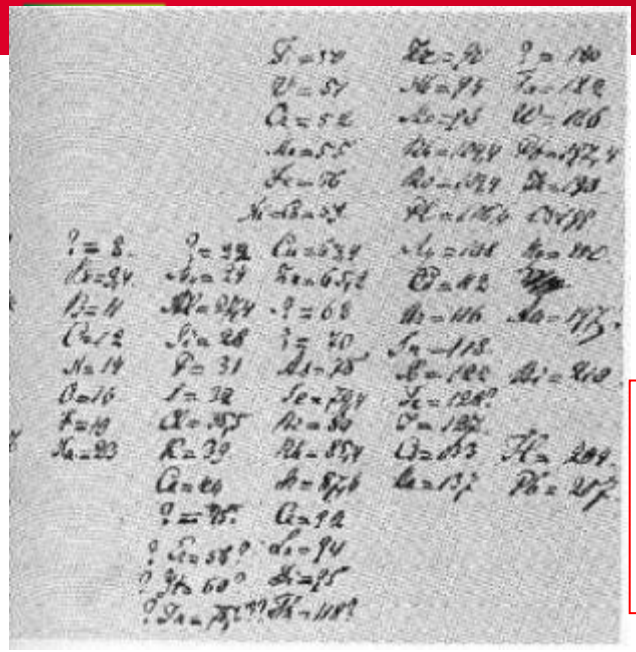
Aims of this course: Highlighting some points of Actinide Chemistry

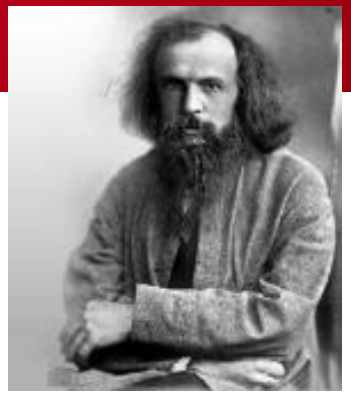
- Extreme variety (wealth) of the aqueous chemistry from Pa to Cm elements

- Existence of regularities in properties of actinide for ions with the same charge

- Fundamental properties of elements of practical importance

Actinide Family





Place of Actinide (An) Family in the Periodic Table of Mendeleev?

From Mendeleev (1869) to XXI century, via G.T. Seaborg (1945)

K	H																	He
L	Li	Be											B	C	N	O	F	Ne
M	Na	Mg											Al	Si	P	S	Cl	Ar
N	K	Ca	Sc							Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
O	Rb	Sr	Y							Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
P	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Q	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

Non métaux

Semi-métaux (métalloïdes)

Métaux

Lanthanides

Actinides

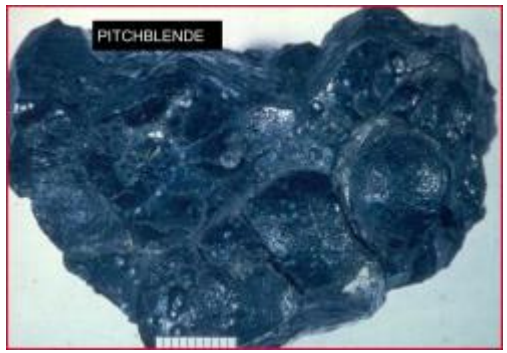
Historic events: 1789 « Chemistry »

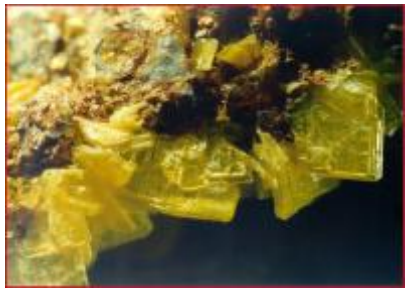
- Discovered in 1789 by the Prussian chemist Martin Heinrich Klaproth, by heating the pitchblende (uranium ore containing UO_2). He named "urane" the compound of uranium that was identified with reference to the discovery of the planet Uranus in 1781.

- In 1841, 50 years later, French Eugène-Melchior Péligot isolates the metal (by reducing UCl_4 with K metal as Berzelius applied before for $ThCl_4$) which he named Uranium.

Uranium is a natural element found in the earth's crust in various chemical forms, 17 isotopes, all radioactive and only three are present in nature

- **^{238} U : 99.28 %** **($T_{1/2}$= 4.5 10^9 yr)** **~ Earth formed 4.54 billion years ago**
- **^{235} U : 0.7180 %** **($T_{1/2}$= 0.7 10^9 yr)**
- **^{234} U : 0.0054 %** **($T_{1/2}$= 0.25 10^6 yr)**





Historic events: Discovery of Natural Actinide Elements « Chemistry » (1828 – 1902 – 1918)

Thorium (Z=90)

1827 - Thorium oxide was discovered by F. Wöhler in a Norwegian mineral

1828 – J.J. Berzellius characterized this material and isolated a new element: thorium (Th) after Thor, a mythological Norse god of thunder and lightening. (Berzelius applied reduction of $ThCl_4$ with potassium).

Actinium (Z=89)

1899 - the earliest discovery of actinium (Ac) is attributed to A. Debierne (from Curie Lab.). however, he never isolated actinium.

1902 - F. Giesel identified and isolated the element Ac in pitchblende. The name actinium is derived from 'aktinos' (Greek word for ray).

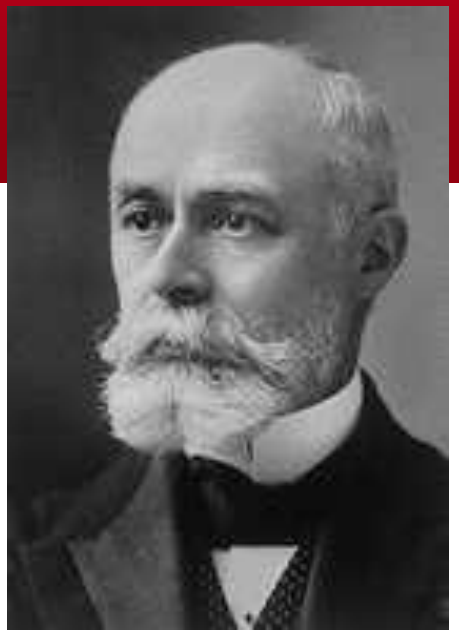
Protactinium (Z=91)

It is the rarest of the naturally occurring actinide elements (mother of Ac)

1913 – identified as short-lived isotope ^{234m}Pa (half-life 1.17 minutes) by K. Fajans and O. H. Goehring during their studies of the ^{238}U decay, and named brevium (latin for 'brief ').

1918 - O. Hahn and L. Meitner (Germany) renamed to "*protoactinium*" (Greek word 'protos' =first) (since 1949 (IUPAC) protactinium).

Historic events: 1896 « Radioactivity and Rays »



Discovery of radioactivity by H. Becquerel
« Natural Radioactivity »

Physicist working of phosphorescence

1896 : works on an uranyl sulfate sample

Experiment with a photographic plate

Nobel prize in physics with
P & M Curie in 1903

1895: Discovery of the “Röntgen“ rays

First radiograph of Bertha Röntgen’s hand

Historic events: 1898 « Analytical Chemistry and Physics Measurments »

1898 : Thesis work on the Becquerel rays

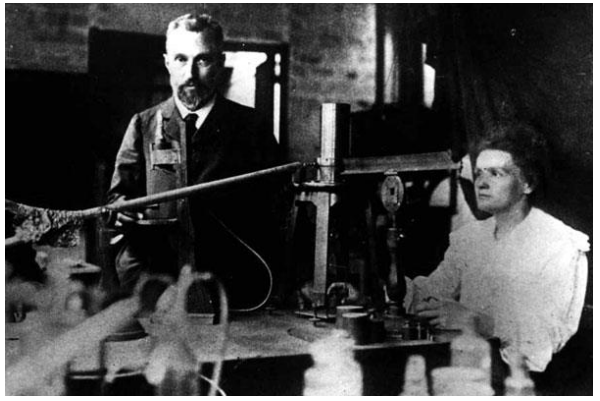
Marie Sklodowska-Curie

Occurrence of a material that is much more radioactive in pitchblende!

- From the pitchblende mineral one element close to Bismuth (around 100 μg/t!!): Polonium(Z=84)
- Second element close to Baryum: Radium (Z=88).

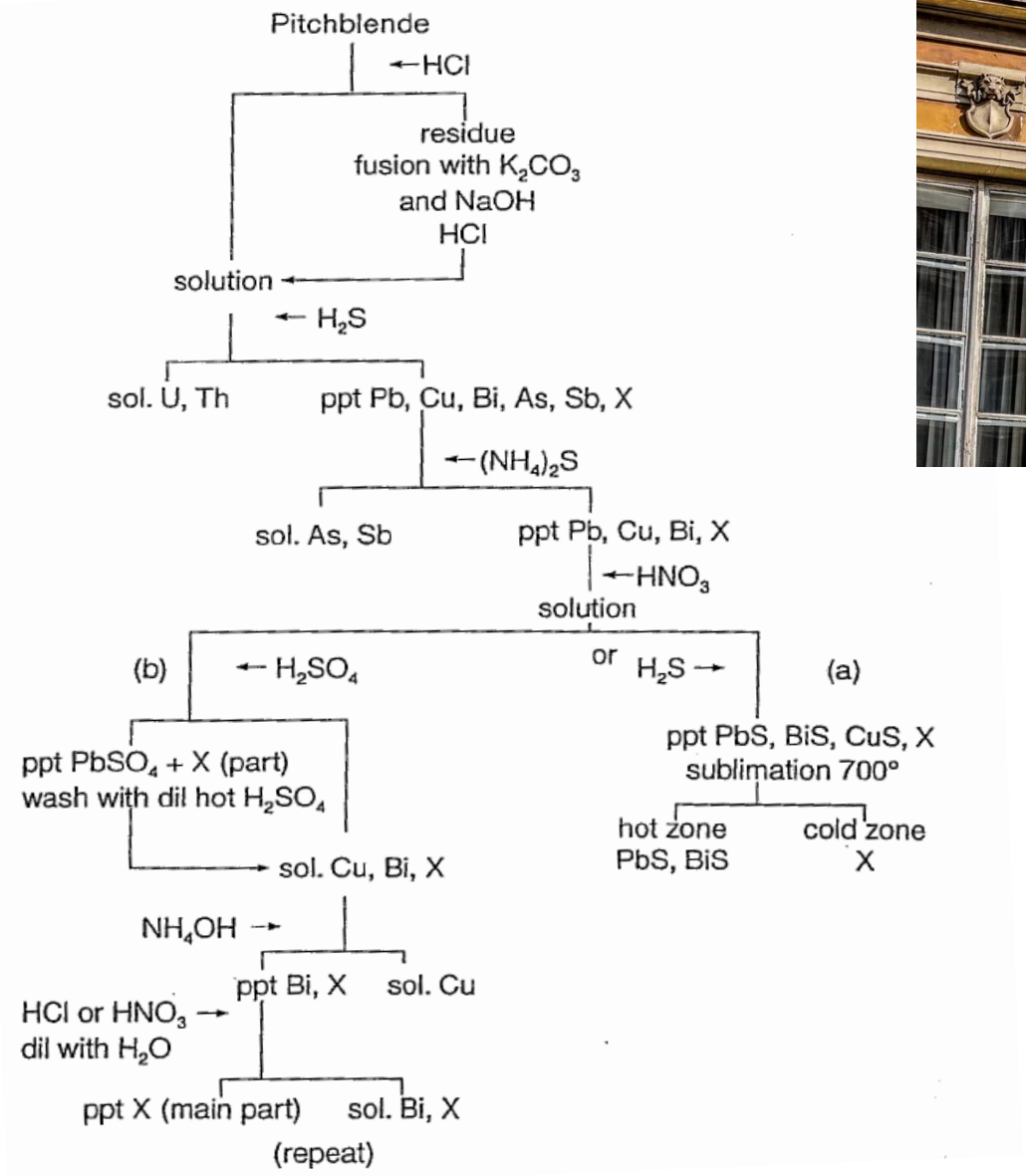
Nobel prize in chemistry in 1911

- **Separation by chemical means** (Analytival Chemistry).
- Residue measured with the **quartz piezo-electric balance** designed by P. Curie.



1883 : P. Curie; Physicist at ESCPI

Chemical separation of Po and Ra

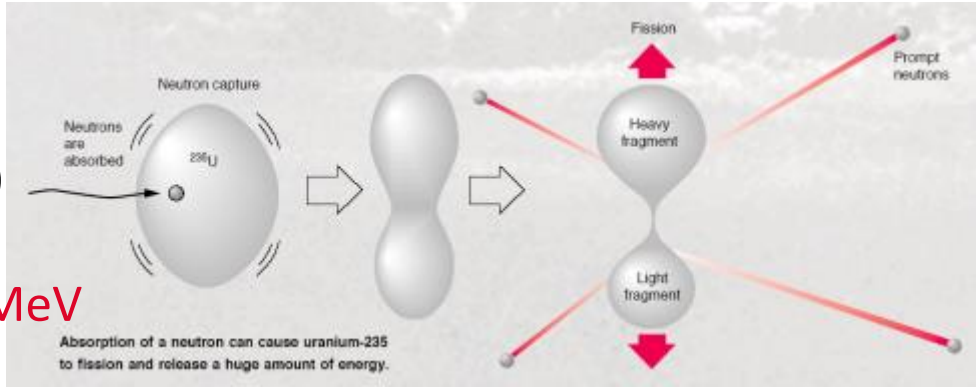


Historic events: 1939 « Transmutation »

1939: Many teams working on nuclear reactions with slow neutrons

- In Paris : I. & F. Joliot-Curie and P. Savitch
- In Berlin : O. Hahn (Chemistry Nobel prize in 1944), F. Strassmann and L. Meitner

In January (1939): O. Hahn discovers that the uranium nuclei produces baryum nuclei (Z=56) and not Ra (Z=88)

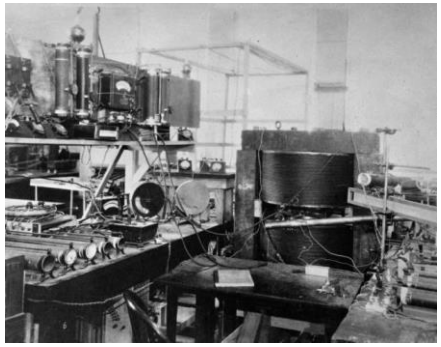


$^{235}U_{92} + {}^{1}n_0 \rightarrow {}^{144}Ba_{56} + {}^{89}Kr_{36} + 3\ {}^{1}n_0 + 200$ MeV

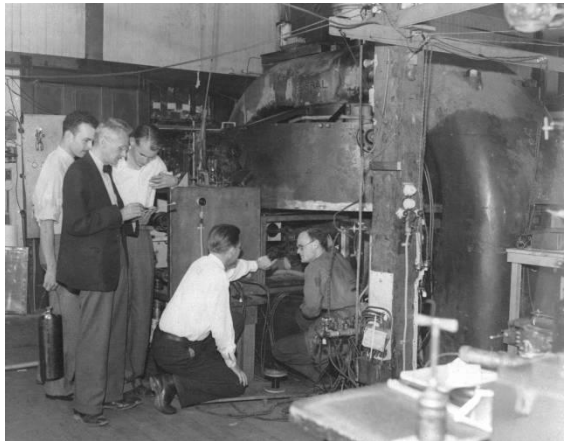
? $^{238}U + {}^{1}n \rightarrow \alpha + {}^{235}Th$ (Curiosum!)

$\rightarrow {}^{231}Ra + \alpha$ (Strassmann)

1931: First cyclotron built by Lawrence and Livingston (Berkeley Nat. Lab.) produce high energy particles (H+ ions at 80 keV) - Nobel prize for Lawrence in 1939



The 11-inch cyclotron installed in Room 329 Le Conte Hall



The 27-inch cyclotron

Historic events: 1935-1938 Bombardement of Uranium by Neutrons

In january 1939: For many scientists (including GT Seaborg) works O. Hahn, L. Meitner and F. Strassmann are clear: uranium is cut in half and the products formed leading to a radioactive release.

This is the fission of uranium!

To prove this, we need to identify the fission products (FP). Many teams will then engage in this work: Germany, France, England and the USA, especially E.M. McMillan in Berkeley with the 60-Inch Cyclotron.

F. Strassmann, L. Meitner and O. Hahn

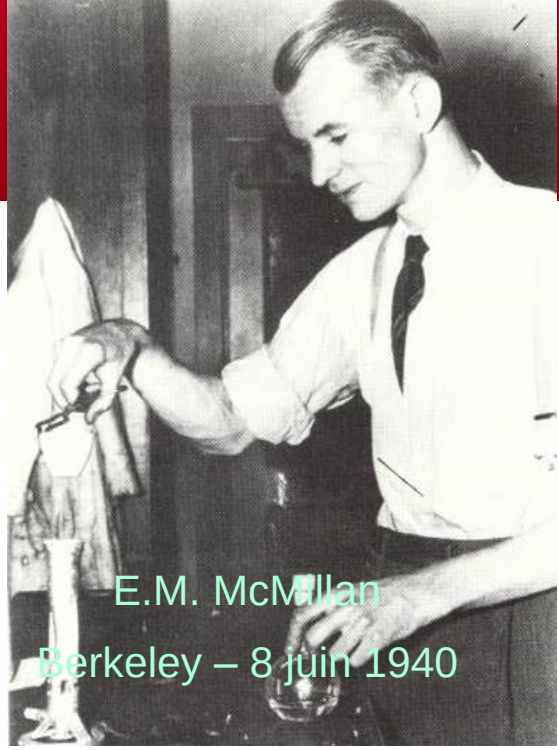
1956 (Mainz – Germany)

$_{93}$Eka-Re^{237}	$T_{1/2}$ = 16 min.
$_{93}$Eka-Re^{239}	$T_{1/2}$ = 2.2 min.
$_{94}$Eka-Os^{237}	$T_{1/2}$ = 12 h.
$_{94}$Eka-Os^{239}	$T_{1/2}$ = 59 min.
$_{95}$Eka-Ir^{239}	$T_{1/2}$ = 3 j.
$_{96}$Eka-Pt^{237}	$T_{1/2}$ = 3 h.

Historic events: 1939
« First artificial element »

Discovery of $^{239}Np_{93}$

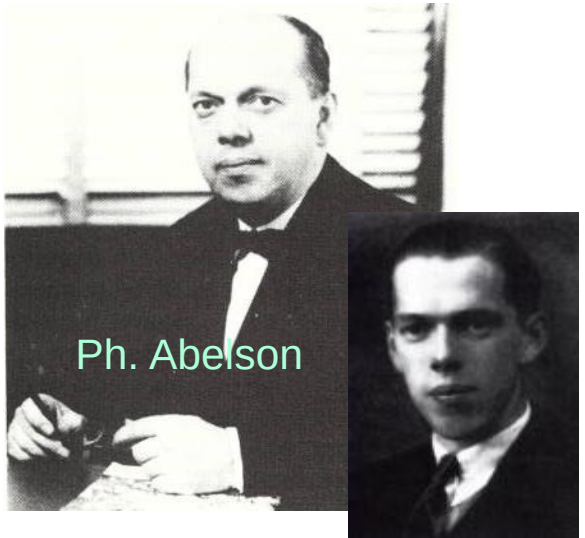
1939: During the study of the fission of uranium (uranium oxide on a cigarette paper) by neutrons (at Berkeley), E.M. McMillan and Ph. Abelson observe the following descent, using radioactivity measurements



$$^{238}U + {}^{1}n_0 \rightarrow {}^{239}U + \beta^- (23\ min.) \rightarrow {}^{239}Np_{93} + \beta^- (2.3\ j.) \rightarrow {}^{239}X_{94}$$

1940: Given the difficulties in identifying the $^{239}X_{94}$ elements (very long half!), a second synthetic route was considered, with deuterons produced by 60-inch/Berkeley but!!!:

$$^{238}U_{92} + {}^{2}d_1 \rightarrow {}^{238}X_{94} + ?$$



Historic events: 1951 Nobel prize

G.T. Seaborg

and

E.M. McMillan

Historic events: 1940 « Plutonium »

December 1940: irradiation of uranium (U_3O_8) by deuterons (60-Inch / Berkeley)

23/24 February 1941: G.T. Seaborg, A.C. Wahl and J.W. Kennedy: separation element $^{238}Pu_{94}$

1941: Production (with neutrons) and separation $^{239}X_{94}$ (G.T. Seaborg, A.C. Wahl, J.W. Kennedy and E. Segre). This isotope ($^{239}X_{94}$) is fissile (with thermal neutrons)!

$$^{238}U + {}^{2}d_{1} \rightarrow {}^{238}Np_{93} + 2\ {}^{1}n_{0}$$

$$^{238}Np_{93} \rightarrow {}^{238}Pu_{94} + \beta^{-}$$

The first plutonium separation from U and FP was performed after oxidation by persulfate ion catalyzed by silver II (Ag) (after discussion with W.M. Latimer!), followed by precipitation (by entrainment by the fluoride ion and the fluoride of La « carriers ») and finally the conversion into dioxide PuO2

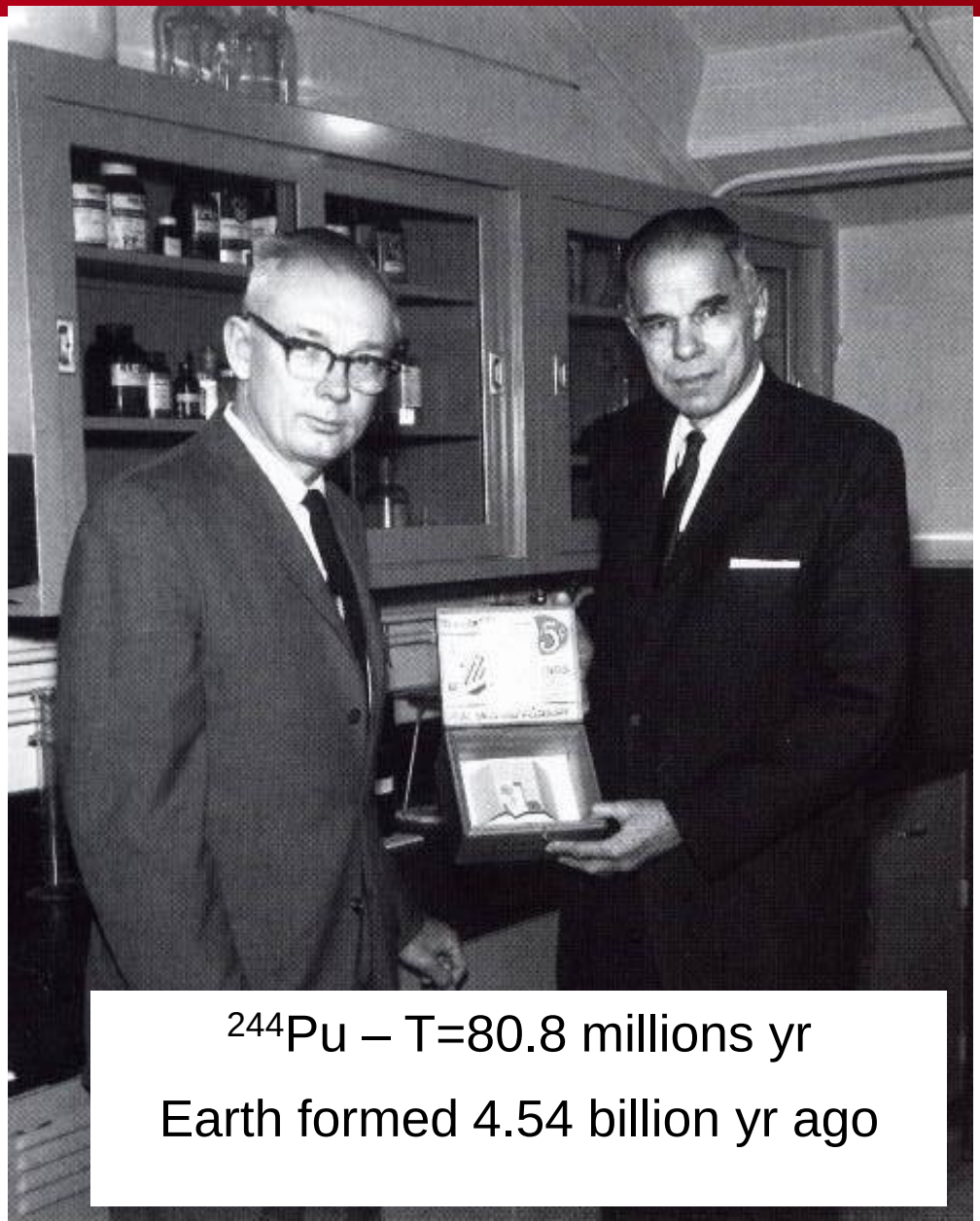
Purification of plutonium

A.C. Wahl et G.T. Seaborg

^{239}Pu – cigare box

« Room 307 »

Gilman Hall - Univ. Berkeley)



^{244}Pu – T=80.8 millions yr

Earth formed 4.54 billion yr ago

Separation Sciences for Plutonium

August 20, 1942; 1 µg Pu (under microscope) as PuO_2 (separation "redox cycle" + precipitation PuF_4 before thermal conversion to PuO_2)

September 1942: Engineers Du Pont come with the goal of industrial adjustment.

The first method used on the Hanford site will be precipitation of bismuth phosphate + Redox (considering the corrosion problems with fluoride ions)

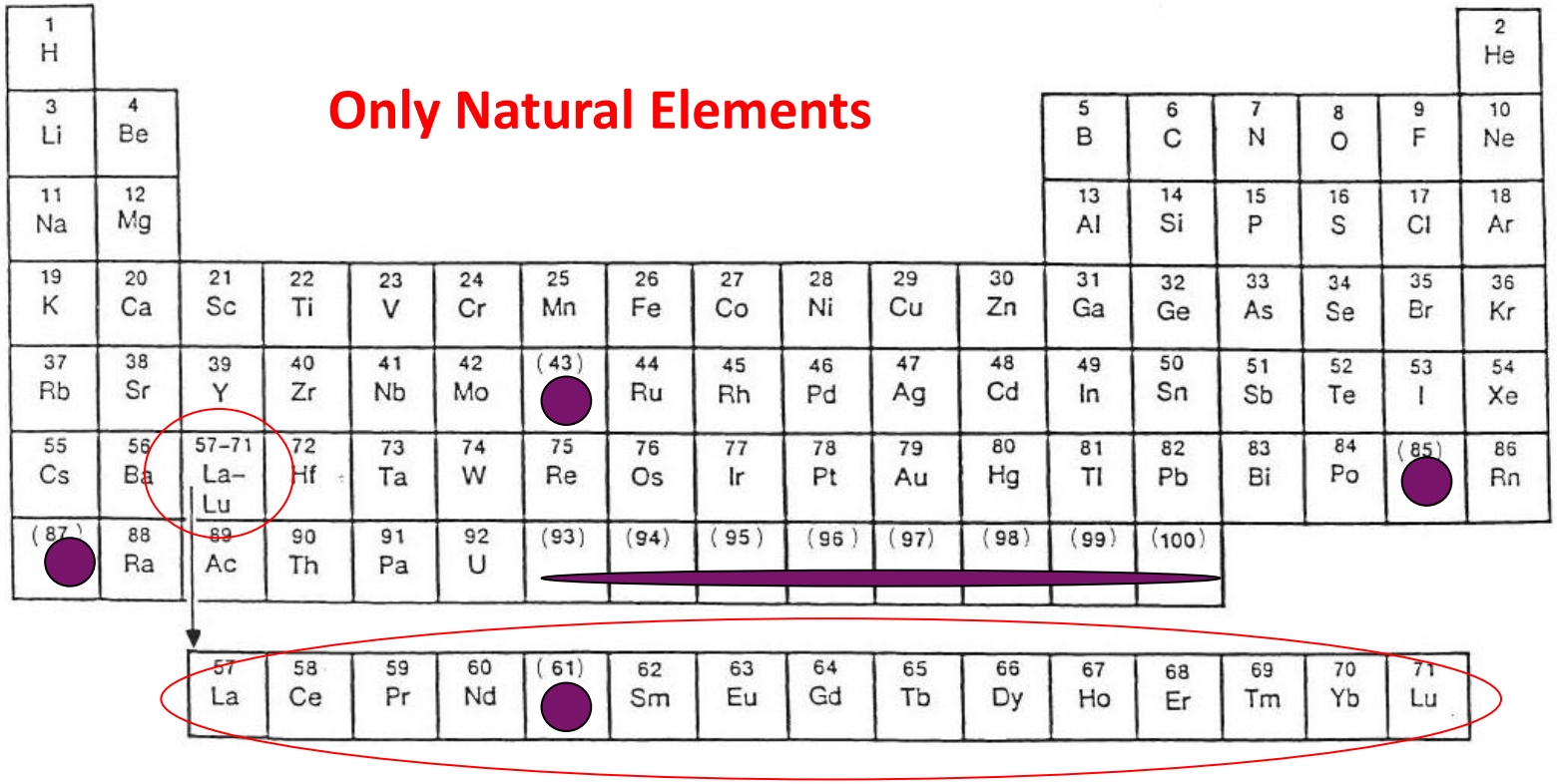
$$(Pu^{4+} + U^{4+}) + NaBiO_3 \rightarrow (PuO_2^{2+} + UO_2^{2+}) + Bi^{3+}$$

$$(PuO_2^{2+} + UO_2^{2+}) + NaNO_2 + PO_4^{3-} \rightarrow BiPO_4(Pu(IV))_{ppt} + UO_2^{2+}$$

ppt (precipitate = "physical" and "chemical" ($Pu_3(PO_4)_4$, $Pu(HPO_4)_2$, $Pu(H_2PO_4)_4$, ...)

This process will be replaced in 1952 by HEXON process (MIBK extractant – CH_3-CO-CH_2-$CH(CH_3)_2$) and then completely abandoned in 1957

The Mendeleev Table before second world war



Discovery of the “rare earth“ (Sc, Y, La-Lu) from 1803 (Ce) to 1947 (Pm)

Discovery of the actinides (Ac - Lr): from 1789 (U) to 1971 (Lr)

The Th_{90}, Pa_{91} and U_{92} elements are elements "6d“ therefore the elements 93, 94, ... will also "6d“ situated below the elements Re, Os, Ir, ...

Formation of Transuranic Elements in Nuclear Fuel or Nuclear Weapons Material