LECTURE SCHEDULE

Mon (Ke3) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Ke5) 10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu & Magnetism
10.	Fri	29.09.	Cu & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

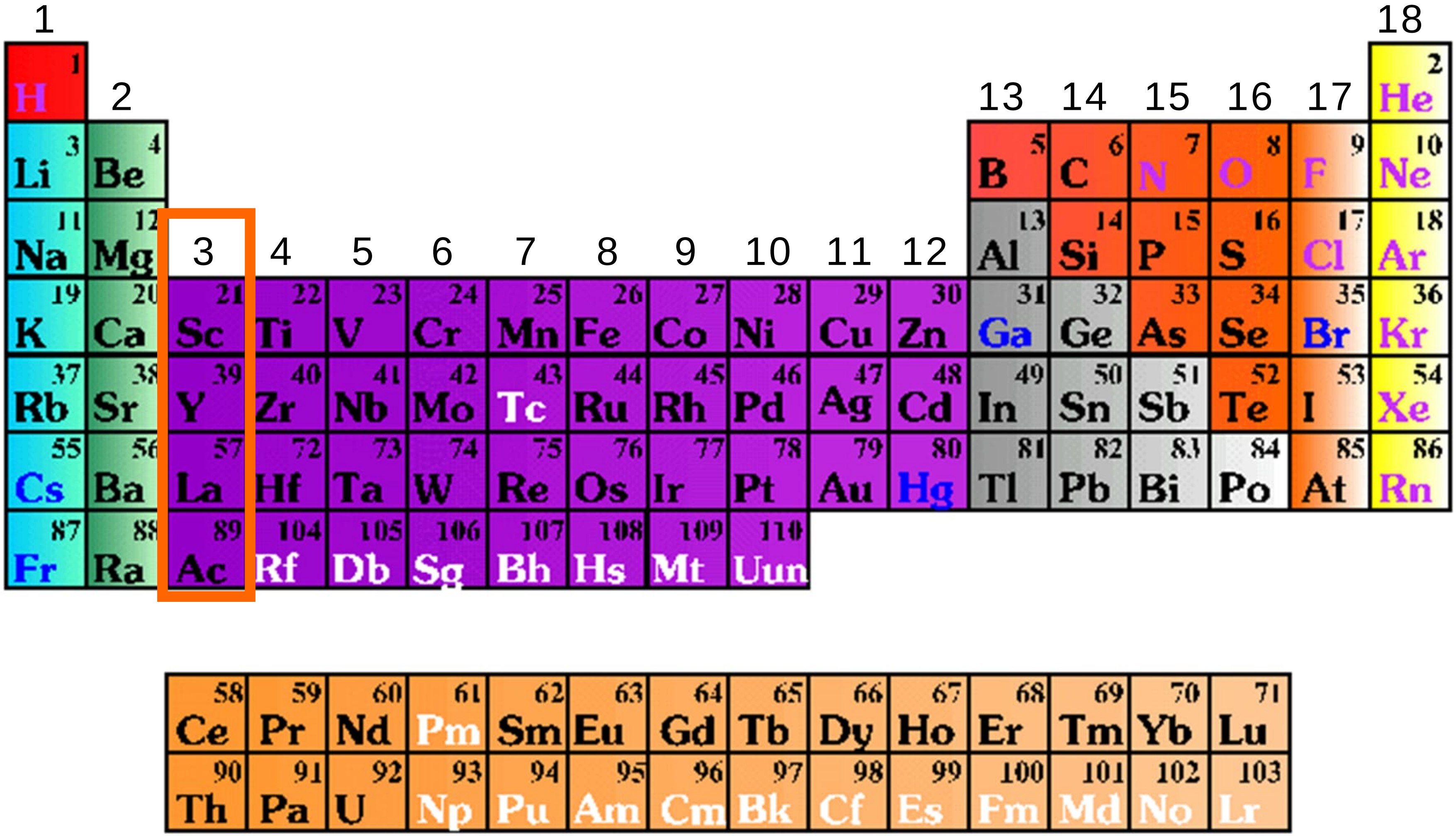
EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Mon	25.09.	Mo:	Maryam Jafarishiad & Saara Siekkinen
Wed	27.09.	Mn:	Naomi Lyle & Sanni Ilmaranta
		Ru:	Miklos Nemeszeghy & Timo de Jonge
Fri	29.09.	Cu:	Koshila Hiruni & Kaushalya Poonanoo
Wed	04.10.	Eu:	Binglu Wang & Mari Heikkinen
		Nd:	Patrich Wiesenfeldt & Tomoki Nakayama
		U:	Miikka Viirto & Ashish Singh
Fri	06.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala & Roger Peltonen

QUESTIONS: Lecture 12

- List all the possible lanthanide ions that have 7 f electrons.
- List all the possible lanthanide ions that have 14 f electrons.
- Why Eu has so low melting point? Which other lanthanide has exceptionally low melting point?



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 La	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 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

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
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

f-BLOCK TRANSITION METALS

- lanthanides [elements after La: Ce ~ Lu]
- actinides [elements after Ac: Th ~ Lr]
- lanthanoids (Ln): La + Lanthanides
- rare earth elements (RE): Ln + Y + Sc

La	lanthanum	Tb	terbium
Ce	cerium	Dy	dysprosium
Pr	praseodymium	Ho	holmium
Nd	neodymium	Er	erbium
Pm	promethium	Tm	thulium
Sm	samarium	Yb	ytterbium
Eu	europium	Lu	lutetium
Gd	gadolinium	Y	yttrium

ABUNDANCES

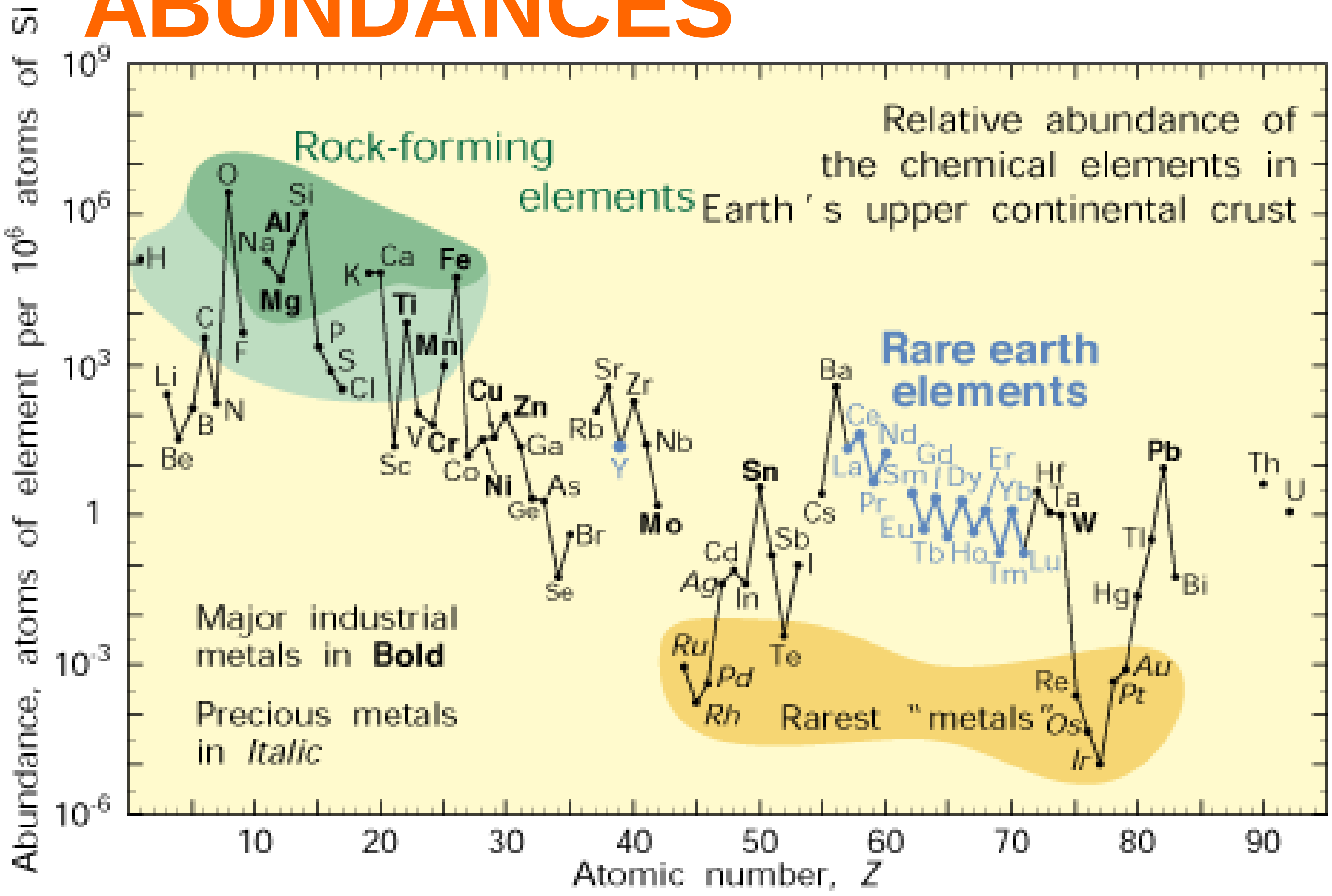


Figure 4. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into (partially overlapping) categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (lanthanides, La–Lu, and Y; labeled in blue); (3) major industrial metals (global production >~3×10^7 kg/year; labeled in bold); (4) precious metals (italic); and (5) the nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid).

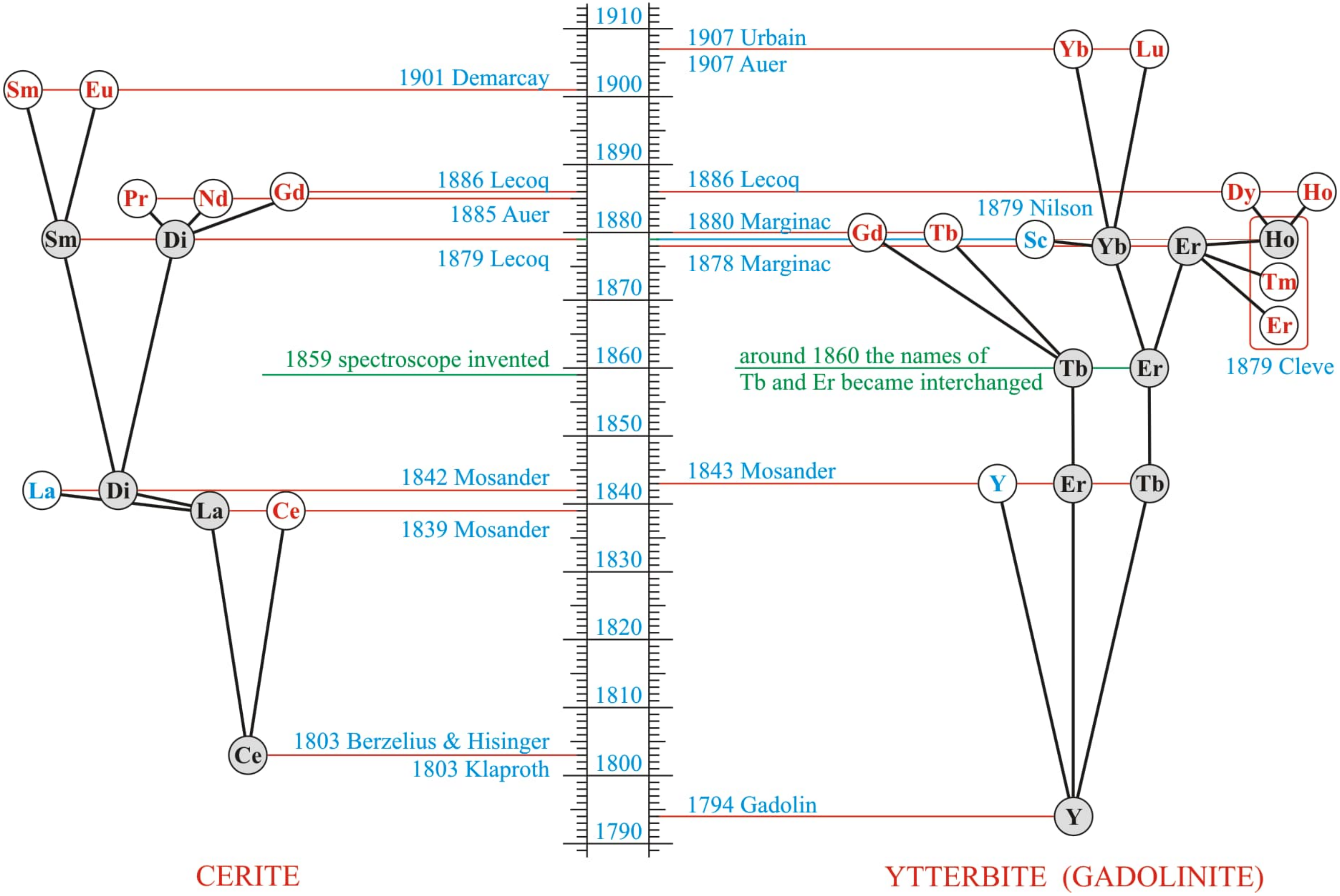
RARE EARTH ELEMENTS (= METALS)

- **Discovery history starts from and ends in Finland:**

  - Johan Gadolin (prof. at Univ. Turku) showed in 1794 that the new mineral found in Ytterby (near Stockholm) contained some new oxide ("earth") of an unknown/new element → yttrium

  - Olavi Erämetsä (inorg. chem. prof. at TKK) found in 1965 from nature small amounts of radioactive promethium (first discovered in USA in 1940s as a fission product in nuclear reactions)

Element	Discoverer	Origin of name
Cerium (Ce)	Klaproth 1803	Ceres (asteroid)
Lanthanum (La)	Mosander 1839	Greek *lanthano* (= to hide)
Terbium (Tb)	Mosander 1843	Ytterby
Erbium (Er)	Mosander 1843	Ytterby
Ytterbium (Yb)	Mariqnac 1878	Ytterby
Holmium (Ho)	Cleve 1878	Holmia (= Stockholm)
Thulium (Tm)	Cleve 1879	Thule (= Nothern country)
Scandium (Sc)	Nilson 1879	Scandinavia
Samarium (Sm)	Boisboudran 1879	Samarskite (mineral)
Gadolinium (Gd)	Marignac 1880	Johan Gadolin
Praseodymium (Pr)	Welsbach 1885	Greek *didymos* (= green twin)
Neodymium (Nd)	Welsbach 1885	Greek *neos didymos* (= new twin)
Dysprosium (Dy)	Boisboudran 1886	Greek *dysprositos prasios* (= difficult to reach)
Europium (Eu)	Demarcay 1896	Europe
Lutetium (Lu)	Urbain 1907	Lutetia (= Paris)



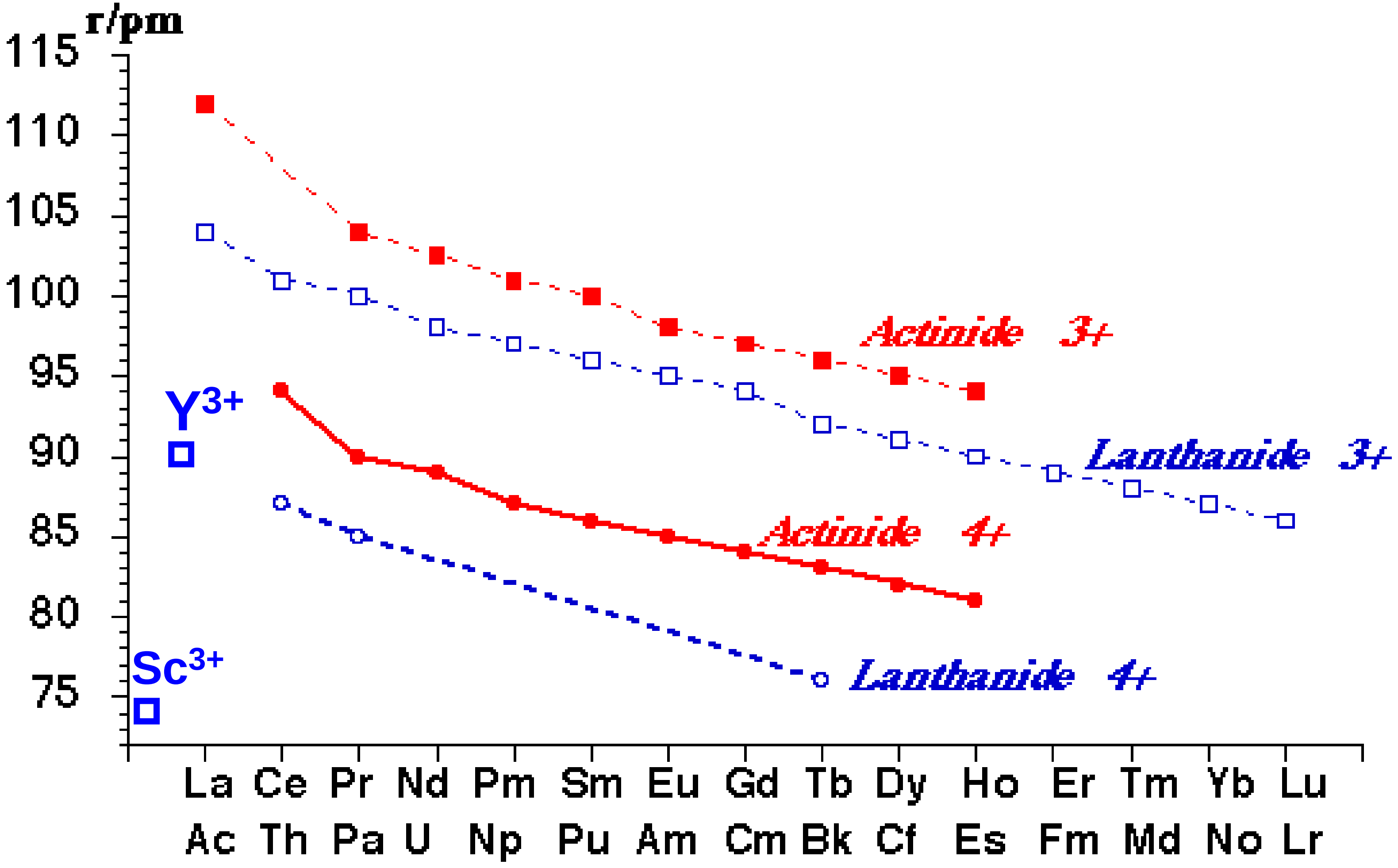
$(Ce,La,Ca)_9(Mg,Fe^{3+})(SiO_4)_6(SiO_3OH)(OH)_3$

Bastnäs, Sweden

$(Y,Ce,La,Nd)_2FeBe_2Si_2O_{10}$

Ytterby, Sweden

LANTHANIDE / ACTINIDE CONTRACTION



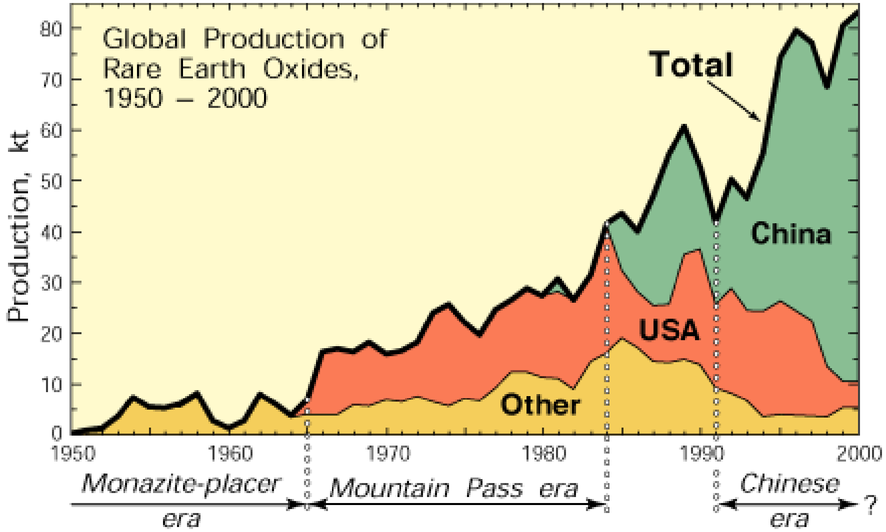
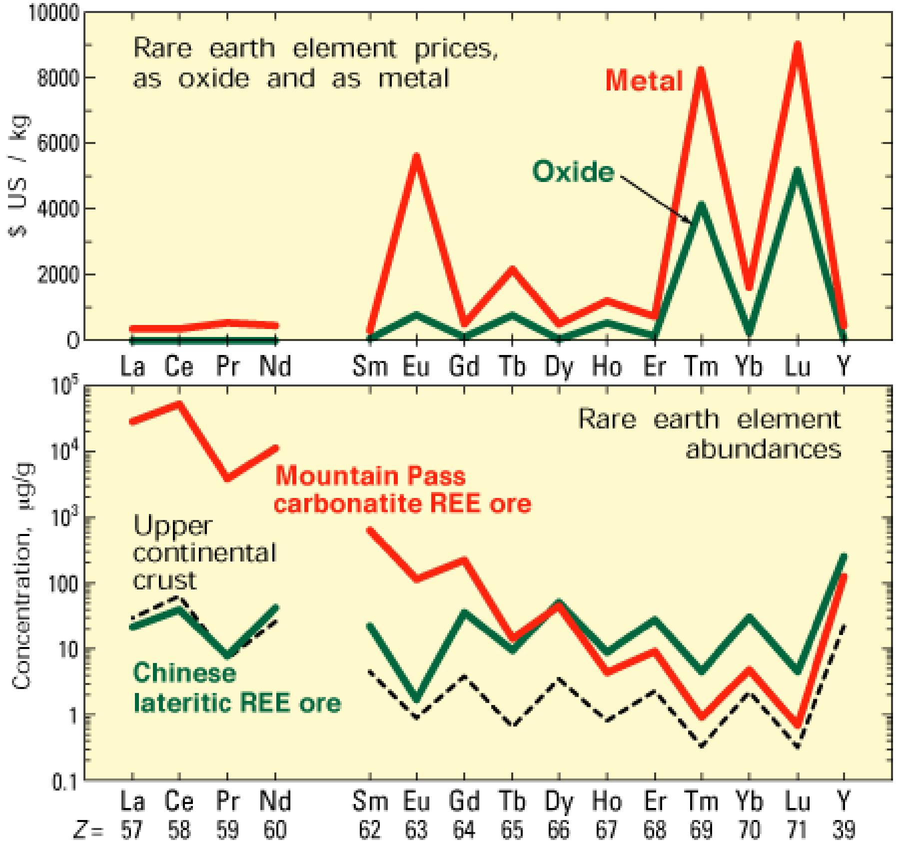


Figure 1. Global rare earth element production (1 kt=10^6 kg) from 1950 through 2000, in four categories: United States, almost entirely from Mountain Pass, California; China, from several deposits; all other countries combined, largely from monazite-bearing placers; and global total. Four periods of production are evident: the monazite-placer era starting in the late 1800s and ending abruptly in 1964; the Mountain Pass era, starting in 1965 and ending about 1984; a transitional perioc from about 1984 to 1991; and the Chinese era, beginning about 1991.

Currently:
China produces >95 %



Atomic numbers:
even more common than uneven

SEPARATION OF RARE EARTH ELEMENTS FROM EACH OTHER

- **Very difficult due to the similarities in chemistry**
- **Cerium and Europium chemically:**

  - oxidation of Ce^{III} to Ce^{IV} plus precipitation as CeO_2 or $Ce(IO_3)_4$

  - reduction of Eu^{III} to Eu^{II} plus precipitation as $EuSO_4$
- **Fractional crystallization (hundreds of steps):**

  as $\mathit{RE}(NO_3)_3 \bullet 2NH_4NO_3 \bullet 4H_2O$ or $\mathit{RE}(BrO_3)_3$
- **Current large-scale separation technique:**

  Continuous solvent extraction (nonpolar organic solvent)

Misch-metal

- German: *Mischmetall* = mixed metal
- Metal alloy of rare earth elements
- Rare earth elements in natural portions (varies)
- Typical composition: 50% Ce + 45% La + Nd, Pr traces
- Use: - in lighter: alloyed with Fe and Mg oxides → ferrocerium
  - in production of FeSiMg alloy to remove free oxygen and sulphur

Scandium (Sc)

- discovered in 1879 by spectral analysis of the minerals euxenite and gadolinite from Scandinavia
- preparation of metallic Sc in 1937
- own rare mineral thortveitite $(Sc,Y)_2Si_2O_7$ (Norway 1911)
- produced as a by-product of rare-earth and uranium production; yearly trade of scandium (oxide) is only 10 tonnes
- first applications for scandium developed in the 1970s
- main use in aluminium alloys
- oxidation state +3; oxide Sc_2O_3
- chemical properties of Sc are intermediate between those of Al and Y
- diagonal relationship between Sc and Mg (ref. Al-Be)

OXIDES

Ln_2O_3

- trivalent oxide most common *Ln* oxide (for all *Ln*)
- strongly basic
- absorbs water/carbon dioxide from air → hydroxide/carbonate salts
- Similarities with alkali earth metal oxides

LnO_2

- CeO_2
- Pr_6O_{11}, Tb_4O_7

LnO

- EuO, YbO: electrical insulators (Ln^{2+} O^{2-})
- EuO ferromagnetic
- NdO, SmO: electrical conductors (Ln^{3+} O^{2-} e^-)

Electronic configurations and oxidation states of lanthanoids

Z	Element	Electronic configuration	Oxidation states
57	Lanthanum (La)	$4f^0 5d^1 6s^2$	+III
58	Cerium (Ce)	$4f^1 5d^1 6s^2$	+III, +IV
59	Praseodymium (Pr)	$4f^2 5d^1 6s^2$	+III
60	Neodymium (Nd)	$4f^3 5d^1 6s^2$	+III
61	Promethium (Pm)	$4f^4 5d^1 6s^2$	+III
62	Samarium (Sm)	$4f^5 5d^1 6s^2$	+III
63	Europium (Eu)	$4f^7 5d^0 6s^2$	+II, +III
64	Gadolinium (Gd)	$4f^7 5d^1 6s^2$	+III
65	Terbium (Tb)	$4f^7 5d^2 6s^2$	+III, +IV
66	Dysprosium (Dy)	$4f^9 5d^1 6s^2$	+III
67	Holmium (Ho)	$4f^{10} 5d^1 6s^2$	+III
68	Erbium (Er)	$4f^{11} 5d^1 6s^2$	+III
69	Thulium (Tm)	$4f^{12} 5d^1 6s^2$	+III
70	Ytterbium (Yb)	$4f^{14} 5d^0 6s^2$	+II, +III
71	Lutetium (Lu)	$4f^{14} 5d^1 6s^2$	+III

MELTING POINTS (^{o}C)

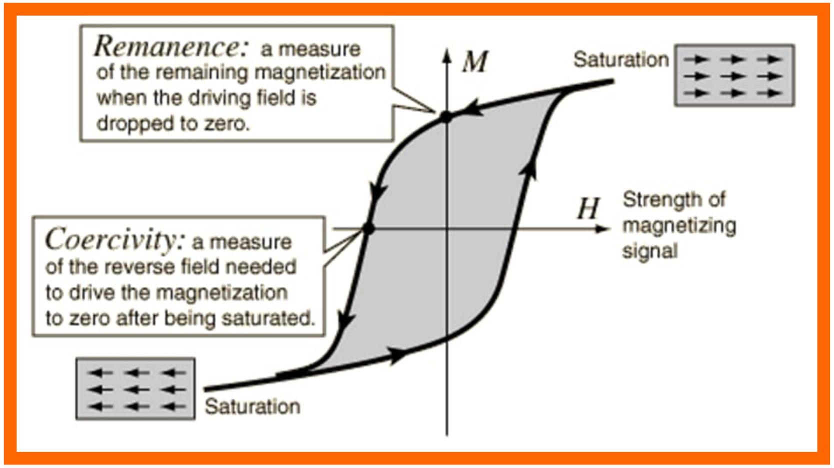
La	920
Ce	795
Pr	935
Nd	1010
Pm	-
Sm	1072
Eu	822
Gd	1311
Tb	1360
Dy	1412
Ho	1470
Er	1522
Tm	1545
Yb	824
Lu	1656

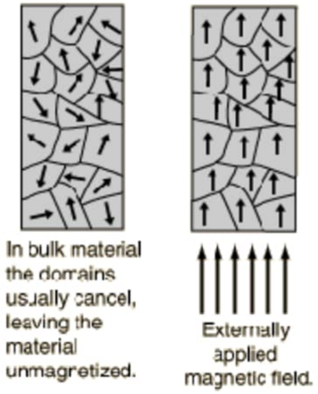
COLOURS OF IONS

- **No strong colours**
  - **colourless: La^{III}, Ce^{IV}, Gd^{III}, Eu^{II} , Yb^{II}, Lu^{III}**
  - **green: Pr^{III}, Tm^{III}**
  - **violet: Nd^{III}, Er^{III}**
  - **yellowish pink: Pm^{III}, Ho^{III}**
  - **yellow: Sm^{III}, Dy^{III}, Yb^{III}**
  - **light pink: Eu^{III}, Tb^{III}**

PERMANENT MAGNETS (ferromagnets)

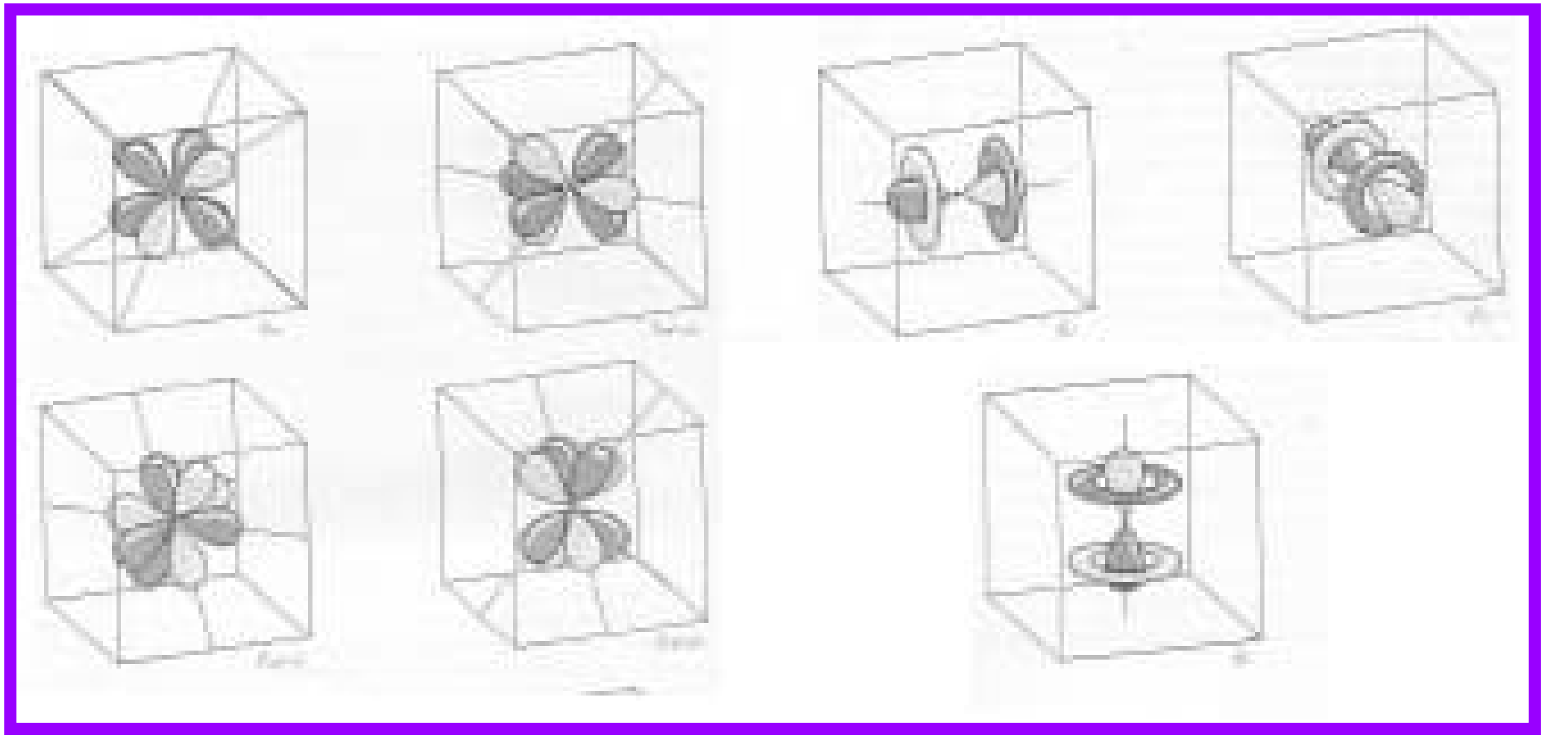
- 1970s: $SmCo_5$, Sm_2Co_{17}
- 1980s: $Nd_2Fe_{14}B$ (= neomagnets; very strong)
- With neomagnets smaller electric motors (e.g. in car industry)





Material	Coercivity [T]	Remanence [T]
$BaFe_{12}O_{19}$	0.36	0.36
Alnico IV	0.07	0.6
Alnico V	0.07	1.35
Alcomax I	0.05	1.2
MnBi	0.37	0.48
$Ce(CuCo)_5$	0.45	0.7
$SmCo_5$	1.0	0.83
Sm_2Co_{17}	0.6	1.15
$Nd_2Fe_{14}B$	1.2	1.2

4f orbitals

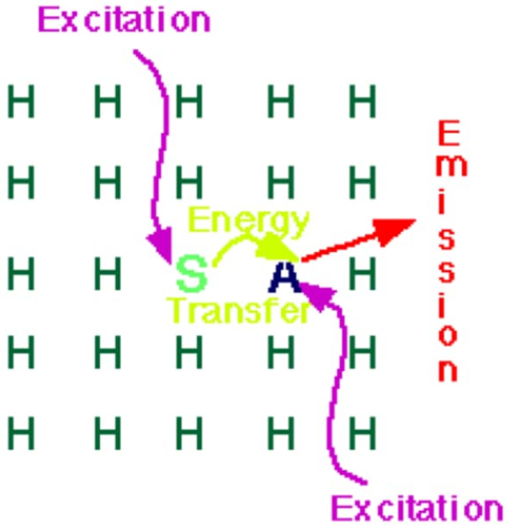


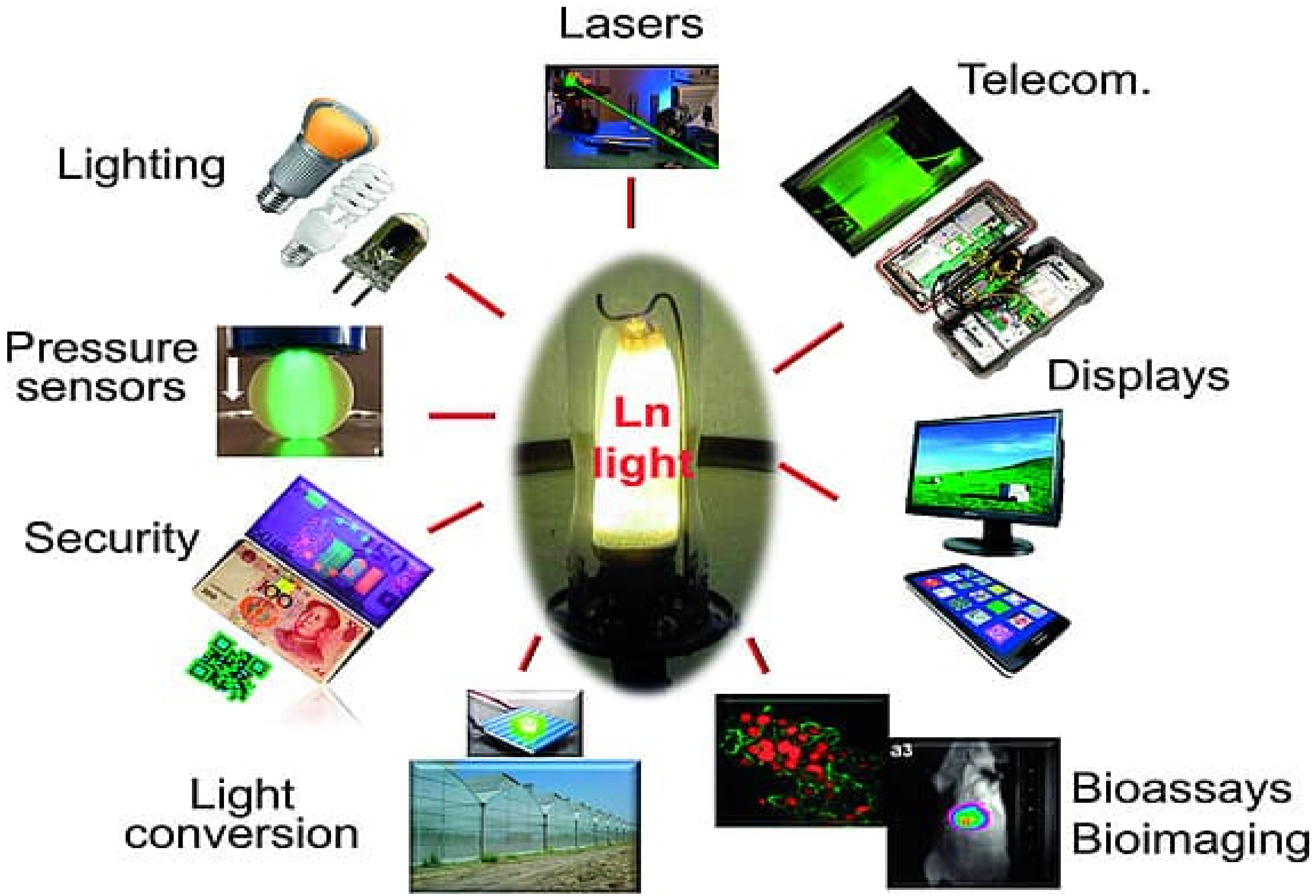
SPECTROSCOPIC PROPERTIES

- Energies of 4f orbitals splitted in crystal/ligand field (ref. d orbitals)
- More complicated splitting scheme than in the case of the d orbitals

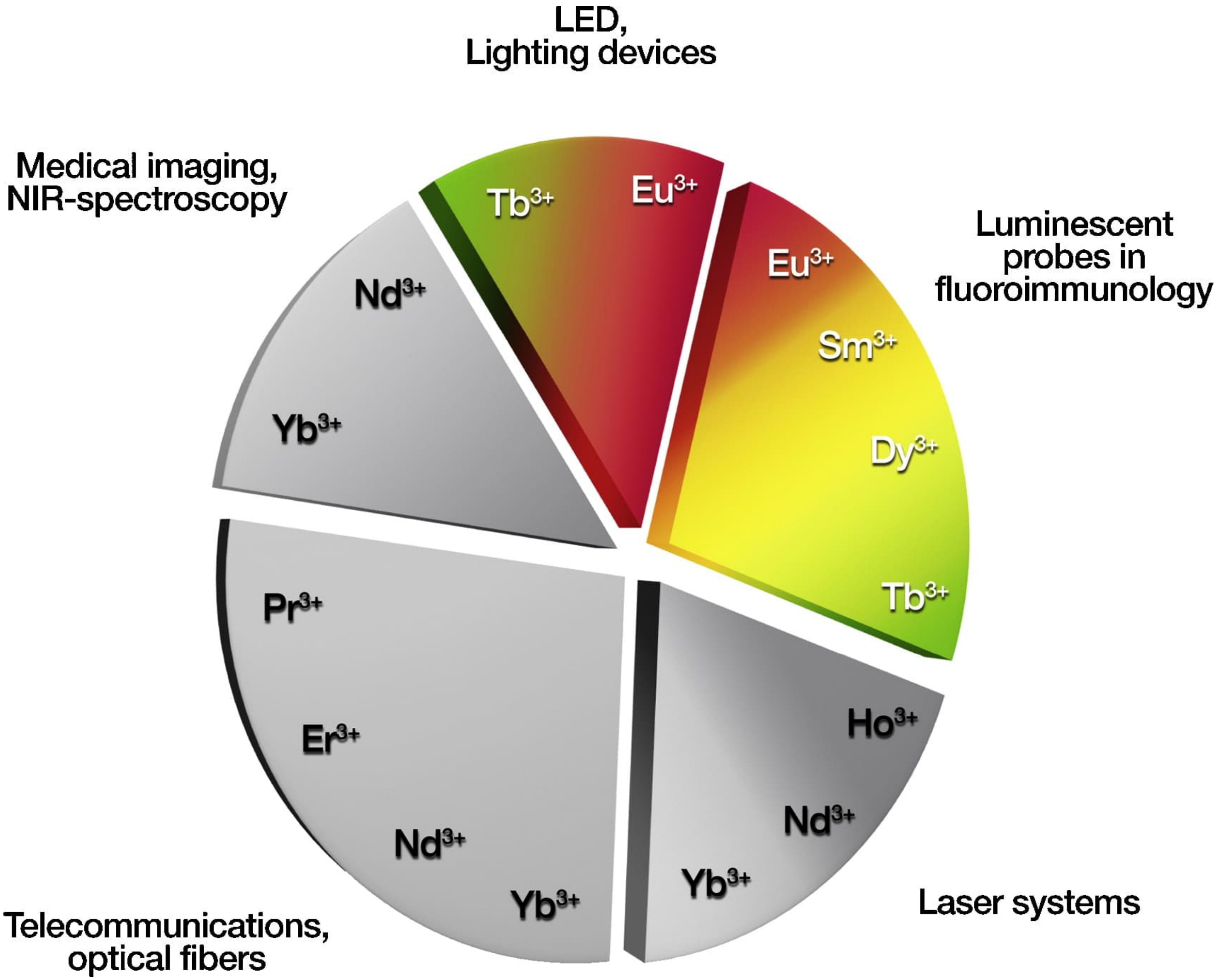
LUMINESCENCE

- Excitation: photo, electro, radio, thermo, chemi, mechano, piezo, bio ...
- Photoluminescence: material absorbs higher-energy photon & emits smaller-energy photon (energy lost as heat)
- Shorter-to-longer wavelength: UV → Vis
- Emitting species embedded in small concentrations in host (H) matrix
- Energy transfer: Sensitizer (S) → Activator (A)
- Applications of Ln photoluminescence: lighting, lasers, telecommunication, security marking, barcoding, luminescent molecular thermometers, immunoassays, medical imaging, etc.

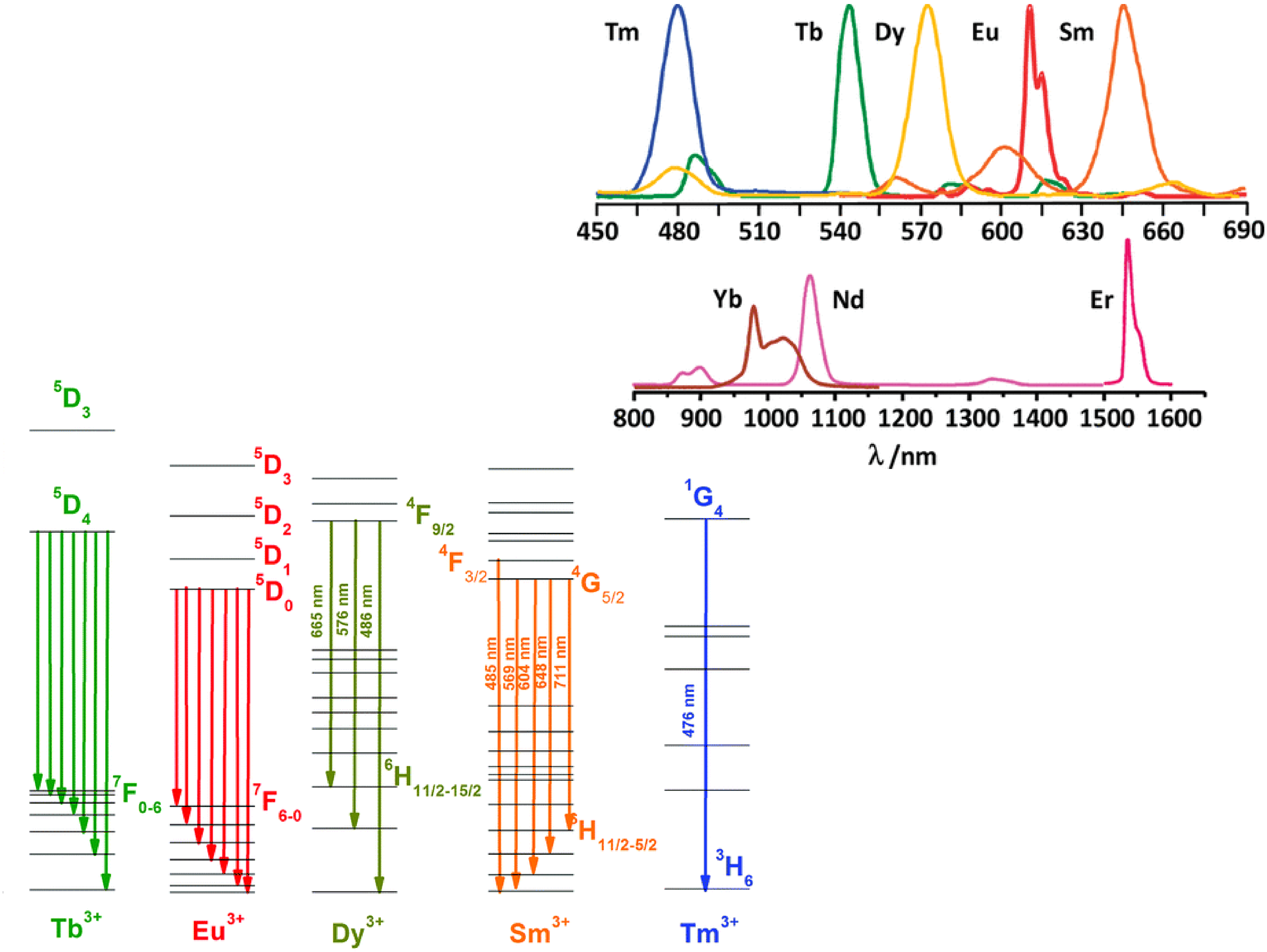




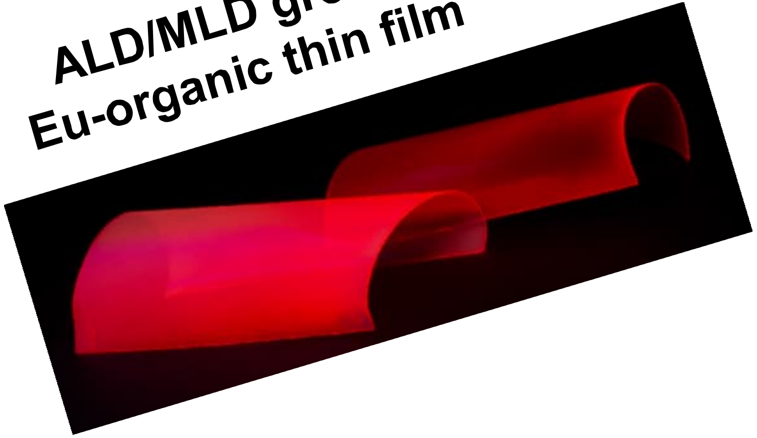
Rising Stars in Science and Technology: Luminescent Lanthanide Materials
Jean-Claude G. Bünzli, https://doi.org/10.1002/ejic.201701201

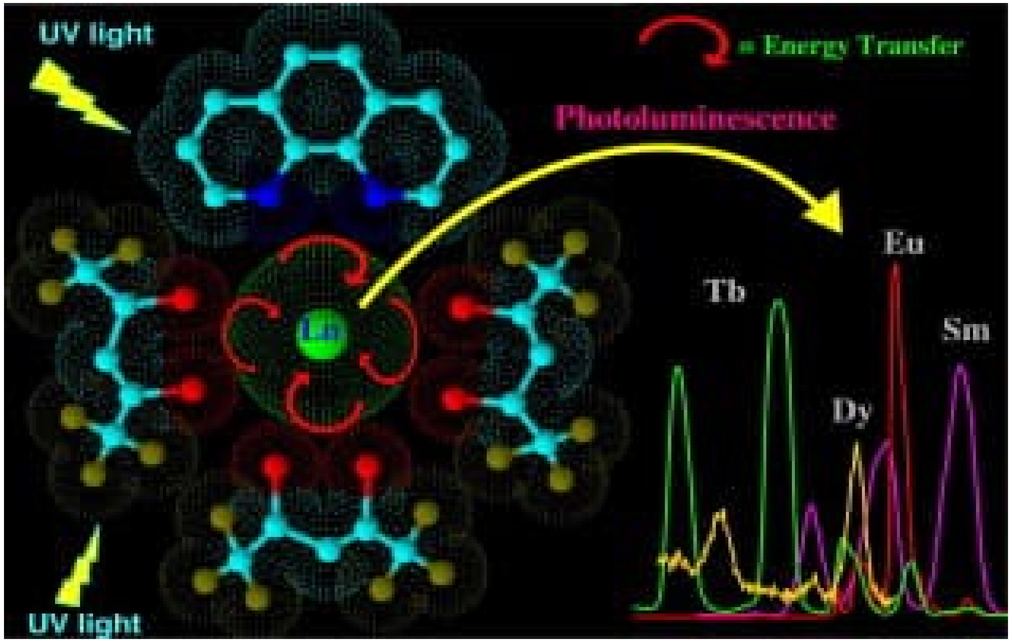


Armelao L.; Quici S.; Barigelletti F.; Accorsi G.; Bottaro G.; Cavazzini M.; Tondello E. Design of luminescent lanthanide complexes: From molecules to highly defficient photo-emitting materials. Coordination Chemistry Reviews 2010, 254, 487.

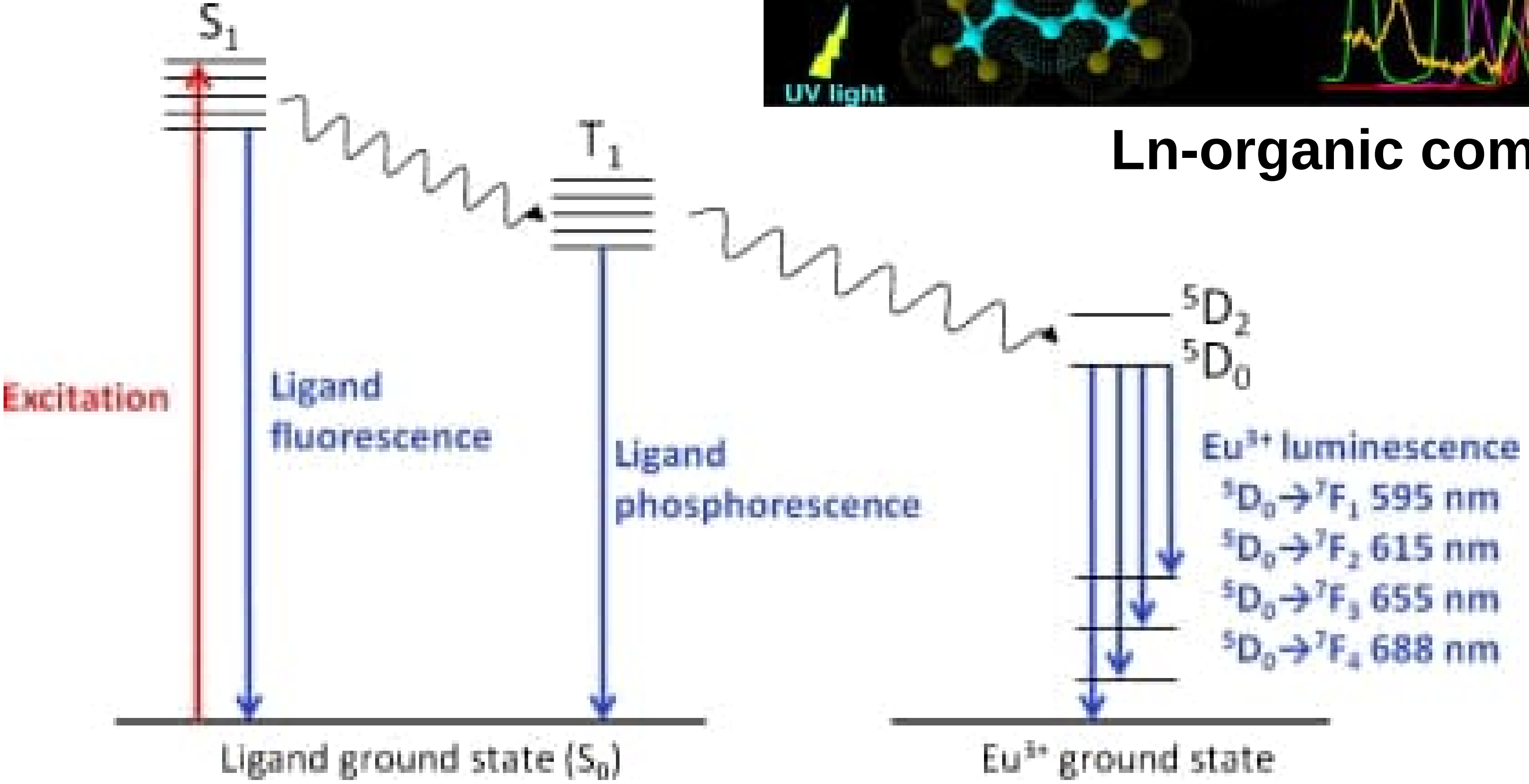

Tm
Tb
Dy
Eu
Sm
450
480
510
540
570
600
630
660
690
Yb
Nd
Er
800
900
1000
1100
1200
1300
1400
1500
1600
λ /nm
$^5D_3$
$^5D_4$
$^7F_{0-6}$
Tb^{3+}
$^5D_3$
$^5D_2$
$^5D_1$
$^5D_0$
$^7F_{6-0}$
Eu^{3+}
$^4F_{9/2}$
665 nm
576 nm
486 nm
$^6H_{11/2-15/2}$
Dy^{3+}
$^4F_{3/2}$
$^4G_{5/2}$
485 nm
569 nm
604 nm
648 nm
711 nm
$^6H_{11/2-5/2}$
Sm^{3+}
$^1G_4$
476 nm
$^3H_6$
Tm^{3+}

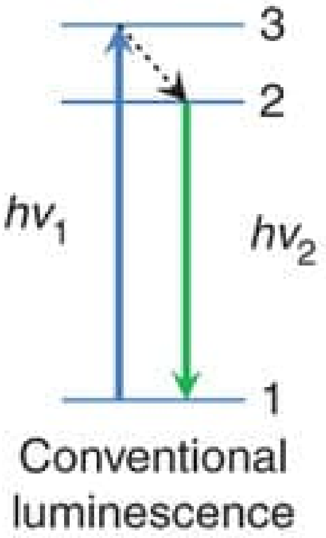
ALD/MLD grown Eu-organic thin film



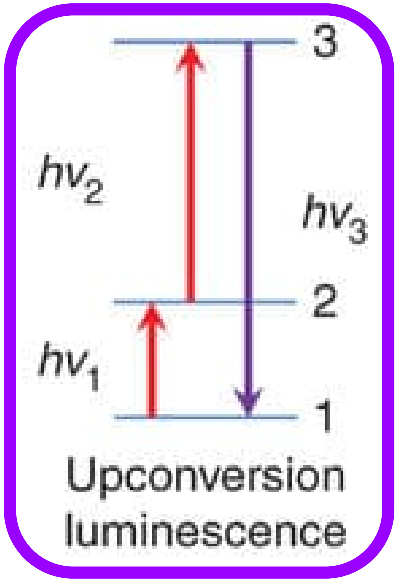


Ln-organic complex





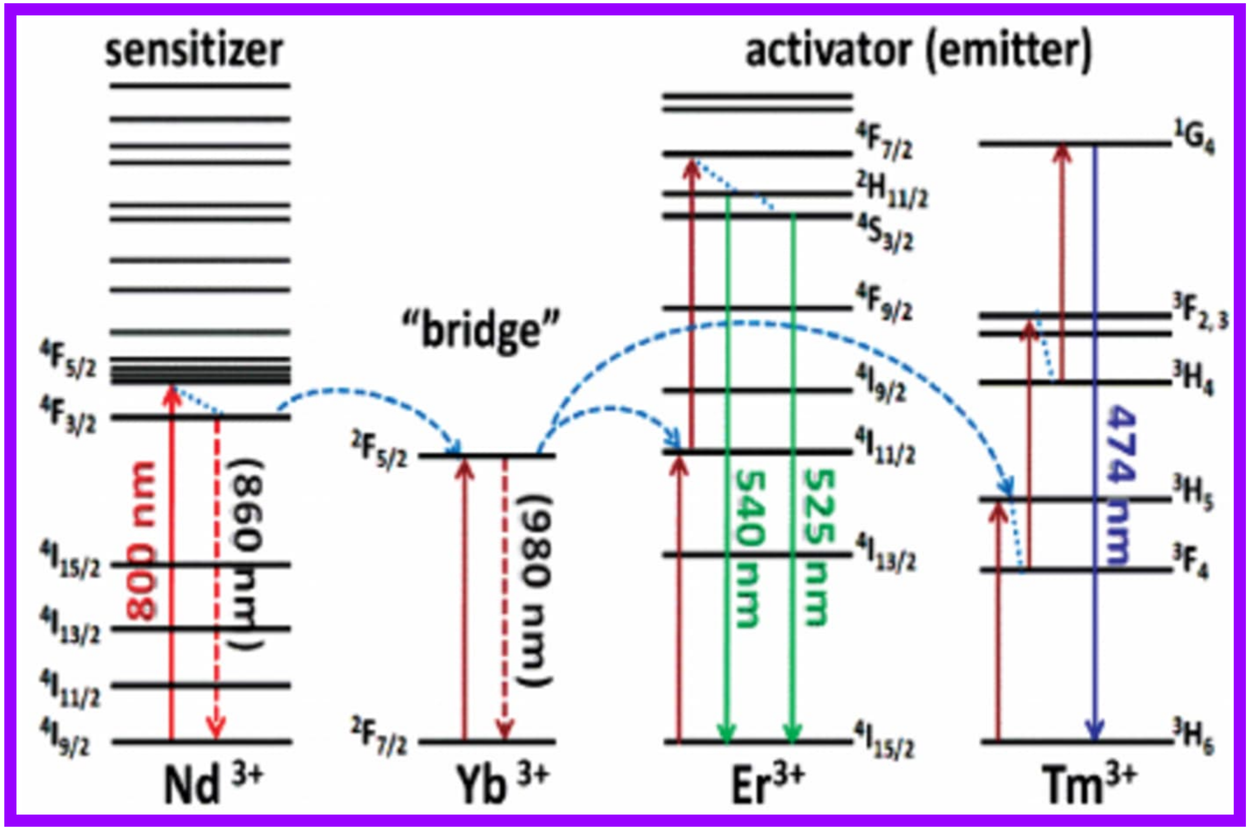
Conventional luminescence



Upconversion luminescence

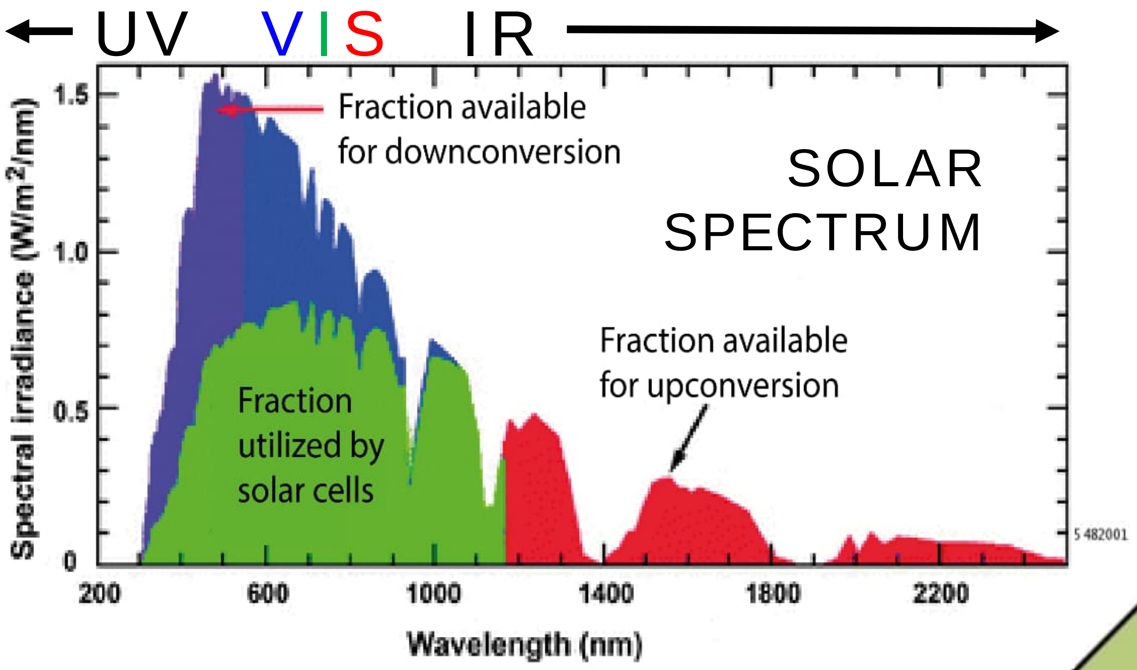
UPCONVERSION EMISSION

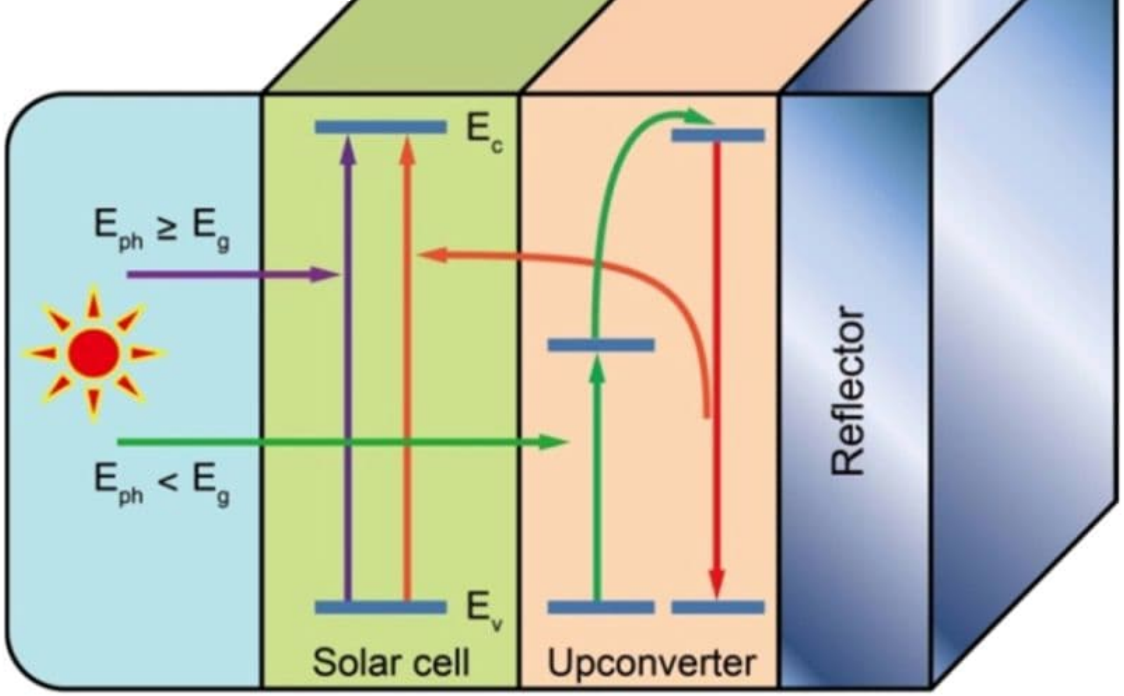
- for example from IR to Visible



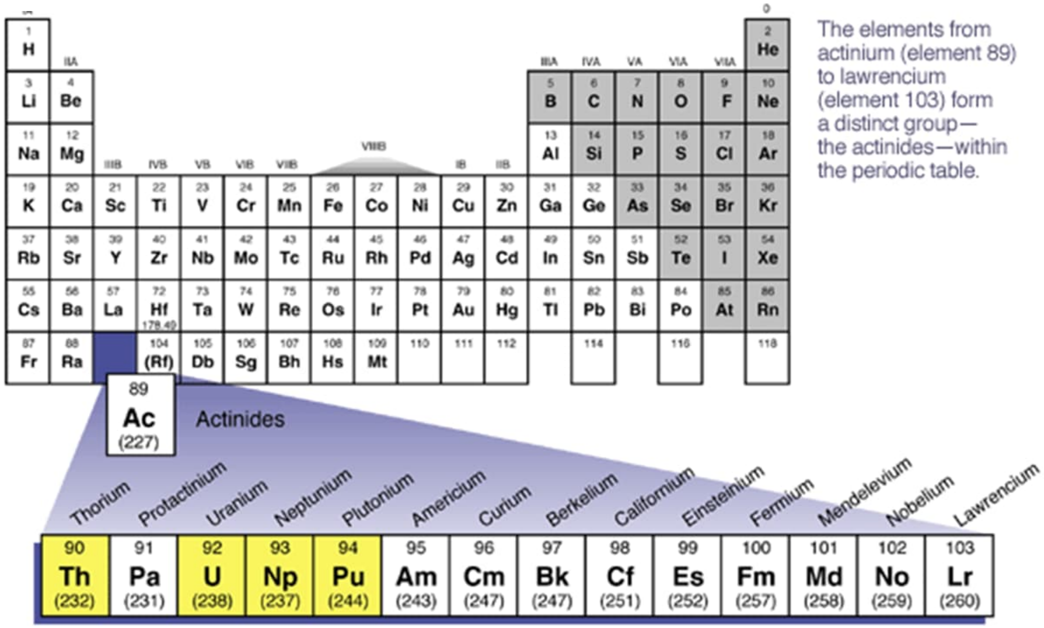
← UV VIS IR →

SOLAR SPECTRUM



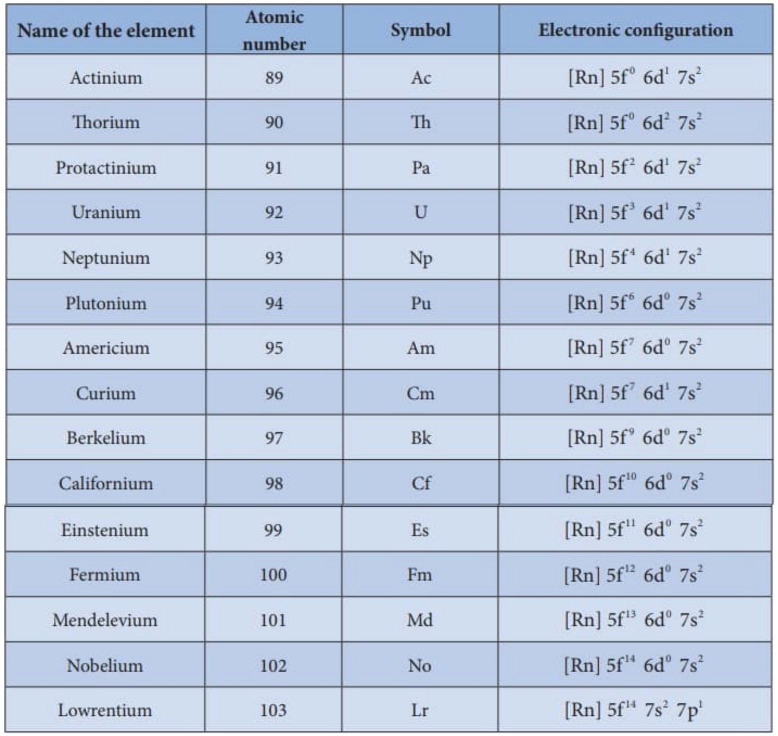


ACTINOIDS

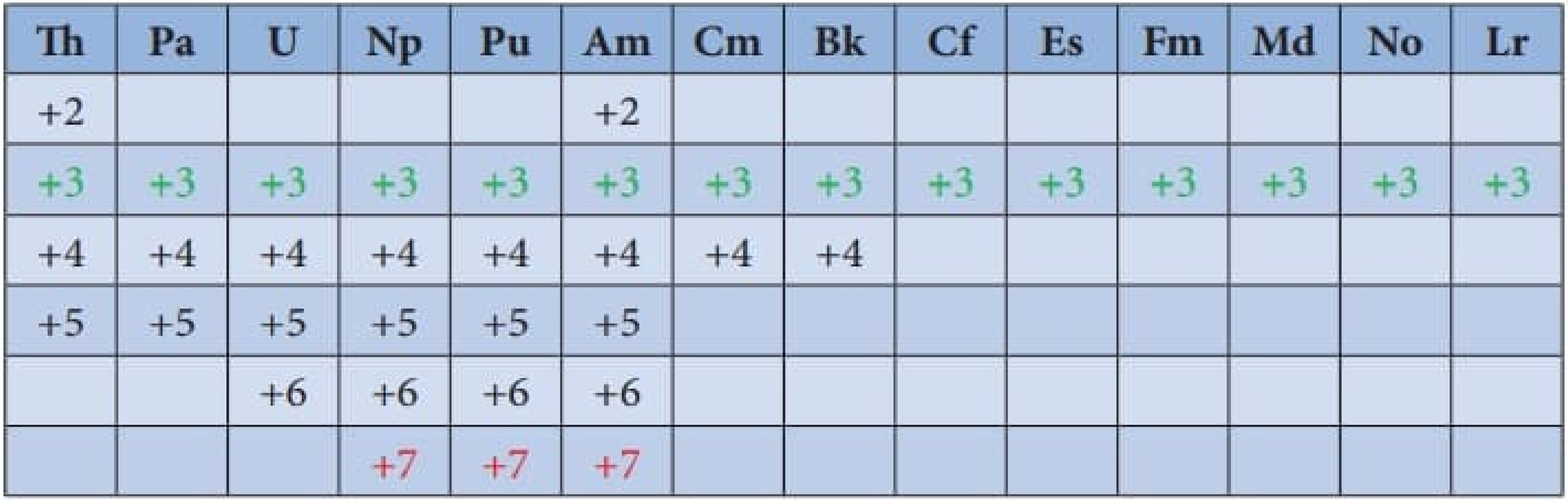


The elements from actinium (element 89) to lawrencium (element 103) form a distinct group—the actinides—within the periodic table.

Table : electronic configuration of actinoids



Name of the element	Atomic number	Symbol	Electronic configuration
Actinium	89	Ac	[Rn] $5f^0$ $6d^1$ $7s^2$
Thorium	90	Th	[Rn] $5f^0$ $6d^2$ $7s^2$
Protactinium	91	Pa	[Rn] $5f^2$ $6d^1$ $7s^2$
Uranium	92	U	[Rn] $5f^3$ $6d^1$ $7s^2$
Neptunium	93	Np	[Rn] $5f^4$ $6d^1$ $7s^2$
Plutonium	94	Pu	[Rn] $5f^6$ $6d^0$ $7s^2$
Americium	95	Am	[Rn] $5f^7$ $6d^0$ $7s^2$
Curium	96	Cm	[Rn] $5f^7$ $6d^1$ $7s^2$
Berkelium	97	Bk	[Rn] $5f^9$ $6d^0$ $7s^2$
Californium	98	Cf	[Rn] $5f^{10}$ $6d^0$ $7s^2$
Einstenium	99	Es	[Rn] $5f^{11}$ $6d^0$ $7s^2$
Fermium	100	Fm	[Rn] $5f^{12}$ $6d^0$ $7s^2$
Mendelevium	101	Md	[Rn] $5f^{13}$ $6d^0$ $7s^2$
Nobelium	102	No	[Rn] $5f^{14}$ $6d^0$ $7s^2$
Lowrentium	103	Lr	[Rn] $5f^{14}$ $7s^2$ $7p^1$



Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+2					+2								
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4	+4	+4	+4	+4	+4						
+5	+5	+5	+5	+5	+5								
		+6	+6	+6	+6								
			+7	+7	+7								

Occurrence of Uranium & Transuranoids

- **only Ac, Th, Pa and U found in nature**
- **transuranoids exist only artificially**

  (trace amounts of Np and Pu in uranium minerals)
- **ca. 100 different uranium minerals, most important being uraninite (pikivälke) UO_x (x = 2 - 2.67) and carnotite $K_2(UO_2)_2(VO_4)_2 \bullet 3H_2O$**
- **U ca. 500 times more common than Au:**

  earth crust 2.1 ppm, ocean water 0.002 - 0.003 ppm
- **occasionally U content may be high enough to create a natural nuclear reactor, e.g. Oklo in Africa billions years ago**
- **15 isotopes (^{226}U - ^{240}U):**

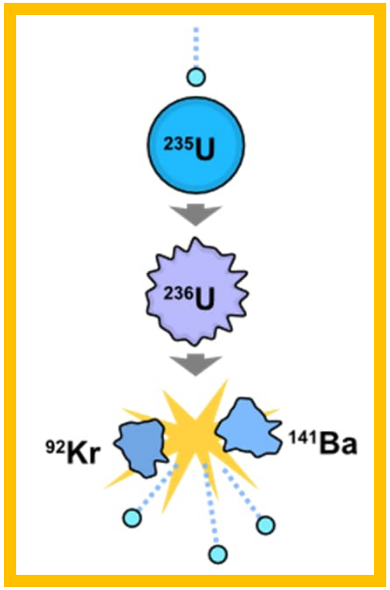
  ^{238}U 99.275 %

  ^{235}U 0.720 %

  ^{234}U 0.005 %
- **all U isotopes unstable**

ENRICHMENT OF URANIUM

- Small carbonate content in ore → acid dissolution/extraction
- Large carbonate content in ore → basic dissolution/extraction



- Concentration after filtering
- Precipitation → yellow cake
  acid solution: $(NH_4)_2U_2O_7$ or MgU_2O_7
  carbonate solution: $Na_2U_2O_7$
- Reduction → UO_2
- Green salt UF_4
- For isotope enrichment: $UF_4(s) + F_2(g) \rightarrow UF_6(g)$
- Isotope enrichment: gas diffusion process, centrifugal separation, electromagnetic separation, laser exitation, jet/spray separation
- Use as a fuel in nuclear reactors: ^{235}U, $^{235}UO_2$, $^{235}UC_2$