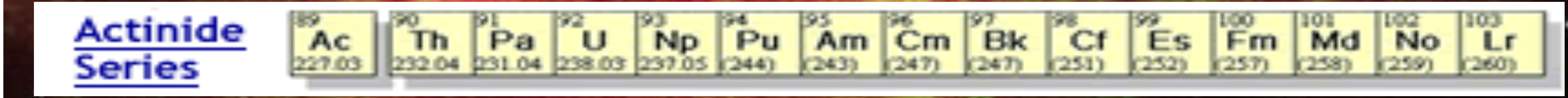
Actinide Chemistry



Actinide Series

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
227.03	232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

Associate Professor Susanna Wold

Understanding fundamental chemistry and the nature of the periodic system

- **Electronic configuration**
- **Oxidation states**
- **The metallic states**
- **Crystal structure**
- Environmental impact

Actinide chemistry – Nuclear energy production

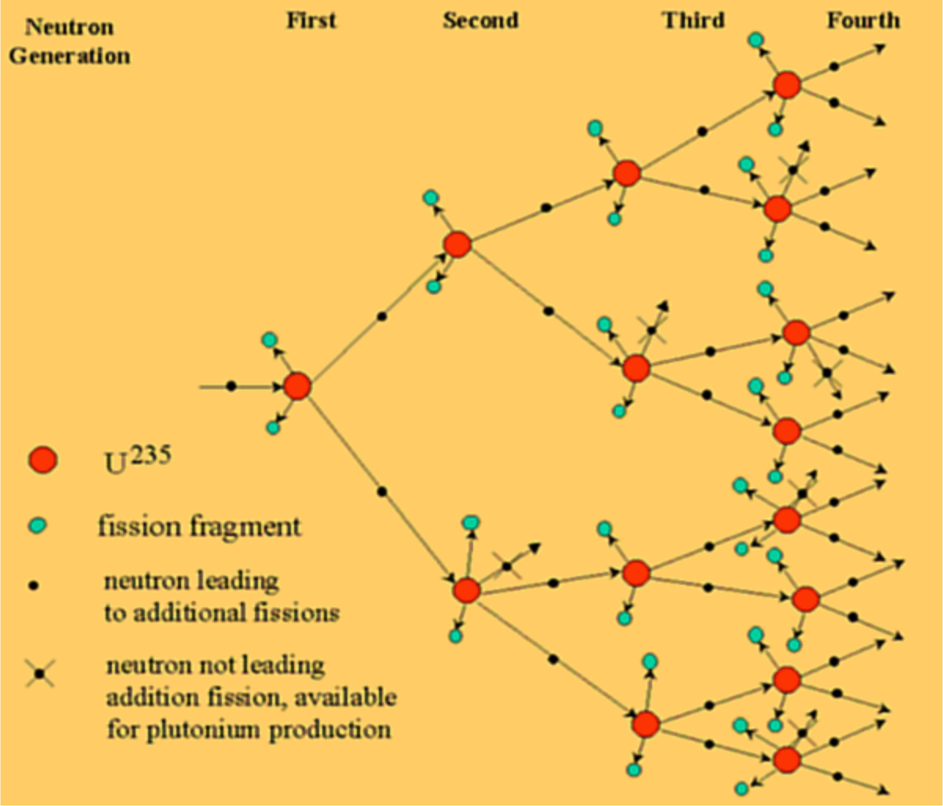
The Nobel Prize in Chemistry 1944

Otto Hahn *"for his discovery of the fission of heavy nuclei".*

1938 Otto Hahn and Fritz Strassman demonstrated fission by bombarding uranium where barium and other lighther elements with around half mass of U.

Lisa Meitner and Otto Frish (working under Nils Bohr) calculated the energy release from fission.

Conformation of $E=mc^2$

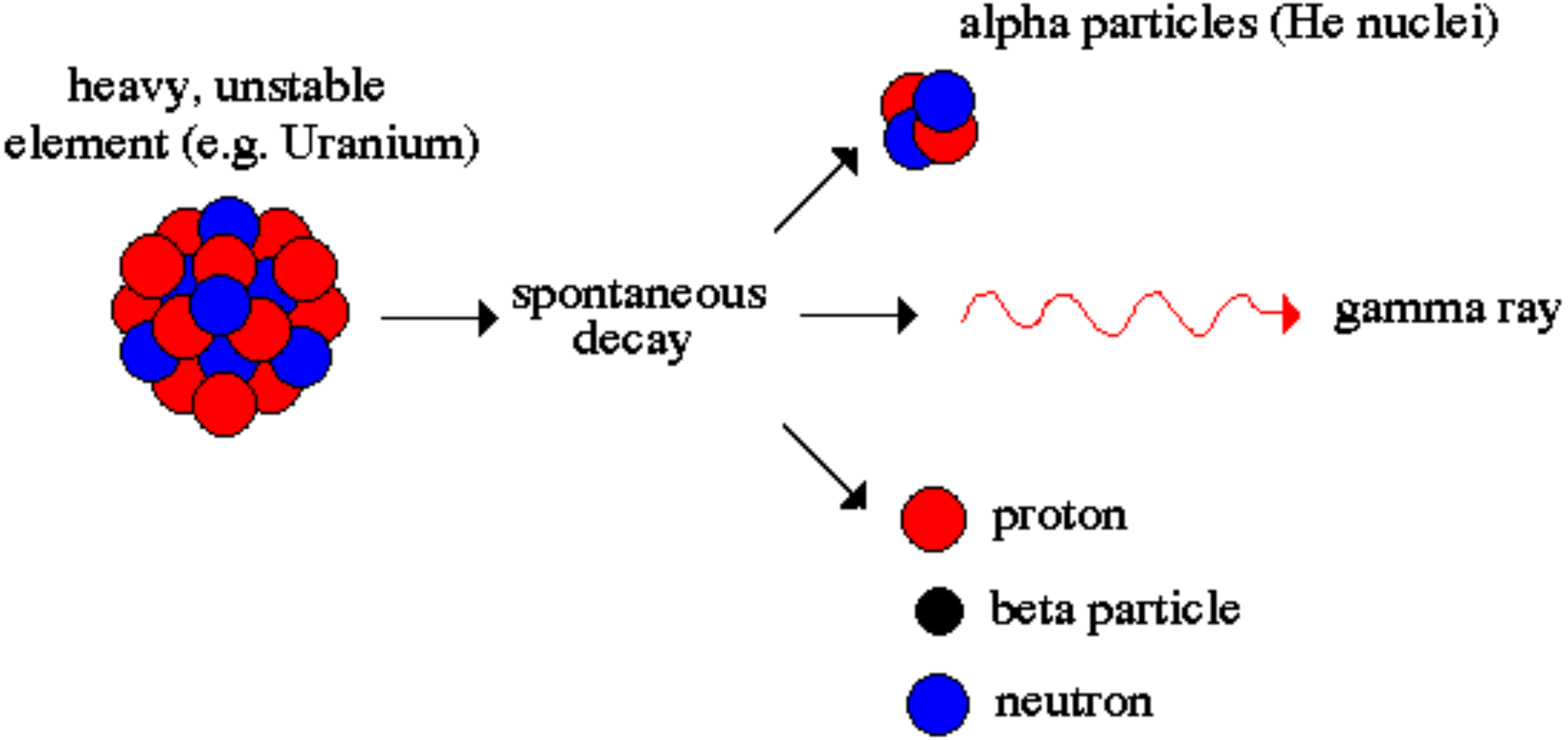


U and Pu are fissile
Th fertile

$$^{235}_{92}U + n \rightarrow fissionproducts + 2.5n + 200\,MeV$$

$$\mathrm{n} + {}^{232}_{90}\mathrm{Th} \rightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow{\beta^-} {}^{233}_{91}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}_{92}\mathrm{U}$$

Radioactivity



heavy, unstable
element (e.g. Uranium)

spontaneous
decay

alpha particles (He nuclei)

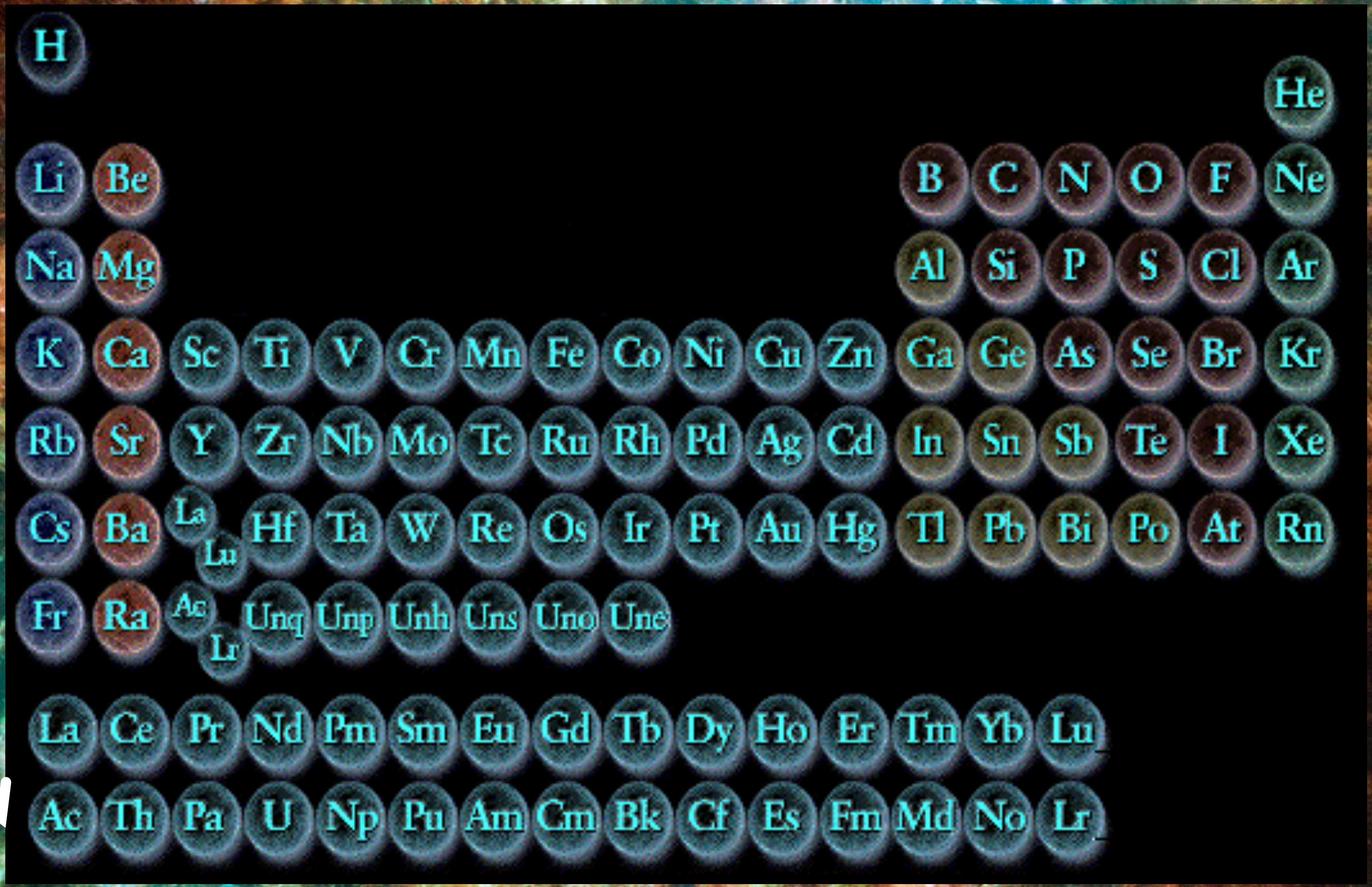
gamma ray

🔴 proton

● beta particle

🔵 neutron

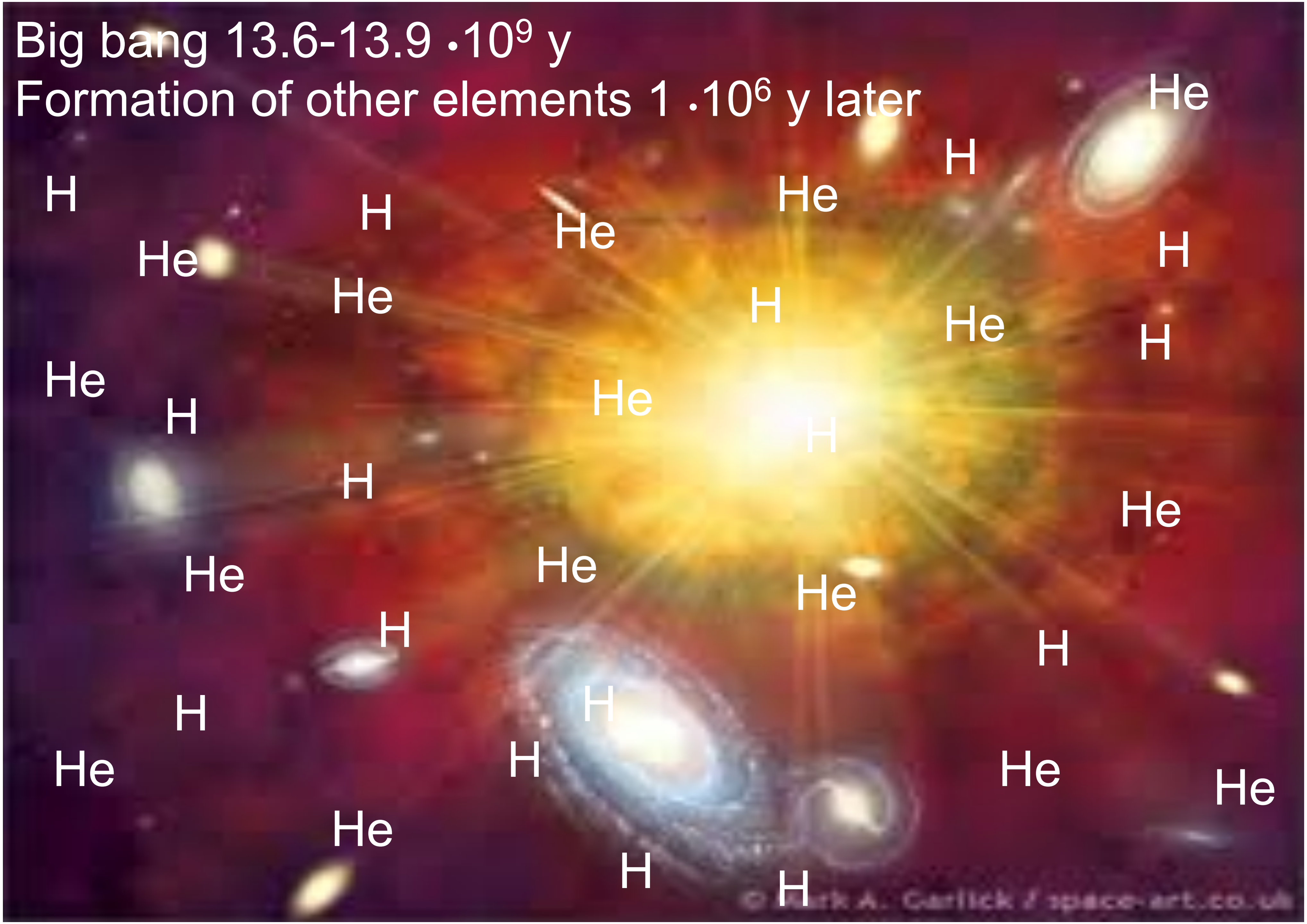
Actinides



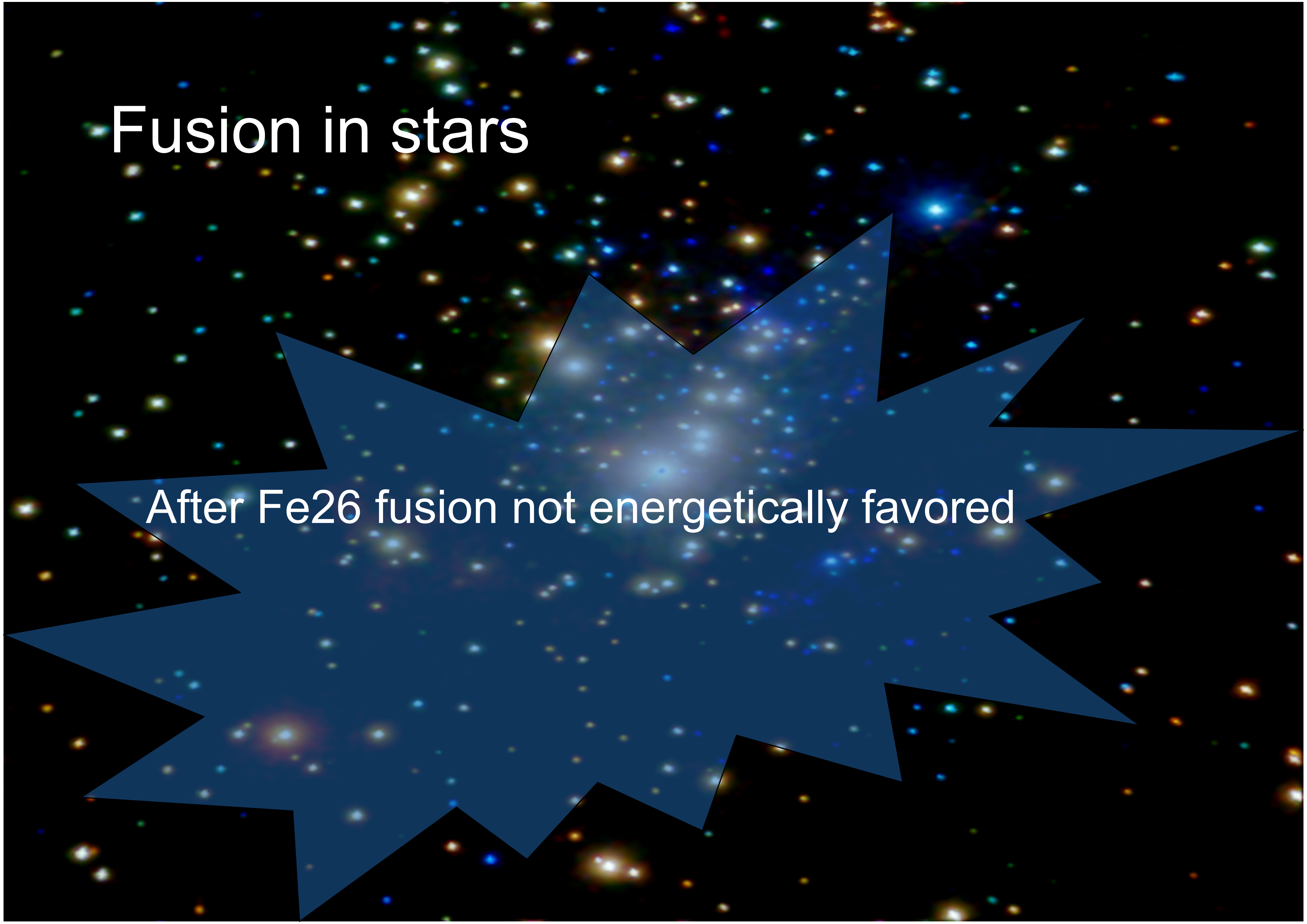
- Heavy
- No stable isotopes
- Radioactive

Big bang 13.6-13.9 $\cdot 10^9$ y

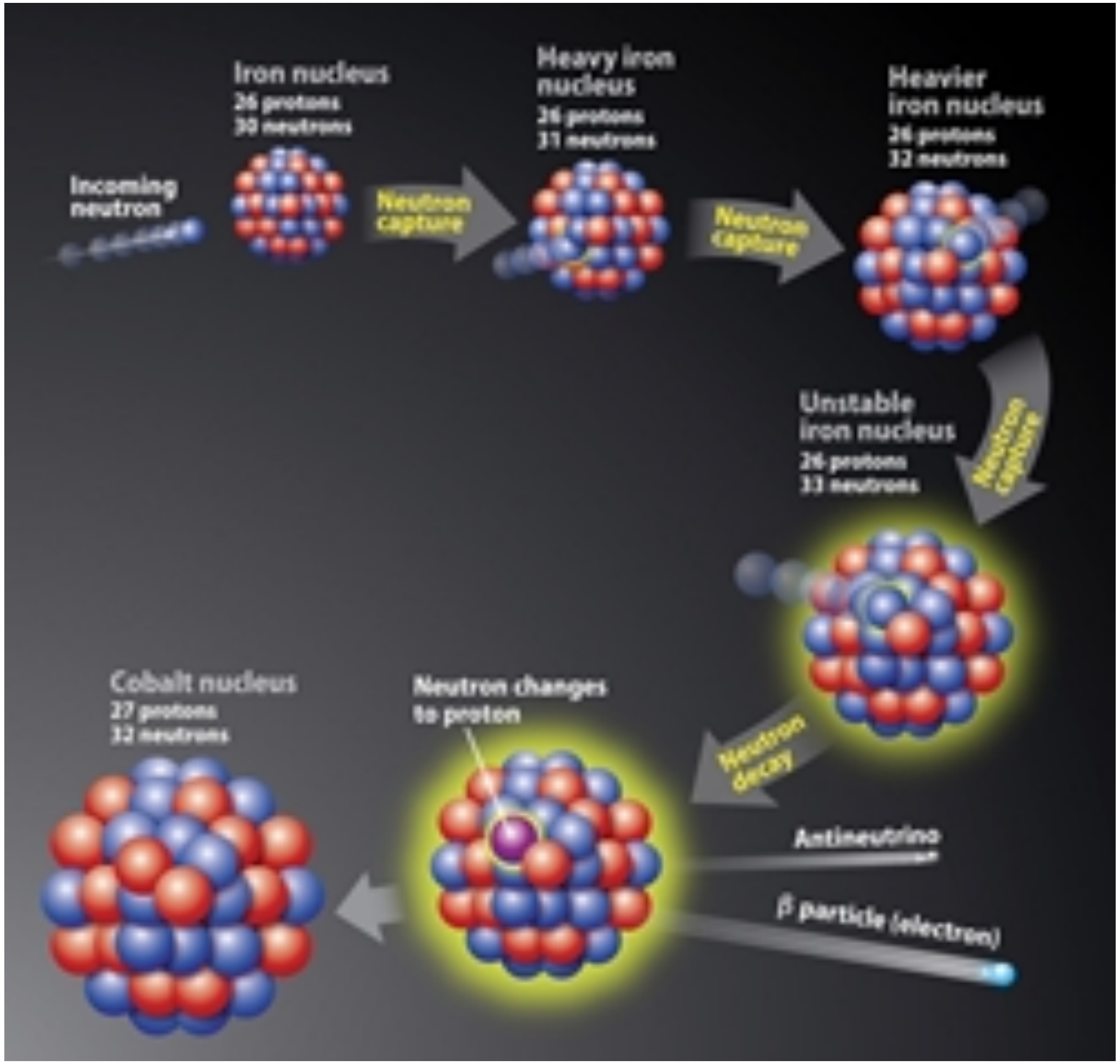
Formation of other elements 1 $\cdot 10^6$ y later



Fusion in stars



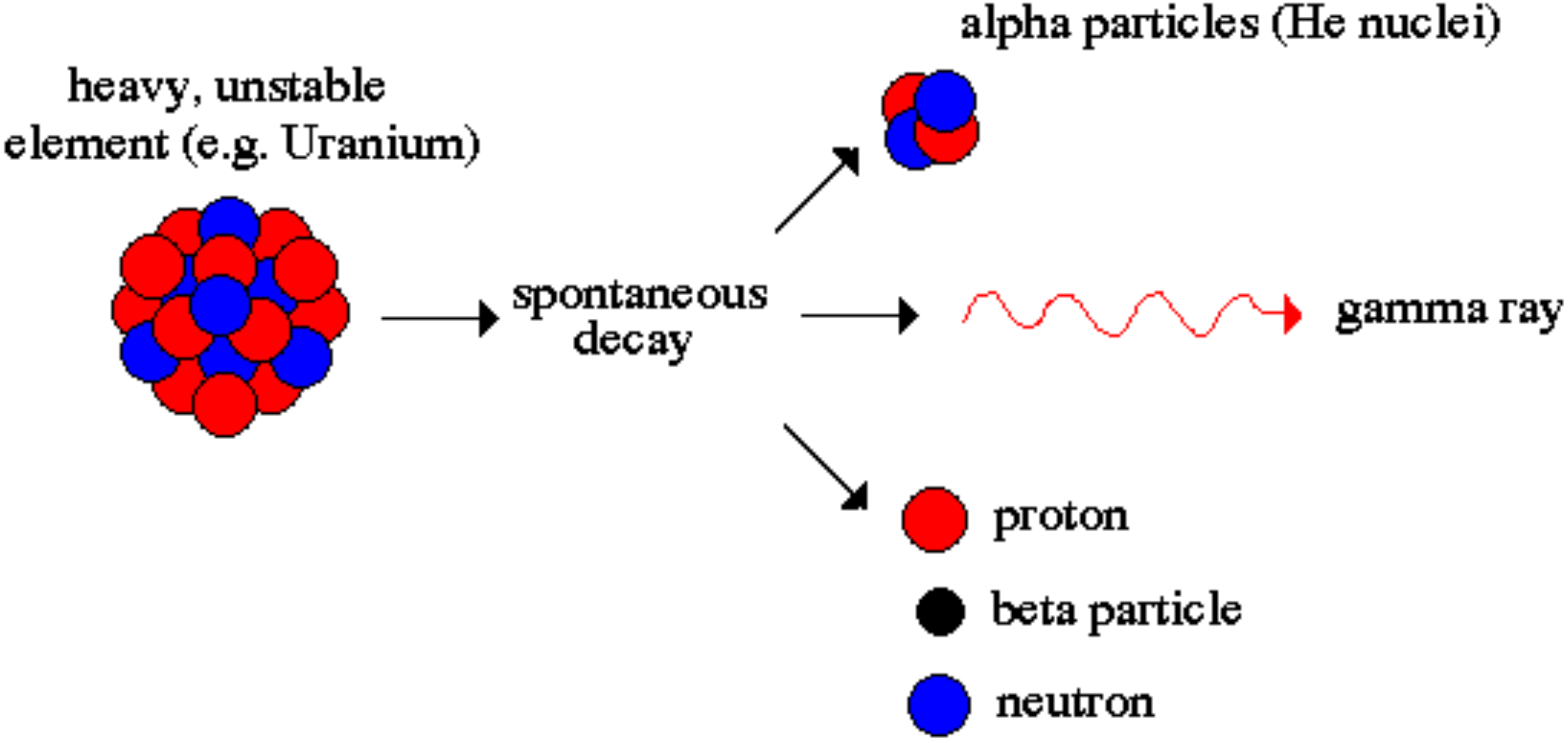
After Fe26 fusion not energetically favored



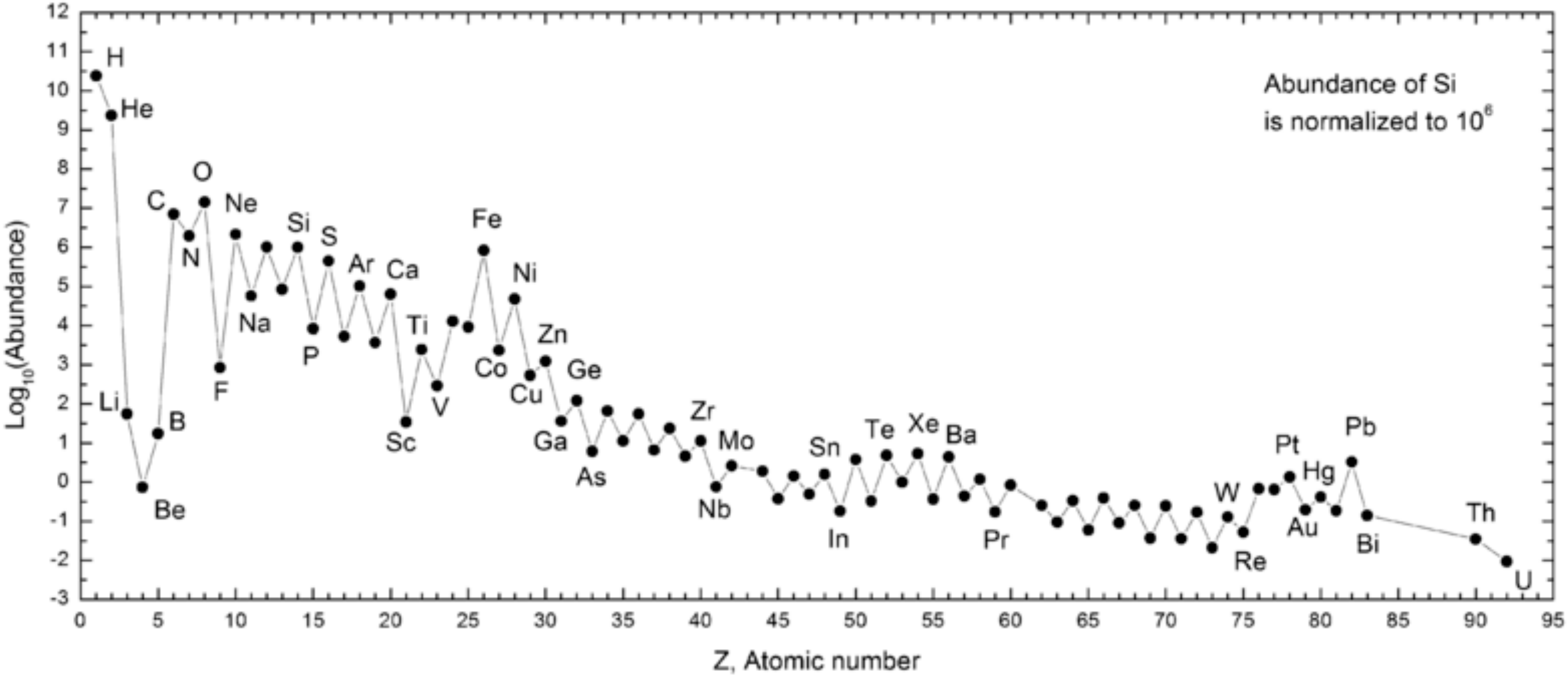
Heavier elements form in supernovas

< 1-2 % other elements than He and H

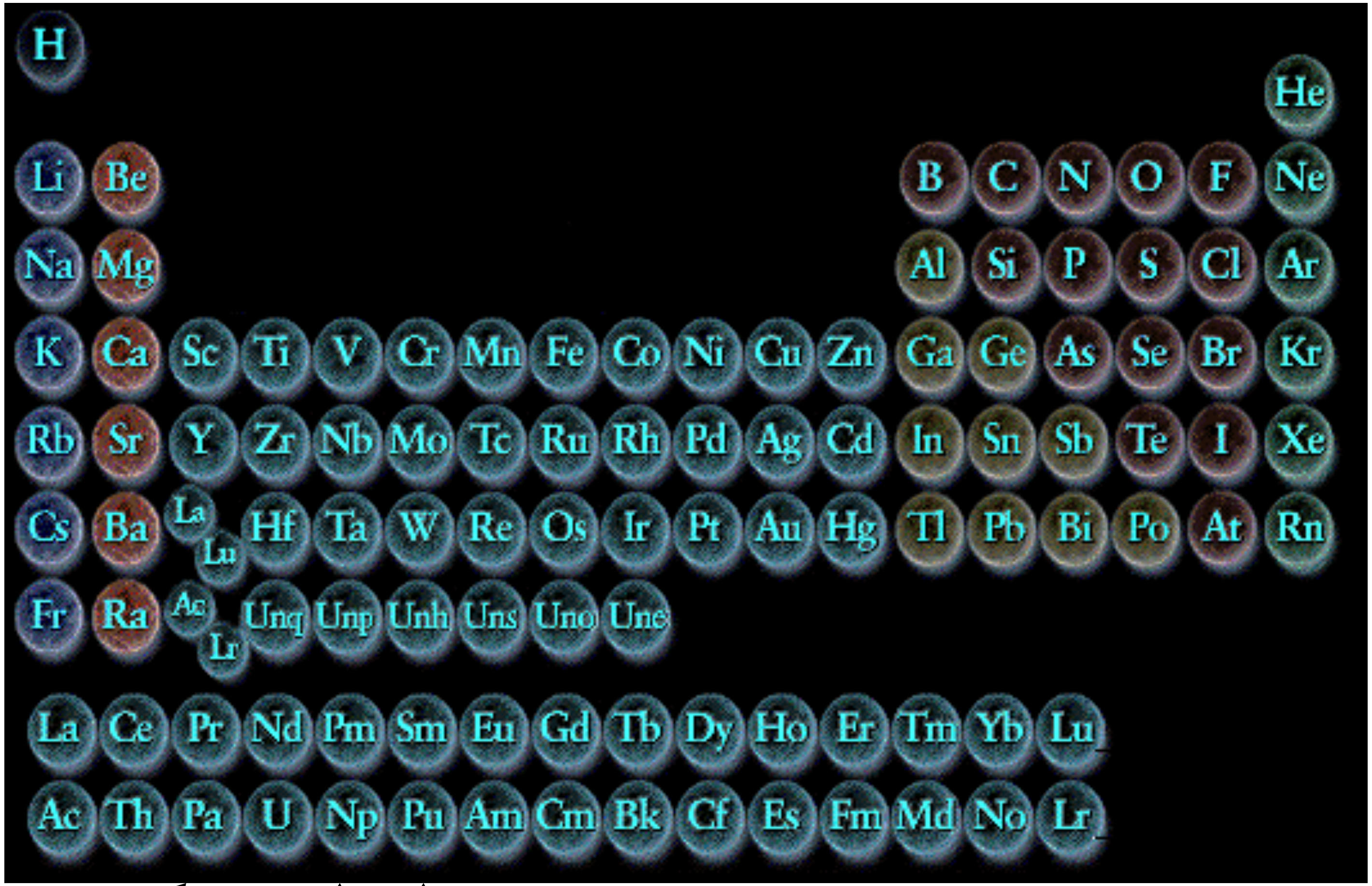
Radioactivity



Abundance of elements on earth / universe



Abundance in nature



Transuranium /transuranic elements

The Np and Pu generated by neutron capture in uranium ore with β-decays (238U → 239U → 239Np → 239Pu).

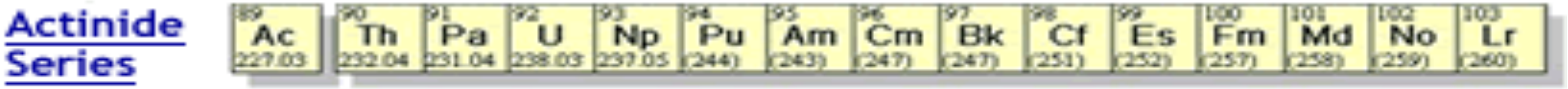
>Z=92 no occurrence in nature

$t^{1/2}$ too short in relation to the formation in supernovas after BB

Form by neutron capture and β-decay (accelerators)

Beyond Fm, halflifes so short that the low equilibrium conc, prevent formation of the elements

Did transuranic elements form at t_0?
Can they form or are we only able to produce them synthetically?



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Whitlockite -Chondrite

$Ca_9(Fe)(PO_4)_6PO_3OH$

^{244}Pu cannot easily be formed in Uranium ores by neutron capture

$$^{242}_{94}Pu + n \rightarrow ^{243}_{94}Pu + n \rightarrow ^{244}_{94}Pu$$

$$^{243}_{94}Pu \rightarrow ^{243}_{95}Am + \beta^{-}\left(t^{1/2}5h\right)$$

Natural decay chains

Isotope		Half-life	Radiation
Thorium-232	232Th	$1,4 \times 10^{10}$ y	α
Radium-228	228Ra	6,7 y	β-
Aktinium-228	228Ac	6,1 h	β-
Thorium-228	228Th	1,9 y	α
Radium-224	224Ra	3,7 d	α
Radon-220	220Rn	55,6 s	α
Polonium-216	216Po	0,16 s	α
Lead-212	212Pb	10,6 h	β-
Bismut-212	212Bi	60,6 m	β-, α
Polonium-212	212Po	$3,04 \times 10^{-7}$ s	α
Tallium-208	208Tl	3,1 m	β-
Lead-208	208Pb	stabile	

Natural??

Isotope		Half-life	Radiation
Neptunium-237	237Np	$2{,}1 \times 10^6$ y	α
Protaktinium-233	233Pa	27 d	β-
Uranium-233	233U	$1{,}6 \times 10^5$ y	α
Thorium-229	229Th	$7{,}3 \times 10^3$ y	α
Radium-225	225Ra	14,8 d	β-
Aktinium-225	225Ac	10 d	α
Francium-221	221Fr	4,8 m	α
Astat-217	217At	0,03 s	α
Bismut-213	213Bi	47 m	β-, α
Polonium-213	213Po	4,2 µs	α
Lead-209	209Pb	3,3 h	β-
Bismut-209	209Bi	stabile	

Isotope		Half life	Radiation
Uranium-238	238U	4,5 × 10^{9} y	α
Thorium-234	234Th	24,1 d	β-
Protaktinium-234m	234mPa	1,2 m	β-
Uranium-234	234U	2,5 × 10^{5} y	α
Thorium-230	230Th	8,0 × 10^{5} y	α
Radium-226	226Ra	1,6 × 10^{3} y	α
Radon-222	222Rn	3,8 d	α
Polonium-218	218Po	3,05 m	α
Lead-214	214Pb	26,8 m	β-
Bismut-214	214Bi	19,7 m β-, α	
Polonium-214	214Po	1,64 × 10^{-4} s	α
Lead-210	210Pb	22,3 y	β-
Bismut-210	210Bi	5,0 d	β-
Polonium-210	210Po	138,4 d	α
Lead-206	206Pb	stabile	

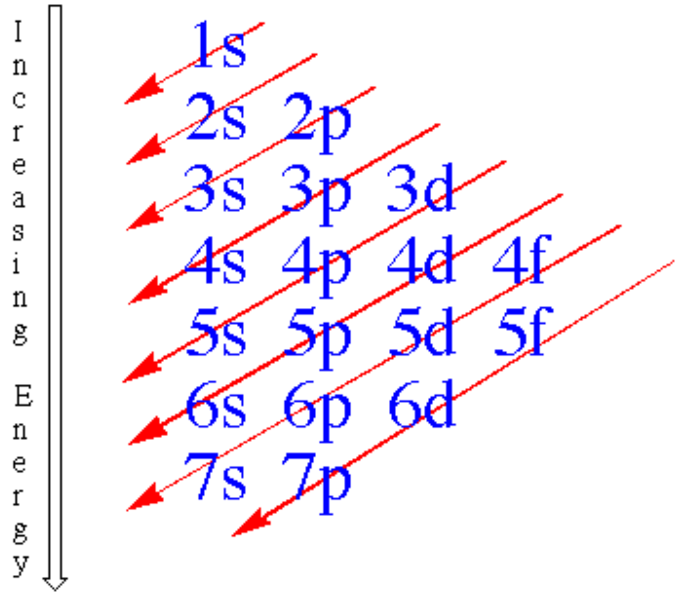
Isotope		Half life	Radiation
Uranium-235	235U	$7{,}1 \times 10^{8}$ y	α
Thorium-231	231Th	25,6 h	β-
Protaktinium-231	231Pa	$3{,}2 \times 10^{4}$ y	α
Aktinium-227	227Ac	21,6 y	β-
Thorium-227	227Th	18,2 d	α
Francium-223	223Fr	22,0 m	β-
Radium-223	223Ra	11,4 d	α
Radon-219	219Rn	4,0 s	α
Polonium-215	215Po	$1{,}77 \times 10^{-3}$ s	α
Lead-211	211Pb	36,1 m	β-, α
Bismut-211	211Bi	2,2 m	α
Tallium-207	207Tl	4,8 m	β-
Lead-207	207Pb	stabile	

Electronic configuration

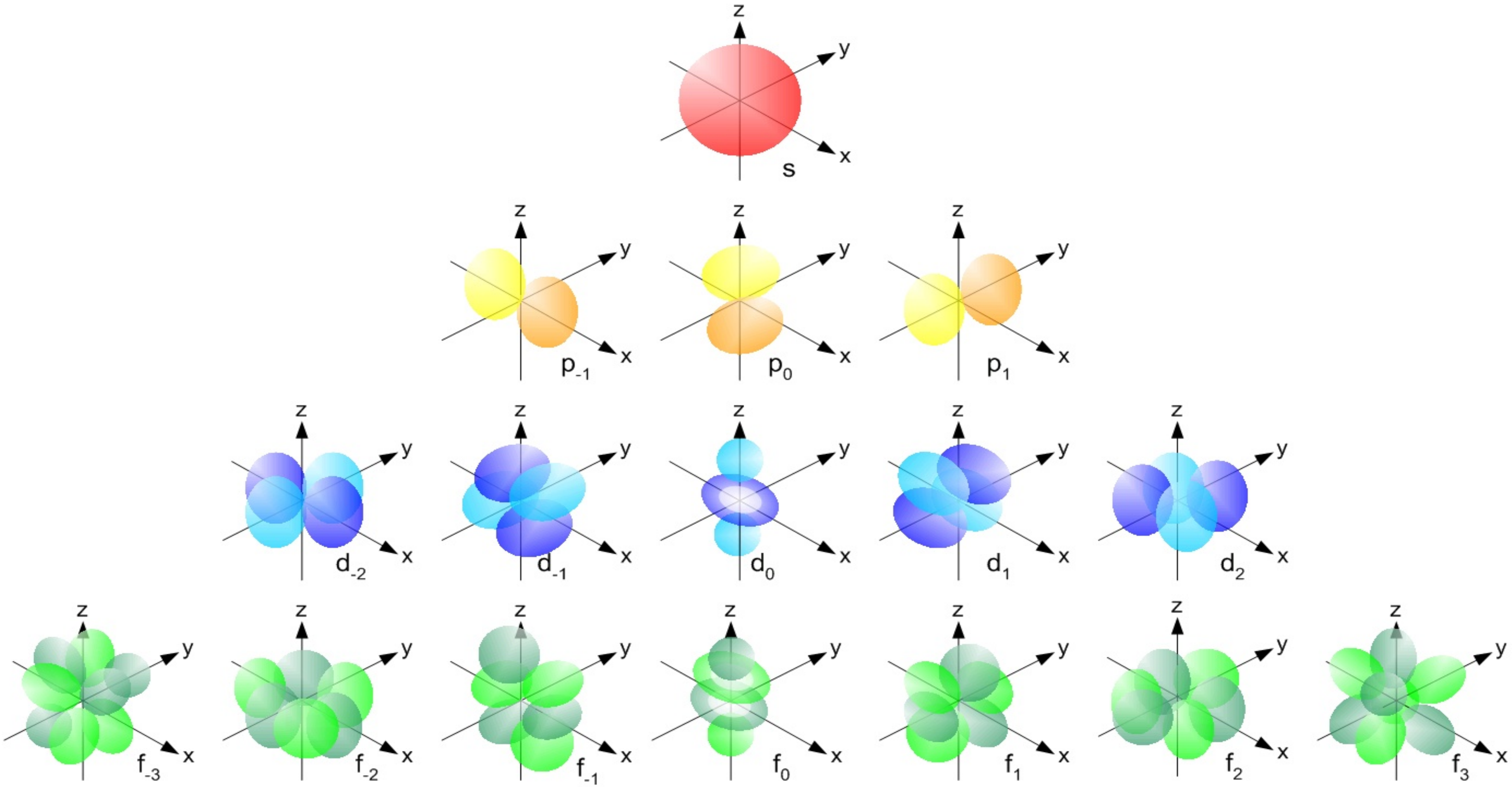
Actinides f-block elements
Filling up the 5f orbitals from Th to Lr

Delocalized electrons to localized electrons

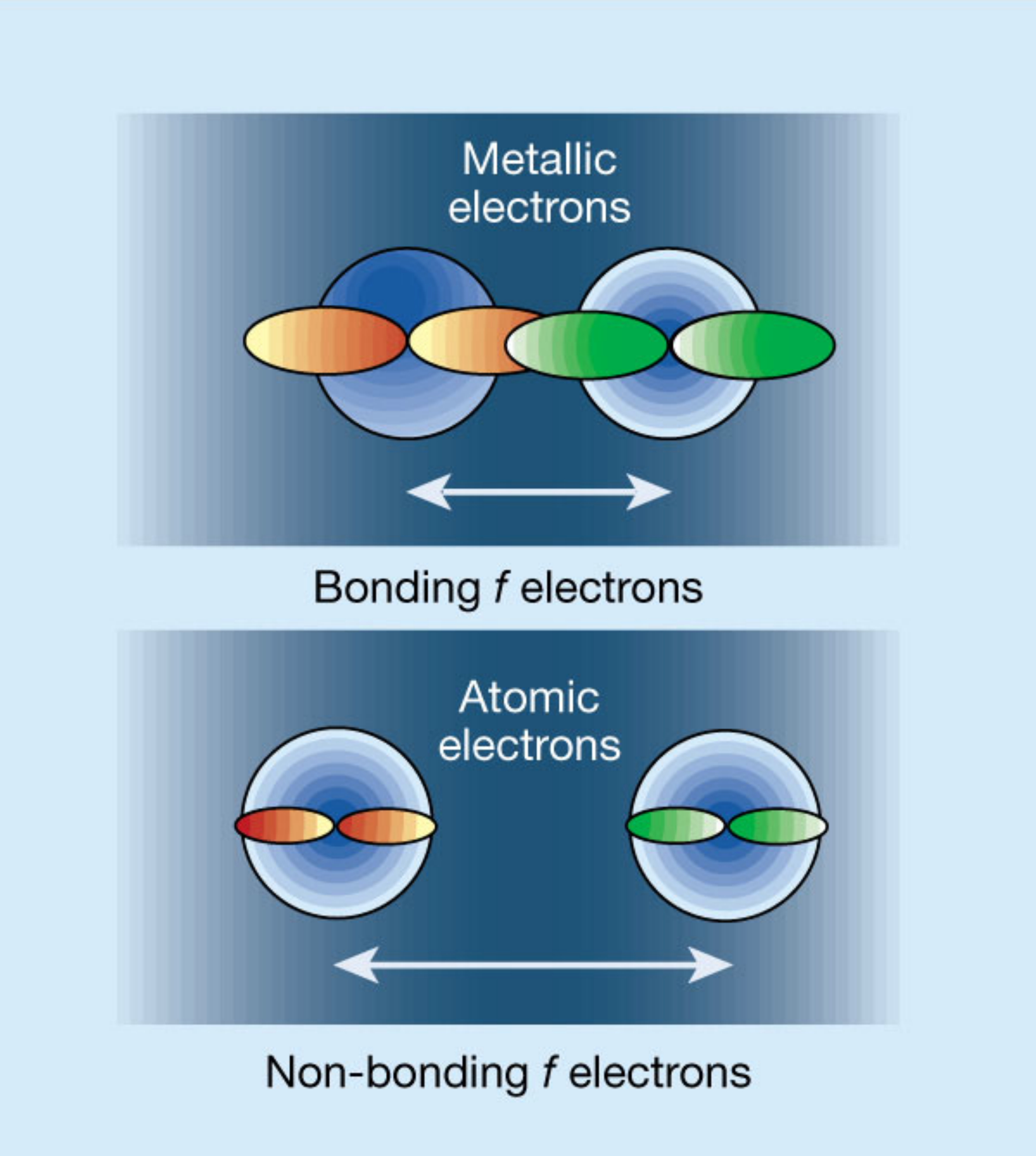
5f close in energy to 6d and 7s in particular in Z=90-94



Orbitals



Delocalized /Localized electrons



The metallic state

Band structure due to delocalized electrons

5f-5f wave function overlap or hybridization with s, p or d electrons

Delocalized electrons Localized electrons

Superconductivity to magnetic phenomena →

General information on actinides

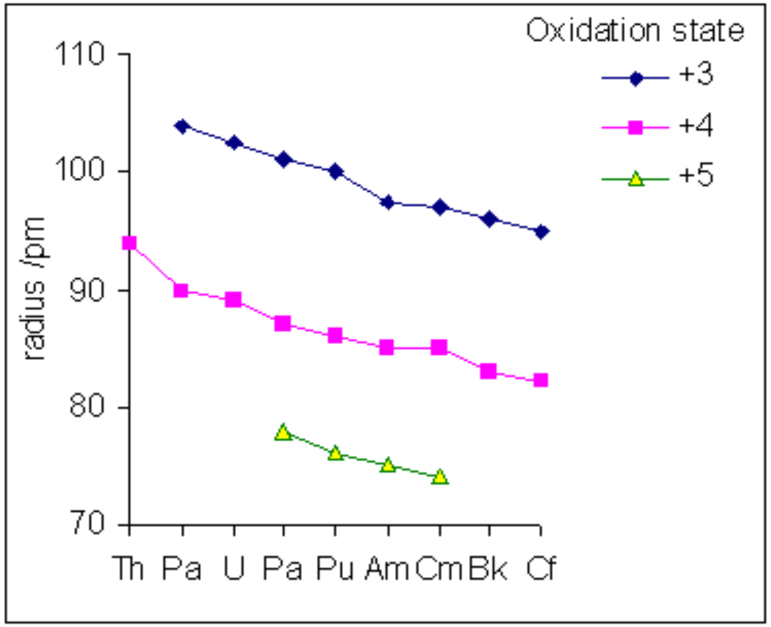
➡ Actinides or the f-block elements:

- Th ($7s^2 6d^2$) to Lr ($7s^2 5f^{14} 7p^1$)

5f electrones are shielded to a greater extent from the nucleus than the 4f in lanthanides, why the energy difference between 5f, 6d and 7s will be smaller than in the lanthanide series

Consequence: Complexes?

Actinide contraction: analogous to the lanthanide contraction.
With increasing atomic number, the outer shell electrons loose the shielding from the nucleus Coulombic interactions. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

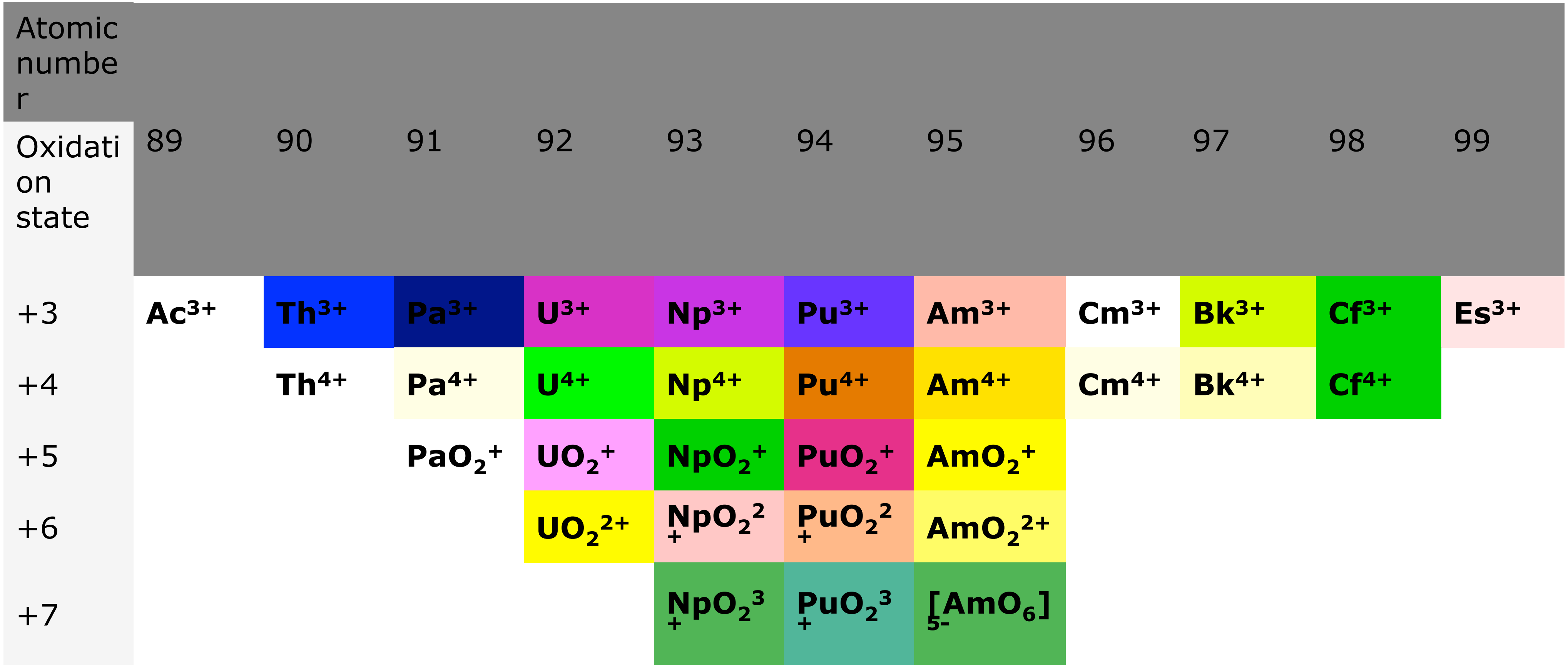


General about actinides

- Similarity in chemical properties between the actinide and lanthanide element used in synthesis and isolation
- Thermodynamical data for the actinide elements are in most cases estimations from experimental data from the lanthanides or results from theoretical calculations, because?
- In nature, asctinides are often carried by natural colloids like clay and humic substances.
- Shorter lived actinides are difficult to analyze.

General information on actinides

The colors in low oxidation states are due to f-f transitions. In the high oxidation states can occur charge transfer transitions. Strong spin-orbit coupling but weak crystal field splitting - there is little color variation in compounds of a given element in a given oxidation state. Transitions between 5f and 6d orbitals are observed in the ultraviolet region.



Atomic number Oxidation state	89	90	91	92	93	94	95	96	97	98	99
+3	Ac^{3+}	Th^{3+}	Pa^{3+}	U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}
+4		Th^{4+}	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}	Bk^{4+}	Cf^{4+}	
+5			PaO_2^+	UO_2^+	NpO_2^+	PuO_2^+	AmO_2^+				
+6				UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}				
+7					NpO_2^{3+}	PuO_2^{3+}	$[AmO_6]^{5-}$				

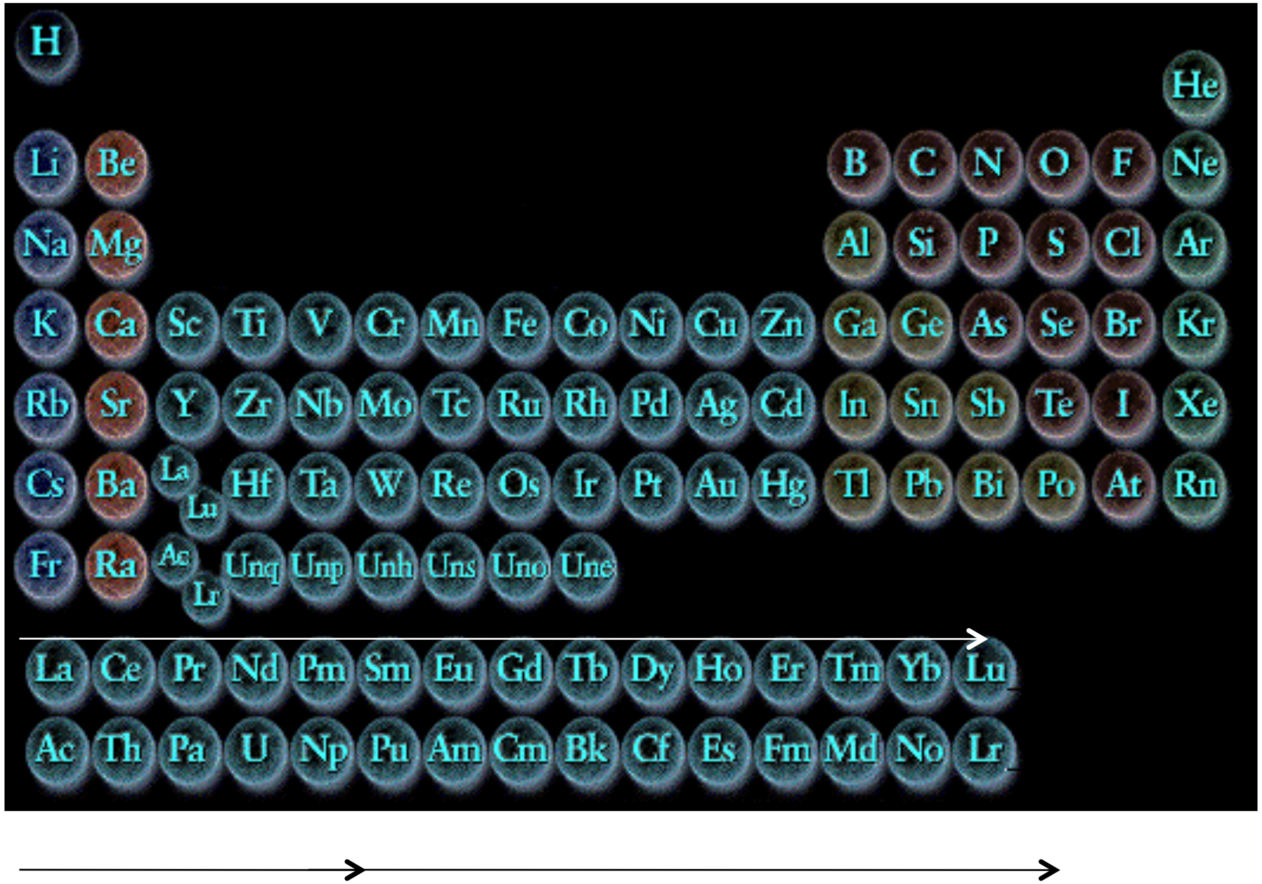
- For the same element, the stability of the complexes varies with the oxidation state in series

- $M^{4+} \geq MO_2^{2+} > M^{3+} \geq MO_2^{+}$

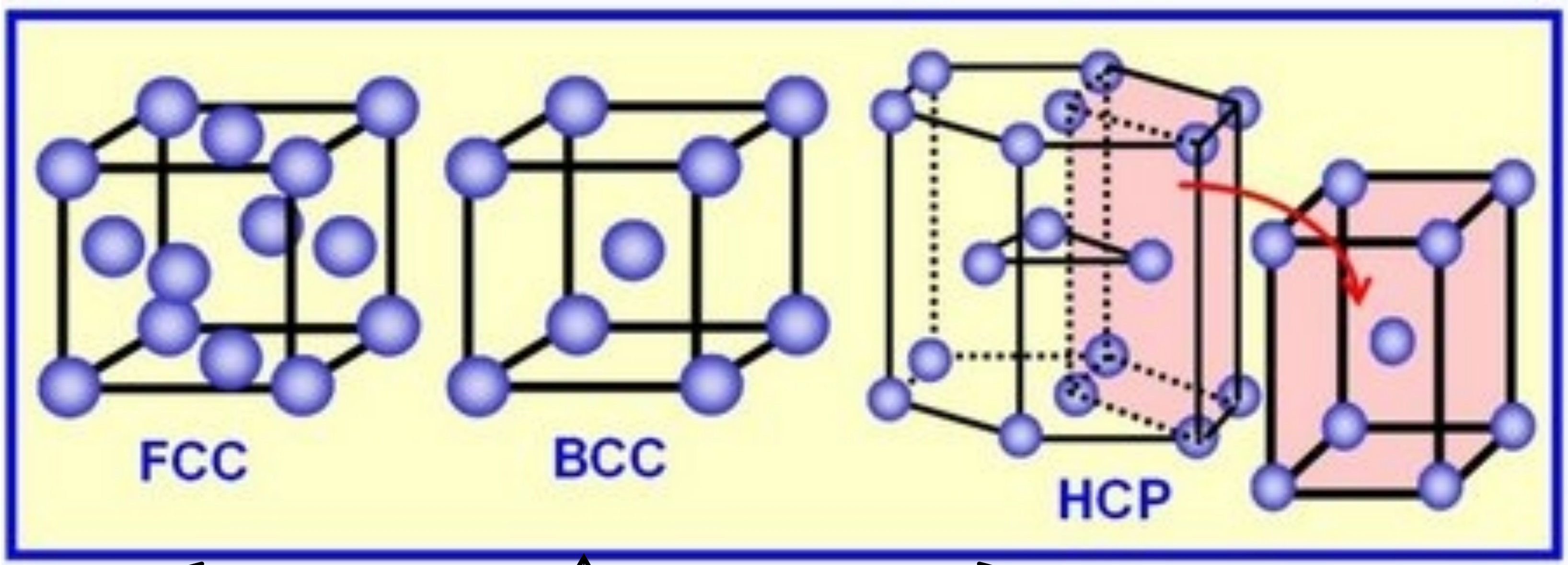
The reversal between M^{3+} and MO_2^{2+} due to hexavalent metal atom in the linear $[OMO]^{2+}$is only partially shed by two oxygen atoms. So MO_2^{2+} has higher charge density than MO_2^{+}

$Ac^{3+} < Am^{3+} < Cm^{3+}$

The crystal structure



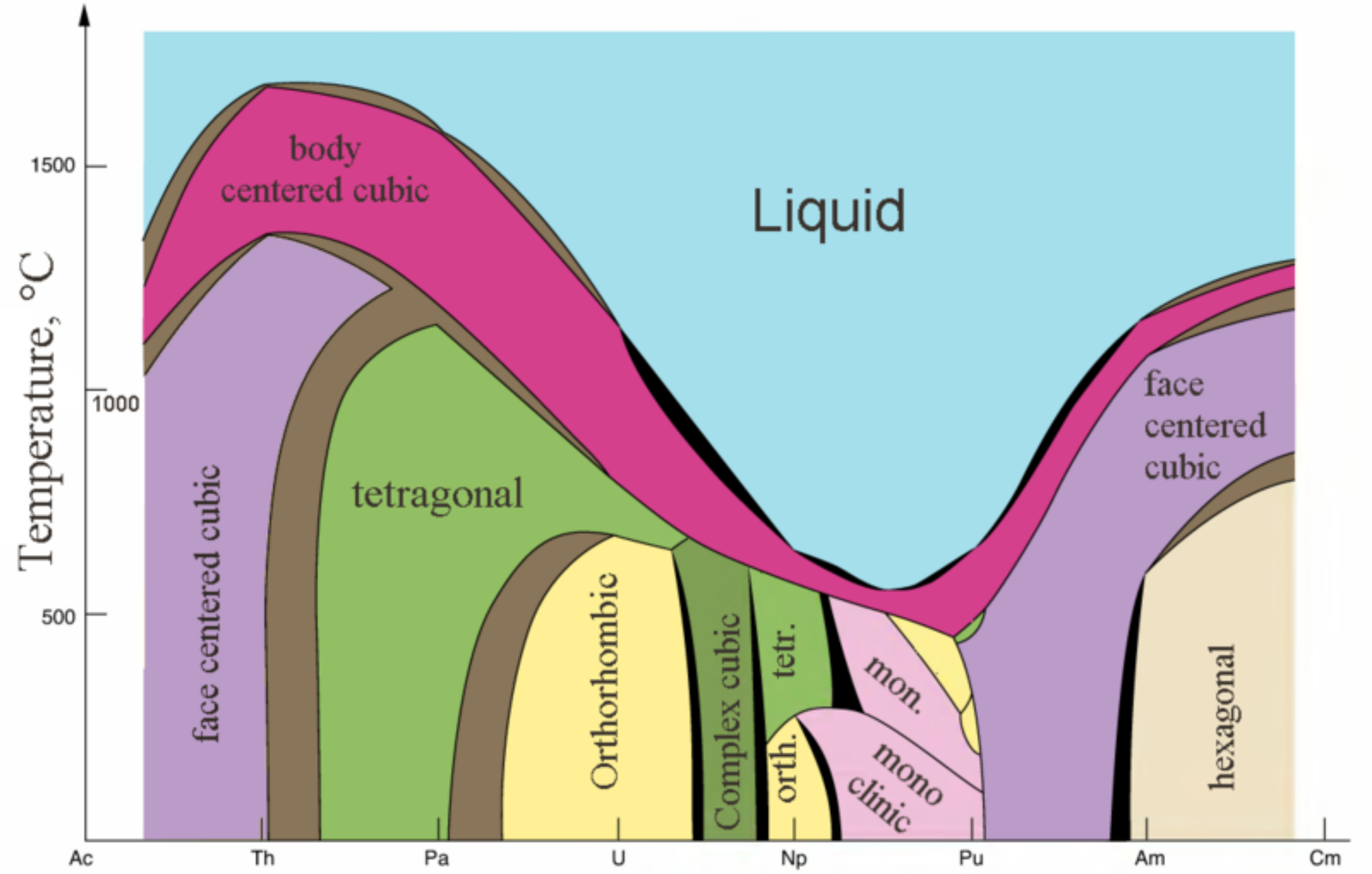
Crystal structure in lanthanides

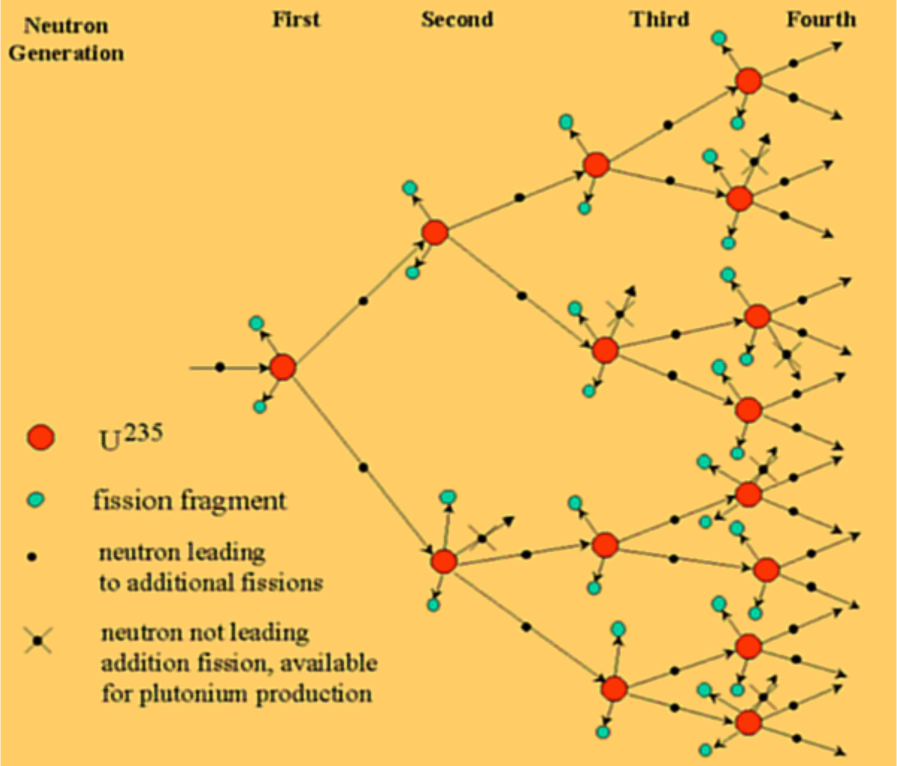


Low temperature

High temperature

Crystal structure in actinides





FISSILE

By early 1942, it was known that the two naturally occurring isotopes of uranium reacted with neutrons as follows:

$$^{235}U_{92} + {}^{1}n_{0} \text{ --> } \text{fission products} + (2.5)\,{}^{1}n_{0} + 200\text{ MeV Energy}$$

$$^{238}U_{92} + {}^{1}n_{0} \text{ --> } {}^{239}U_{92}$$

$$^{239}U_{92} \text{ --> } {}^{239}Np_{93} + \beta^{-1} \qquad t_{1/2}=23.5\text{ min.}$$

$$^{239}Np_{93} \text{ ---> } {}^{239}Pu_{94} + \beta^{-1} \qquad t_{1/2}=2.33\text{ days}$$

Each U-235 that undergoes fission produces an average of 2.5 neutrons. In contrast, some U-238 nuclei capture neutrons, become U-239, and subsequently emit two beta particles to produce Pu-239. The plutonium was fissile also and would produce energy by the same mechanism as the uranium.

FERTILE

$$n + {}^{232}_{90}\mathrm{Th} \rightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow{\beta^-} {}^{233}_{91}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}_{92}\mathrm{U}$$

Advantages with using Th instead of U:

Abundant recource (in ppm) much more than U

Less longlived elements in the waste

Less radioactive waste

Tonnes (2010)Country	**Reserves**
United States	440,000
Australia	300,000
Brazil	16,000
Canada	100,000
India	290,000
Malaysia	4,500
South Africa	35,000
Other Countries	*90,000*
World Total	*1,300,000*

Th-reactors

Problems to solve:
high cost of fuel fabrication

U-233 contaminated with traces of U-232 (69 year half-life but whose daughter products such as thallium-208 are strong gamma emitters with very short half-lives).

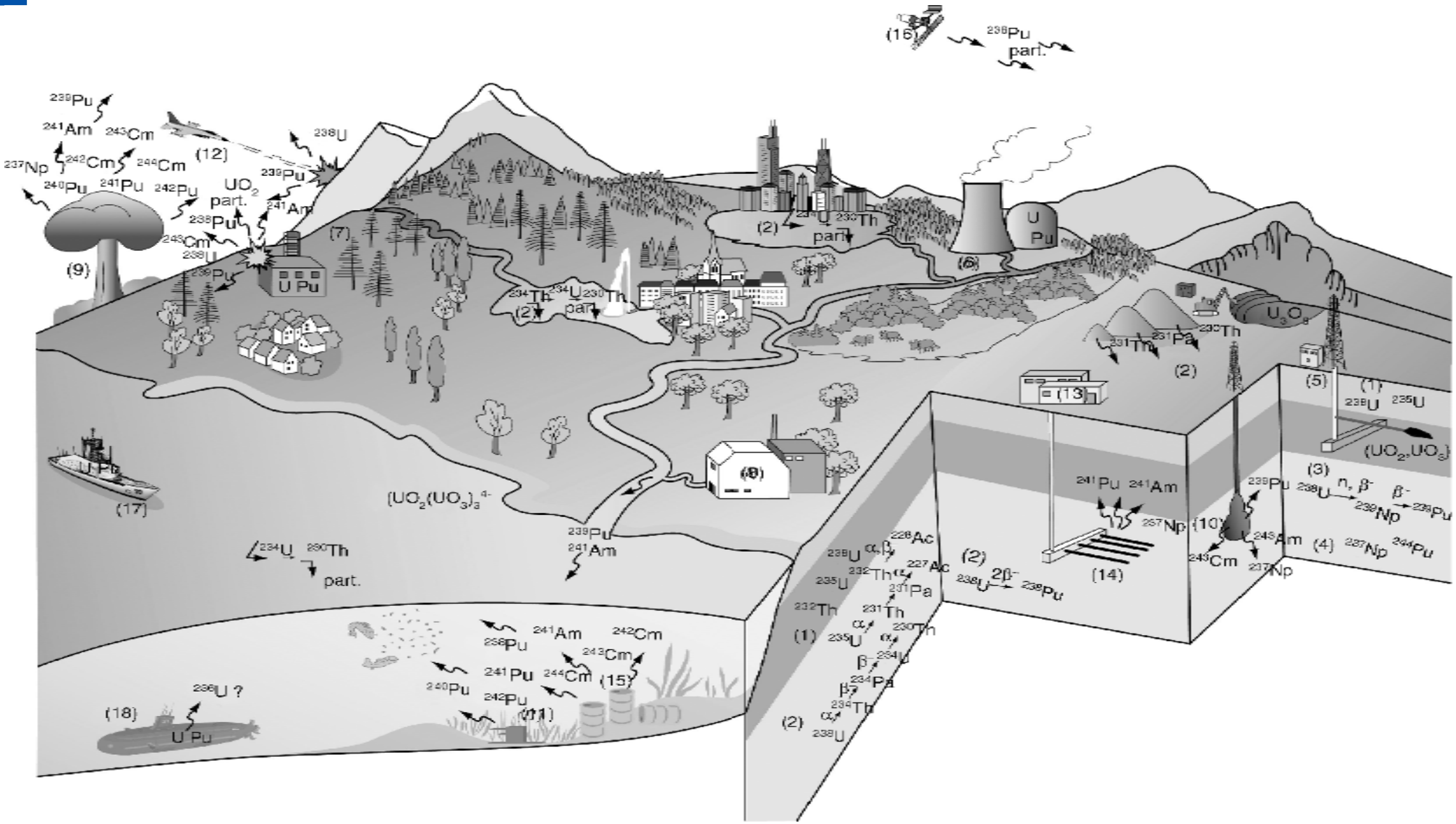
Recycling thorium hard due to radioactive Th-228 (an alpha emitter with two-year half life)

Other applications

- Technical applications

smoke detectors (neutron source)
small power generators
ϒ-radiation source for measuring metal thickness
medical treatments
etc. etc.

Actinides in the environment



Natural and anthropogenic actinide species in the environment.

Actinides in the environment

- Natural:
  - Natural occurring major actinides: ^{232}Th, ^{235}U, ^{238}U, ^{226}Ac
  - Natural occurring minor actinides: ^{234}Th, ^{234}Pa, ^{243}U, ^{230}Th, ^{238}Pu
  - Actinides at the ultratrace level: ^{239}Np, ^{239}Pu, ^{237}Np, ^{244}Pu

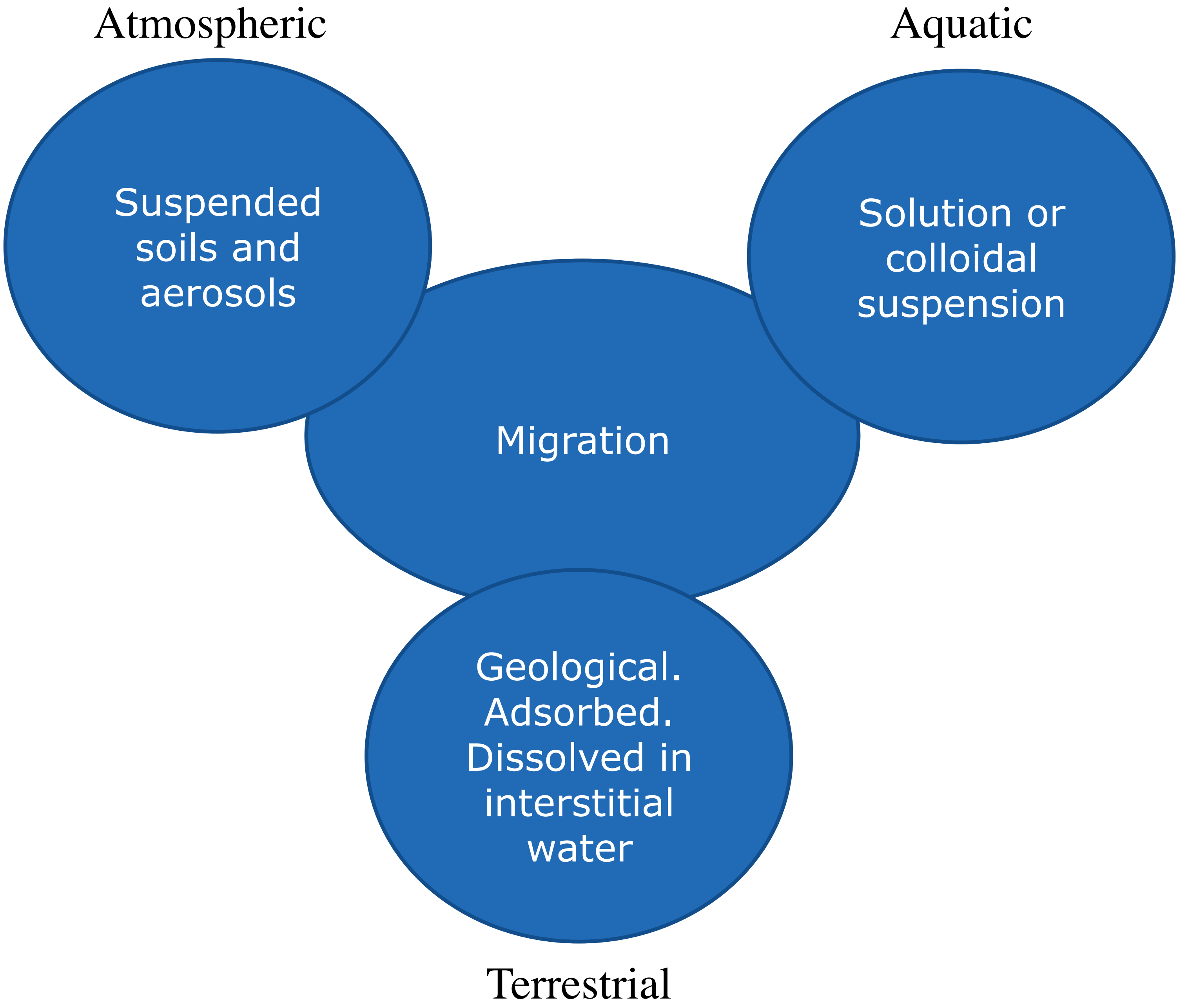
- Anthropogenic:

  ^{241}Am, ^{244}Cm, ^{243}Cm, ^{242}Cm, ^{237}Np, ^{236}Pu, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{234}U, ^{235}U, ^{236}U, ^{238}U

➡ Anthropogenic actinides origin:

- Released intentionally below legal norms from nuclear power plants, released by accident, or reprocessing facilities.
- Actinides released from military activities: weapons production (atmospheric tests, underground detonations, objects from nuclear naval vessels and depleted uranium warheads).
- Nuclear waste management activities: intermediate, geologic and oceanic disposal.
- Unexpected events from nuclear power sources: satellite reentry in the atmosphere, nuclear icebreakers, or nuclear submarine sinking.

Actinides in the environment



Atmospheric

Aquatic

Suspended soils and aerosols

Solution or colloidal suspension

Migration

Geological. Adsorbed. Dissolved in interstitial water

Terrestrial

Actinides in natural waters

Actinide solubility in water depends on:

- pH of the media
- Redox potential of the media
- Reactions with complexing agents (carbonates, phosphates, humics…)
- Sorption to surface of minerals and/or colloids

Actinides have strong ion-dipole interaction with water molecules and the binding of water of hydration extends beyond the first hydration sphere.

The extent of hydration of the cation is dependent of its effective charge and the number of coordination sites not occupied by ligands.

The case of Pu

- Pu isotopes are regarded as highly hazardous pollutants due to:
  - Their radiological toxicities
  - Their very long radioactive half-lives – 87.7 up to 8.08 x 10^{7} y
  - They are released into the environment as a result of human activity – nuclear weapons testing, satellite and reactor accidents…

In 1989 the total fallout of Pu releases in the environment was estimated as:

- 330 TBq → ^{238}Pu
- 7.4 PBq → ^{239}Pu
- 5.2 PBq → ^{240}Pu
- 170 PBq → ^{241}Pu
- 16 TBq → ^{242}Pu

Distribution strongly influenced by the different environmental compartments: atmosphere, terrestrial environment, aquatic environment.

Actinides in natural waters - Pu

The speciation as a function of pH poses a challenge when it comes to model the speciation behavior of Pu in water. In the same oxidation state, Pu can exist in a variety of forms at different pH values:

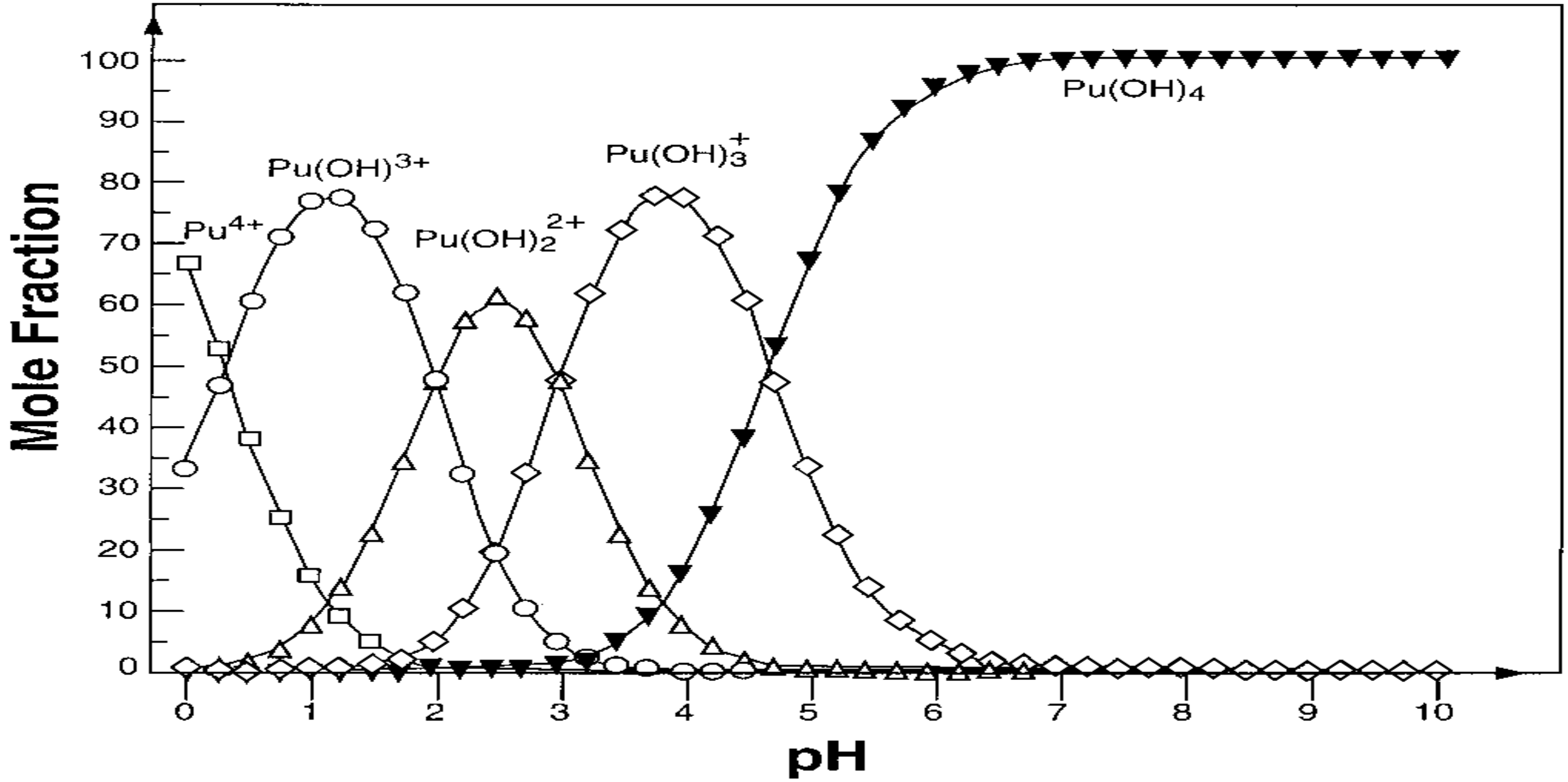


Fig. 5. Speciation diagram of Pu(IV) as a function of pH in oxic waters.

Pu in natural waters - sorption

- The strength of the actinide – carbonate complexation makes the carbonate minerals as excellent surfaces for actinide sorption.

- Pu sorbs strongly in the (III) and (IV) states. In the Baltic sea 99% of Pu(IV) is sorbed to sediments.

- Because of the strong affinity of $Pu(OH)_4$ for sediments and suspended particulates, Pu(IV) sorption is a limiting factor in Pu transport processes.

Actinides in natural waters, role of humics and colloids

- In sea waters the size of humics falls in the range of colloidal particles.

- Humic acid can readily reduce Pu(V)O_2^+ and Pu(VI)O_2^{2+} to the insoluble Pu(IV).

- The tetravalent state of Pu is very susceptible to hydrolysis. The hydrolytic products of Pu(IV) can precipitate, sorb to solids or colloidal species.

- In sea water colloids are usually carbonates or oxide minerals very often with a surface coating of humic acid (pseudo-colloids) which can sorb the hydrolyzed species even stronger than simple colloids.

Actinides in natural waters

Complexation strength for Pu: Pu(IV) $>$ Pu(III) $\approx$ Pu(VI)O_2^{2+} $>$ Pu(V)O_2^{+}

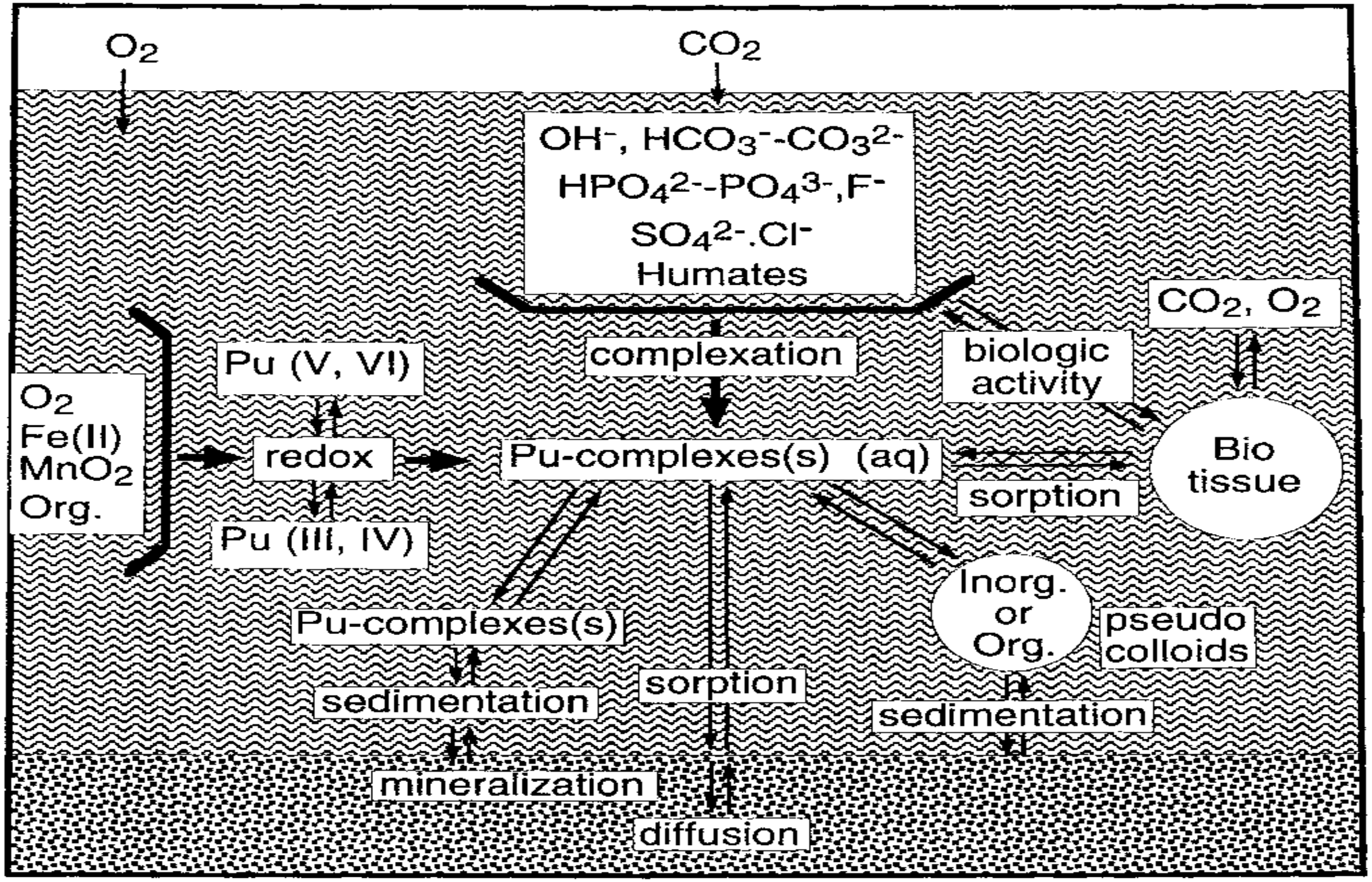


Diagram of possible reactions of plutonium in natural waters.