Actinides – The Basics

LISA Specialized Training 1 – JGU Mainz

Christoph E. Düllmann (JGU Mainz / GSI Darmstadt / HIM Mainz)

LASER IONISATION AND SPECTROSCOPY OF ACTINIDES

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The Actinides in the Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The Actinides in the Periodic Table of the Elements

The Actinides:

The actinide series of elements encompasses all the 15 chemical elements that have properties attributable to the presence of low-lying 7p, 6d, and 5f orbitals such that their tri-positive ions have electronic configurations $7p^0 6d^0 5f^n$, where n = 0,1,2,. . .,14.

From textbook by Morss, Edelstein & Fuger

→ colloquially: „in the actinides, the 5f-shell is filled“

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Actinium (Ac, element 89) – discovery

1899: Debierne (in the Curie's laboratory):

reports finding of a new radioactive substance, with chemical similarity to Ti.
Six months later: Ti fraction no longer very active; radioactive material he was now recovering showed chemistry similar to Th.

→ Claims right of discovery; name "actinium" (aktis, ray).

(Was accepted uncritically at the time, but, with today's knowledge, it is clear that his 1899 preparation contained no actinium at all!)

1902: Giesel

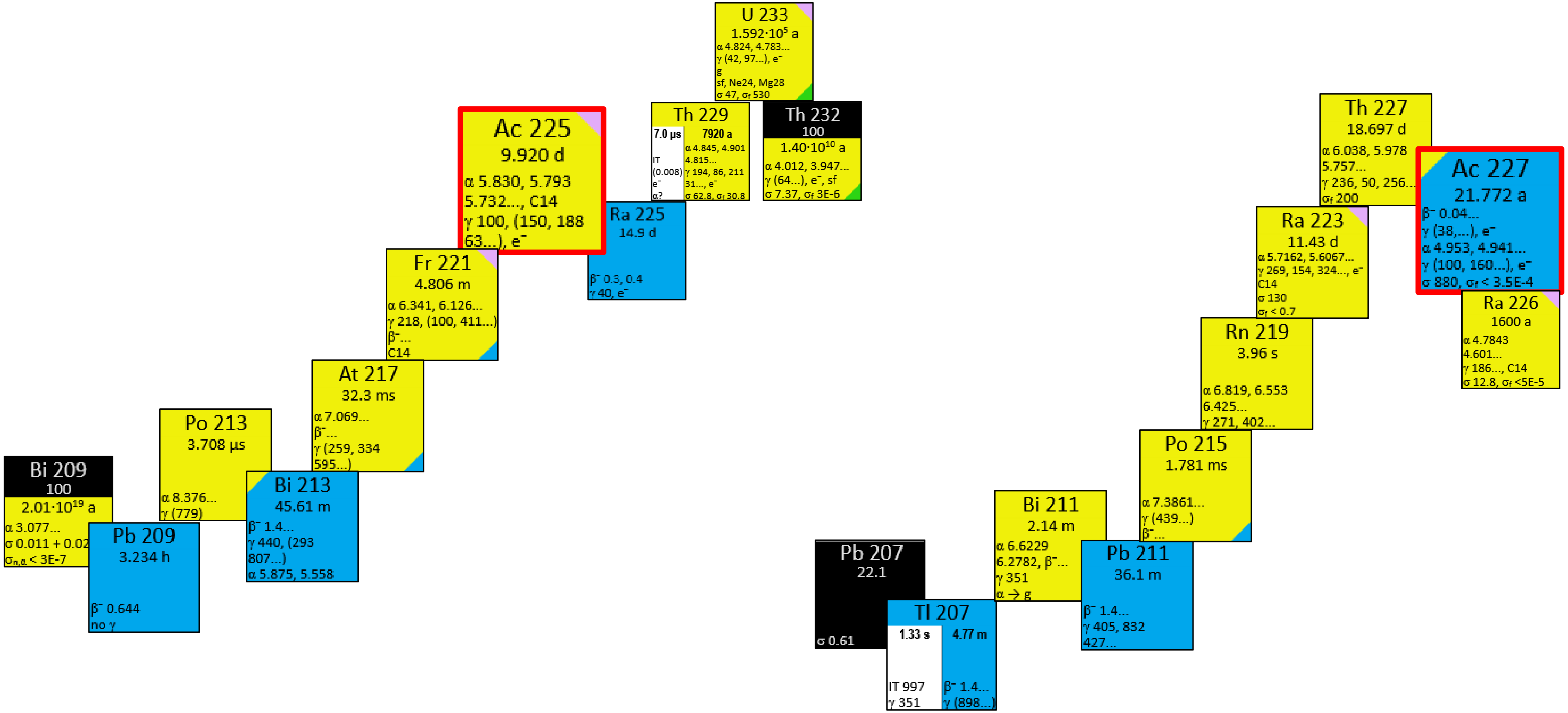
reports new 'emanation-producing' substance among impurities separated with Ra from pitchblende residues.
Establishes many chemical properties correctly.

→ After further purification work, he proposes name "emanium" in 1904.

Debierne vigorously attacks Giesel. Debierne's claim prevailed, and has been propagated by historians, largely because of the prestige of the Curies and the support of Rutherford.

Actinium (Ac, element 89) – applications

Chemistry of Ac large similar to that of La



Thorium (Th, element 90)

1815: Berzelius

Analyses a rare earth mineral from Falun. Assumes this to contain a new element

→ name "thorium" (ancient Scandinavian god of thunder and weather, Thor)

10 years later: mineral turned out to be xenotime (yttrium phosphate)

1828: Berzelius

was given a mineral by Reverend Hans Morten Thrane Esmark.
In there, Berzelius really discovered a new element; gave it the same name.

Mineral from which he isolated the new element named thorite;
contains significant amounts of U → $(Th,U)SiO_4$.

ThO_2 is a high-temperature resistant; from 1895 on used in incandescent gas mantle (gas lamps) etc. (now mostly replaced by Y-containing mantles)

https://www.wikiwand.com/de/Glüstrumpf

1898: Radioactivity of Th recognized

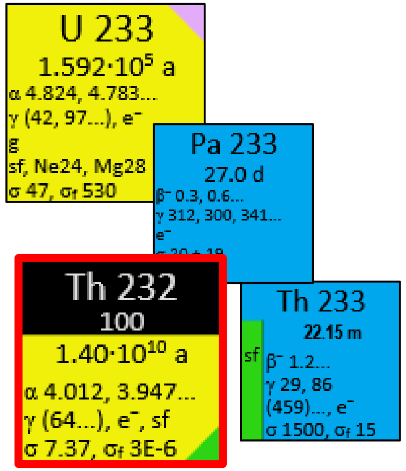
Thorium (Th, element 90)

Natural occurrence:

in various minerals, in monazite sand (contains up to 20% Th, up to 450 kBq/kg).
Natural radioactivity in Iran in rooms from local building materials >100 mSv/a.

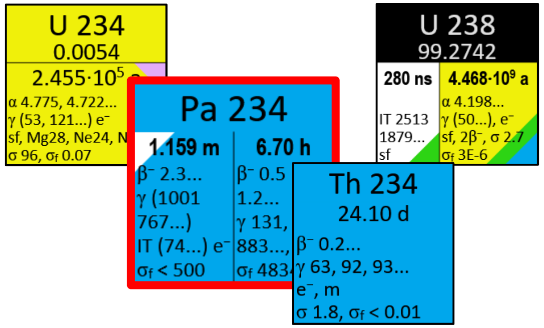
Often associated with Zr, is not separated from it during Zr extraction.

Chemistry: typically 4-valent. Most important compound: ThO_2.



Potential basis of Th-based nuclear reactors, burning ^{233}U as alternative to ^{235}U; these have not yet gained acceptance. However, Th inventories are significantly larger than ^{235}U inventories.

Protactinium (Pa, element 91)

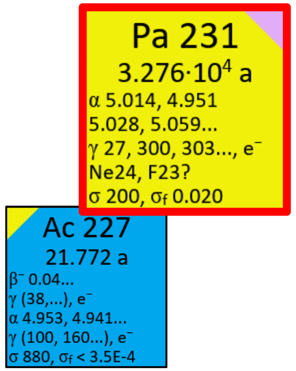


1913: Fajans and Göhring:

Discovery of ^{234m}Pa during search of missing β^--emitter connecting ^{238}U with ^{234}U.

Half-life ~1 min

→ Half-life ~1 min: name "brevium".



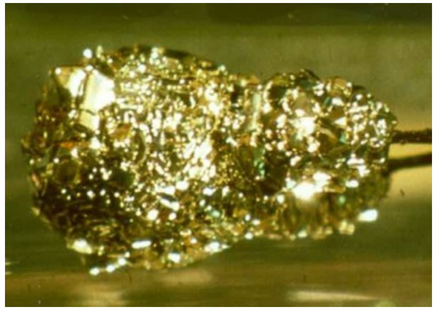
1918: Soddy and Cranston; almost contemporaneously Hahn and Meitner:

Identification of the precursor of ^{227}Ac: ^{231}Pa. Origin (from yet unknown ^{235}U) was unclear.

→ Half-life >1200 a: "brevium" inappropriate. Name: "prot(o)actinium".

1927: first isolation of weighable amounts (2 mg) by Grosse

1949: IUPAC fixes the name as "protactinium"



(wikipedia)

Chemical properties: stable 5+ oxidation state, differs from homolog Pr (3+).
Resembles Ta more closely; also its neighbors Th and U.
No current applications

Uranium (U, element 92)

In use as a colorant since Roman times

1789: Klaproth

discovers U to be constituent of pitchblende

→ Named after planet Uranus (discovered 1781)

This itself was named after the Greek deity of the Heavens

The name for the planet was commonly used only after ~1850

1896: Becquerel discovers radioactivity

Uranium keywords:

-natural reactors in Oklo, Gabon

-application as nuclear fuel; isotopics $^{235}U/^{238}U$

-range of U at current consumption rates (20-200 a)

-chemistry: dominant oxidation states 1+ – 6+; importance of UO_2^{2+})

-proliferation of ^{235}U

-reprocessing, nuclear waste disposal…

Abundances of the natural actinides in the Earth's crust

$_{89}Ac$	$6 \cdot 10^{-14}$ %
$_{90}Th$	10^{-3} %
$_{91}Pa$	$9 \cdot 10^{-11}$ %
$_{92}U$	$3 \cdot 10^{-4}$ %

In sea water: 3 mg/m^3, total $4 \cdot 10^9$ t

for comparison:

$_{8}O$	49.4 %
$_{2}He$	$4 \cdot 10^{-7}$ %
$_{79}Au$	$5 \cdot 10^{-7}$ %

RESEARCH

Science

NUCLEAR ASTROPHYSICS

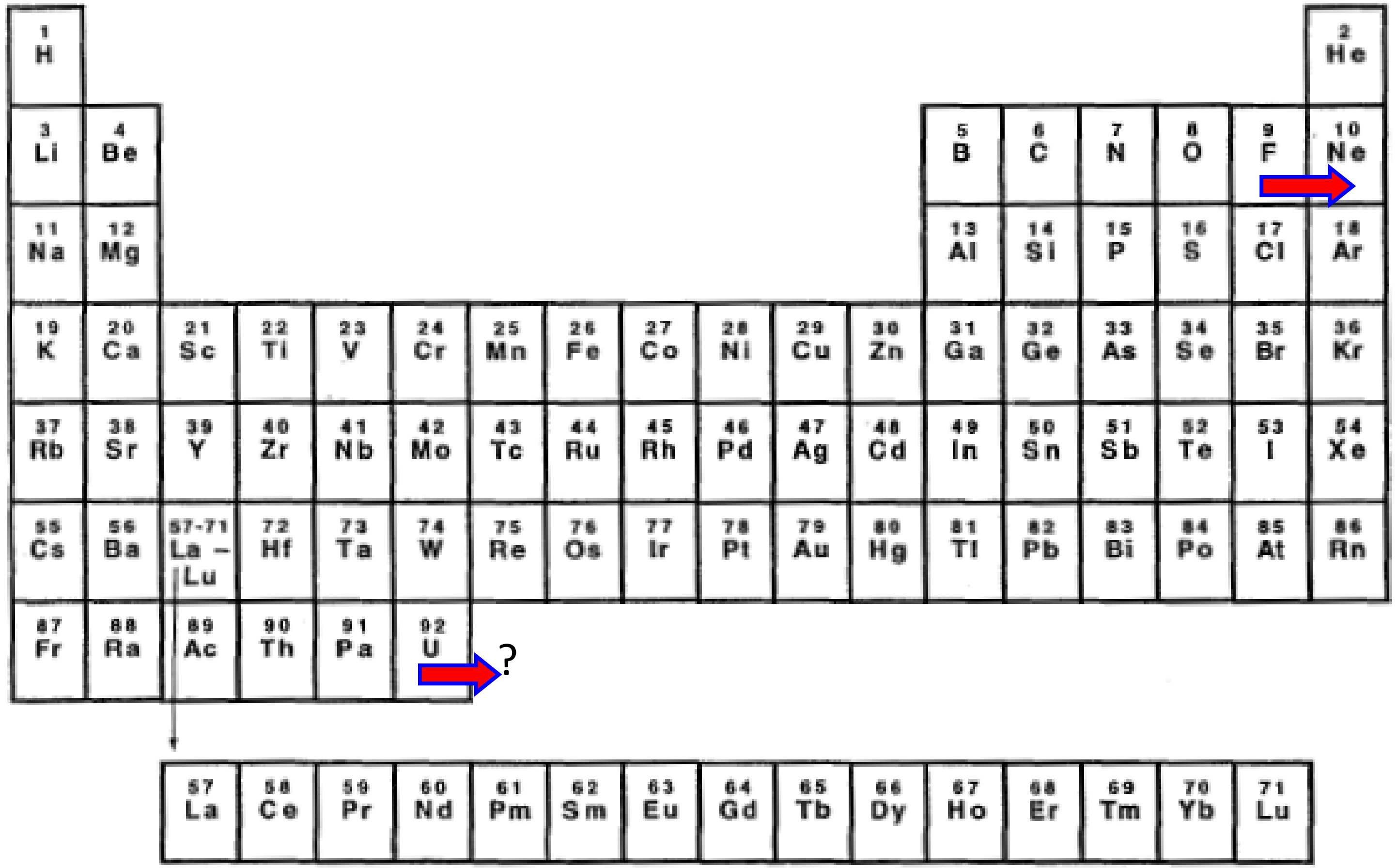
^{60}Fe and ^{244}Pu deposited on Earth constrain the r-process yields of recent nearby supernovae

A. Wallner[1,2]*, M. B. Froehlich[1], M. A. C. Hotchkis[3], N. Kinoshita[4], M. Paul[5], M. Martschini[1]†, S. Pavetich[1], S. G. Tims[1], N. Kivel[6], D. Schumann[6], M. Honda[7]‡, H. Matsuzaki[8], T. Yamagata[8]

Wallner *et al.*, *Science* **372**, 742–745 (2021)

„The averaged extraterrestrial ^{244}Pu incorporation rate was (71 ± 8) and $11.5^{+7.8}_{-5.8}$ atoms cm^{-2} Myr^{-1} for 0 to 4.6 Ma and 4.6 to 9 Ma, respectively

The beginning of the search for transuranium elements



$^{19}F+n$
$\rightarrow {}^{20}F$
$\beta^{-}\rightarrow {}^{20}Ne$

G.T. Seaborg, J. Radioanal. Nucl. Chem. 203 (1996) 233

The misleading trail…

Irradiating U with neutrons produces a wealth of β-decaying isotopes!

Publication of a multitude of "decay chains of transuranium elements", e.g:

$_{92}$U	$_{93}$Eka-Re	$_{94}$Eka-Os	$_{95}$Eka-Ir	$_{96}$Eka-Pt	$_{97}$Eka-Au
10 sec →	2,2 min →	59 min →	66 h →	2,5 h →	?
40 sec →	16 min →	5,7 h →	60 d →	?	
23 min →	93 ?				

O. Hahn, L. Meitner, F. Strassmann, Juli 1938

55 Cs	56 Ba	57-71 La – Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	(93)	(94)	(95)	(96)	(97)	(98)

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy

Already in his letter of Dec. 19, 1938, Otto Hahn writes to Lise Meitner: „there could be another most strange coincidence. But more and more we come to the terrible conclusion: our Ra isotopes do not behave like Ra but like Ba. … Maybe you can suggest some fantastic explanation. We know ourselves that it *cannot* actually burst into Ba. Now we want to check whether Ac isotopes formed from Ba do not behave like Ac but like La.“

Answer L. Meitner: „the idea of bursting is very difficult to accept. Are highter transuranics excluded?“

….that led to the discovery of the fission process

Hahn in a letter to Meitner (Dez. 1938)

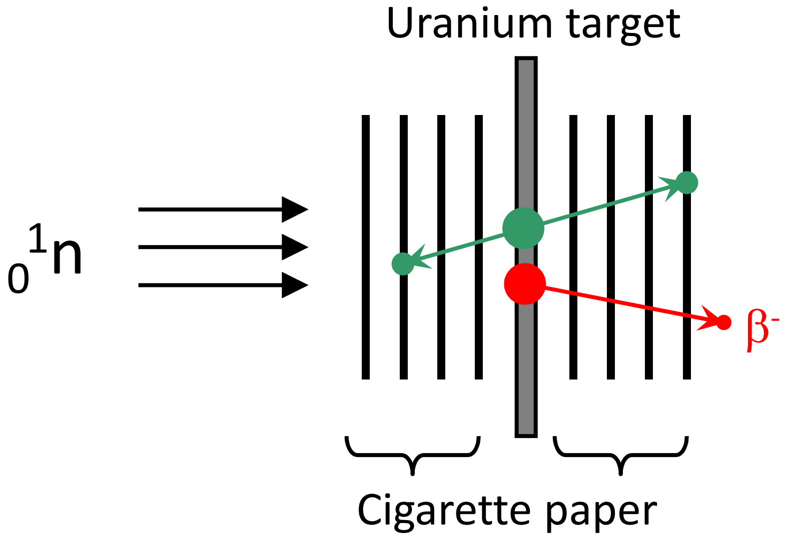
“According to our Ra-evidence, we conclude that as chemists we must conclude that the three studied isotopes are not Ra at all but are Ba from the chemist's point of view. Also the Ac resulting from the isotopes is not Ac, but obviously La!”

“As chemists, based on our briefly described experiments, we should actually rename the above scheme and – instead of Ra, Ac, Th – should use the symbols Ba, La, Ce. As ‘nuclear chemists’ who are in a certain way close to physics, we cannot yet decide to make this leap, which contradicts all previous experiences in nuclear physics.”

Hahn et al., Naturwissenschaften 27 (1933) 11-15

Studies of fission fragments

Experimental setup of E. Segrè:



Studies of the radioactivities in the cigarette paper and in the target.

Resultat: identical in most aspects, but the main activities of the target are missing in the cigarette paper: one activity with 23 min half-life and one with 2.3 d half-life.

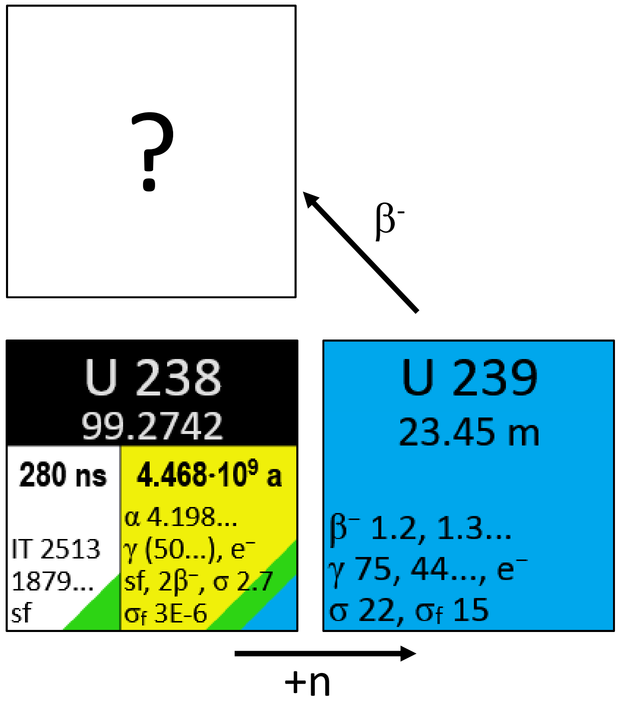
Segrè about his "cigarette paper" experiments

An Unsuccessful Search for Transuranic Elements

The nonrecoiling activity showed practically only two periods, the uranium [...] and a 2.3-day period due to a rare earth. This second chemical identification is shown by the fact that this activity does not precipitate with hydrogen sulfide in 6*n* or 0.3*n* hydrochloric acid [...] using rhenium [...] as a carrier, that it is precipitated from acid solution by hydrofluoric acid or oxalic acid with lanthanum as a carrier, [...]

On the other hand, the 23-minute uranium must decay into a substance with atomic number 93, hence a search was made for an alpha-emitter.

A sample showing very strong β-activity due to the 23-minute period showed no alpha-activity [...].



The necessary conclusion seems to be that the 23-minute uranium decays into a very long-lived 93 and that *trans-uranic elements have not yet been observed.*

E. Segrè, Phys. Rev. 55 (1939) 1104

Neptunium (Np, element 93)

McMillan discovers the wrong interpretation of Segrè.

Chemistry of Np resembles that of U, but not that of Re!

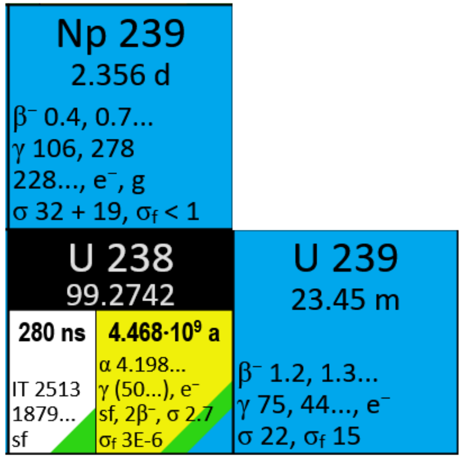
Repeats the cigarette paper experiments, finds activities in the first three sheets. The decay properties are similar for the three sheets.

In uranium: an additional 23-min activity and a further, very strong ~2-day activity

23 min nuclide: ^{239}U, was known from the n,γ-reaction with ^{238}U

2 d nuclide: because the ratio of the two activities is always identical, these must be genetically linked.

Therefore, the 2-day activity should be ^{239}Np (β^- daughter of ^{239}U).



Neptunium (Np, element 93)

Abelson + McMillan:

repeated separation of freshly ingrowing activity from the decay of 23-min ^{239}U proofs element 93

Radioactive Element 93

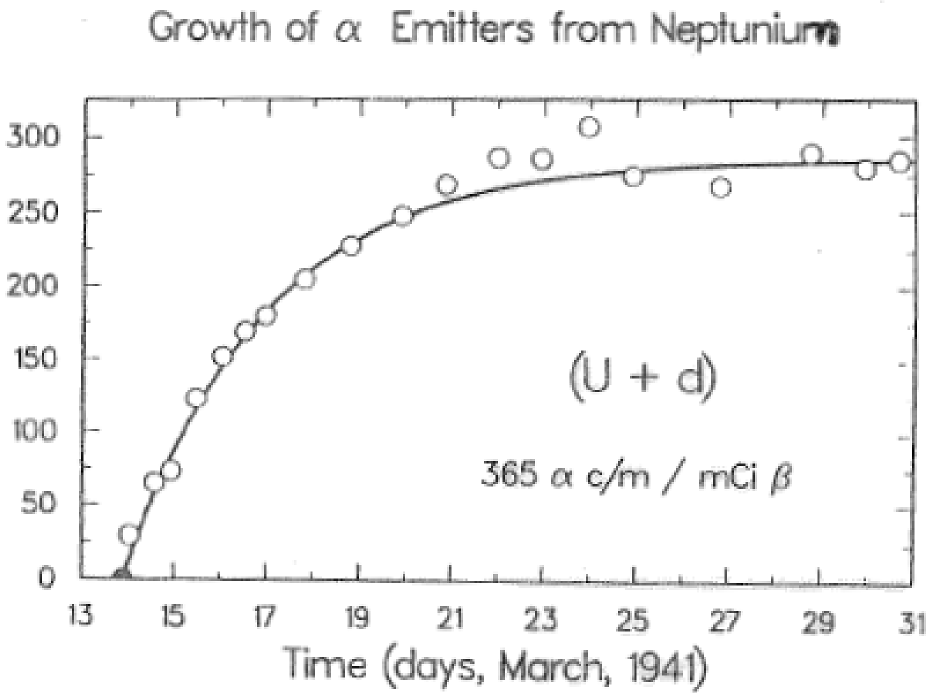
It is interesting to note that the new element has little if any resemblance to its homolog rhenium; for it does not precipitate with H_2S in acid solution, is not reduced to the metal by zinc in acid solution, and does not have an oxide volatile at red heat. This fact, together with the apparent similarity to uranium, suggests that there may be a second "rare earth" group of similar elements starting with uranium.

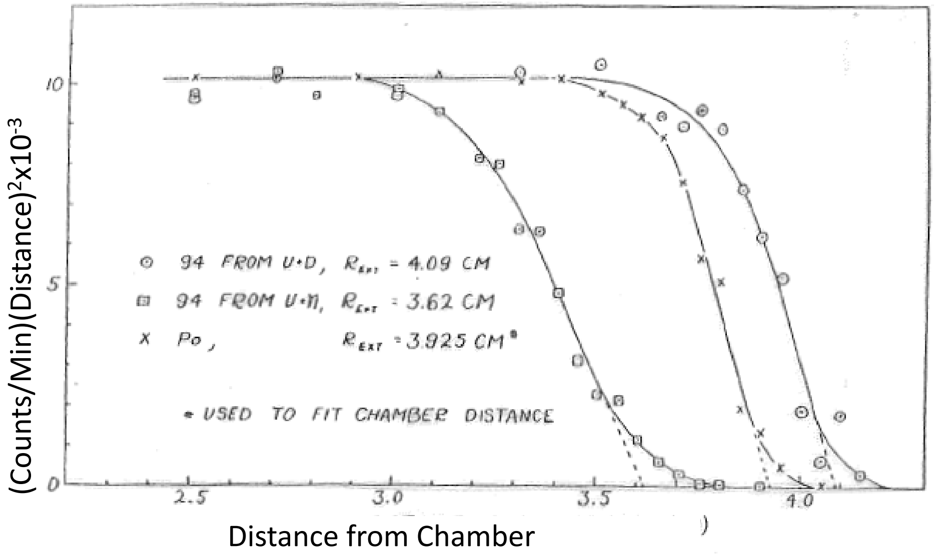
E. McMillan + P.H. Abelson, Phys. Rev. 57 (1940) 1185

Plutonium (Pu, element 94)

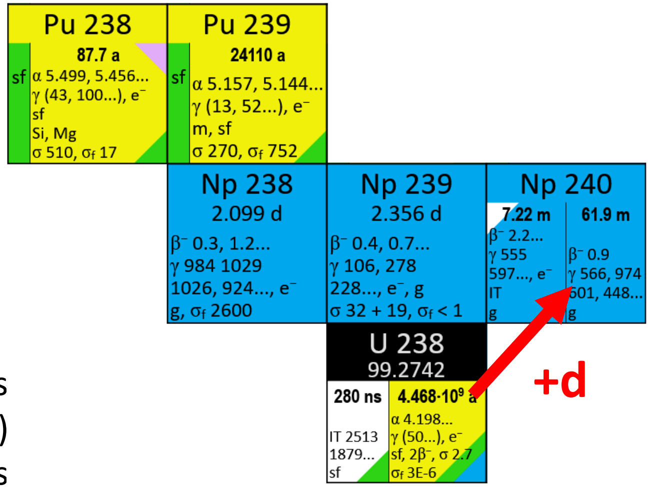
1) McMillan searches for the daughter of 2.3 d ^{239}Np $\rightarrow$ No success ($T_{1/2}$(^{239}Pu): 24'000 a)

2) A.C. Wahl: U irradiation with d, chemical Np isolation ($^{238/239}$Np), hoping that another isotope than the unidentifiable ^{239}94 will be produced. Finds an ingrowing α-emitter (^{238}Pu, $T_{1/2}$ ~50 a)





Absorption by air of alpha particles from plutonium that was produced by irradiating uranium with neutrons (U+n, ^{239}Pu) and with deuterons (U+D, ^{238}U), compared to alpha particles from ^{210}Po (Po).



Chemistry is similar as that of Th and U, but not Os (no volatile tetroxide)

$\rightarrow$Eka-Os is not a suitable name. Proposed name: "Plutonium"

A.C. Wahl, PhD Thesis, Berkeley, 1942

Chemistry of Pu

-$^{238}U(p,n)^{238}Np$
-Np-separation
-^{238}Pu grows in
→chemical studies

1) Cannot be oxidized with BrO_3^- (as Np can), but only with $S_2O_8^{2-}$
2) In oxidized state: does not co-precipitate with LaF_3 (almost no α's in precipitate).
LaF_3 co-precipitates 3-/4-valent species.
3) Reduction with SO_2, Br^-, Mn^{2+}, or (as shown in the schematic on the right) via evaporation to dryness. SO_3-fumes indicate complete absence of $S_2O_8^{2-}$; thus, Pu is reduced to Pu(IV).

Now, 94 co-precipitates with LaF_3
→ Preparation of very clean samples possible

Separation of the Alpha Emitter from LaF_3
(February 23 & 24, 1941)

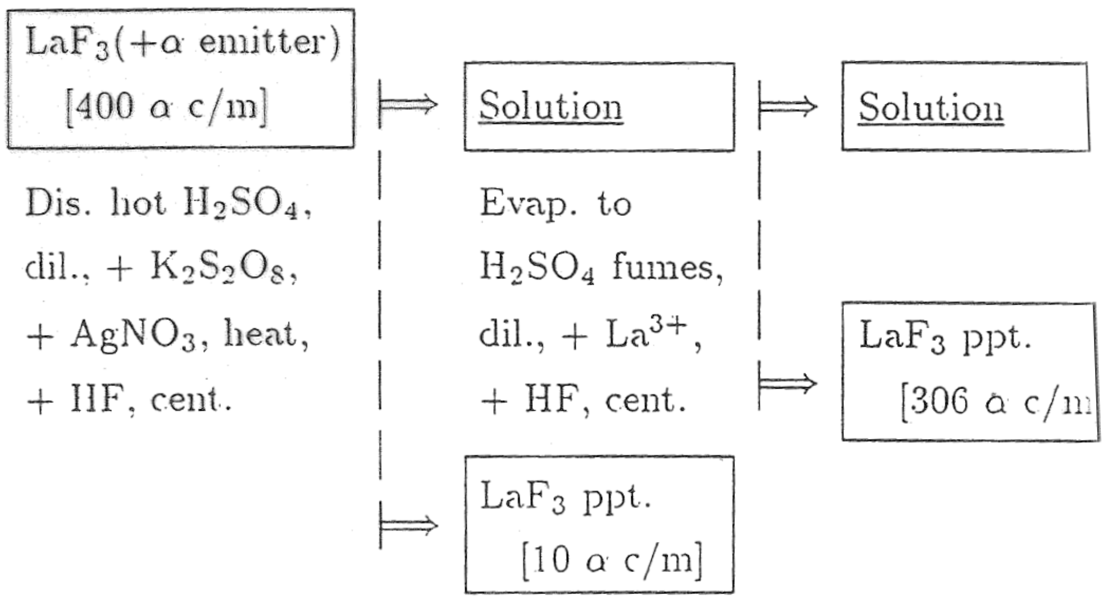


FIGURE 3
Diagram of the chemical procedure used for separating the alpha emitter from lanthanum fluoride, showing that the alpha emitter had different chemical properties than the rare-earth-like elements and thorium. The alpha radioactivities are shown in brackets for the several chemical fractions measured; the activities were measured as counts/minute (c/m) with a screened-window ionization chamber connected to a linear amplifier.

A.C. WAHL

Movie: Glenn Seaborg about plutonium

Movie 1: Pu

The path to the Pu bomb

About 1941: hardly any more American publications on Pu (these were submitted to Phys. Rev. but published only in 1946).

($\rightarrow$This made the Russians, especially G.N. Flerov, suspicious).

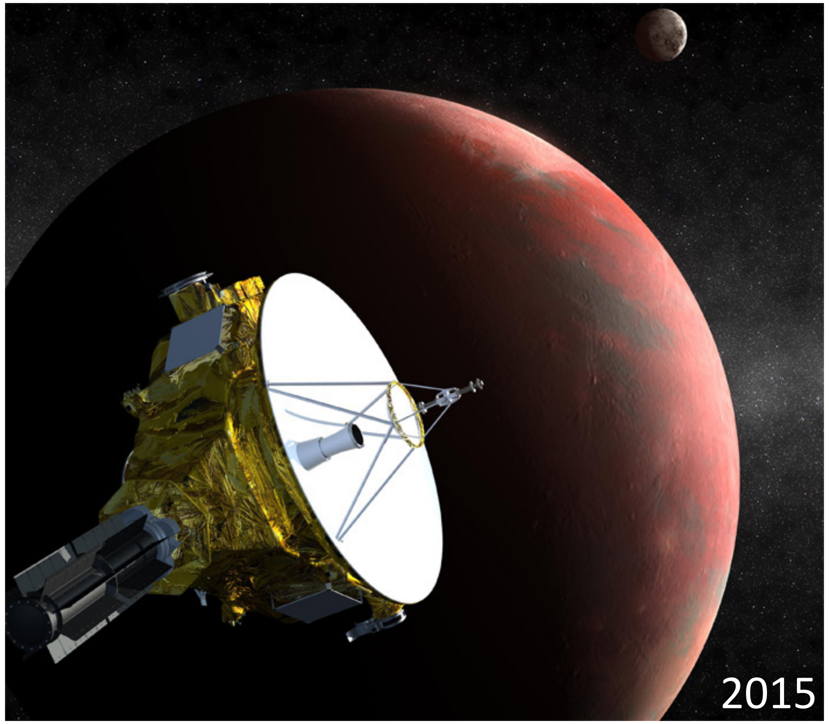
The path to the atomic bomb seemed to be via enrichment of ^{235}U or via the mass production of ^{239}Pu. In August 1941, the first amount of ^{239}Pu visible to the naked eye was obtained by cyclotron irradiation.

On December 2, 1942, the first controlled chain reaction occurred in a reactor in Chicago (Fermi and Co.), opening the way to mass production of Pu. Beginning in December 1944, Pu was separated at Hanford. By the summer of 1945, enough material had been separated for a Pu bomb, which was detonated as the "Trinity" test at Alamogordo (New Mexico, USA).

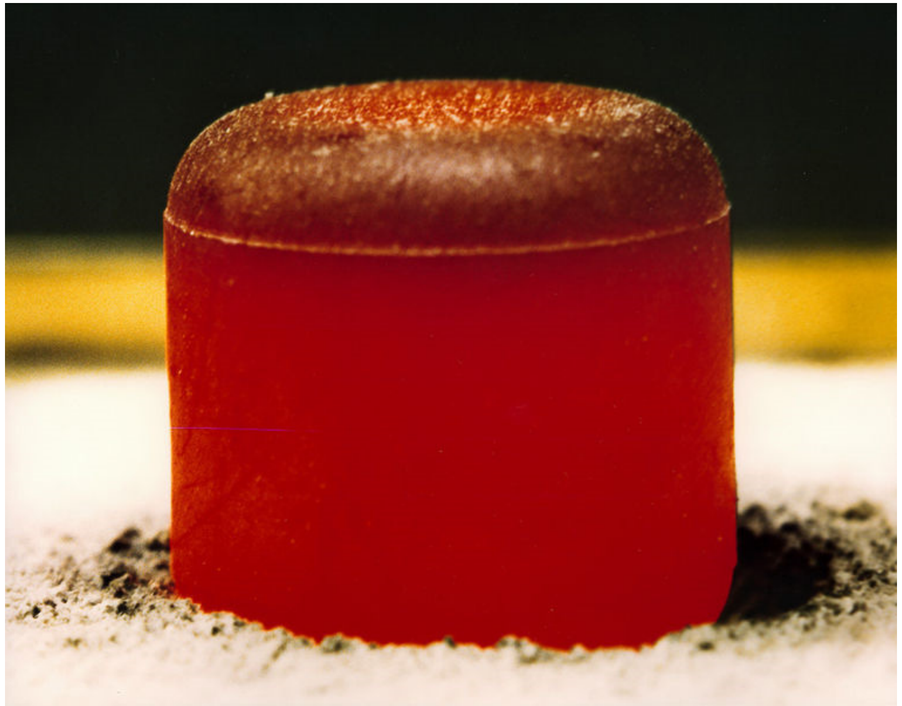
06 August 1945: Bomb on Hiroshima (^{235}U)

09 August 1945: Bomb on Nagasaki (^{239}Pu)

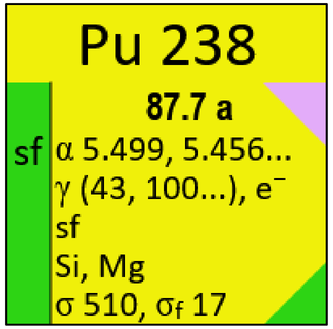
The present: harvesting Pu power to travel the solar system



“New Horizons” at Pluto
200 W power from 11 kg ^{238}Pu
radioisotope thermoelectric
generator (RTC)
aka „radioisotope battery“



One ^{238}Pu pellet generating 62 W.
It is glowing red due to heat from
radioactive decay



https://rps.nasa.gov/missions/7/new-horizons/
https://en.wikipedia.org/wiki/Actinide

Back to 1944: the uranid-series

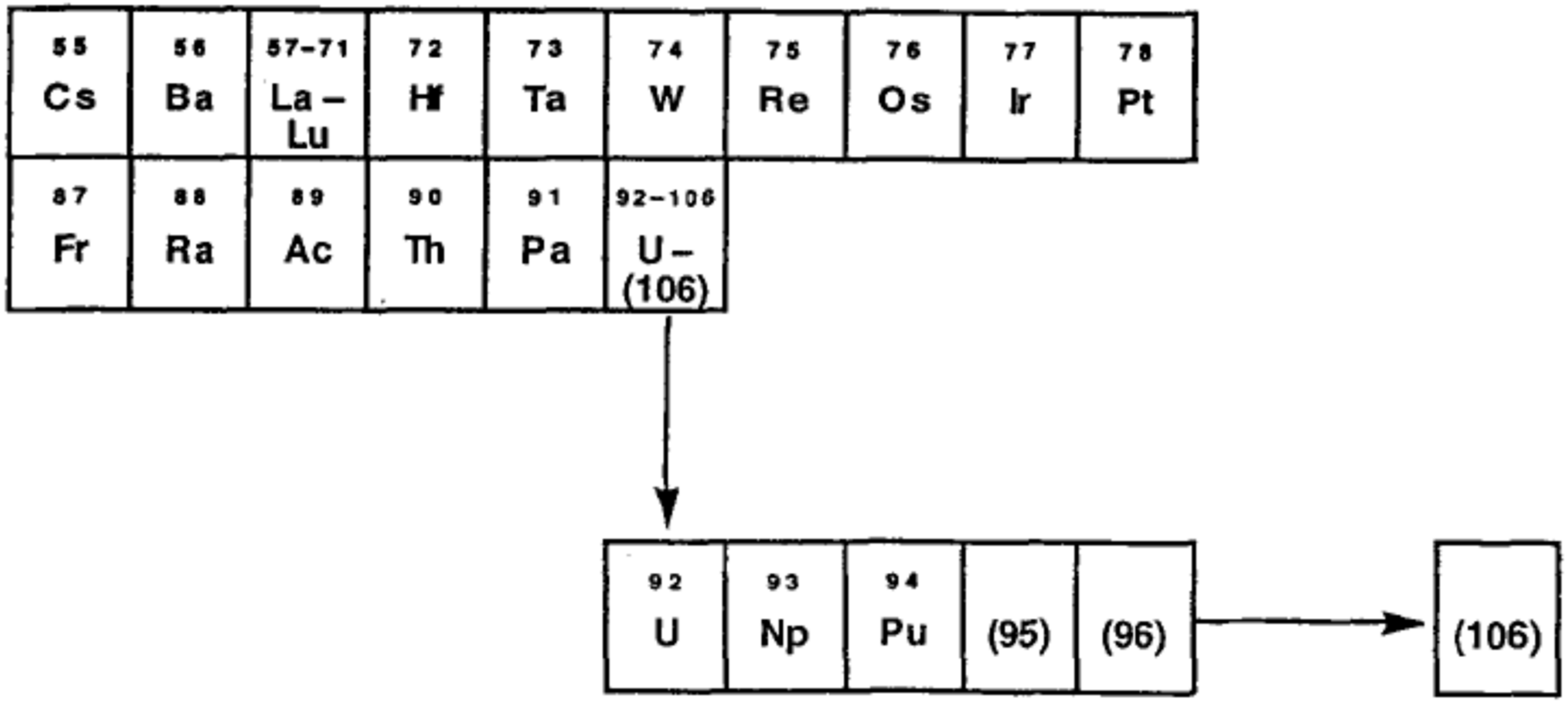


Fig. 3. By 1944 two new transuranium elements (95 and 96) had been placed in an "uranide" group.

The periodic table of 1944 therefore implied that the chemical properties of elements 95 and 96 should be very much like those of neptunium and plutonium.

The search for element 95

Unsuccessful attempts to identify element 95:

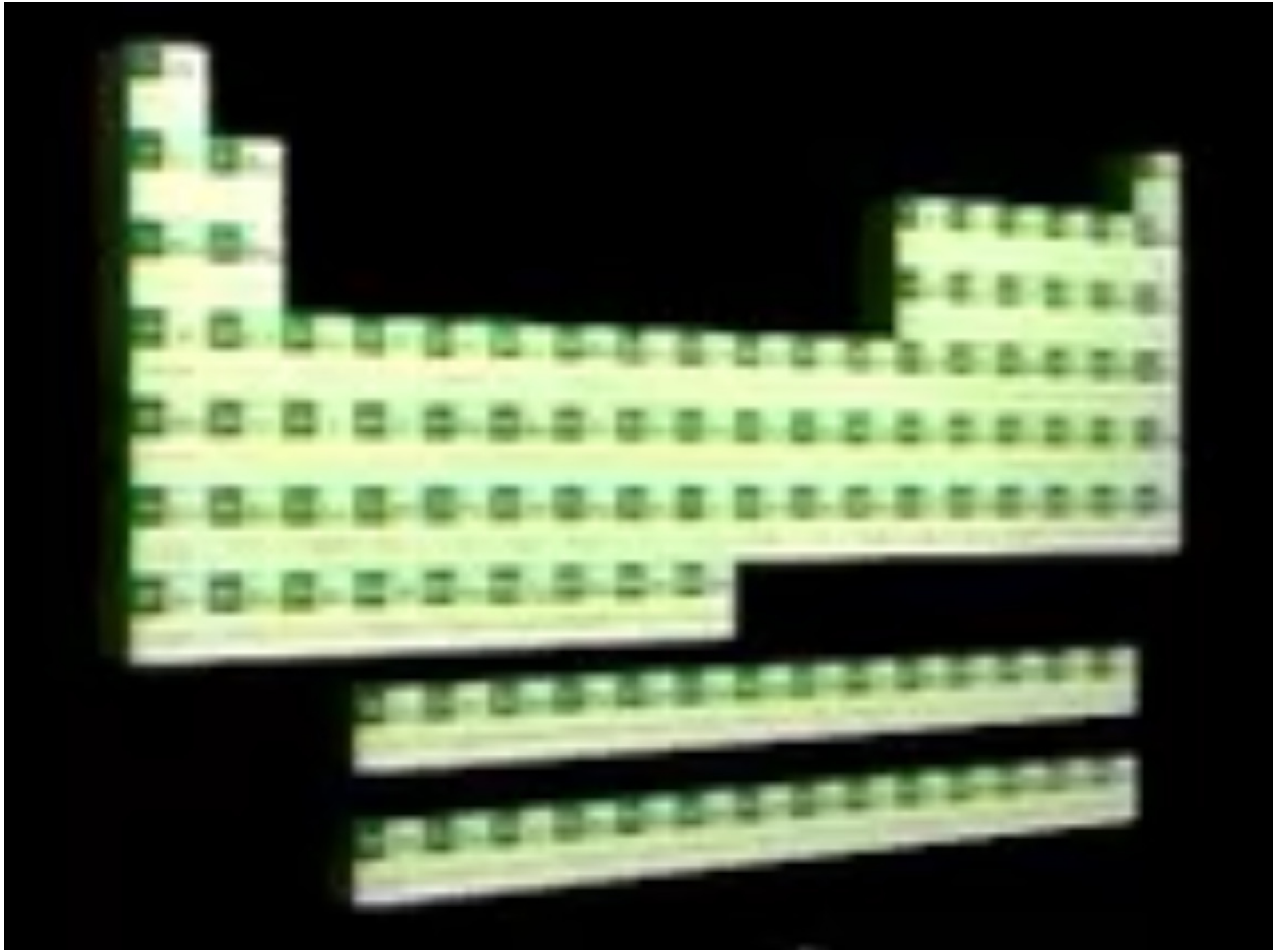
1) Irradiation of 1 mg ^{239}Pu (!) with d, chemical isolation of element 95, search for α-emitters.
   ($\rightarrow$ produced isotope decay via electron capture decay)

2) Neutron irradiation of ^{239}Pu, to produce ^{240}Pu and heavier Pu-isotopes, which decay via β^--decay to element 95.
   ($\rightarrow$ α-energies of ^{239}Pu about the same as ^{240}Pu $\rightarrow$ ^{240}Pu not detectable)

3) Reports from Berkeley about the probably identification of element 95 turned out to be wrong. The fission product ^{91}Y ($T_{1/2}$=57 d) had been measured.

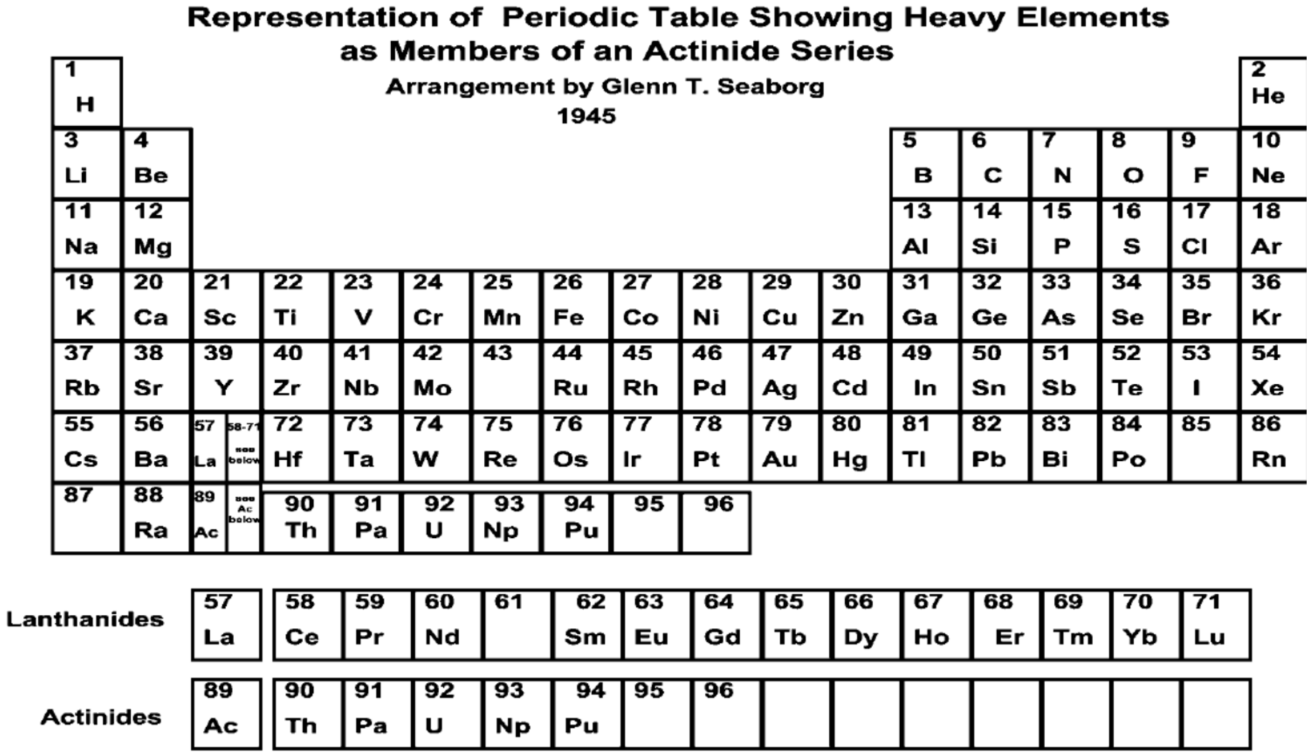
Glenn Seaborg explains the actinide concept

Movie 2: actinide concept



The actinide concept – Nobel prize in chemistry 1951

Elements 90 to 94 lie in corresponding positions just below the 6th period transition elements Hf to Os, in which the 5d electron shell is being filled. The transition elements Hf to Os are similar in their chemical properties to the corresponding 4d transitions elements in the 5th period (Zr to Ru). Although the first members ($_{90}$Th, $_{91}$Pa) of the group 90 to 94 show great resemblance in chemical properties to the first members ($_{72}$Hf, $_{73}$Ta) in the 5d transition series and to the first members ($_{40}$Zr, $_{41}$Nb) in the 4d transition series, the later members ($_{93}$Np, $_{94}$Pu) show practically no resemblance to $_{75}$Re and $_{76}$Os and to $_{43}$Tc and $_{44}$Ru. This suggests that it is the 5f electron shell which is being filled, although it is not possible to deduce from this chemical evidence alone whether uranium is the first element in the series for which this is the case. While it is beyond the scope of this discussion to give all the supporting evidence, we would like to advance the attractive hypothesis that this rare-earth-like series begins with actinium in the same sense that the "lanthanide" series begins with lanthanum. On this basis it might be termed the "actinide" series and the first 5f electron might appear in Th. Thus, the characteristic oxidation state – i.e., the oxidation state exhibited by those member containing seven 5f and fourteen 5f electrons – for this transition series is III.



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19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La 58-71 see below	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85	86 Rn
87	88 Ra	89 Ac see Ac below	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96								

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95	96							

Americium (Am, element 95) and curium (Cm, element 96)

Actinide concept: Am cannot be oxidized in aqueous solution into states that form soluble fluorides.
Only states III und IV can be reached, whose fluorides are not soluble.

Irradiation of ^{239}Pu with ^{4}He in Berkeley, air transport to Chicago.

Oxidation of the target in aqueous solution to Pu(VI) (soluble fluoride).
LaF_3-co-precipitation of the presumed insoluble fluorides of 95 and 96 (and minute amounts of Pu).
Dissolution, next oxidation, repetition of LaF_3 co-precipitation $\rightarrow$ Further Pu separation. Third cycle.

In the final sample:
0.004% of the original Pu (0.09 μg), leads to 12000 α/s.

Measurement of the range of α-particles in Mica
$\rightarrow$ Fraction of long-range α-particles (a few hundred α/s).

Most probable assignment:
$^{242}95$ via (α,p)-reaction
$^{242}96$ via (α,n)-reaction
$^{241}96$ via (α,2n)-reaction

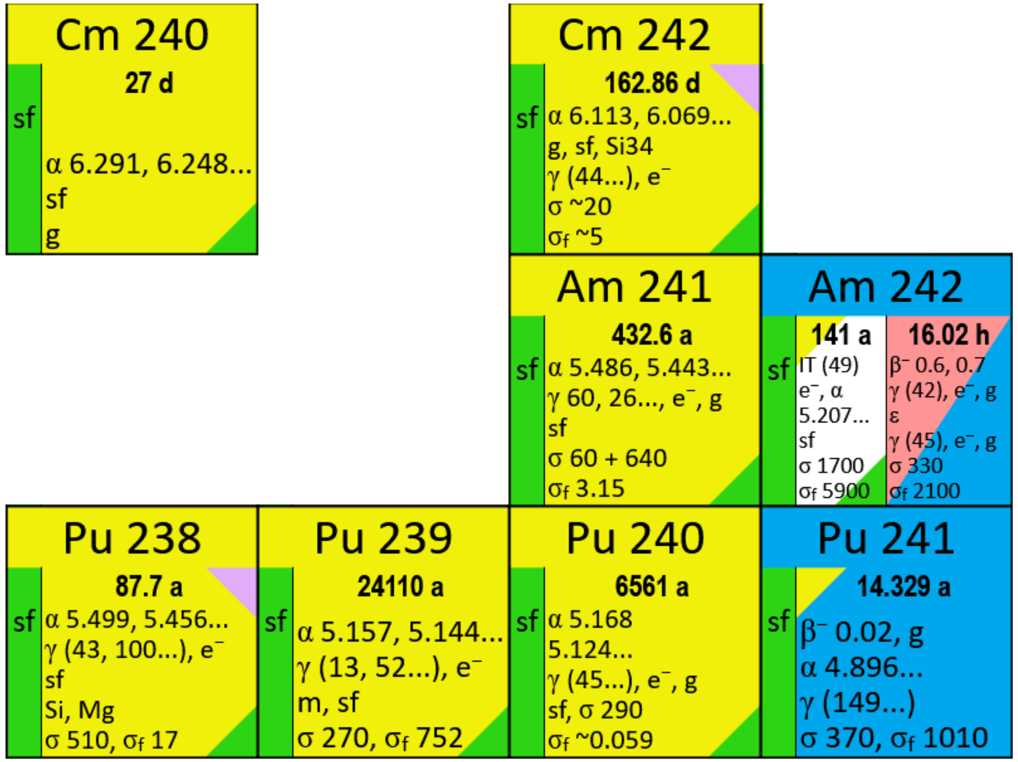
Further oxidation cylces for further reduction of Pu content

Americium (Am, element 95) and curium (Cm, element 96)

Further experiments with

1) Irradiation of larger (reactor-produced) Pu-samples (up to 250 mg) with ^{4}He of various energies and
2) various n-irradiations led to the identification of

^{241}Pu	^{239}Pu(n,γ)$\rightarrow$^{240}Pu(n,γ)
^{238}Pu	α-decay product of ^{242}Cm
^{241}Am	β^{-}-daughter of ^{241}Pu
^{242}Am	^{241}Am(n,γ)
^{240}Cm	^{239}Pu(α,3n)
^{242}Cm	^{239}Pu(α,n)
	^{241}Am(n,γ) as confirmation of the interpretation



Separation of Am and Cm from lanthanides difficult!

$\rightarrow$ Naming: Am in analogy to Eu, Cm in analogy to Gd.

The search for element 97

After the war: Seaborg and Ghiorso back to Berkeley, wanted to search for heavier elements.

Plan: $^{239}Pu + n + n \longrightarrow {}^{241}Pu \longrightarrow {}^{241}Am$ as target material, irradiation with ^{4}He.

Expected chemistry: according to actinide concept.

Problems:

-Sufficient amounts of ^{241}Am

-Handling of this highly radioactive target in the accelerator experiment.

-Separation of the new element (chemistry unknown!), whose chemistry is probably very similar to that of the target.

Berkelium (Bk, element 97)

First experiments: search for α-emitter was negative.

→ Change of setup to be sensitive to EC/β^+ emitter.

New experiments (Dec. 1949):

-irradiation of 7 mg ^{241}Am with ^{4}He, dissolution of the target.

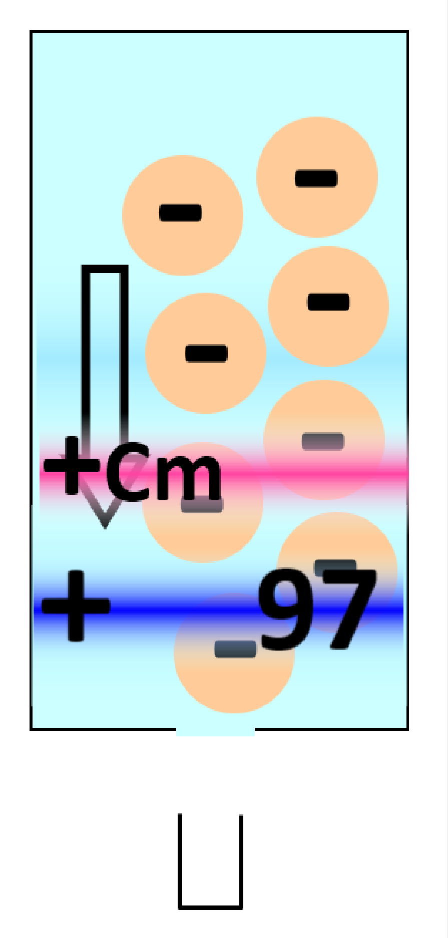
-oxidation to Am(VI) (was discovered to be possible under certain conditions only shortly before)

-precipitation of the suspected insoluble fluorides.

→ many fission products form insoluble fluorides!

-An ↔ Ln separation in conc. HCl on an ion exchanger.

-Purified An fraction was subjected to single element separation (citric acid CIX).



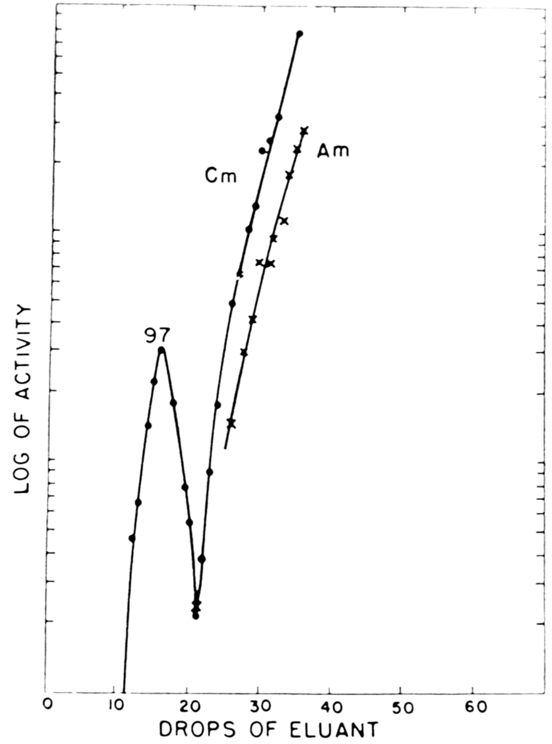


Fig.: Original elution data corresponding to the discovery of berkelium

Start of chromatography of heaviest elements!

→ Measurement of the radioactive decay of element 97. $T_{1/2}$=4.5 h (^{243}Bk)

Californium (Cf, element 98)

Meanwhile, sufficient ^{241}Am was bred in a high-flux reactor, so that $^{241}\text{Am} + n \rightarrow {}^{242}\text{Am} \rightarrow {}^{242}\text{Cm}$ provided sufficent Cm material for a target.

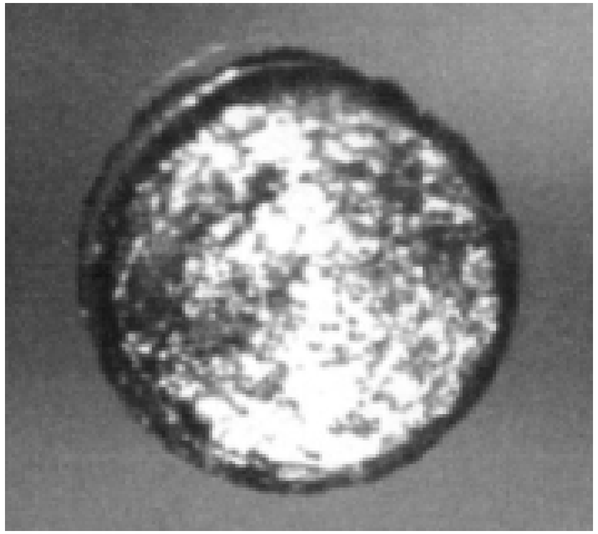
-Irradiation of 7 μg (!) ^{242}Cm with ^{4}He. Target activity: 10^8 α/s!

-Just in front of the elution peak of element 97, a fraction with 80 α/s was eluted; $E_\alpha = 7.1$ MeV (significantly higher than from 97)

The peak position together with the higher α-energy were proof for the new element.

In the discovery experiment: ~5000 atoms isolated

"This number is substantially smaller than the number of students attending the University of California at Berkeley..."



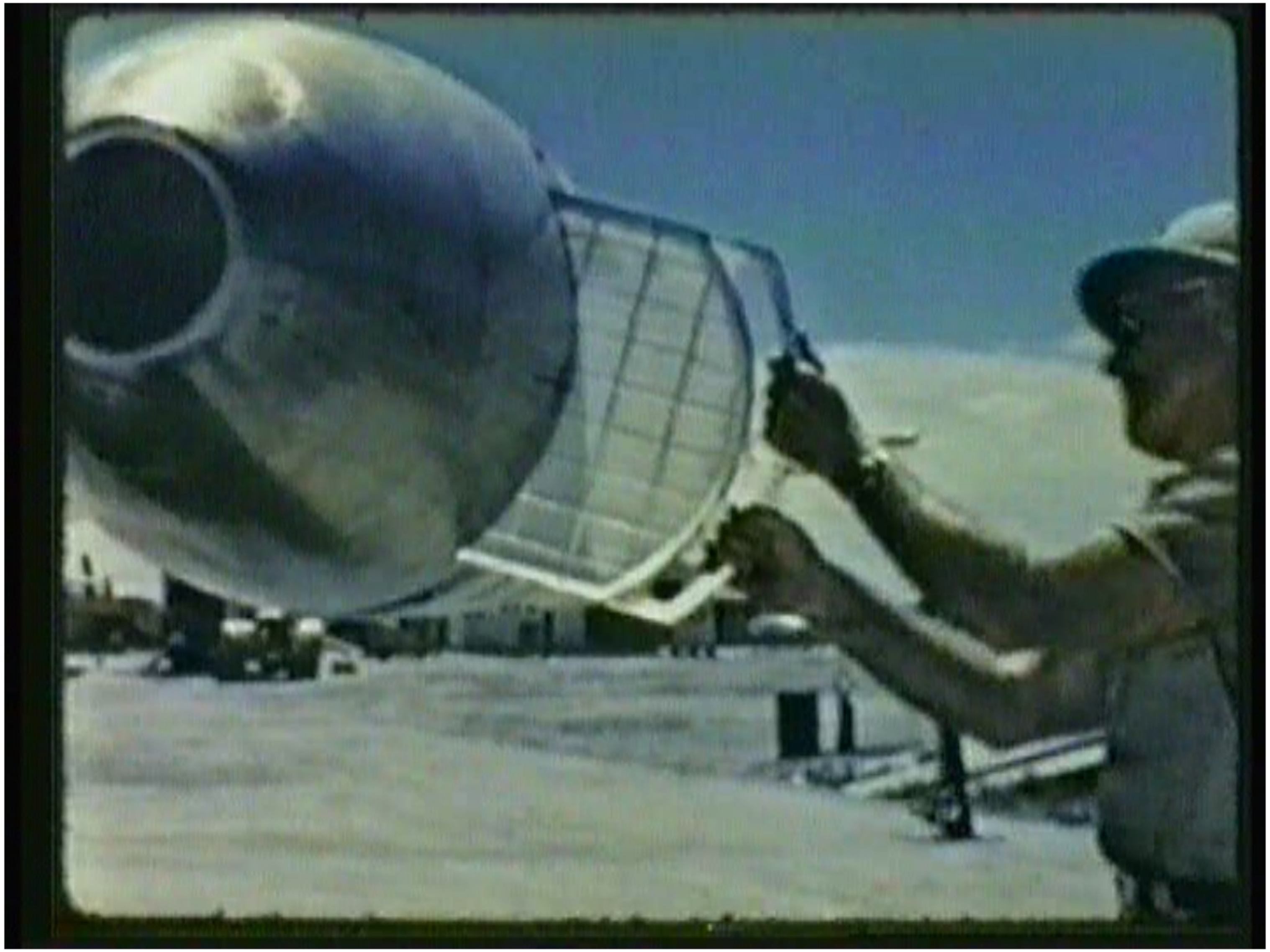
A 10 mg disc of ^{249}Cf metal. Diameter on the order of 1 mm.
https://en.wikipedia.org/wiki/Actinide

The elements from the bomb…

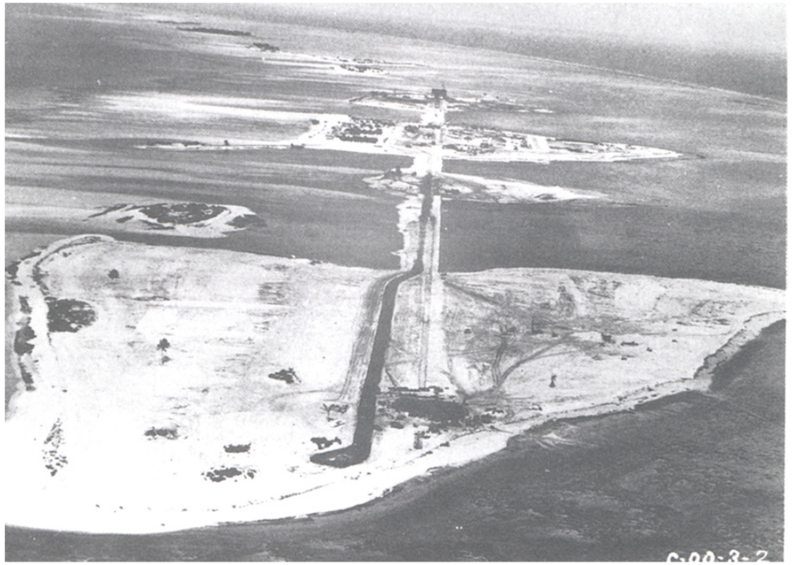
First American thermonuclear explosion "Ivy Mike", 10 MT; 01 November 1952, Eniwetok Atoll (Marshall Islands).
Early phase of the cloud photographed from a few km away. (from "The Transuranium People")

Studies in the wake of “Ivy Mike”

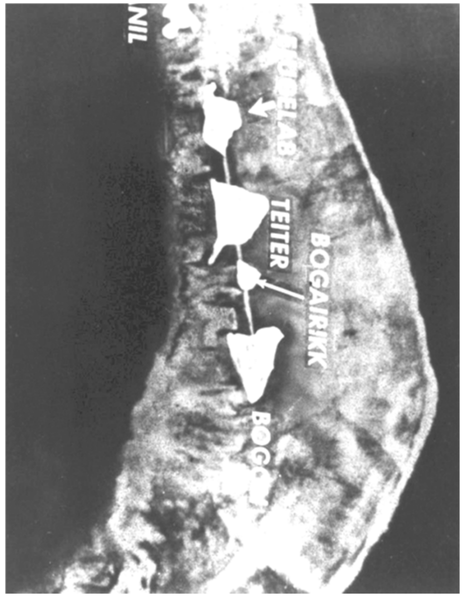
Movie 3: U.S. DOE

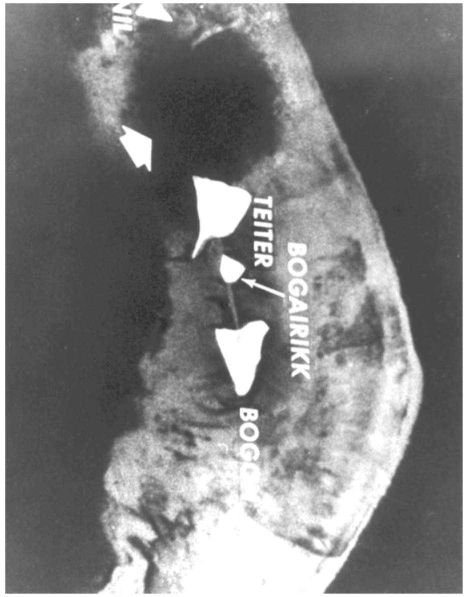


Studies in the wake of “Ivy Mike”



Before
Mike





After
Mike

Einsteinium (Es, element 99) and fermium (Fm, element 100)

F86 aircraft with filters fly through cloud to collect samples.
Detection of ^{244}Pu, and of "transplutonium-α emitters with 6.6 and 7.1 MeV".
Ghiorso + Co: they know nothing about Mike, as they are not involved in nuclear weapons testing.

Ghiorso's thoughts after hearing about ^{244}Pu findings:

-Knows that ^{244}Pu has been detected. This is only possible by MS. Typical detection limit: 0.1% of ^{239}Pu content.

-Assumption 1: large amounts of ^{238}U in the bomb

-Assumption 2: ^{238}U has instantaneously captured many neutrons

-Assumption 3: yield along the isotope chain decreases logarithmically with increasing mass

The yield line is then defined by $^{239}Pu/^{244}Pu=10^{-3}$

-Assumption 4 (based on former own experience): 10^{14} atoms collected

-Speculation: accumulation of 16 neutrons, yield ~10^{-9} → formation of ^{254}U

β^--decays lead to the formation of element 100

-Systematics of decay properties: α-emitter, $T_{1/2}$ ~ 1 month.

→ Expectation: detection of 1 α-particle / min of element 100.

Einsteinium (Es, element 99) and fermium (Fm, element 100)

Separation of actinides and lanthanides

CIX for the separation of individual actinides

Detection of 6.6-MeV α-particles in "trans-Cf fraction".

Further experiments:

Detection of an ingrowing ~1-d activity (7.1-MeV α-particles), which is formed by a long-lived Z=99 mother

This, along with position of peaks:

Elements 99 and 100 discovered!

Discovery of the "rapid neutron capture" process (r-process)

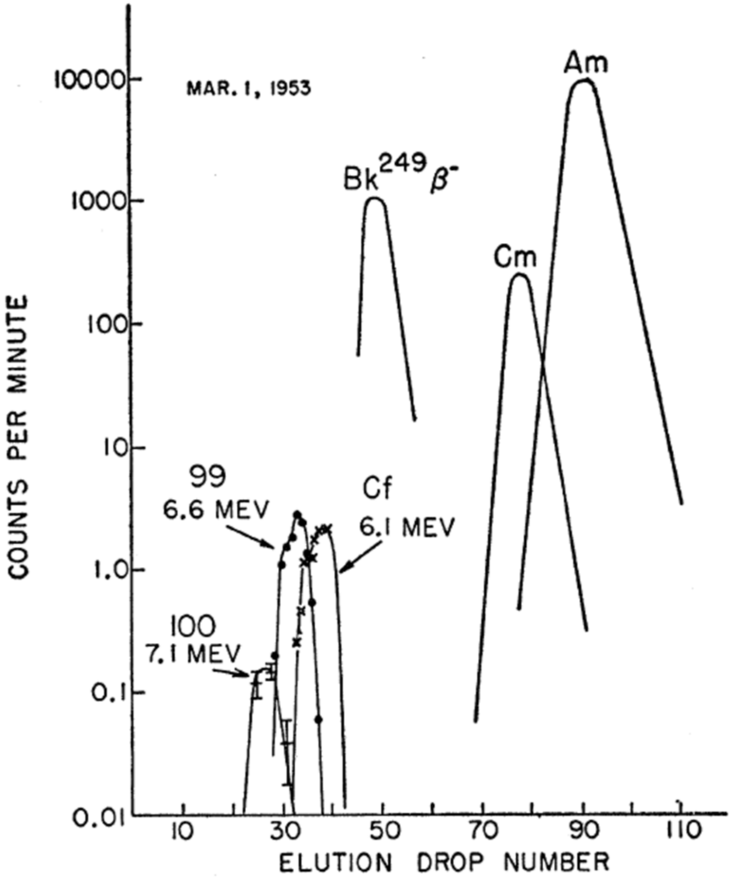
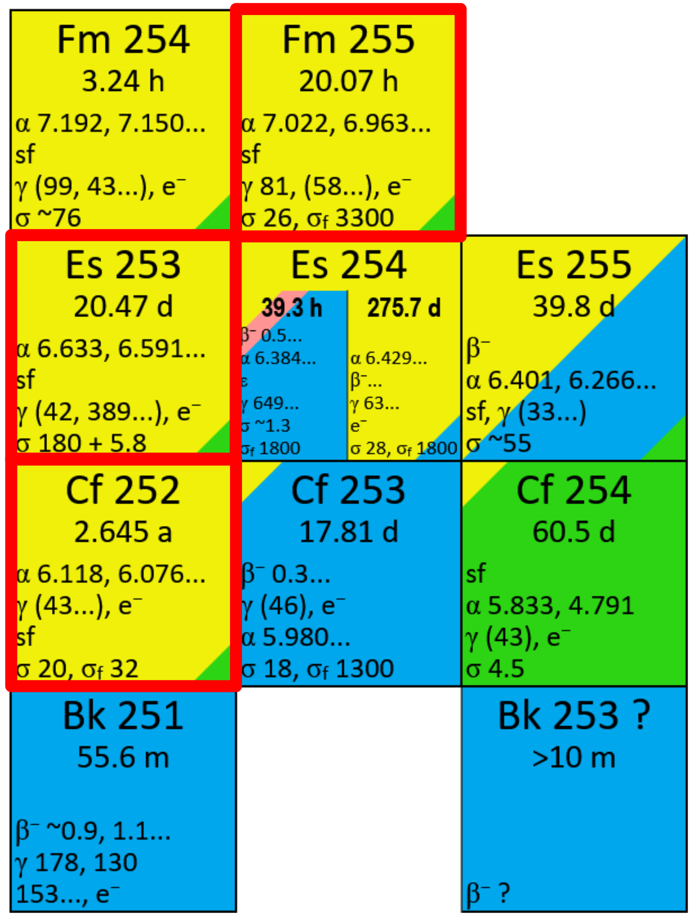


Fig. 2. Elution of element 100 relative to other actinide elements (citrate eluant).

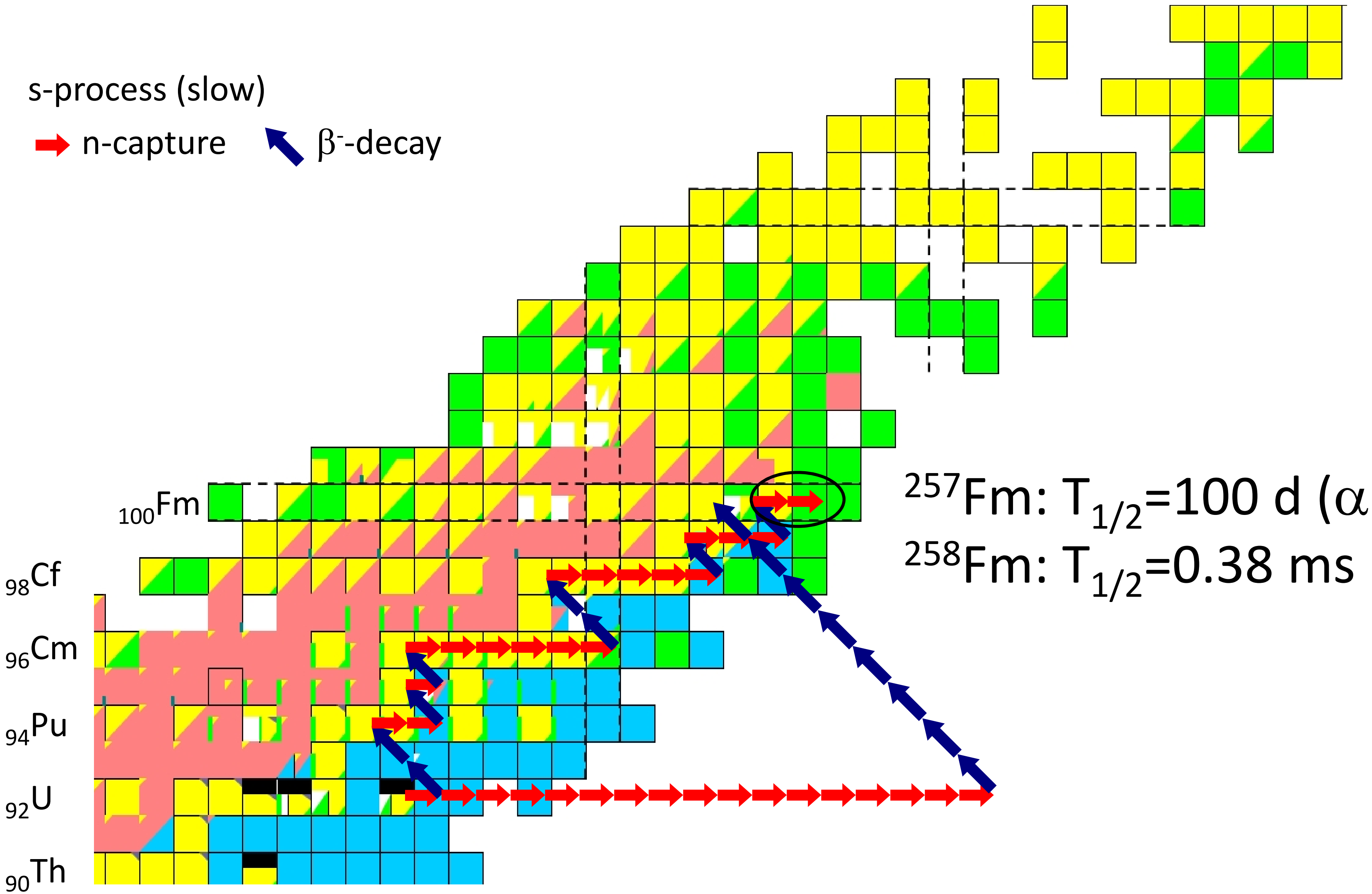
Phys. Rev. 99 (1955) 1048



Production of heavy elements in n-induced reactions

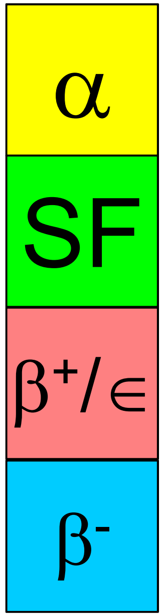
s-process (slow)

n-capture β⁻-decay



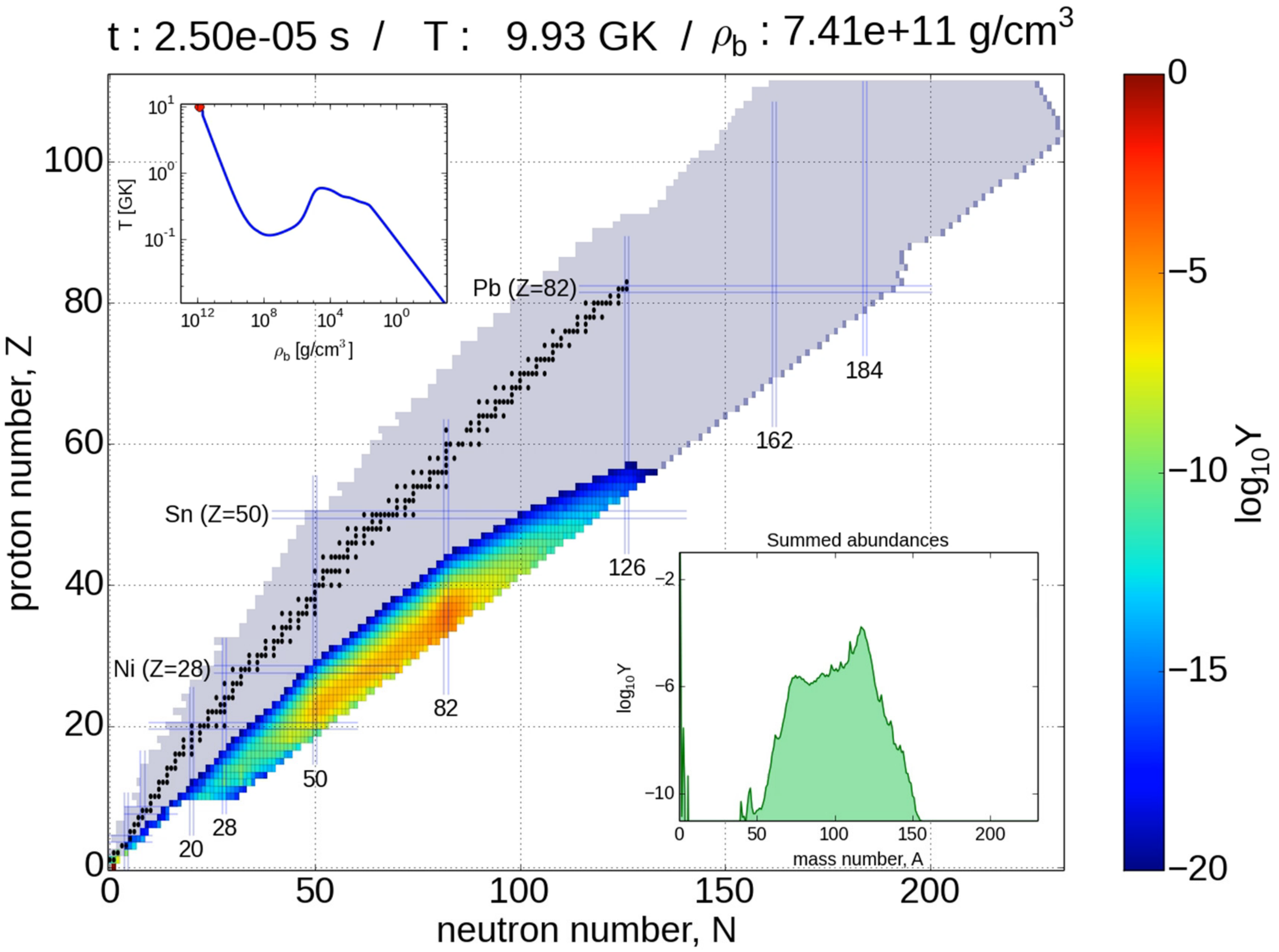
^{257}Fm: $T_{1/2}$=100 d (α)

^{258}Fm: $T_{1/2}$=0.38 ms (SF)



Production of heavy elements in the r-process

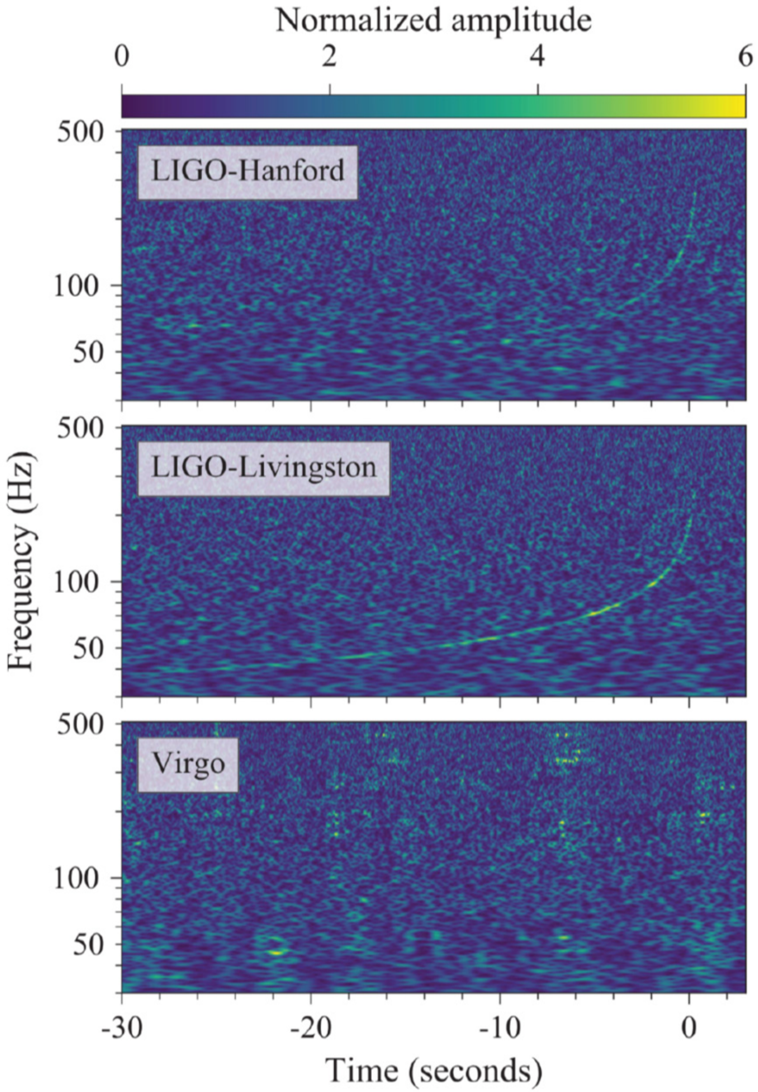
Movie 4: r-Prozess (I)



Movie from
G. Martinez-Pinedo

Detection of gravitational waves – the event on Aug. 17, 2017

GW170817

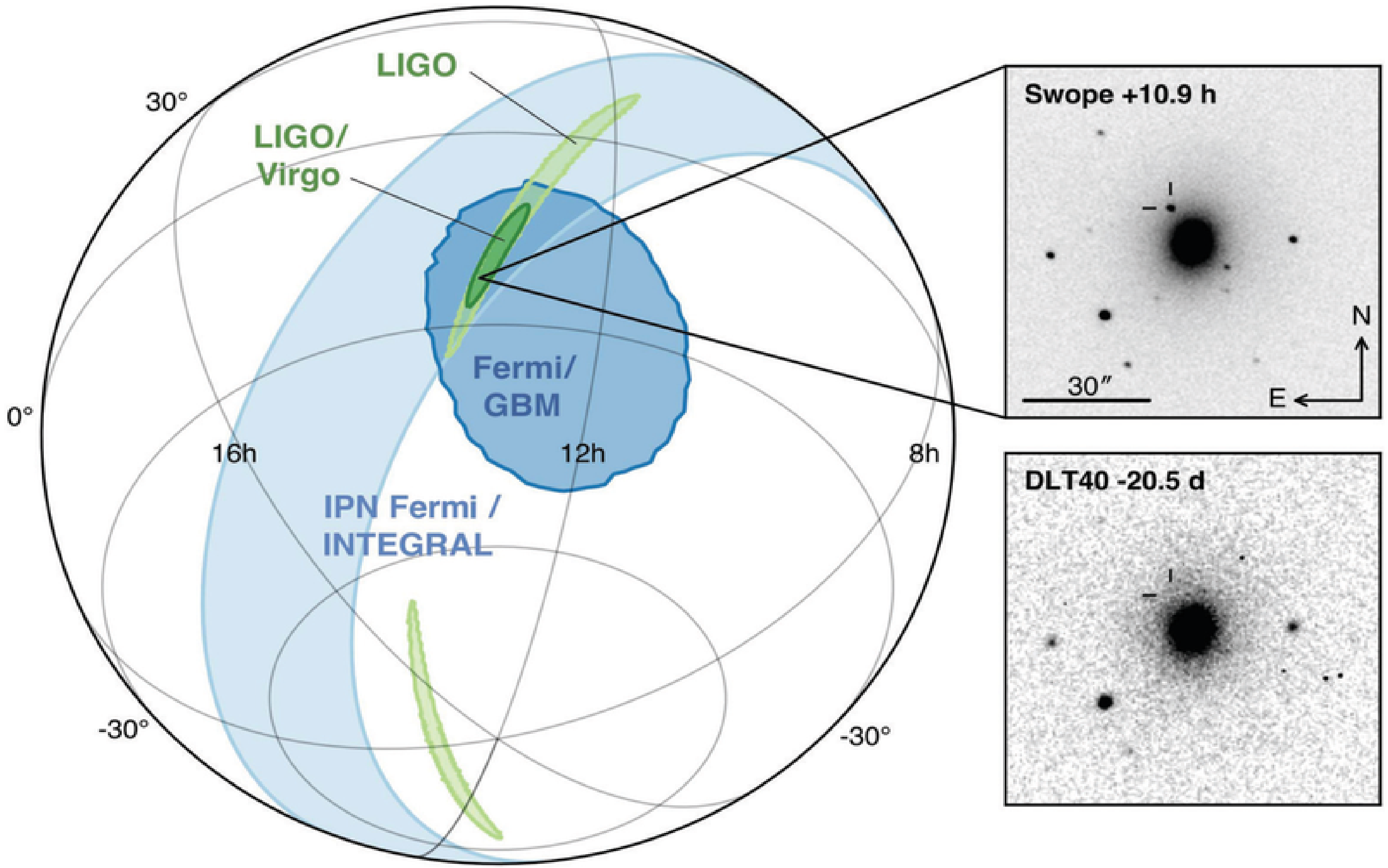


Slide curteousy of
Almudena Arcones

This GW signal was much much slower than all previous ones

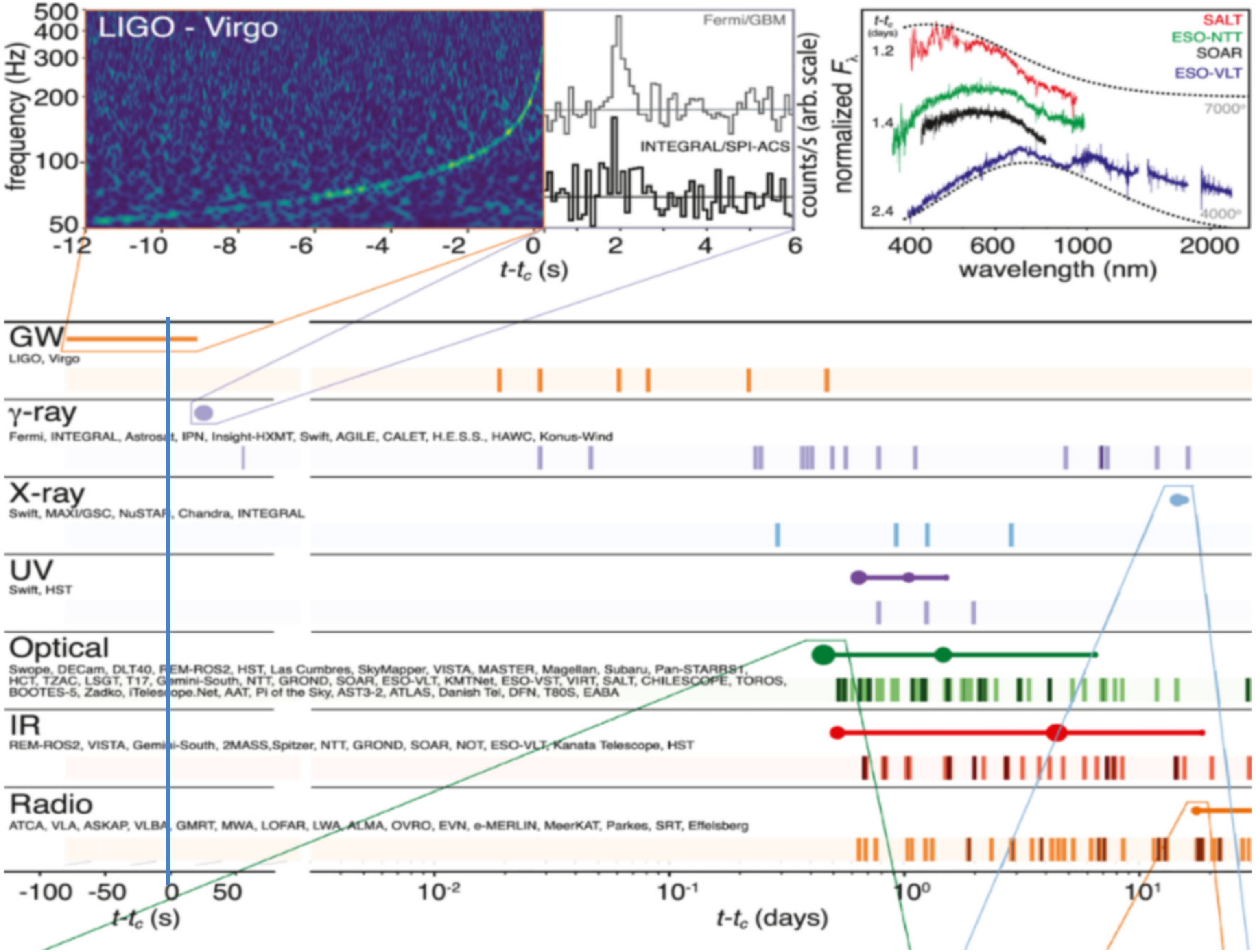
Identification of the optical transient

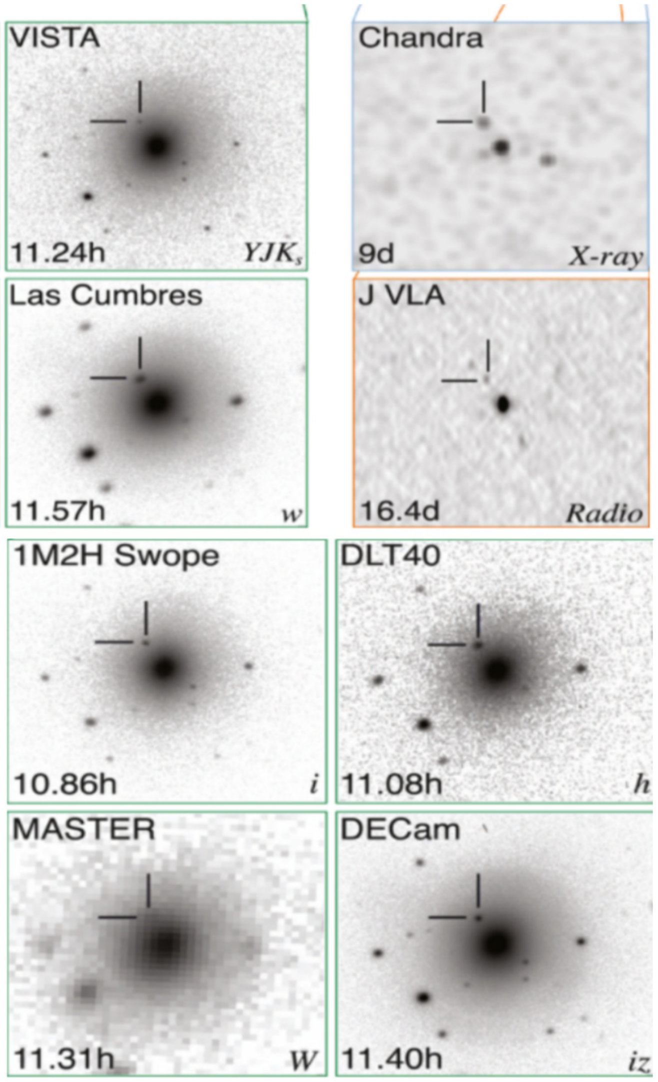
Kilonova identified 10.9 hours after the LIGO/Virgo GW signal on August 17, 2017, in the galaxy NGC 4993 in the constellation of Hydra (southern hemisphere)



Slide courtesy of
G. Martinez-Pinedo

Start of the Multimessenger Era

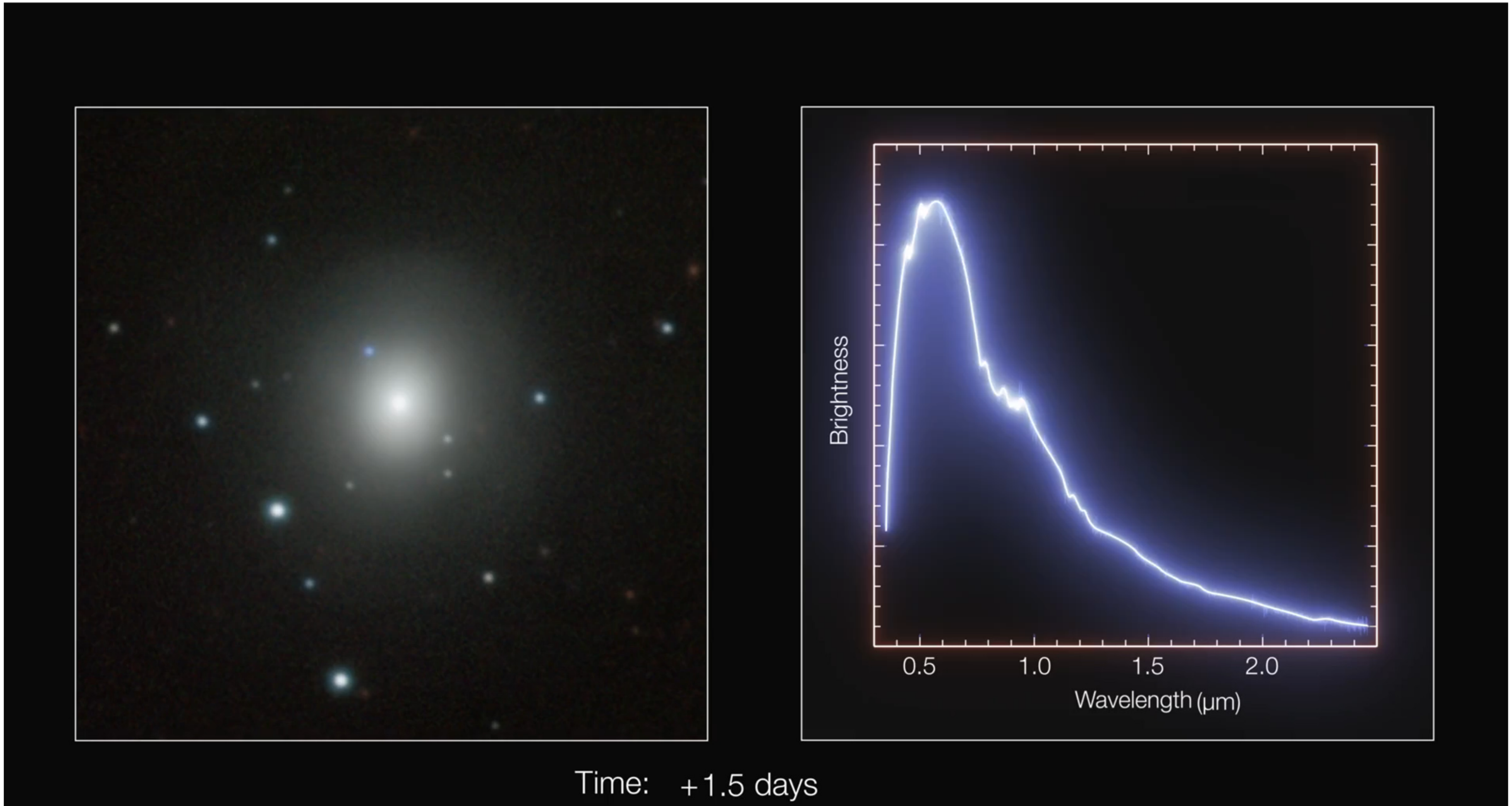




Slide from G. Martinez-Pinedo

Temporal evolution of the optical signal

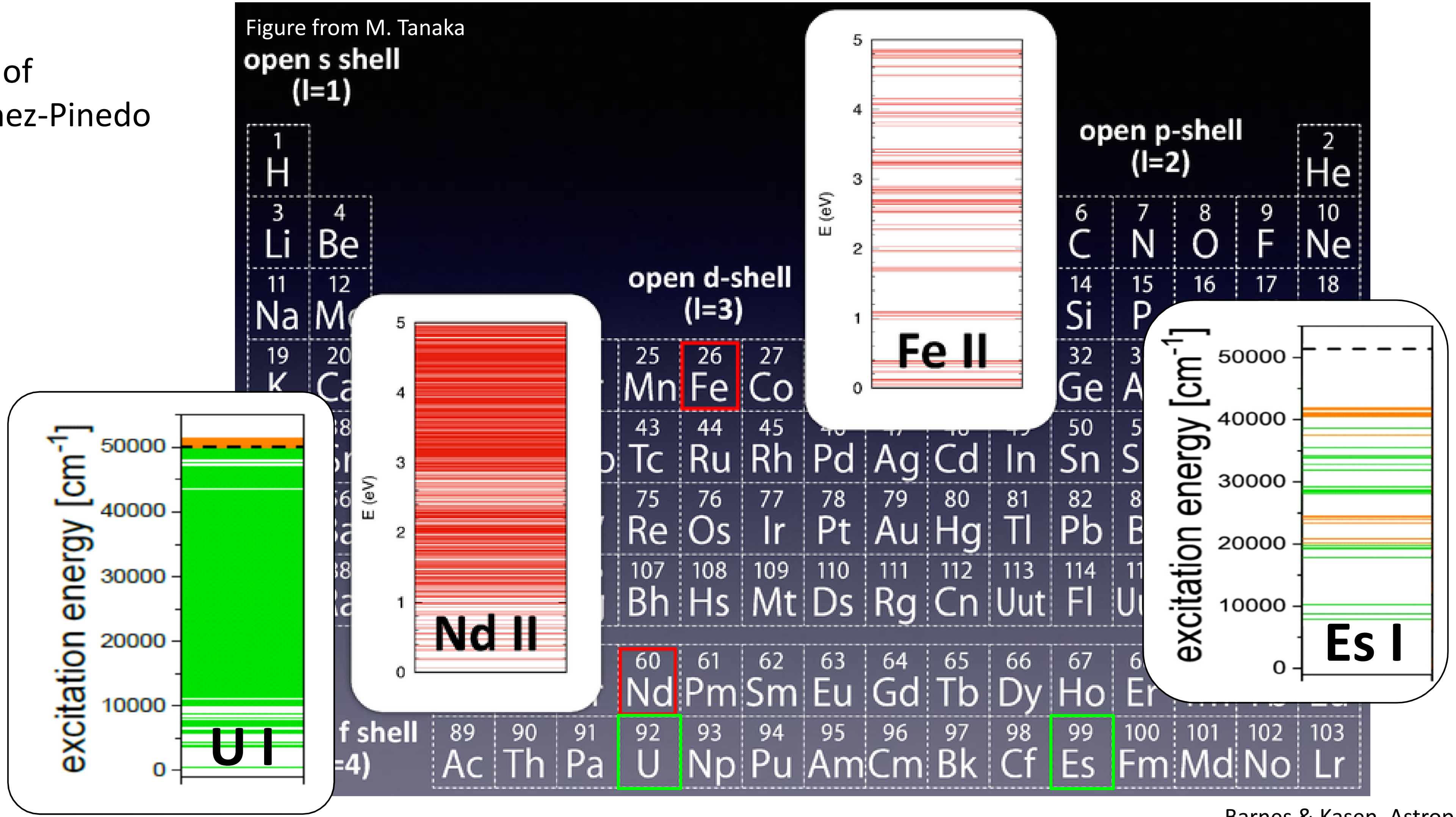
Movie 5: r-process II



Slide courtesy of Gabriel Martinez-Pinedo

Influence of f elements

Courtesy of
G. Martinez-Pinedo
and

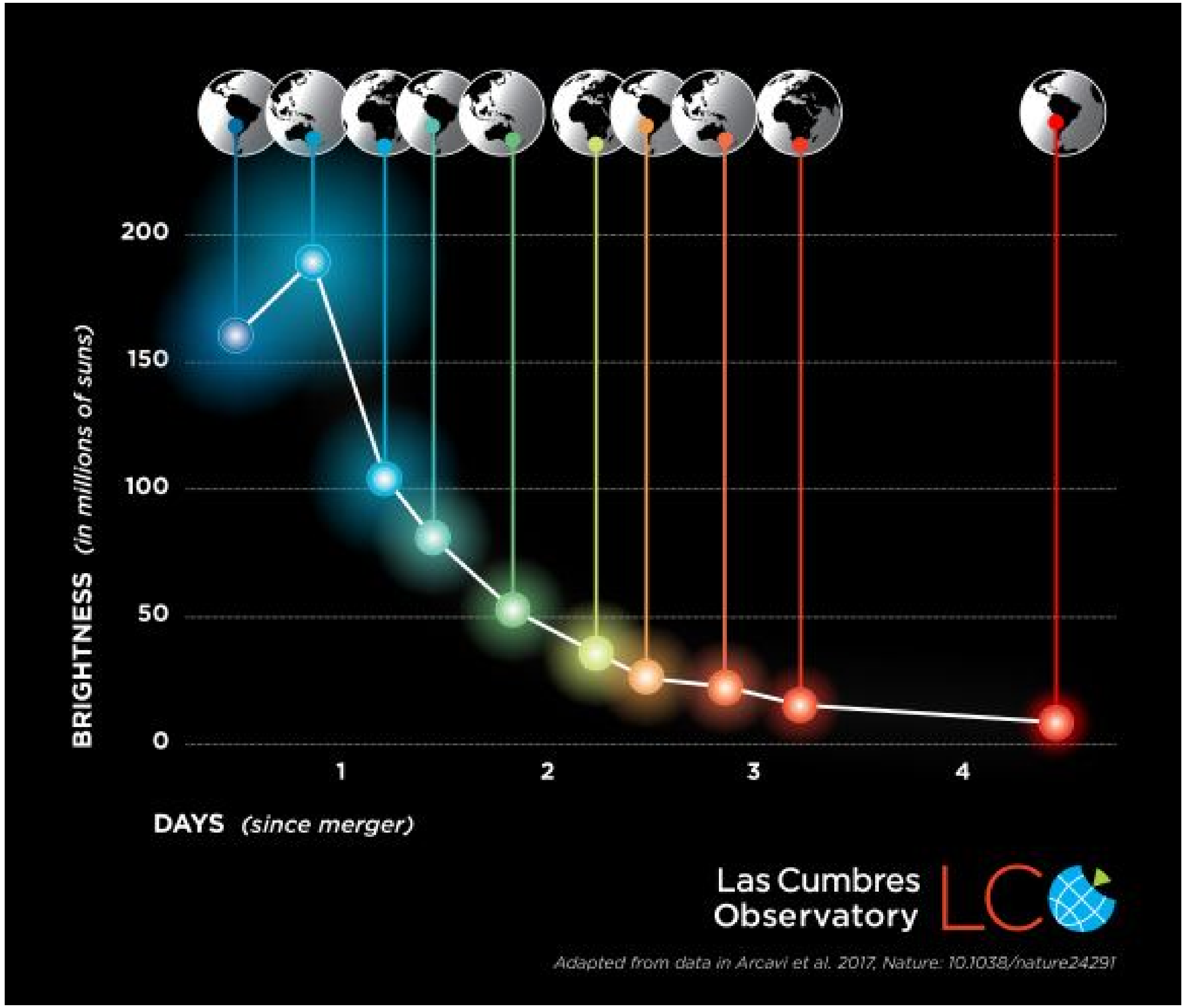


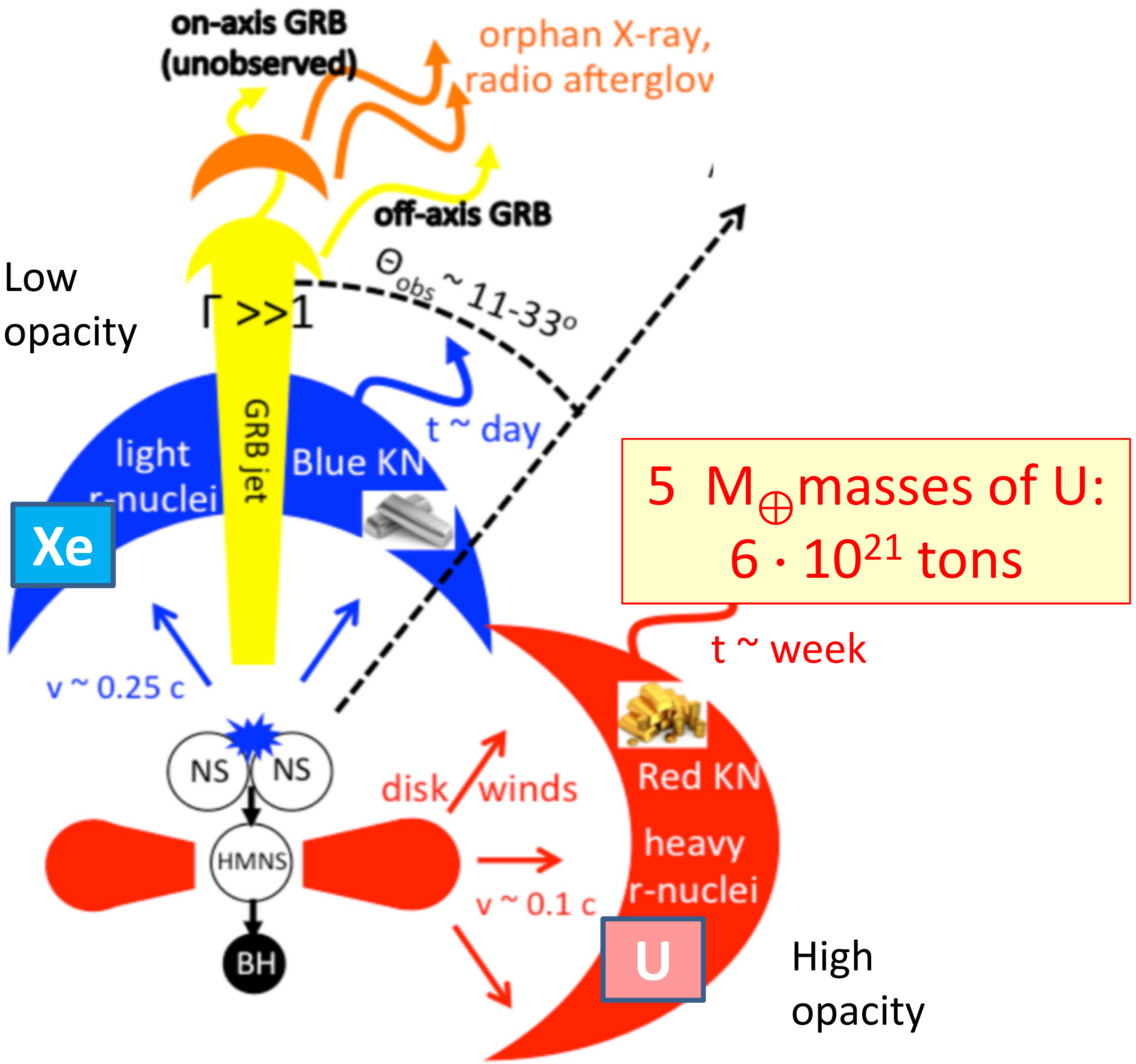
More valence-e$^-$
→ more lines
→ higher opacity

High density of states in lanthanides and actinides leads to large opacity

Barnes & Kasen, Astrophys. J. 775, 18 (2013)
Tanaka & Hotokezaka, Astrophys. J. 775, 113 (2013)
Block & Laatiaoui & Raeder, PPNP 116, 103834 (2021)

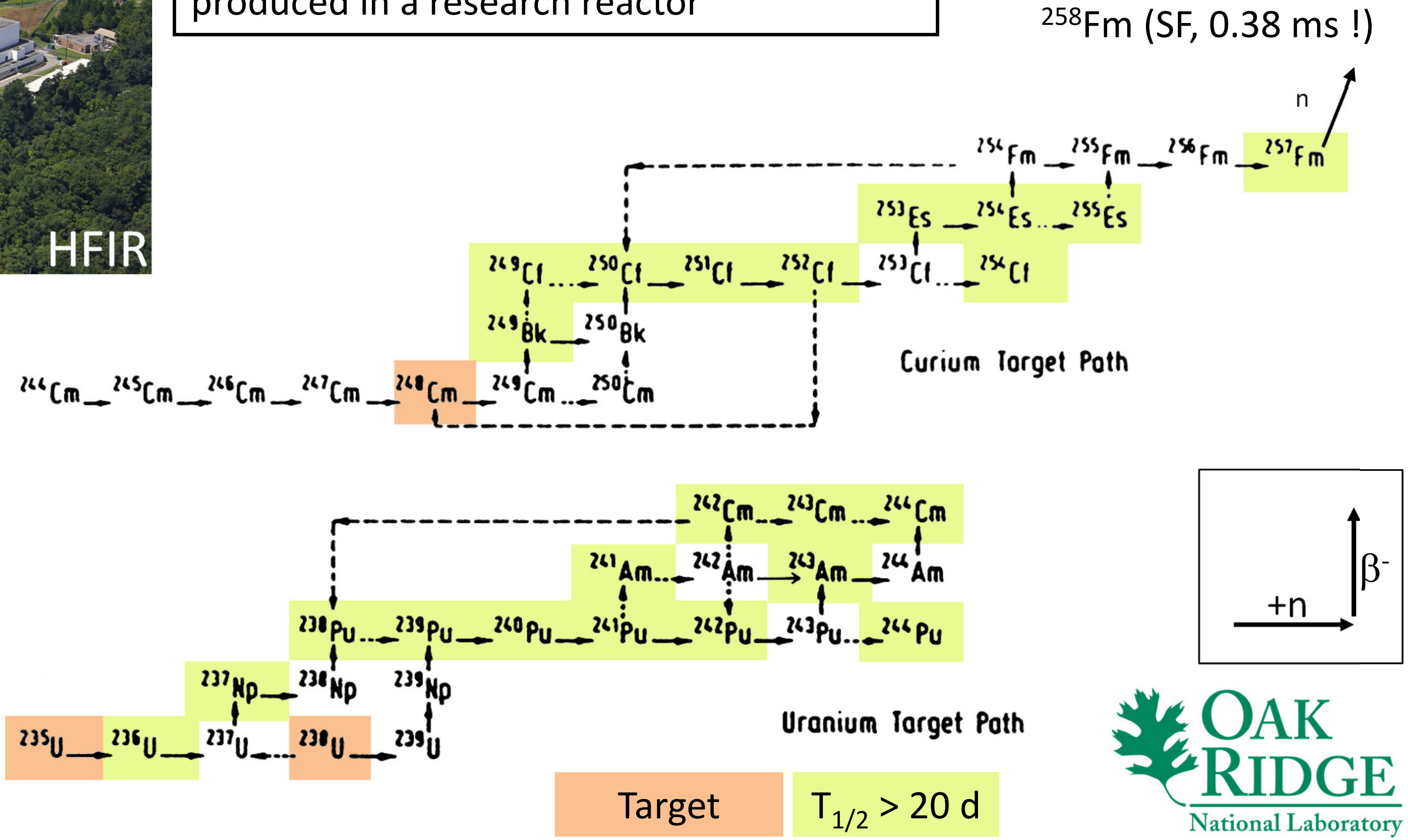
Temporal evolution of color and intensity of the optical signal





Back to Earth – production of transuranium elements in the s-process in a high-flux research reactor

Fm is the heaviest element that can be produced in a research reactor



OAK RIDGE National Laboratory

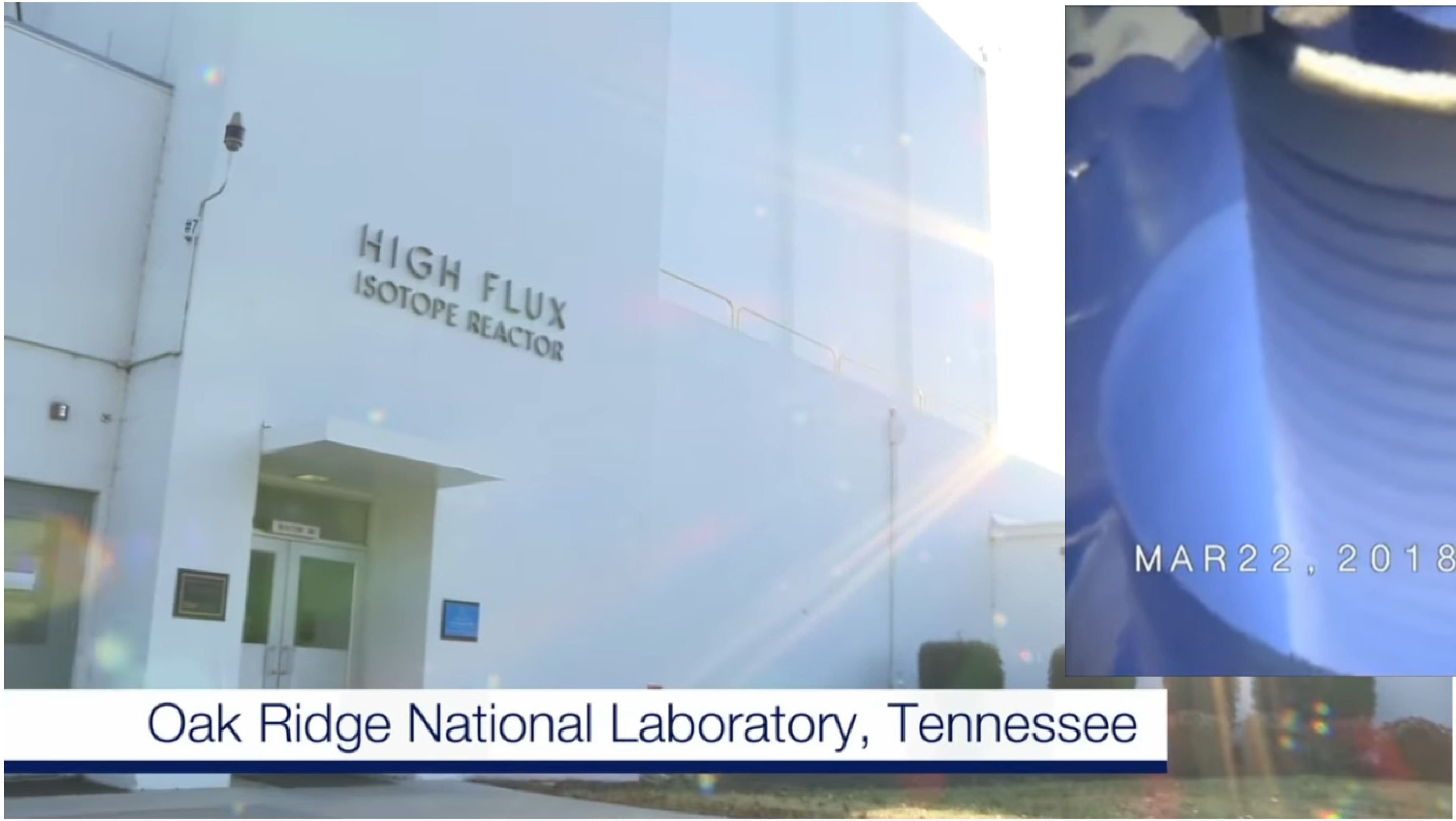
Macroscopically available transuranium isotopes

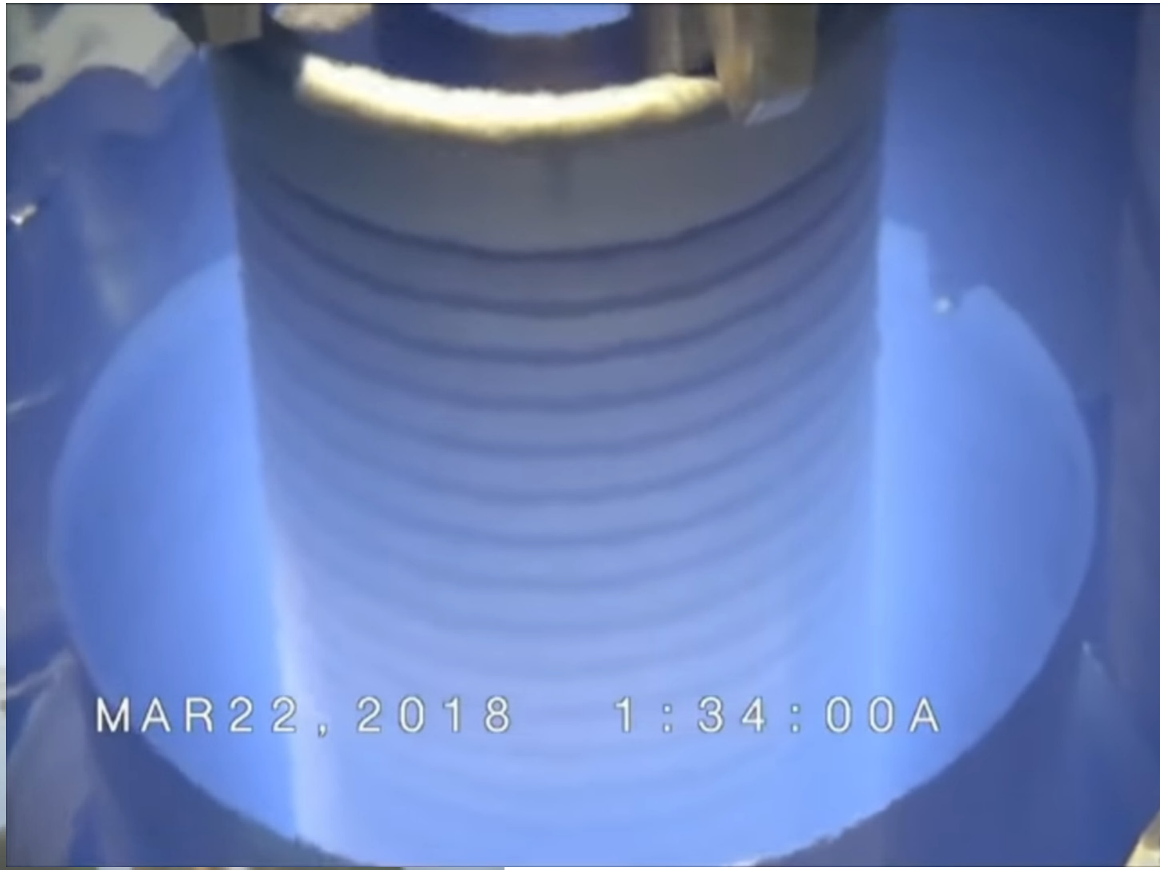
TABLE 5.1 Availability of Transuranium Element Materials

Nuclide	$t_{1/2}$	Decay Mode	Amounts Available	Specific Activity (dpm/μg)
^{237}Np	2.14×10^6 years	α,SF(10^{-10}%)	kg	1565.
^{238}Pu	87.7 years	α,SF(10^{-7}%)	kg	3.8×10^7
^{239}Pu	2.41×10^4 years	α,SF(10^{-4}%)	kg	1.38×10^5
^{240}Pu	6.56×10^3 years	α,SF(10^{-6}%)	10–50 g	5.04×10^6
^{241}Pu	14.4 years	β,α,(10^{-3}%)	1–10 g	2.29×10^8
^{242}Pu	3.76×10^5 years	α,SF(10^{-3}%)	100 g	8.73 10^3
^{244}Pu	8.00×10^7 years	α,SF(0.1%)	10–100 mg	39.1
^{241}Am	433 years	α,SF(10^{-10}%)	kg	7.6×10^6
^{243}Am	7.38×10^3 years	α,SF(10^{-8}%)	10–100 g	4.4×10^5
^{242}Cm	162.9 days	α,SF(10^{-5}%)	100 g	7.4×10^9
^{243}Cm	28.5 years	α,ϵ(0.2%)	10–100 mg	1.15×10^8
^{244}Cm	18.1 years	α,SF(10^{-4}%)	10–100 g	1.80×10^8
^{248}Cm	3.40×10^5 years	α,SF(8.3%)	10–100 mg	9.4×10^3
^{249}Bk	320 days	β,α,(10^{-3}%), SF(10^{-8}%)	10–50 mg	3.6×10^9
^{249}Cf	350.6 years	α,SF(10^{-7}%)	1–10 mg	9.1×10^6
^{250}Cf	13.1 years	α,SF(0.08%)	10 mg	2.4×10^8
^{252}Cf	2.6 years	α,SF(3.1%)	10–1000 mg	1.2×10^9
^{254}Cf	60.5 days	SF,α(0.3%)	μg	1.9×10^{10}
^{253}Es	20.4 days	α,SF(10^{-5}%)	1–10 mg	5.6×10^{10}
^{254}Es	276 days	α	1–5 μg	4.1×10^9
^{257}Fm	100.5 days	α,SF(0.2%)	1p g	1.1×10^{10}

Loveland + Seaborg, The elements beyond uranium

High-Flux Isotope Reactor, Oak Ridge National Laboratory





Inside a nuclear reactor (24 min)

https://www.youtube.com/watch?v=P99C051arMo

The Periodic Table 1955

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac-Lr															

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm			

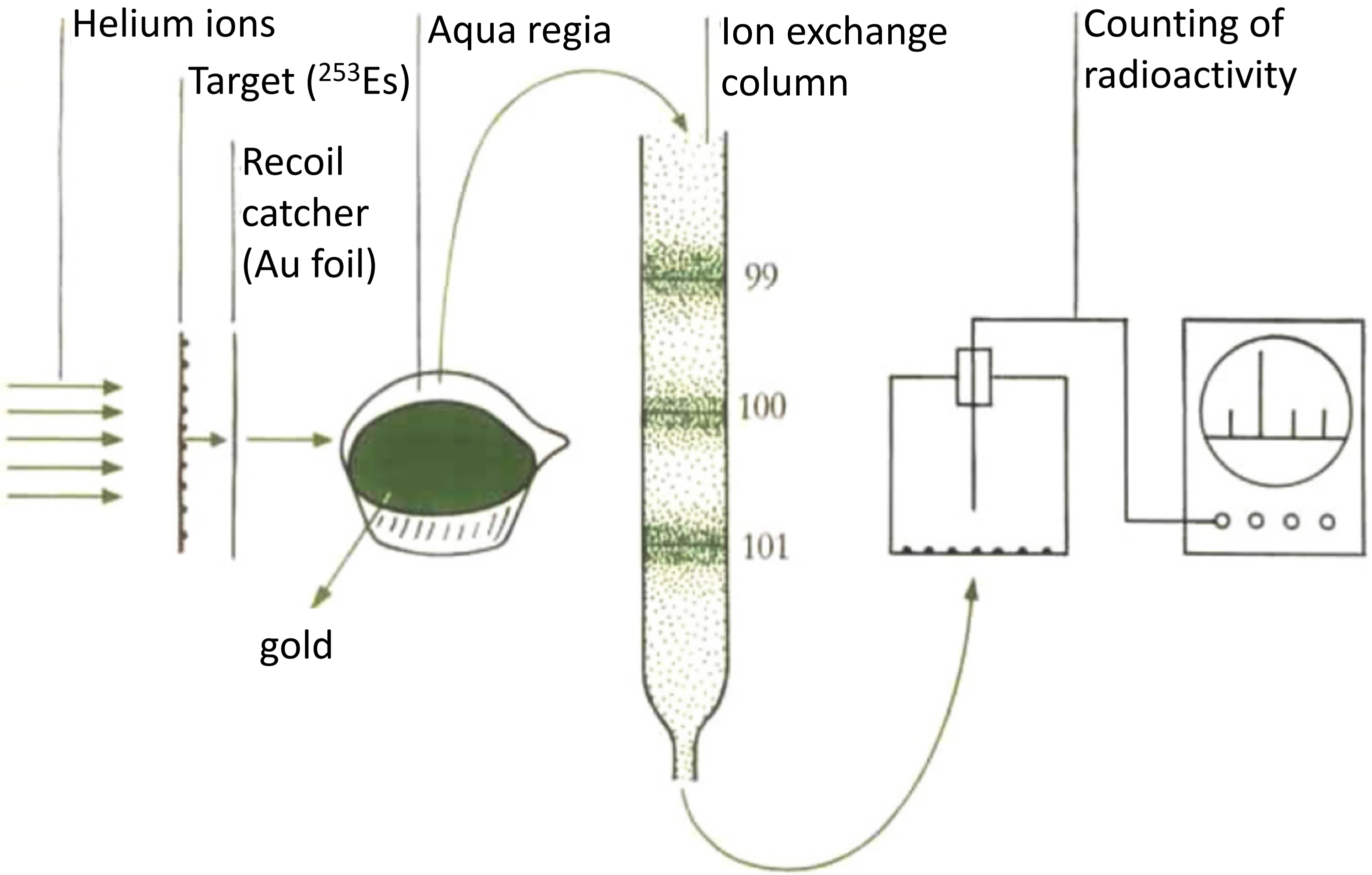
tons **mg / µg / pg**

Mendelevium (Md, element 101)

Target: 10^9 atoms (invisible!) ^{253}Es ($T_{1/2}$=20 d).

Recoil technique allows for physical separation of reaction products from target

→ No need to dissolve the target after every experiment.



Chemistry: Dissolve the Au recoil catcher foil in Aqua Regia; extraktion of Au with ethyl acetate. Aqueous phase: (AIX) with 6 M HCl for complete Au removal.
2. column (CIX) with α-HIB for separation of different actinides

Mendelevium: the way it was

http://www.youtube.com/watch?v=DrssJRb301k

Mendelevium (Md, element 101)

Registration of SF in "101"-Fraction. $T_{1/2}$ = 3.5 h → identical with $T_{1/2}$(^{256}Fm).

→ ^{256}101 decays via electron capture decay (EC) to ^{256}100

Result: 17 fissions from element 101

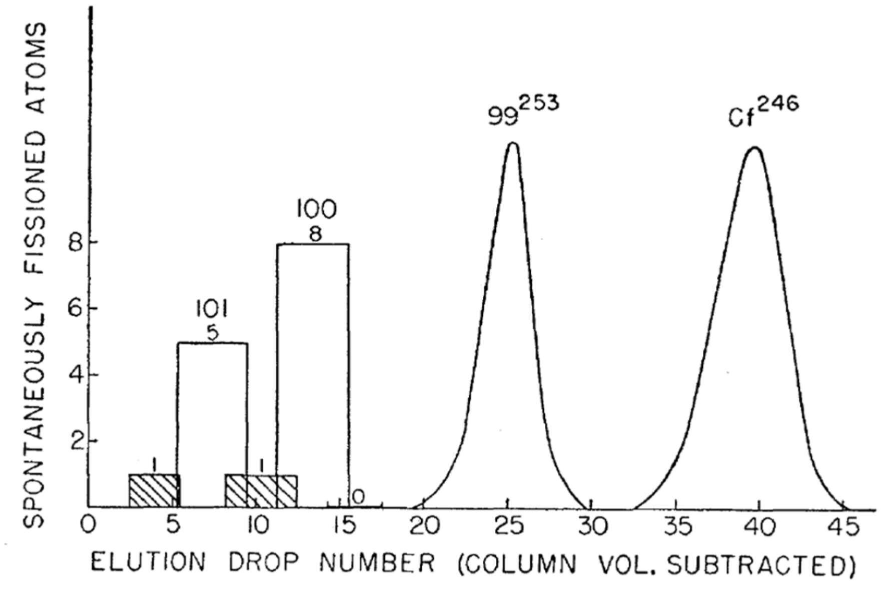
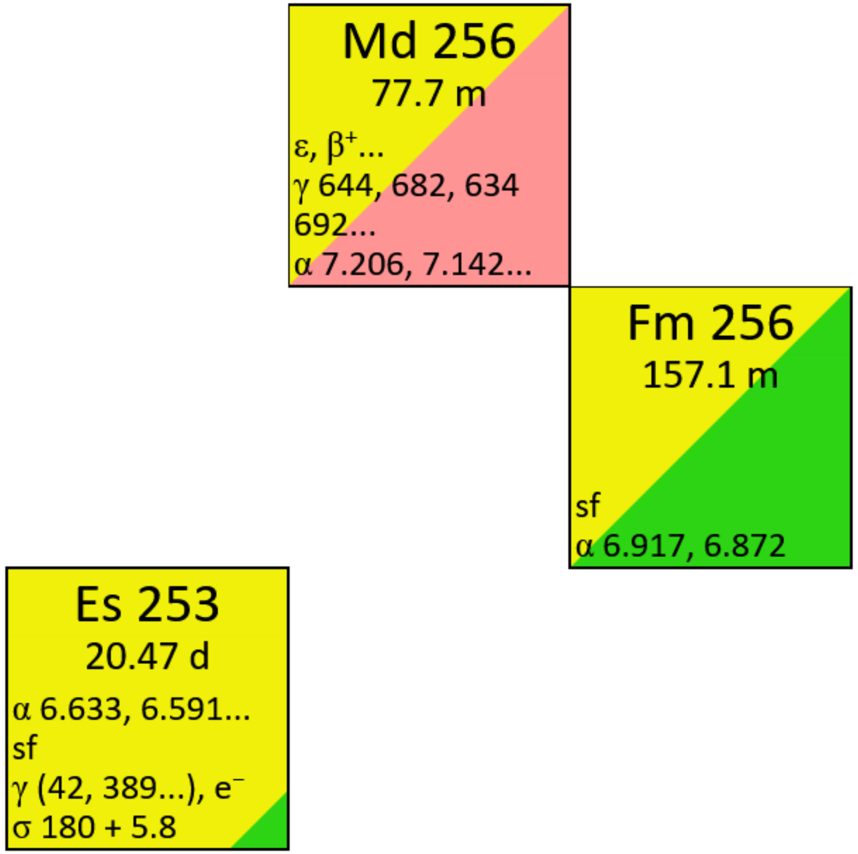


FIG. 1. Elution of elements 98–101 from Dowex-50 column with ammonium α-hydroxy-isobutyrate.

A. Ghiorso et al.,
Phys. Rev. 98 (1955) 1518

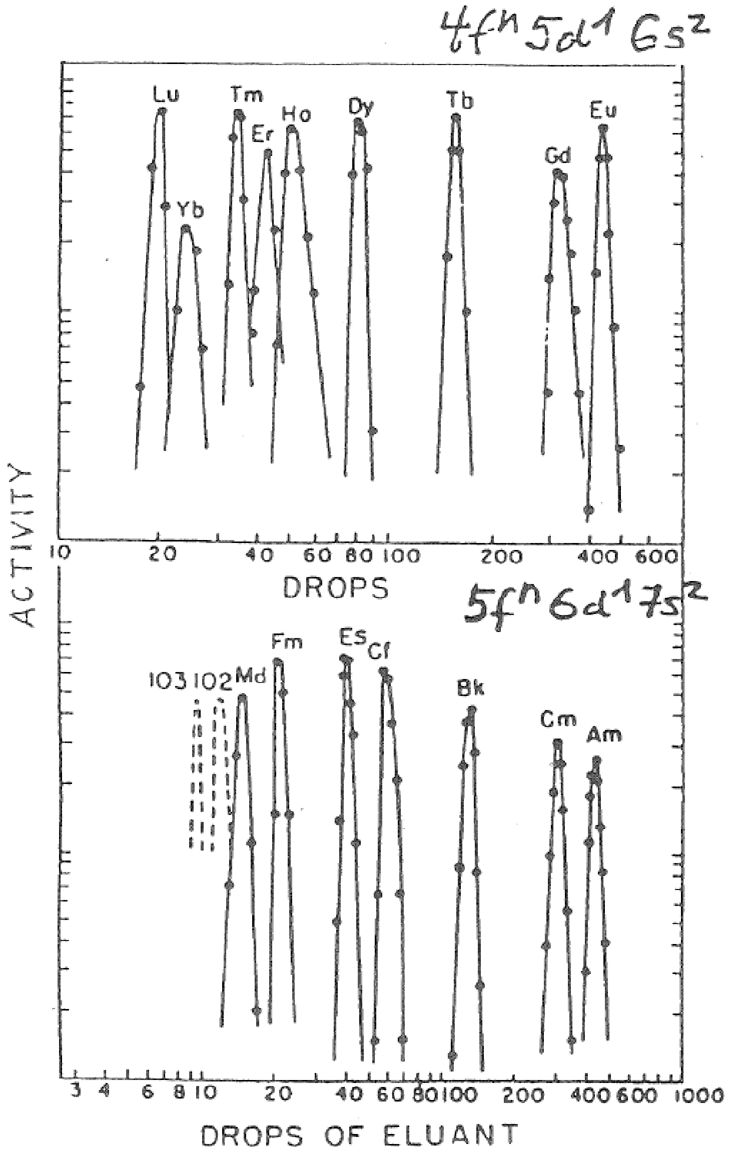


Md is the first element to be discovered via "single-atom chemistry".

Note: in the midst of the cold war, American researchers named a new element after a Russian scientist!

Similarities of the lanthanide and actinide series

CIX with α-hydroxy isobuteric acid (α-HIB)



Search for element 102

Production of elements Z > 101 needs beams > ^{4}He, as no targets of isotopes with Z>99 exist.

Worldwide: only 3 "heavy ion" accelerators: in Berkeley, Moscow and Stockholm.

Stockholm, 1957

First experiment: Stockholm, 1957; ^{244}Cm+^{13}C,

Collection of recoil products in plastic foils.

8.5 MeV α-particle, $T_{1/2}$ ~10 min.

α-HIB CIX (elution of trivalent cations) confirmed this result.

Publication in Phys. Rev. proposed name for element 102: "nobelium".

Berkeley, 1957-1958

α-energy appears high, half-life too long.

Attempt to reproduce the results fails, despite higher sensitivity than in the Stockholm experiments.

Nobelium (No, element 102)

LBNL Experiment $^{244,246}Cm + ^{12}C$

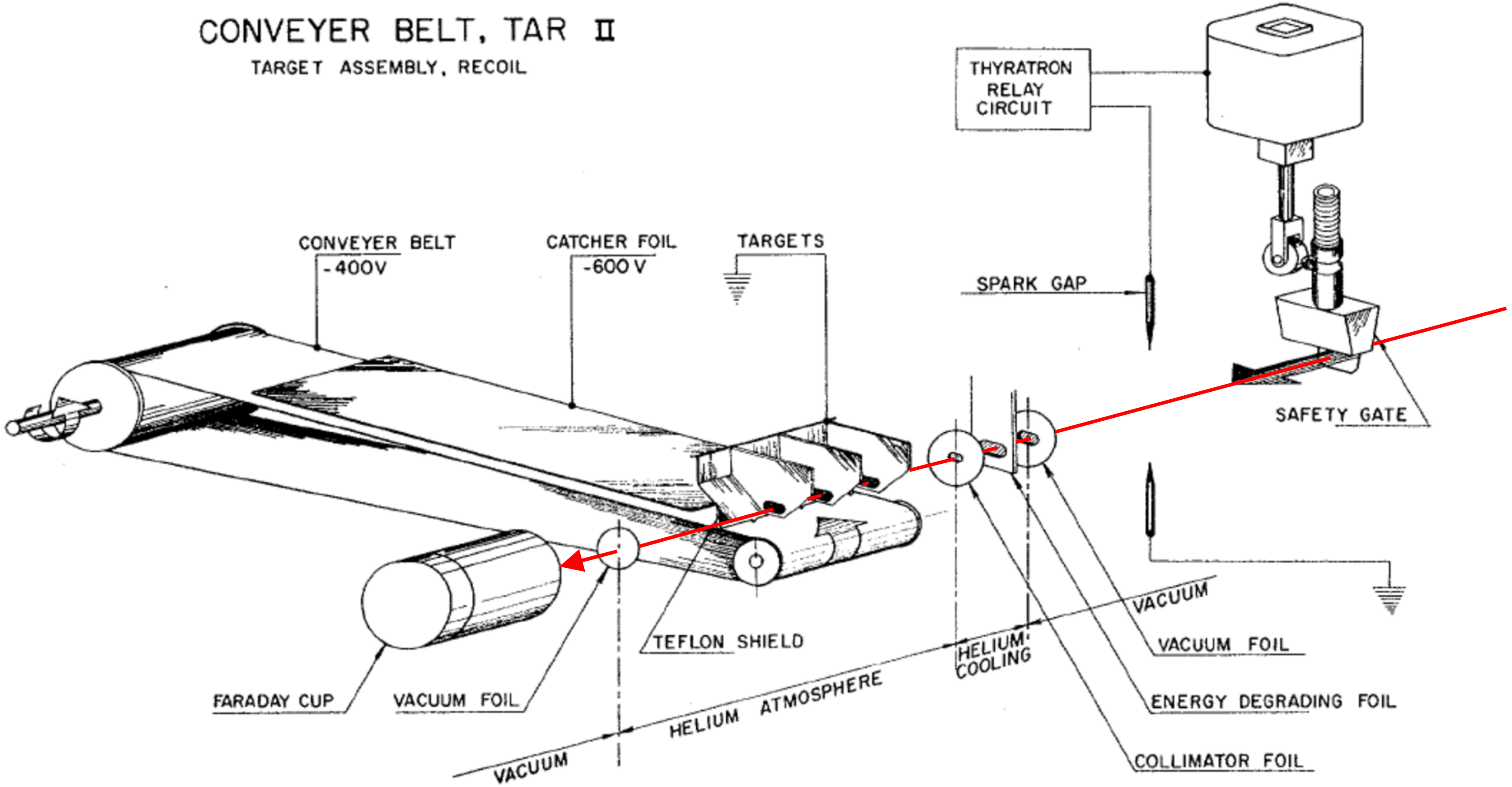


FIG. 1. Schematic diagram of conveyor belt experiment.

Chemical identification of ^{250}Fm on catcher foil

A. Ghiorso et al., Phys. Rev. Lett. 1 (1958) 18

Nobelium (No, element 102)

LBNL published ^{254}No with ~3 s half-life.

FLNR studies various reactions: $T_{1/2}(^{254}No)$=55 s, not 3 s (known now: this was ^{252}No from $^{12}C+^{244}Cm$).

Finally, LBNL studies all six reactions $^{12,13}C+^{244,246,248}Cm$, FLNR half-life is correct.

Chemistry experiments show the most stable oxidation state in aqueous solution to be 2+, not 3+

→ Consistent with Seaborg's actinide concept.

The Stockholm chemistry work could not have observed No, since those experiments were designed for trivalent species only!

The sum of the JINR and LBNL work leads to the discovery of nobelium.

The name "nobelium" remains, because it was already used for more than 10 years in the scientific world, although it comes from a refuted work.

Lawrencium (Lr, element 103)

Discovered at LBNL, using $^{10,11}B$ + $^{249,250,251,252}Cf$ (no isotopically pure target was available)

Chemical properties

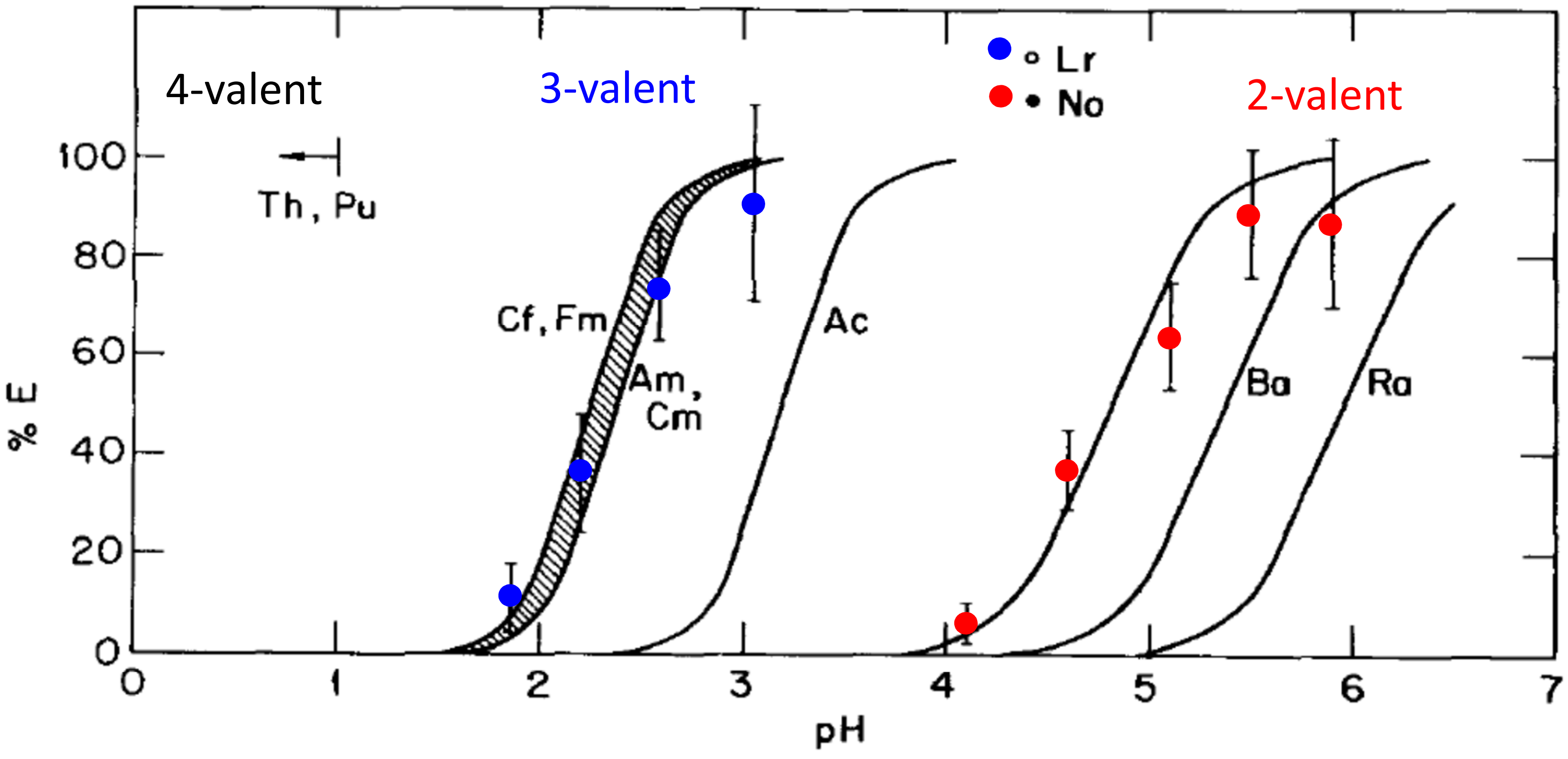


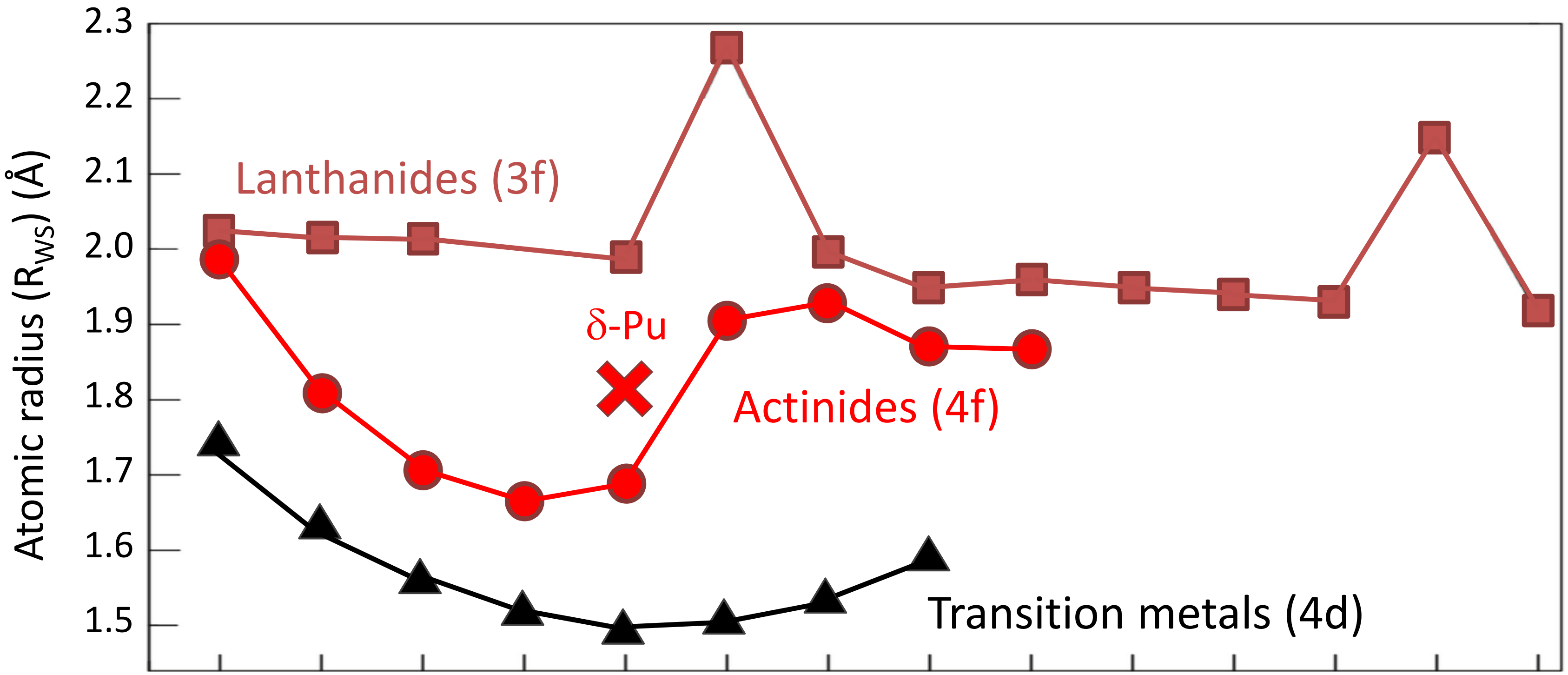
FIG. 1

Percent extracted into the organic phase as a function of the pH of the aqueous phase. Solid lines are summary of data given in Ref. 8.

R. Silva et al., Inorg. Nucl. Chem. Lett. 6 (1970) 733.

Atomic radii of the actinides

Early actinides: itinerant f-electrons lead to transition metal-like trends. Beyond Pu: localized f-electrons, like the lanthanides



Transition metals (5d)

72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**

Lanthanides (3f)	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
Actinides (4f)	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

Periodic Table 2021: actinides are not the end

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
119 ---	120 ---																

<1 atom month^{-1}

1 atom min^{-1}

3 atoms day^{-1}

<1 atom day^{-1}

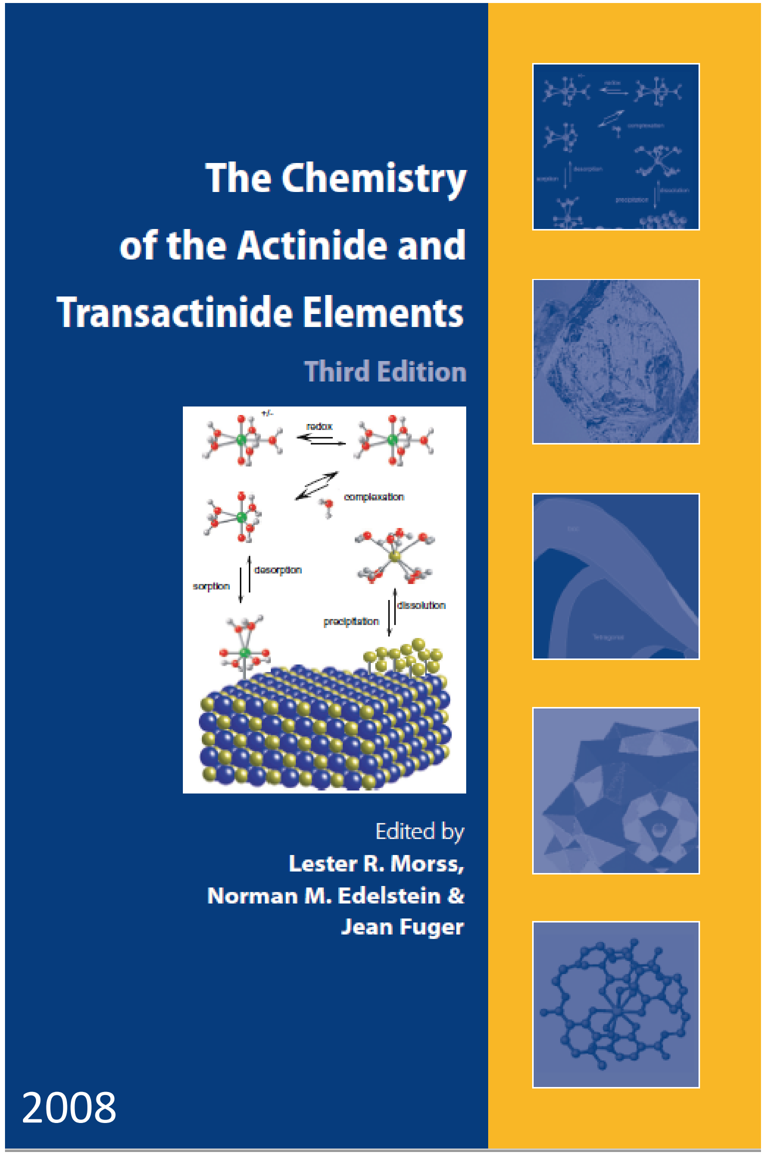
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

tons

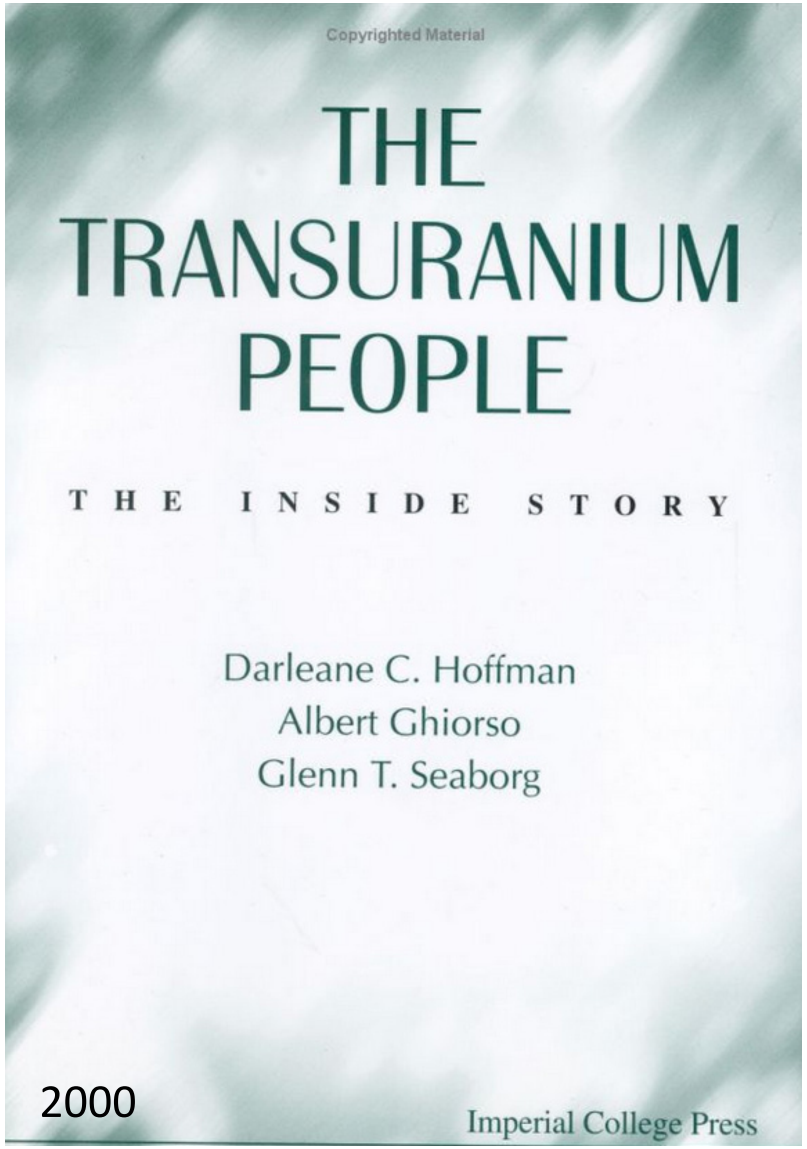
mg / µg / pg

50 atoms min^{-1}

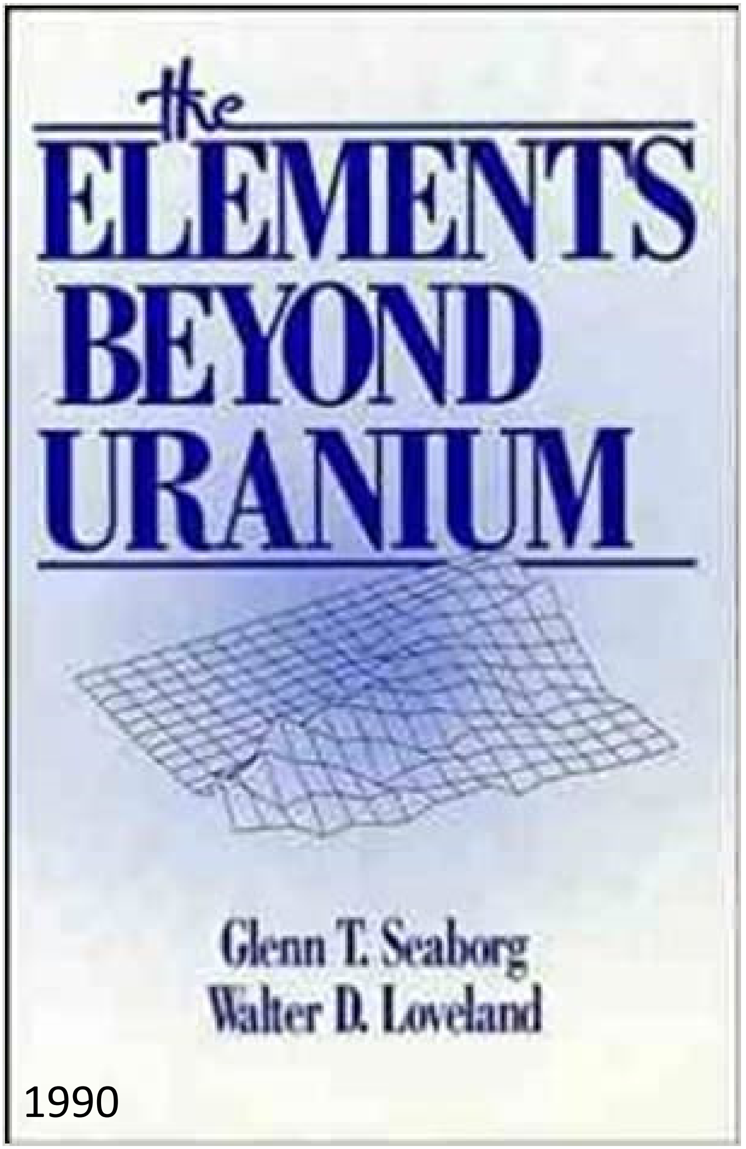
Further reading



2008



2000



1990