Chemistry of Elements

CHEM-E4130 (5 cr)

Lectures (14 x): Monday (Pt) 12.15 – 14.00
Wednesday (Ke2) 10.15 – 12.00
Friday (Pt) 10.15 – 12.00

Lecturers: Maarit Karppinen
Antti Karttunen (one lecture)
Linda Sederholm (one lecture)

- Lectures: 14 x 2 h
- Home problem solving 30 h
- Independent homework 60 h
- Exam 3 h

MARKING

- **Exam:** 50 points
- **Lecture exercises:** 25 points
  13 x 2 p → 26; one extra point possible
- **Seminar:** 25 points

The course covers the basics of the chemistry of elements.

Emphasis on the d-block transition metals and lanthanides.

After the course the student will be able to:

1. Explain the basic features of the transition metal chemistry
2. Derive the basic chemical and physical properties of d-block and f-block transition metals from their electron structures
3. Describe different types of metal complexes and metal-organics
4. Describe the most important compounds of transition elements and name their applications
5. Find and read basic scientific literature on a given topic related to the chemistry of elements

Positive Overlapp:
CHEM-E4101 Lab. Course by Eeva Rautama

REFERENCE BOOKS

- Descriptive Inorganic Chemistry, G. Rayner-Canham & T. Overton, W.H. Freeman and Company.
- Chemistry of the Elements, N.N. Greenwood & A. Earnshaw, Pergamon Press.
- Inorganic Chemistry, C.E. Housecroft & A.G. Sharpe, Pearson.

LECTURE SCHEDULE

Mon (Pt) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Pt) 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
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
10.	Fri	29.09.	Cu & Magnetism & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
	Fri	06.10.	
13.	Wed	11.10.	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

INSTRUCTIONS for LECTURE EXERCISES

- These are simple questions/small exercises meant to help you to follow the lecture and to test your learning
- The questions/exercises are given to you in MyCourses at the same time as the lecture slides
- You should be able to easily answer to the questions during the lecture or just after the lecture; this should typically not take more than 15 ~ 20 min
- Then the deadline for returning your answer file is next day by the noon.
- Each exercise is evaluated in the scale: 0 ~ 2 points
- All together you can collect 13 x 2 = 26 (1 extra!) points in maximum

QUESTIONS: Lecture 1

Name your file Exe-1-Familyname; Return by noon tomorrow into MyCourses drop-box

1. Which element(s) was/were discovered

- As a result of huge interest in burning reactions in 1700s
- Based on accurate measurements of air in 1890s
- Thanks to the progress in electrochemical techniques in 1800-1810
- Thanks to the progress in spectroscopy techniques in 1860s
- For the first time from outside of the Earth (1868)
- Much earlier in South America by native Indians than in Europe (in 1750~1850)
- By a Finnish professor
- The discovery was rewarded by a Nobel prize in 1906
- Based on quantum chemical considerations

2. Indicate **(with short explanation !)** for each of the following pairs the larger atom/ion:
Na–K, K–Ca, Fe^{2+}–Fe^{3+}, Ti^{3+}–Ti^{4+}, Ti^{4+}–Zr^{4+}, La–Lu

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Presentation (~20 min) is given in a group of two (or three) persons
- It is evaluated in the scale: 15 ~ 25 points
- Presentation is given in English, and the slides are put up in MyCourses afterwards
- Content of the presentation:

- ELEMENT: discovery, origin of name, abundancy, world production, special features if any, etc.

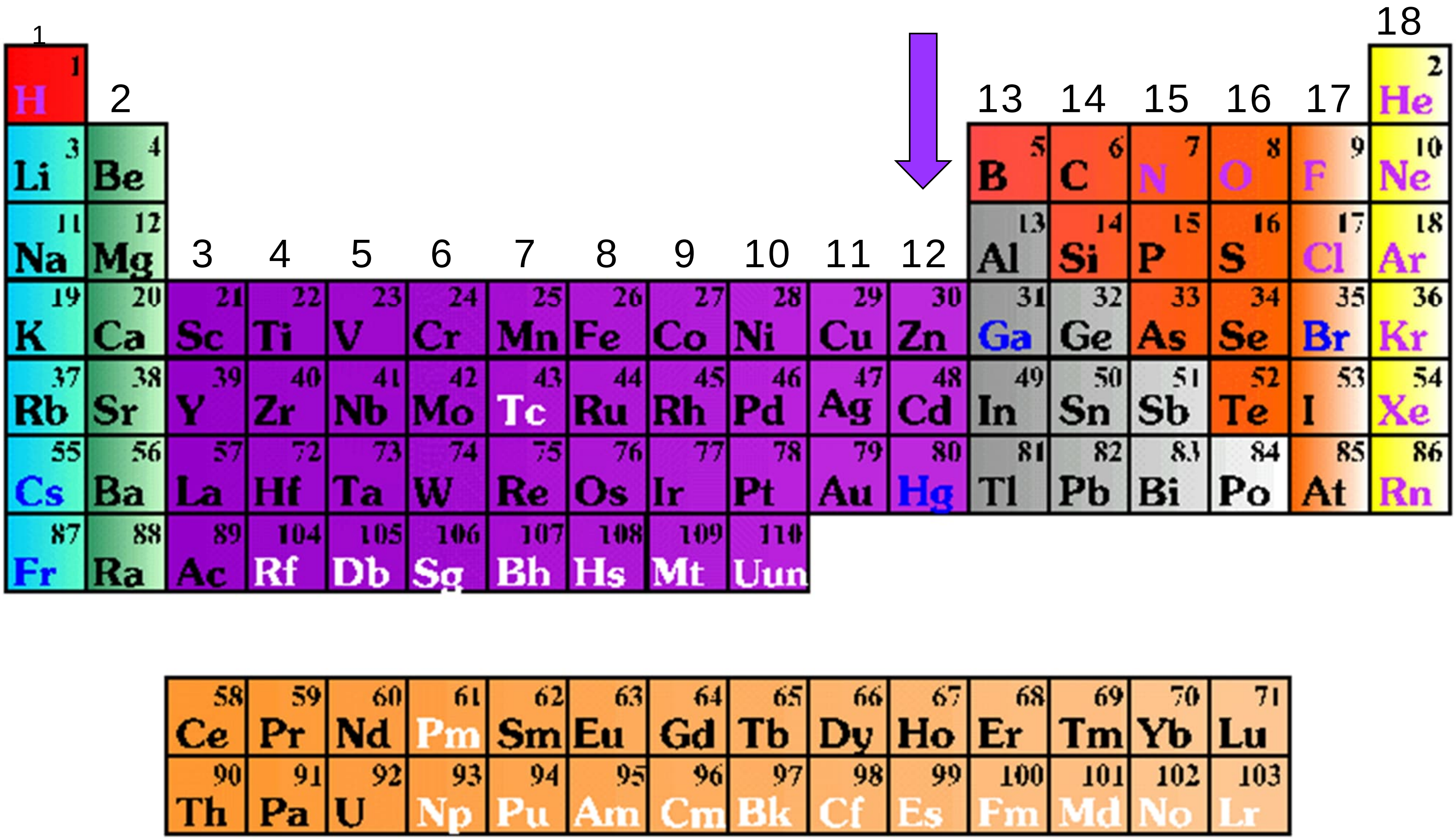
- CHEMISTRY: position in Periodic Table, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc.

- COMPOUNDS: examples of important compounds, their properties and applications, etc.

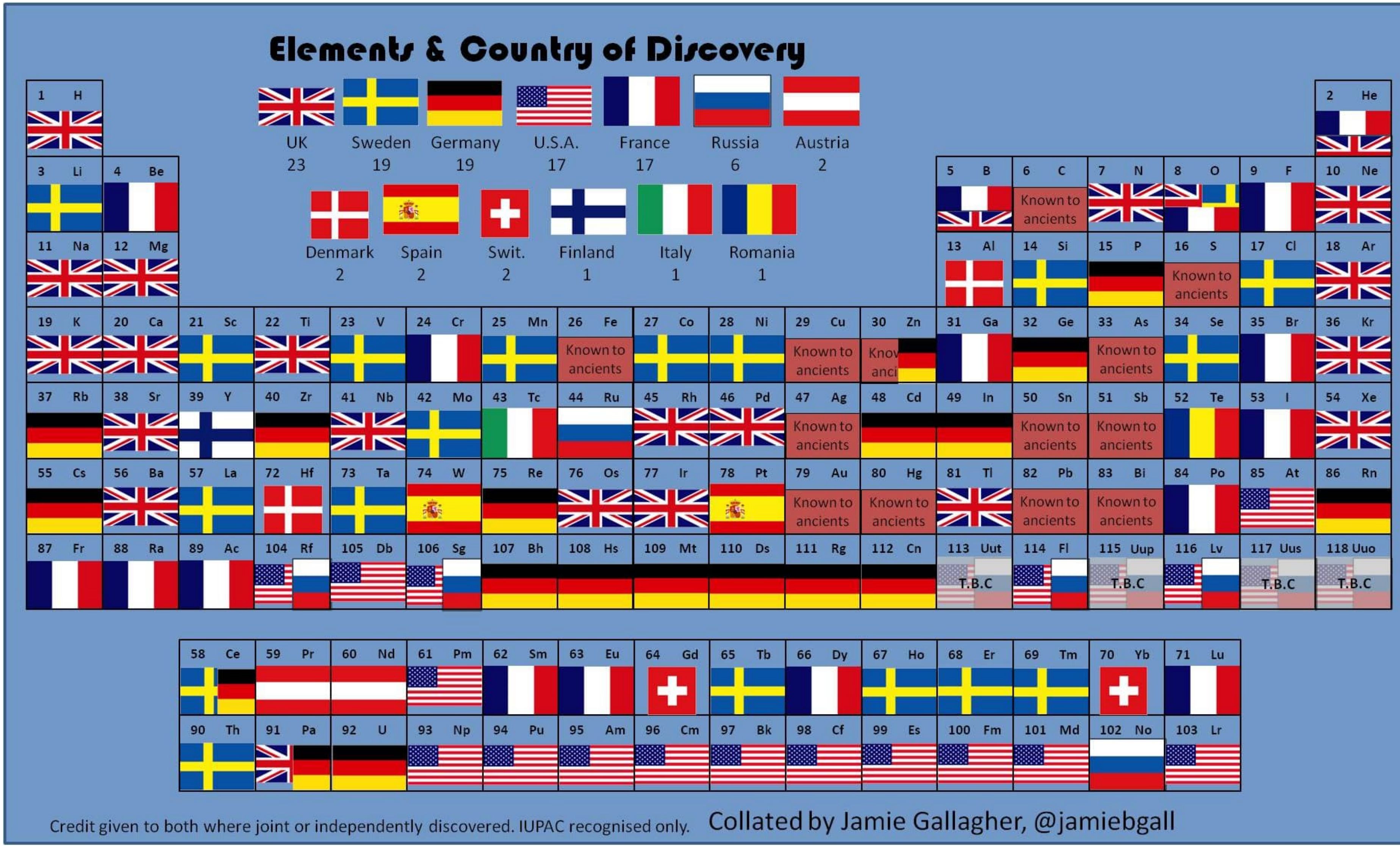
- SPECIFIC FUNCTIONALITIES/APPLICATIONS: Two or three examples of exciting functionalities/applications of the element or its compounds. <u>Here the meaning is to discuss why this specific element is needed in each selected application.</u> You will be given one (or two) scientific article for a reference, and you should search for couple of more (recent) articles to be discussed in the presentation.

PRESENTATION TOPICS/SCHEDULE

Wed	20.09.	Nb:
Mon	25.09.	Mo:
Wed	27.09.	Mn:
		Ru:
Fri	29.09.	Cu:
Wed	04.10.	Eu:
		Nd:
		U:
Wed	11.10.	Co:
		In:
		Te:



Alkali metals
Alkaline earth metals
Halogens
Noble gases
Transition metals
Lanthanides
Actinides


Elements & Country of Discovery
UK 23
Sweden 19
Germany 19
U.S.A. 17
France 17
Russia 6
Austria 2
Denmark 2
Spain 2
Swit. 2
Finland 1
Italy 1
Romania 1
1 H
2 He
3 Li
4 Be
5 B
6 C
Known to ancients
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
Known to ancients
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
Known to ancients
27 Co
28 Ni
29 Cu
Known to ancients
30 Zn
31 Ga
32 Ge
33 As
Known to ancients
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
Known to ancients
48 Cd
49 In
50 Sn
Known to ancients
51 Sb
Known to ancients
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
Known to ancients
80 Hg
Known to ancients
81 Tl
82 Pb
Known to ancients
83 Bi
Known to ancients
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 Ds
111 Rg
112 Cn
113 Uut
T.B.C
114 Fl
115 Uup
T.B.C
116 Lv
117 Uus
T.B.C
118 Uuo
T.B.C
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
Credit given to both where joint or independently discovered. IUPAC recognised only.
Collated by Jamie Gallagher, @jamiebgall

PREHISTORIC METALS (= Metals of Antiquity)

- **Seven metals** known (and actively used) already since prehistoric times:

  - Gold, Silver, Copper, Tin, Lead, Iron & Mercury

- **Occurrence:**

  - Iron 4th (4.1 %), Copper 26th (50 ppm), Lead 37th (14 ppm), Tin 49th (2.2 ppm), Silver 65th (70 ppb), Mercury 66th (50 ppb), Gold 72nd (1.1 ppb)

- **Melting points (in ^{o}C):**

  - Mercury −38.8, Tin 231, Lead 327, Silver 961, Gold 1064, Copper 1084, Iron 1538

- **Extraction:** - Gold & silver occur frequently in native form
  - Mercury compounds reduced to elemental mercury by low-T heating (500 °C)
  - Tin & iron oxides reduced with carbon monoxide (CO known; from charcoal)
  - Copper & lead compounds roasted to oxides, then reduced with CO

Metal	Celestial body	Week day
Gold	Sun	Sunday
Silver	Moon	Monday
Iron	Mars	Tuesday
Mercury	Mercury	Wednesday
Tin	Jupiter	Thursday
Copper	Venus	Friday
Lead	Saturn	Saturday

OXYGEN and NITROGEN

- **End of 18th century (Priestley, Scheele, Lavoisier): burning reactions in air → discoveries of O_2 & N_2**
- **Oxygen: Greek *oxys genes* (= acid forming)**
- **Nitrogen: Greek *nitron genes* (= nitrate forming)**

NOBLE GASES

- **End of 19th century (Ramsay & Rayleigh): All stable noble gases found through accurate measurements/experiments of air**

- **Element | Year | Origin of name**

Element	Year	Origin of name
Argon (Ar)	**1894**	**Greek *argon* (= inert)**
Krypton (Kr)	**1898**	**Greek *krypton* (= hidden)**
Neon (Ne)	**1898**	**Greek *neos* (= new)**
Ksenon (Xe)	**1898**	**Greek *xenon* (= strange)**

ALKALI and ALKALINE EARTH METALS

(mostly through electrochemistry)

- **Sodium (Na):** Lat. *natrium*;
  Compounds known since ancient times,
  preparation in metallic form by Davy in 1807
- **Potassium (K):** Lat. *kalium,* Arab. *qali* (= base); Davy 1807
- **Lithium (Li):** Greek *lithos* (= stone); Arfwedson 1817
- **Magnesium (Mg):** Greek *Magnesia* (name of a place)
- **Calcium (Ca):** Lat. *calx* (= Chalk); Davy 1808
- **Barium (Ba):** Greek *baryta* (= heavy);
  Scheele showed in 1774 that the oxide made from baryte (raskassälpä) is different from calcium oxide,
  preparation in metallic form by Davy in 1808
- **Strontium (Sr):** *Strontia* (Scottish town);
  Hope siscovered in 1791 from Scotland ($SrSO_4$ mineral), metallic form by Davy in 1808
- **Beryllium (Be):** Greek *beryllos*
  Vauguelin discovered in 1798 from beryllos mineral,
  preparation in metallic form in 1828 (reduction by K)

ELEMENTS DISCOVERED by means of SPECTROSCOPY

▪ **Cesium (Cs):**	**Lat. *caesius* (= sky blue); Bunsen & Kirchoff in 1860 from mineral water, separation twenty years later**
▪ **Rubidium (Rb):**	**Lat. *rubidius* (= deep red); Bunsen & Kirchoff in 1861**
▪ **Thallium (Tl):**	**Greek *thallos* (= green spring); Crookes 1861**
▪ **Indium (In):**	***indigon* (blue/violet); Reich & Richter 1863**
▪ **Helium (He):**	**Greek *helios* (= sun); - first discovered outside of the Earth (Janssen 1868; spectrum of the Sun); - then from the spectral line of material erupted from Mount Vesuvius (Palmieri 1881)**

PLATINUM METALS (Noble metals)

- **Known in South America (native Indians used in jewelry) much before “discovered” in Europe**

Element	Discoverer	Origin of name
Platinum (Pt)	**de Ulloa 1748**	**Spanish *platina***
Palladium (Pd)	**Wollaston 1803**	***Pallas* (asteroid)**
Osmium (Os)	**Tennart 1803**	**Greek *osme* (= smell)**
Iridium (Ir)	**Tennart 1803**	**Lat. *iris* (= rainbow)**
Rhodium (Rh)	**Wollaston 1804**	**Greek *Rhodon* (= rose)**
Rutenium (Ru)	**Claus 1844**	**Lat. *Rutenia* (= Russia)**

HALOGENS

- **Chlorine (Cl):** **Greek *kloros* (= yellowish green);**
  Scheele 1774: oxidation of HCl
  Davy 1807: understood as a new element
- **Iodine (I):** **Greek *iodes* (= violet);**
  Courtois: from seaweed ash
- **Bromine (Br):** **Greek *bromos* (= to stink (bad smell));**
  Balard 1861: from salt solutions
- **Fluorine (F):** **Lat. *fluere* (= to flow);**
  Use of fluorspar in metallurgy (flux agent) known since 1500s;
  Moissan 1886: elemental fluorine through electrolysis of HF (Nobel 1906)

RARE EARTH ELEMENTS (= METALS)

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

  - Johan Gadolin (Univ. Turku) 1794: the new mineral found in Ytterby (Stockholm) contains a new metal oxide ("earth") of an unknown element → yttrium

  - Olavi Erämetsä (Helsinki Univ. Tech.) 1965: small amounts of radioactive promethium from nature (first discovered in USA as a fission product in nuclear reactions) from nature

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)

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- based on accurate measurements of air in 1890s
- thanks to the progress in electrochemical techniques in 1800-1810
- thanks to the progress in spectroscopy techniques in 1860s
- for the first time from outside of the Earth (1868)
- much earlier in South America by native Indians than in Europe (in 1750~1850)
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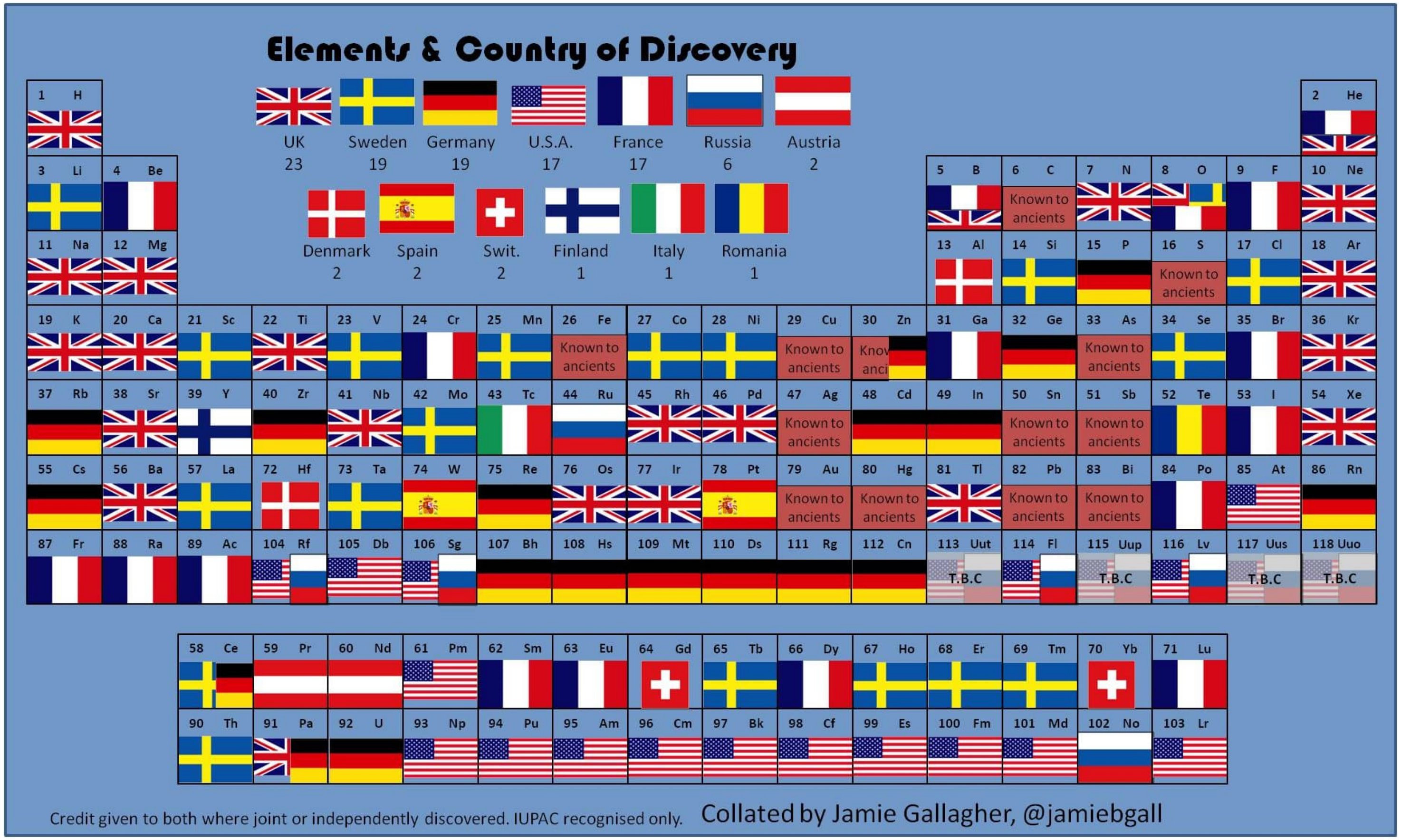
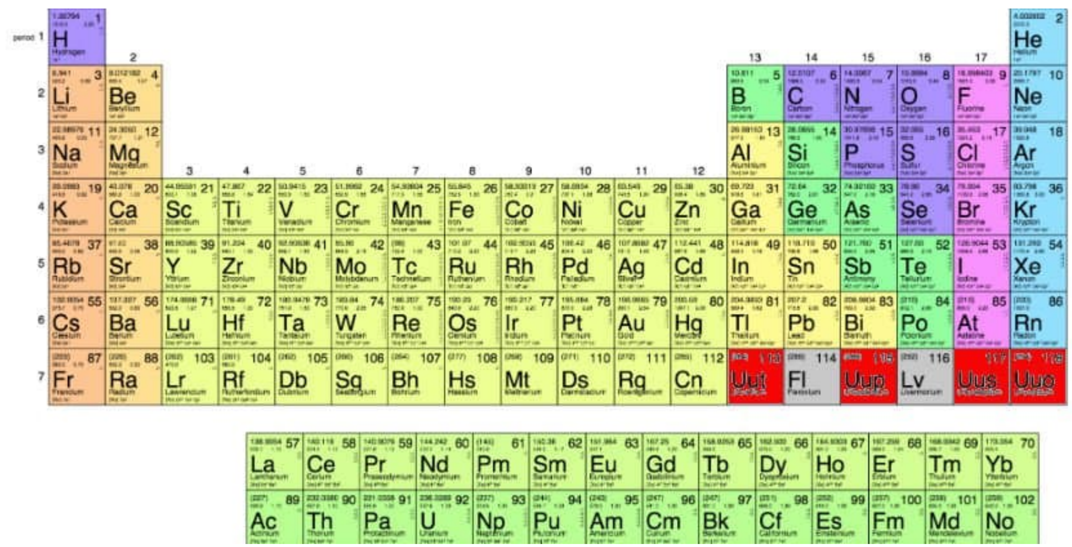
- the discovery was rewarded by a Nobel prize in 1906
- **based on quantum chemical considerations**



IUPAC (International Union of Pure and Applied Chemistry)

- Based on the Greek/Latin names of numbers
- For example: element no. **119**: un un enn → **Ununennium** (**Uue**)

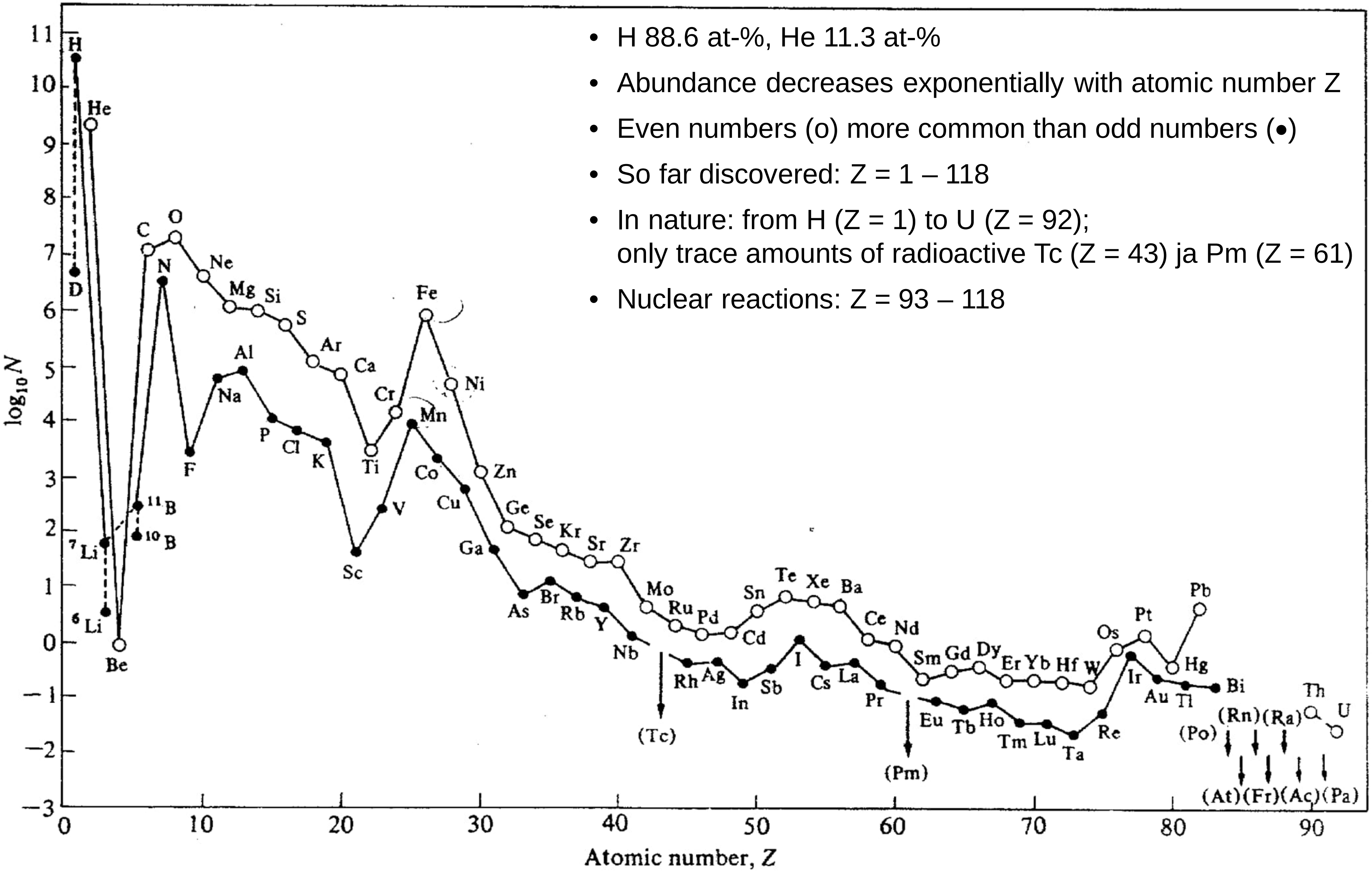
Number	Name	Number	Name
0	nil	5	pent
1	un	6	hex
2	bi	7	sept
3	tri	8	oct
4	quad	9	enn



Z = 113: nihonium Nh
Z = 115: moscovium Mc
Z = 117: tennessine Ts
Z = 118: oganesson Og

Nuclear fusion: Dubna, RIKEN, OakRidge

RELATIVE ABUNDANCE OF ELEMENTS (in universe)



- H 88.6 at-%, He 11.3 at-%
- Abundance decreases exponentially with atomic number Z
- Even numbers (o) more common than odd numbers (•)
- So far discovered: Z = 1 – 118
- In nature: from H (Z = 1) to U (Z = 92);
  only trace amounts of radioactive Tc (Z = 43) ja Pm (Z = 61)
- Nuclear reactions: Z = 93 – 118

LITHIUM ISOTOPES

- Lithium has two stable isotopes: ^6Li and ^7Li (92.5 %) + 7 unstable isotopes
- For both isotopes: nuclear fission possible → Lithium less common than expected
- The two natural isotopes behave differently in many natural processes, such as mineral formation, metabolism and ion exchange
- For example: ^6Li has higher preference for octahedral coordination than ^7Li → ^6Li enriched in clay minerals based on octahedral Mg or Fe
- **^6Li** is important for nuclear physics and **nuclear weapons**:
  - absorber of neutrons in nuclear fusion reactions
  - source material for the production of tritium ^3H

  → In commercial Li chemicals ^6Li content often visibly low (7.5 → 3.75 %)
- Nowadays even in nature (e.g. rivers) lower ^6Li contents detected (because of its long-lasting extraction)

$$^{6}_{3}Li + ^{1}_{0}n \dashrightarrow ^{4}_{2}He + ^{3}_{1}H$$

https://en.wikipedia.org/wiki/Lithium

ATOMIC MODEL & ELECTRON CONFIGURATIONS

IMPORTANT HISTORICAL STEPS

- **Thomson 1898-1903:** existence of electrons
- **Rutherford 1911:** small and dense nucleus + electron cloud
- **Einstein 1905:** wave and particle nature of electromagnetic radiation
- **Bohr 1913:** simple atom model (classical physics + some quantum theory features)
- **de Broglie 1924:** wave nature of particles
- **Davisson & Germes 1927:** diffraction of electrons
- **Heisenberg 1926:** uncertainty principle (exact position and momentum of electron)
- **Schrödinger 1926:**
  wave nature of electrons → quantum mechanical atom model
- **Compton 1921 and Goudsmit & Uhlenbeck 1925:** electron spin
- **Pauli 1925:** “exclusion principle”
- **Hund 1925:** minimum energy → maximum number of unpaired electrons

QUANTUM MECHANICAL ATOM MODEL

- **Electrons have simultaneously both wave and particle nature**
- **In an atom electron behaves like standing wave**
- **Schrödinger wave function:**
  - **wavefunction ψ is a solution of Schrödinger equation**
  - **ψ describes the behaviour of electron**
  - **in chemistry: wavefunction $\rightarrow$ atomic orbital**
  - **Schrödinger equation has several possible solutions (= orbitals)**
  - **each orbital is described with a set of three quantum numbers: n, l and m**
  - **There is a certain energy corresponding to each wave function**
  - **Energy quantization is derived from the Schrödinger equation**

QUANTUM NUMBERS

n	l	m	Orbital	Number
1	0	0	1s	1
2	0	0	2s	1
	1	-1, 0, 1	2p	3
3	0	0	3s	1
	1	-1, 0, 1	3p	3
	2	-2, -1, 0, 1, 2	3d	5
4	0	0	4s	1
	1	-1, 0, 1	4p	3
	2	-2, -1, 0, 1, 2	4d	5
	3	-3, -2, -1, 0, 1, 2, 3	4f	7

Principal quantum number (n): 1, 2, 3, …
- size and energy of the orbital

Angular momentum quantum number (l): 0, 1, … , (n-1)
- shape of the orbital

Magnetic quantum number (m): -l, (-l+1), …, (+l-1), +l
- orientation of the orbital in 3D space

Spin quantum number (s): -½, ½

Pauli’s exclusion principle

It is impossible for two electrons in the same atom to have the same set of quantum numbers: n, l, m and s

Aufbau (“building up”) principle

Orbitals are filled in the order of increasing energy:
1s–2s–2p–3s–3p–4s–3d–4p–5s–4d–5p–6s–4f–5d–6p–7s–5f–6d–7p

Hund’s rule (not necessarily obeyed when the energy levels splitted, ref. crystal field theory)

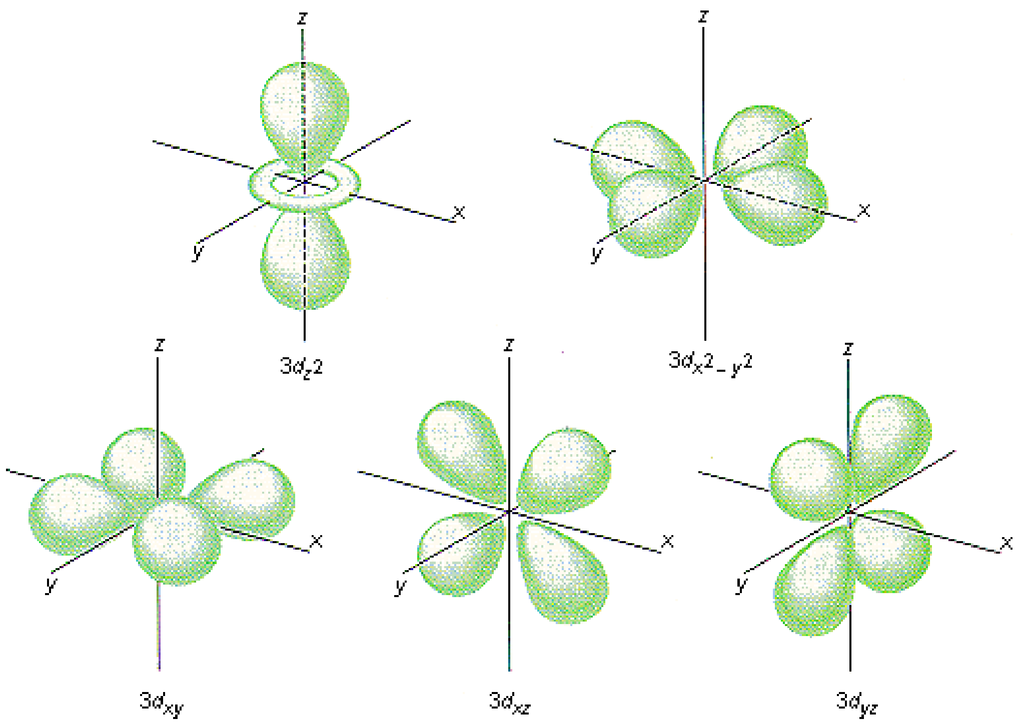
All orbitals in a subshell are first occupied with one electron before two electrons start to occupy the same orbital
(to minimize the electron-electron repulsions)

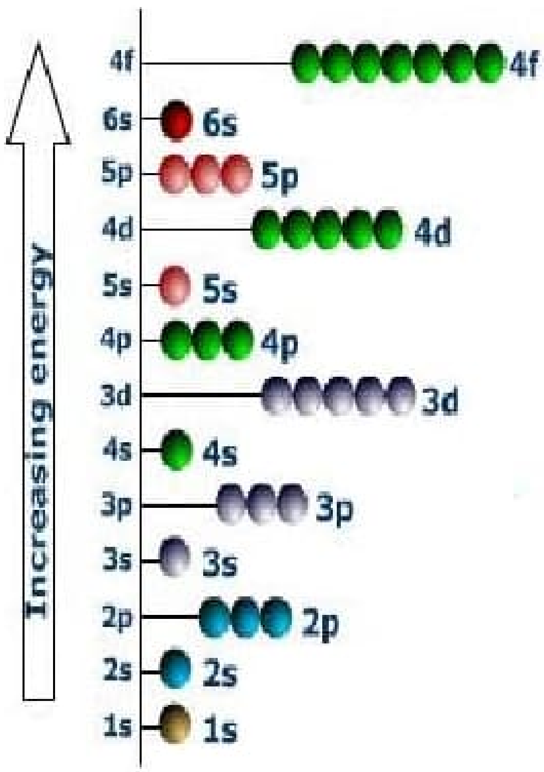
Atom orbitals

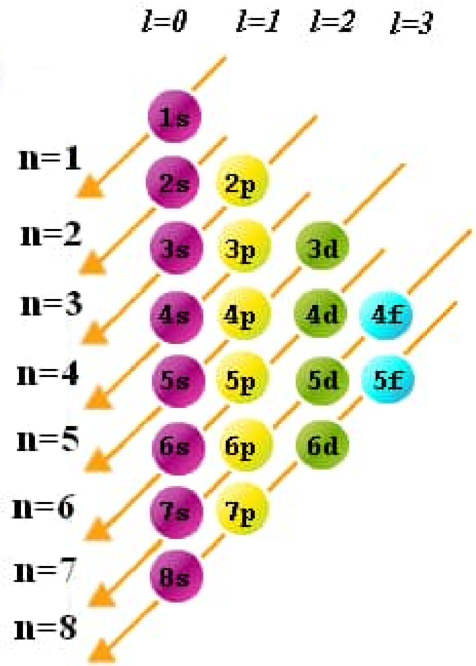
- ψ (wave function):
  does not tell the location or path of electron
  (c.f. Heisenberg uncertainty principle)

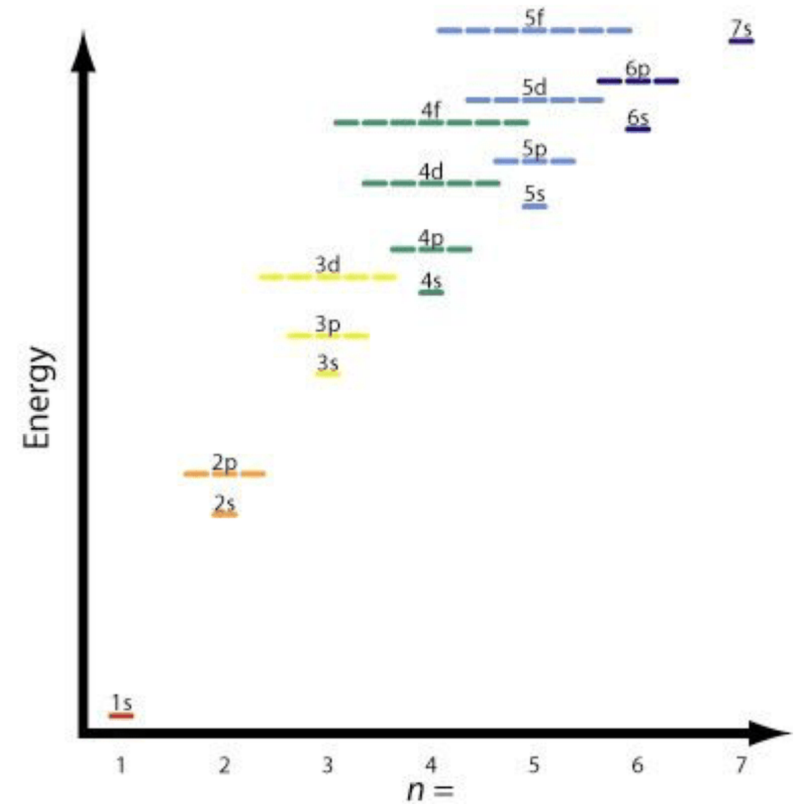
- ψ2 (square of wave function):
  probability of electron to be located in a certain location

  → PROBABILITY DENSITY / ELECTRON DENSITY MAP
  → **”shape” of the orbital**









Relative Orbital Energies

- These diagrams show situation: - for empty orbitals
  - in a single isolated atom
- Once an orbital is occupied by electron(s), its relative energy changes
- Once an atom is surrounded by neighbouring atoms, the energies of its (outer) d and f orbitals are splitted (*Crystal Field Splitting*)

s

d

Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	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
Period 5	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
Period 6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

p

Lanthanide series →	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
Actinide series →	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

f

Electron configurations of 3d metals:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^x$$

			3d				4s
Scandium (Sc)	↑						↑↓
Titanium (Ti)	↑	↑					↑↓
Vanadium (V)	↑	↑	↑				↑↓
Chromium (Cr)	↑	↑	↑	↑	↑		↑
Manganese (Mn)	↑	↑	↑	↑	↑		↑↓
Iron (Fe)	↑↓	↑	↑	↑	↑		↑↓
Koboltti (Co)	↑↓	↑↓	↑	↑	↑		↑↓
Nikkeli (Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓
Kupari (Cu)	↑↓	↑↓	↑↓	↑↓	↑↓		↑
[Sinkki (Zn)]	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓

Electron configurations and oxidation states of lanthanoids

(to be discussed later in this course)

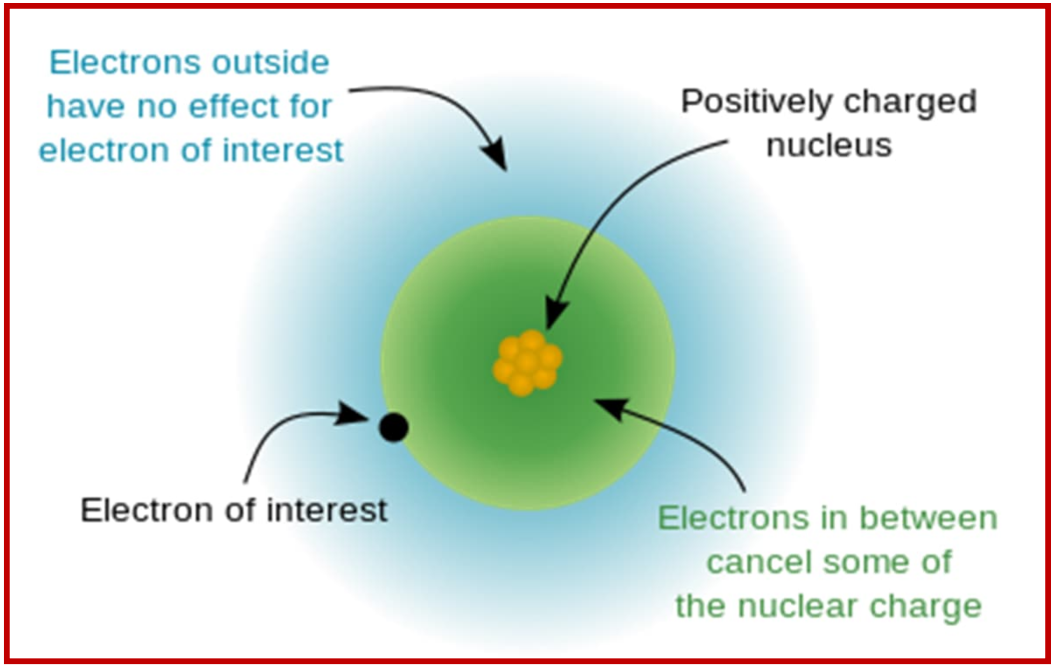
Z	Element	Electronic configuration	Oxidation states
57	Lanthanum (La)	$4f^0 5d^1 6s^2$	+III
58	Cerium (Ce)	$4f^1 5d^1 6s^2$	+III, +IV
59	Praseodymium (Pr)	$4f^2 5d^1 6s^2$	+III
60	Neodymium (Nd)	$4f^3 5d^1 6s^2$	+III
61	Promethium (Pm)	$4f^4 5d^1 6s^2$	+III
62	Samarium (Sm)	$4f^5 5d^1 6s^2$	+III
63	Europium (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

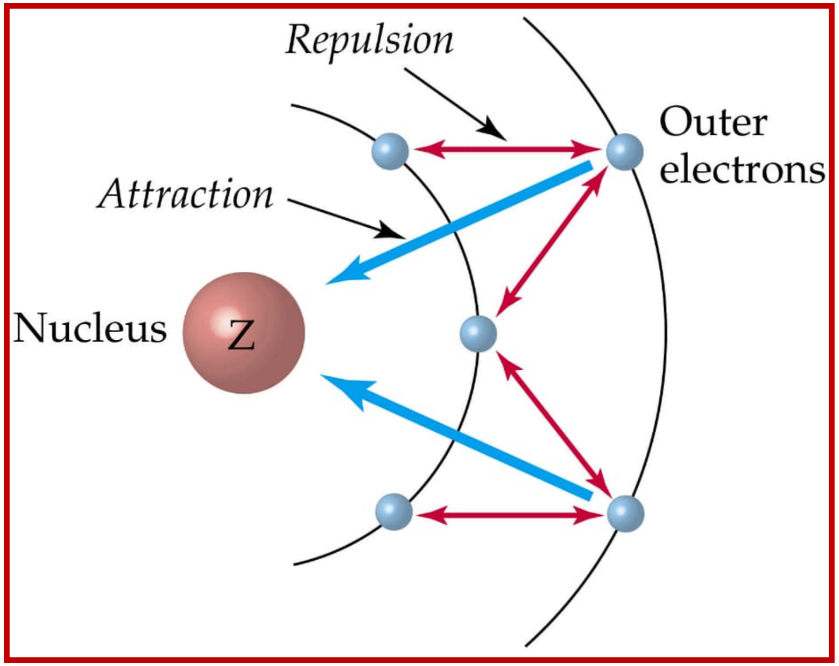
PERIODIC PROPERTIES

- effective nuclear charge
- atomic radius and ionic radius
- ionization energy
- electron affinity
- electronegativity
- oxidation numbers
- density
- melting and boiling points
- reactivity and stoichiometries of compounds
- properties of compounds
- etc.

EFFECTIVE NUCLEAR CHARGE (Z_{eff})

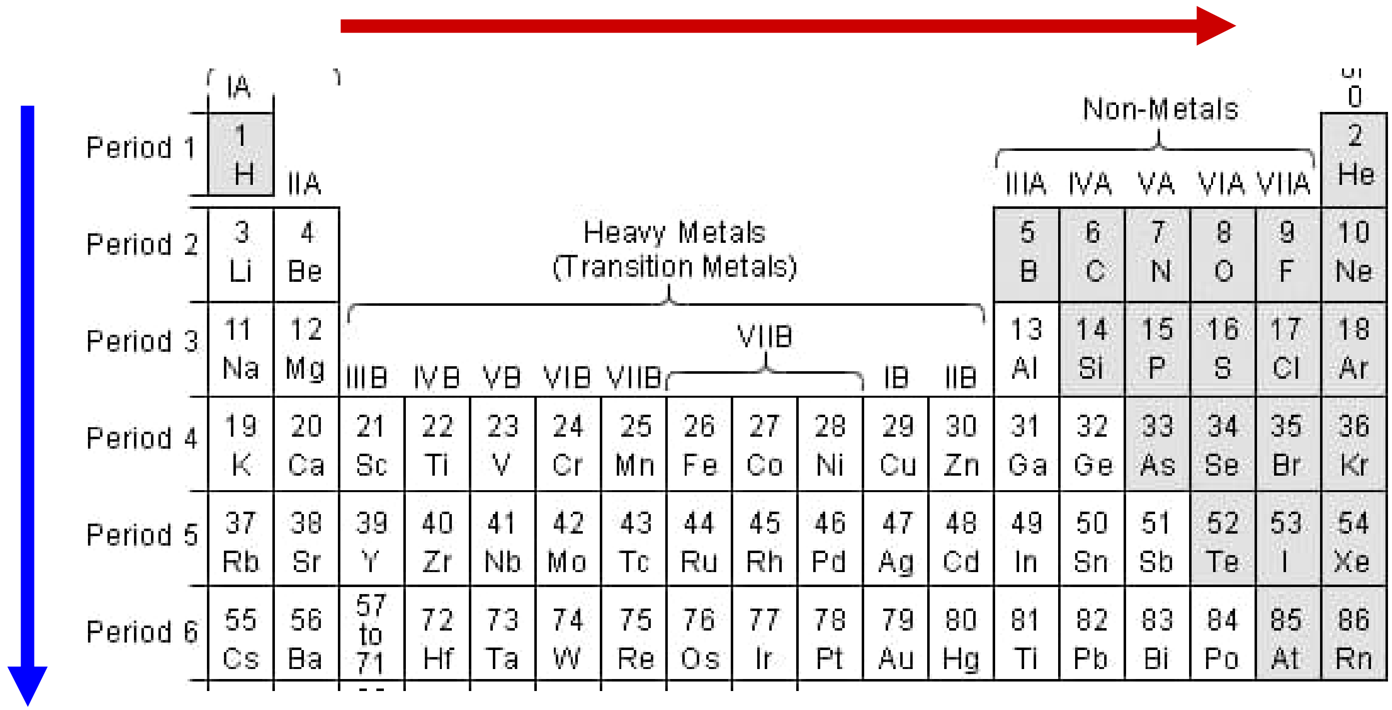
- Atomic number (Z) = number of protons = (true) positive nuclear charge
- Z_{eff}: positive charge experienced by an electron in a multi-electron atom
- Z_{eff} is smaller than Z due to the shielding effect of the other (inner) electrons in the same atom
- Only the electrons that are closer to the nucleus contribute to the shielding effect (not electrons on the same orbitals)
- $+e < Z_{eff} < Z$





Z_{eff} increases, r_{atom} decreases

$Z_{eff} \approx$ constant:
r_{atom} increases

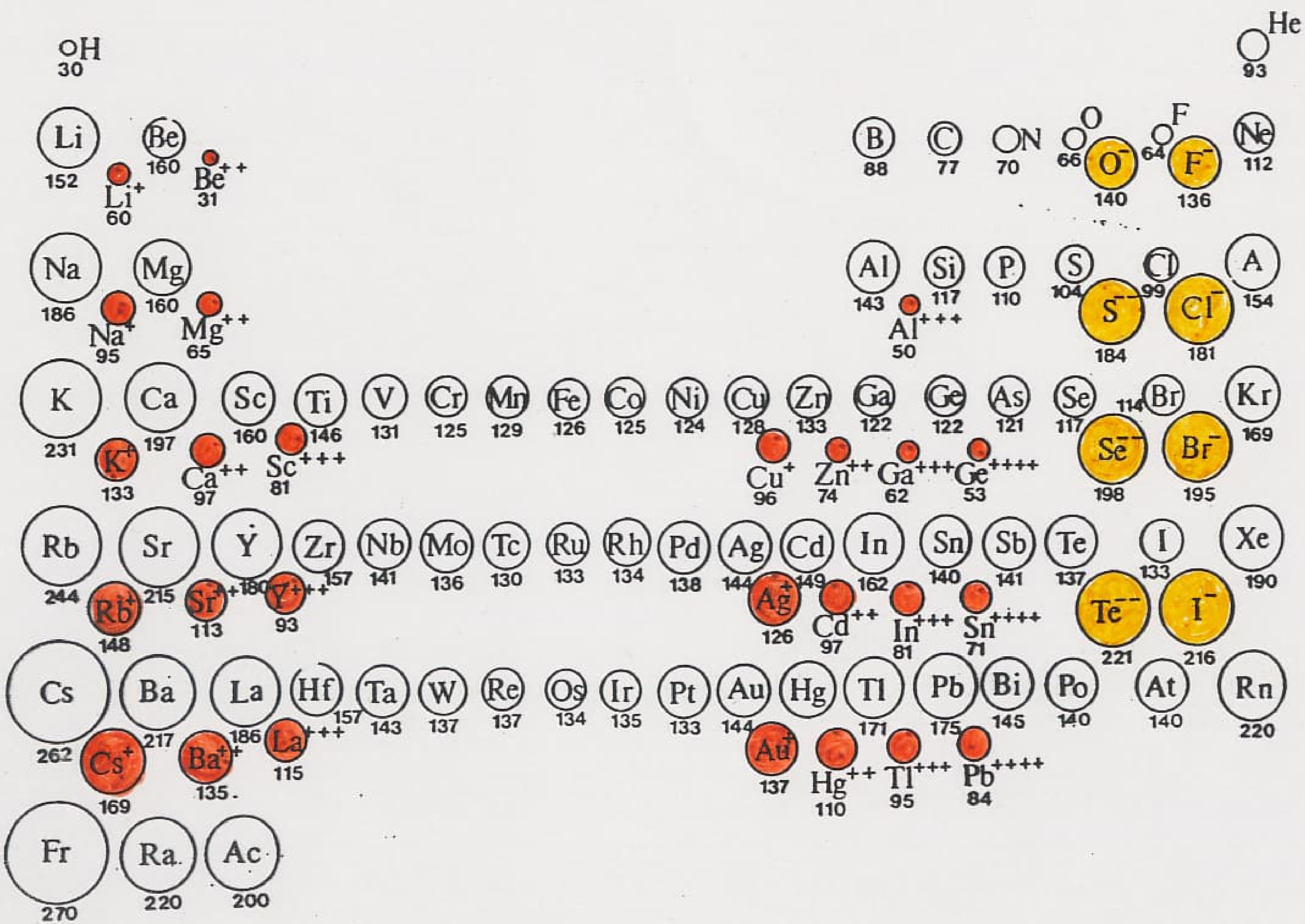


IONIC RADIUS

- **Ionic radius values can not be measured directly**
- **The values are estimated (using statistical techniques) for each ion from a large data set for experimentally determined bond lengths in different ionic compounds**
- **The values are tabulated (originally) in:**

R.D. Shannon, Acta Cryst. A 32, 751 (1976)

You can find ionic radius values at: http://abulafia.mt.ic.ac.uk/shannon/ptable.php



H 30
He 93
Li 152
Be 160
Li+ 60
Be++ 31
B 88
C 77
N 70
O 66
F 64
Ne 112
O− 140
F− 136
Na 186
Mg 160
Na+ 95
Mg++ 65
Al 143
Si 117
P 110
S 104
Cl 99
A 154
Al+++ 50
S−− 184
Cl− 181
K 231
Ca 197
Sc 160
Ti 146
V 131
Cr 125
Mn 129
Fe 126
Co 125
Ni 124
Cu 128
Zn 133
Ga 122
Ge 122
As 121
Se 117
Br 114
Kr 169
K+ 133
Ca++ 97
Sc+++ 81
Cu+ 96
Zn++ 74
Ga+++ 62
Ge++++ 53
Se−− 198
Br− 195
Rb 244
Sr 215
Y 180
Zr 157
Nb 141
Mo 136
Tc 130
Ru 133
Rh 134
Pd 138
Ag 144
Cd 149
In 162
Sn 140
Sb 141
Te 137
I 133
Xe 190
Rb+ 148
Sr++ 113
Y+++ 93
Ag+ 126
Cd++ 97
In+++ 81
Sn++++ 71
Te−− 221
I− 216
Cs 262
Ba 217
La 186
Hf 157
Ta 143
W 137
Re 137
Os 134
Ir 135
Pt 133
Au 144
Hg
Tl 171
Pb 175
Bi 145
Po 140
At 140
Rn 220
Cs+ 169
Ba++ 135
La+++ 115
Au+ 137
Hg++ 110
Tl+++ 95
Pb++++ 84
Fr 270
Ra 220
Ac 200

Ionic radius [Å]

earth-alkaline metals: oxidation state +II

CN	4	6	8	9	10	12
Be	0.27	0.45	-	-	-	-
Mg	0.57	0.72	0.89	-	-	-
Ca	-	1.00	1.12	1.18	1.23	1.34
Sr	-	1.18	1.26	1.31	1.36	1.44
Ba	-	1.35	1.42	1.47	1.52	1.66

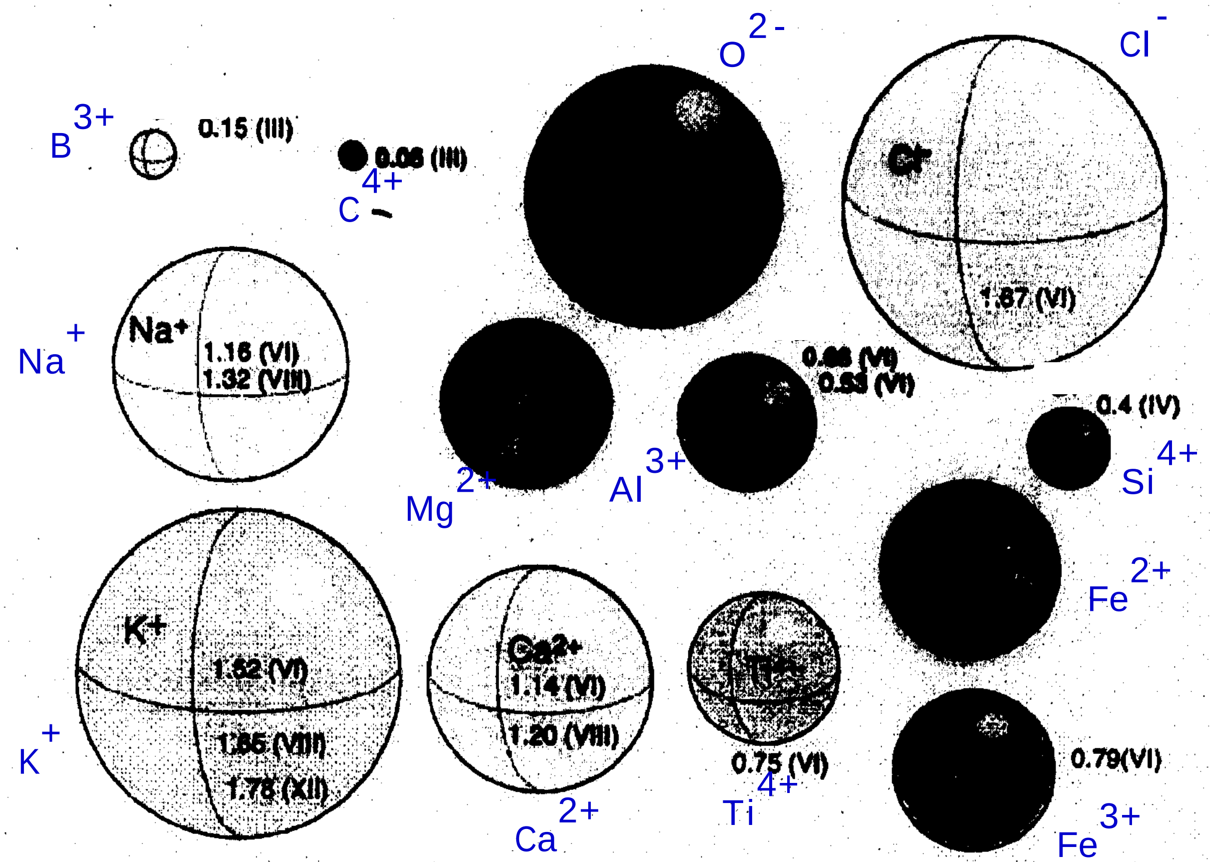
3d cations: CN = 6

Ox. state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+II	0.86	0.79	0.80	0.83	0.78	0.75	0.69	0.73	0.74
+III	0.67	0.64	0.62	0.65	0.65	0.61	0.60	0.54	-
+IV	0.61	0.58	0.55	0.53	0.59	0.53	0.48	-	-

anions: CN = 6

OH^- 1.37	H^- 1.67
O^{2-} 1.40	F^- 1.33
S^{2-} 1.84	Cl^- 1.81
Se^{2-} 1.98	Br^- 1.96
Te^{2-} 2.21	I^- 2.20

Ionic Radii (Shannon, 1976)



LANTHANIDE CONTRACTION