Chemistry of Elements

CHEM-E4130 (5 cr)

Lectures (14 x):	Monday (Ke4)	12.15 – 14.00
	Wednesday (Ke2)	10.15 – 12.00
	Friday (Ke4)	10.15 – 12.00

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

- Lectures: 15 x 2 h
- Home problem solving 30 h
- Independent homework 60 h
- Exam 3 h

MARKING

- **Exam:** 50 points
- **Lecture exercises:** 25 points
  14 x 2 p → 28; 3 extra points 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.

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 14 x 2 = 28 (3 extra!) points in maximum

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 scientific article for a reference, and you should search for couple of more (recent) articles to be discussed in the presentation.

TENTATIVE LECTURE SCHEDULE

Mon (Ke4) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Ke4) 10.15 – 12.00

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Metal Complexes & MOFs
9.	Wed	28.09.	Cr, Mo, W & 2D materials
10.	Fri	30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
10.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
11.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
12.	Mon	10.10.	EXTRA
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

PRESENTATION TOPICS/SCHEDULE

Fri	16.09.	Ti:
		Zn:
Mon	26.09.	Nb:
Wed	28.09.	Mo:
Fri	30.09.	Mn:
		Cu:
		Ru:
Fri	07.10.	Eu:
		Nd:
		U:
Wed	12.10.	Co:
		In:
		Te:

QUESTIONS: Lecture 1

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

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

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

Alkali metals
Alkaline earth metals
Halogens
Noble gases

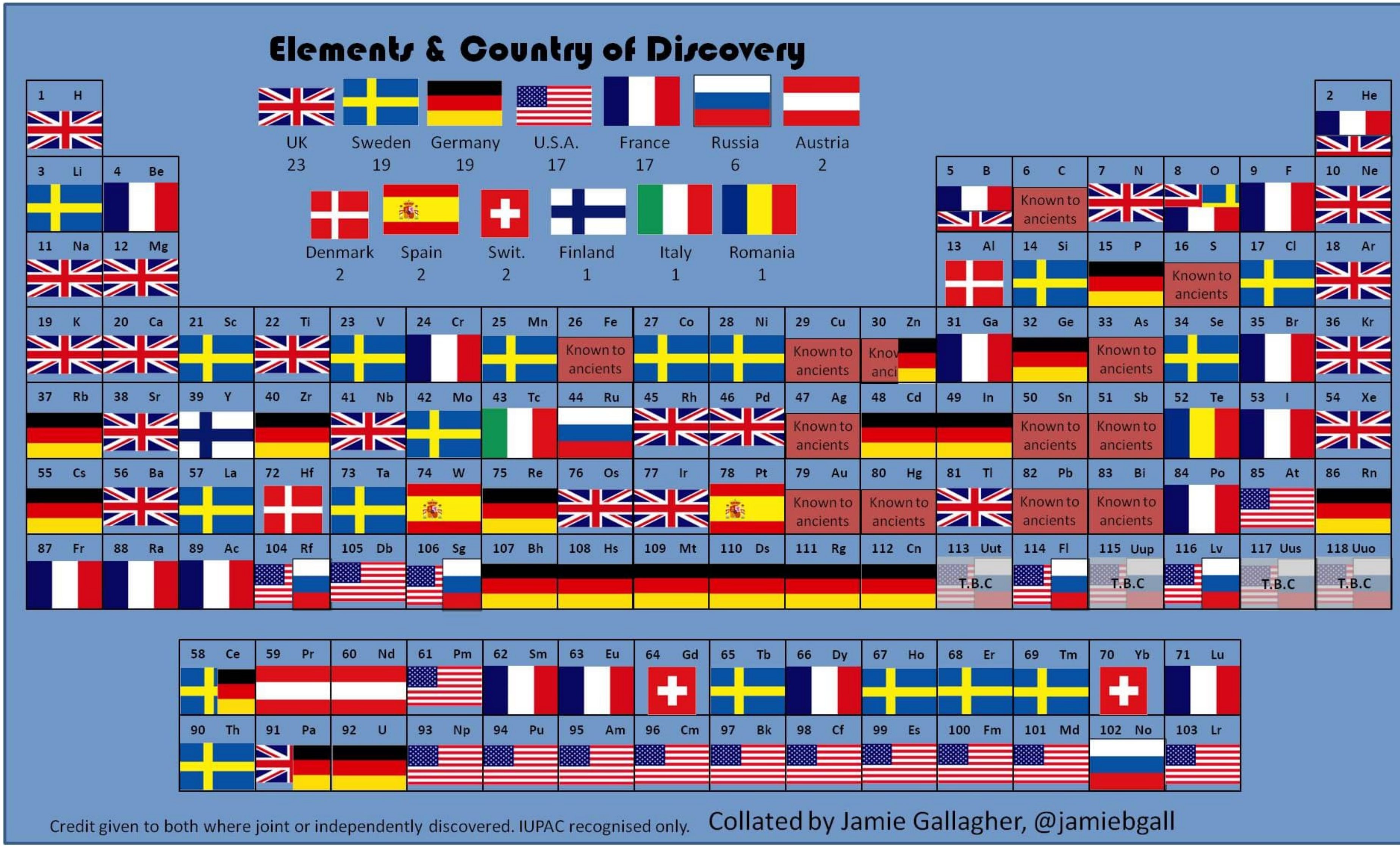
Transition metals
Lanthanides
Actinides

TRANSITION METALS

- A variety of possible oxidation states and spin-configurations → exciting properties

- d-block transition metals
  - [Sc ~ Cu(Zn)] + [Y ~ Ag(Cd)] + [La ~ Au(Hg)]

- f-block transition metals
  - lanthanides [14 elements after La: Ce ~ Lu]
  - actinides [14 elements after Ac: Th ~ Lr]
  - lanthanoides (Ln): La + Lanthanides
  - rare earth elements (RE): Ln + Y + Sc


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:**

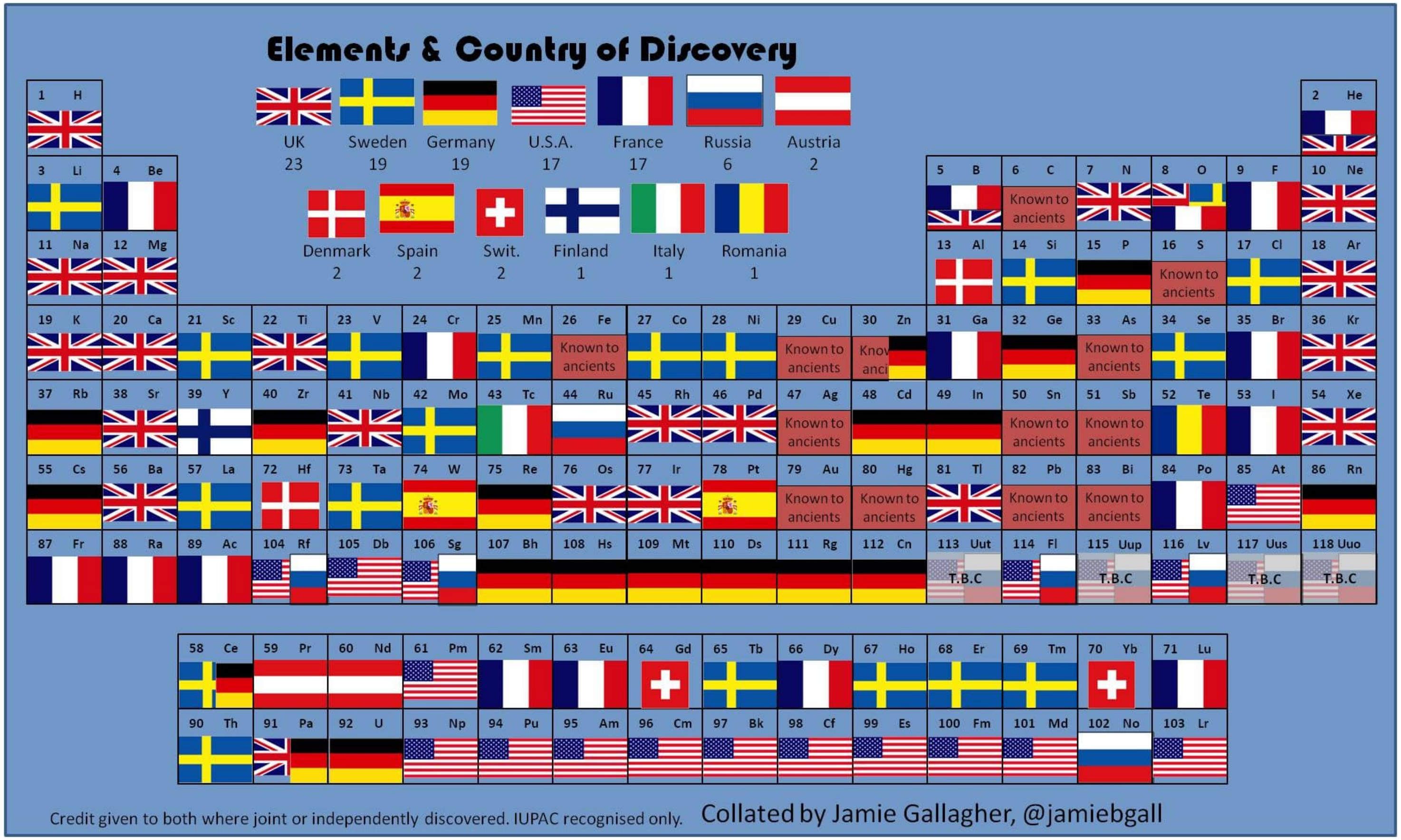
  - Johan Gadolin (Univ. Turku) 1794: the new mineral found in Ytterby (Stockholm) contains a new metal oxide ("earth") of an unknown element → yttrium

  - 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)

Which element(s) was/were discovered

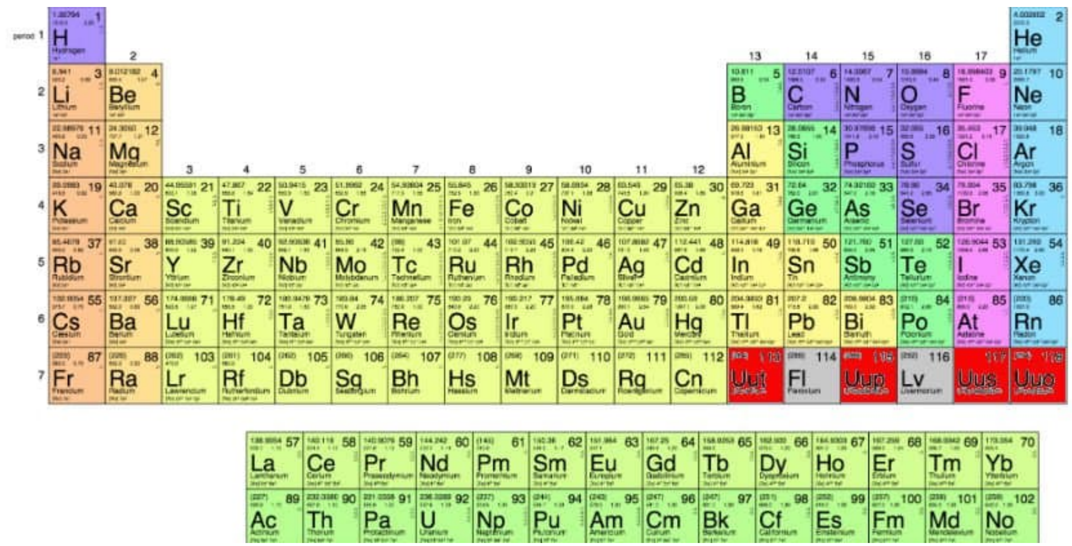
- as a result of huge interest in burning reactions in 1700s
- based on accurate measurements of air in 1890s
- thanks to the progress in electrochemical techniques in 1800-1810
- thanks to the progress in spectroscopy techniques in 1860s
- for the first time from outside of the Earth (1868)
- much earlier 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**



IUPAC (International Union of Pure and Applied Chemistry)

- Based on the Greek/Latin names of numbers
- For example: element no. **119**: un un enn $\rightarrow$ **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

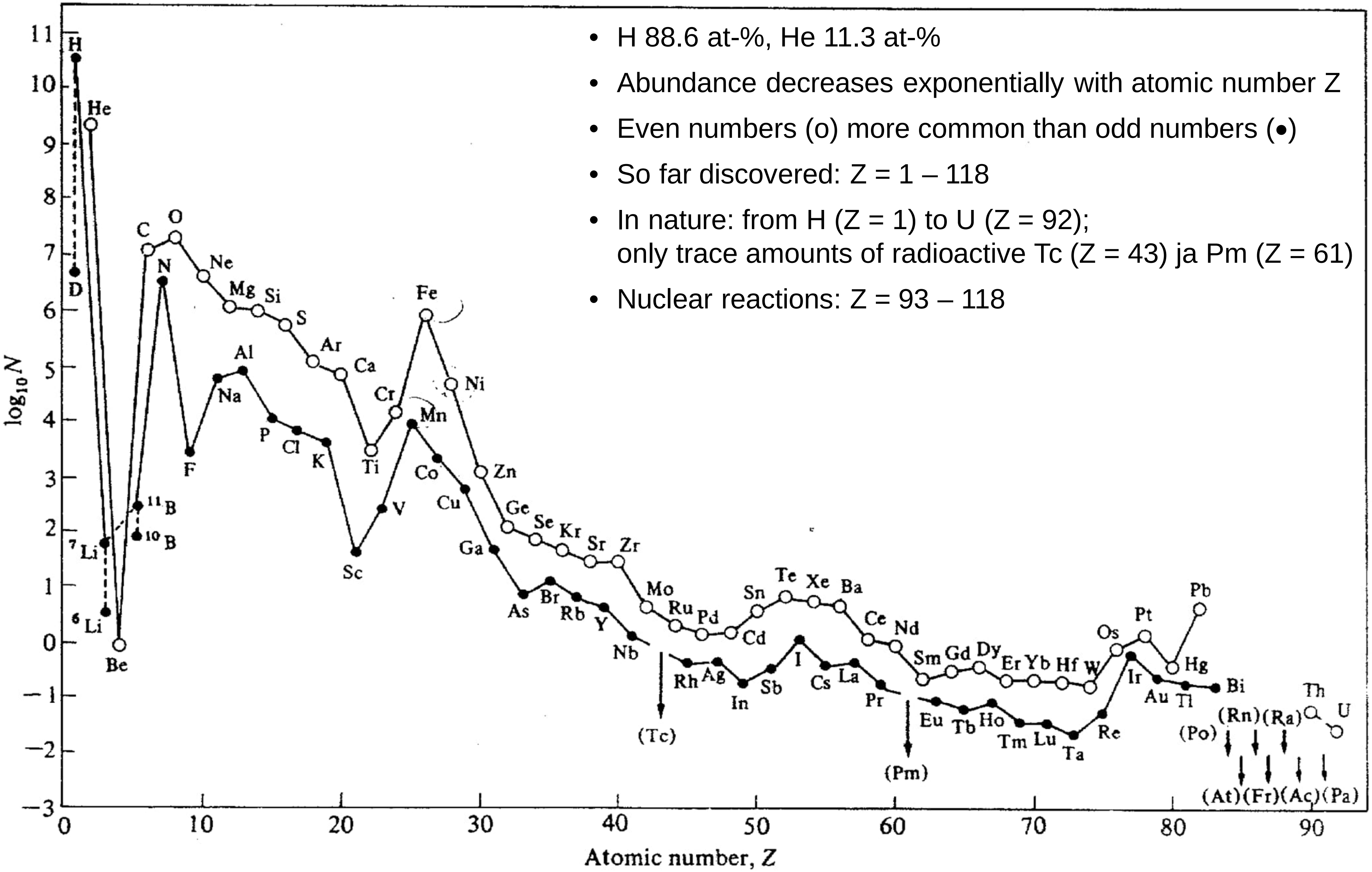


Z = 113: nihonium Nh
Z = 115: moscovium Mc
Z = 117: tennessine Ts
Z = 118: oganesson Og

Nuclear fusion: Dubna, RIKEN, OakRidge

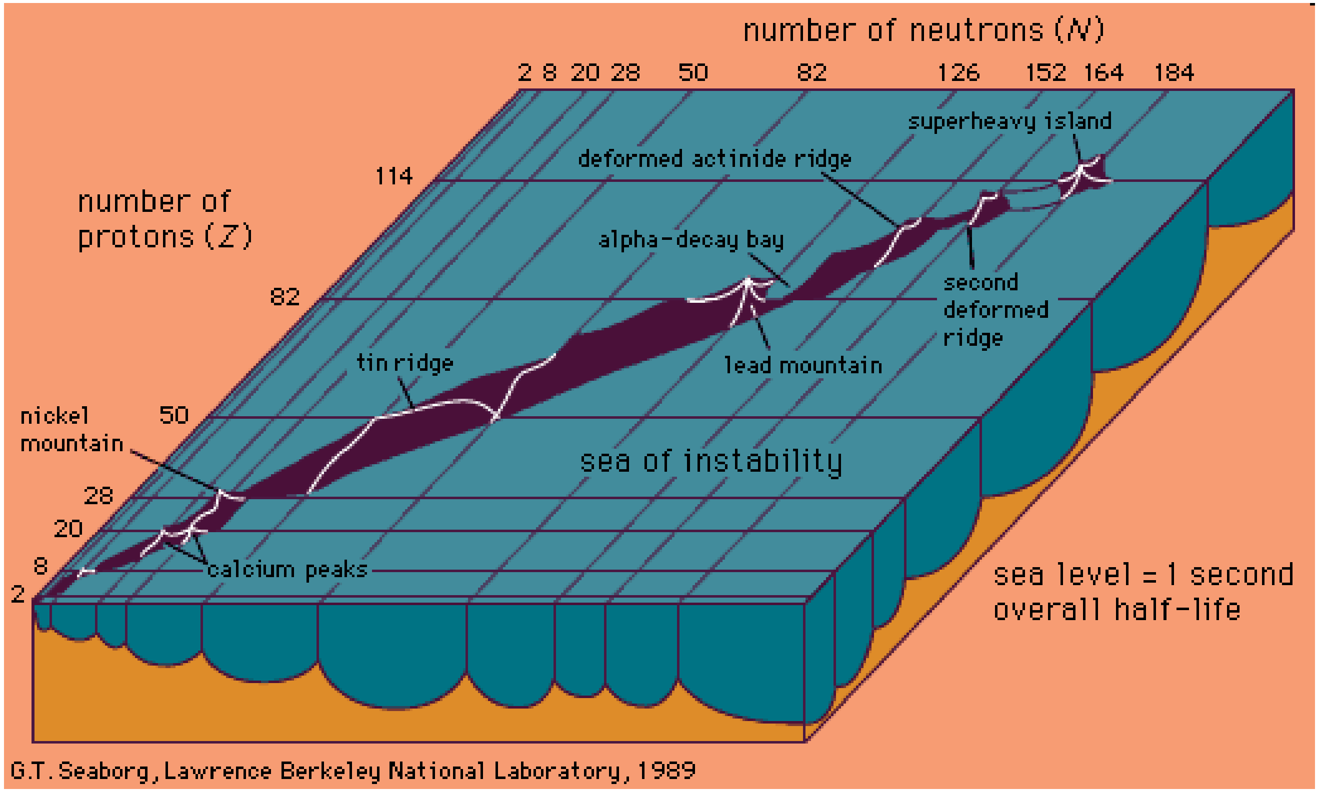
RELATIVE ABUNDANCE OF ELEMENTS (in universe)

- 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



MAGIC NUMBERS

- In nucleus fixed energy levels for protons and neutrons (c.f. electrons & orbitals)
- With certain atomic numbers (Z) and neutron numbers (N) more stable nuclii
- So-called magic numbers: Z or N = 2, 8, 20, 28, 50, 82, 126
- Most stable: both Z and N magic numbers: ^{4}He (Z = 2), ^{16}O (Z = 8), ^{208}Pb (Z = 82)



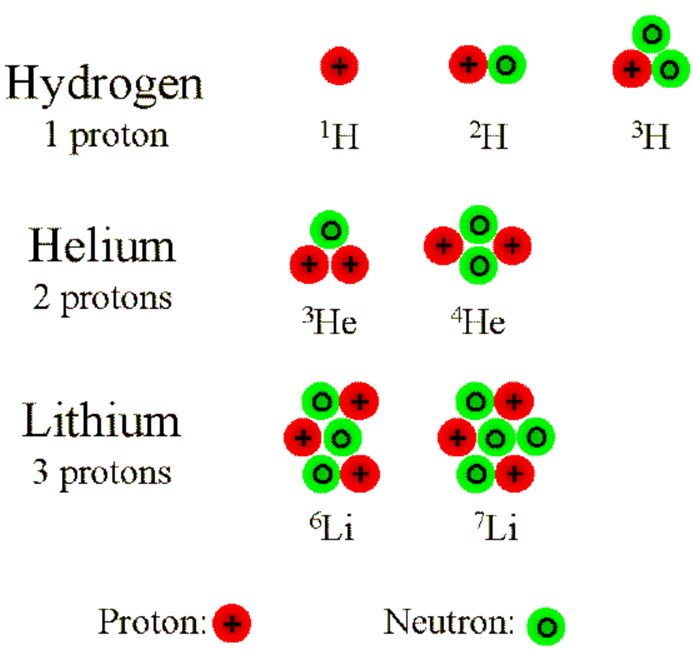
Artificial Elements

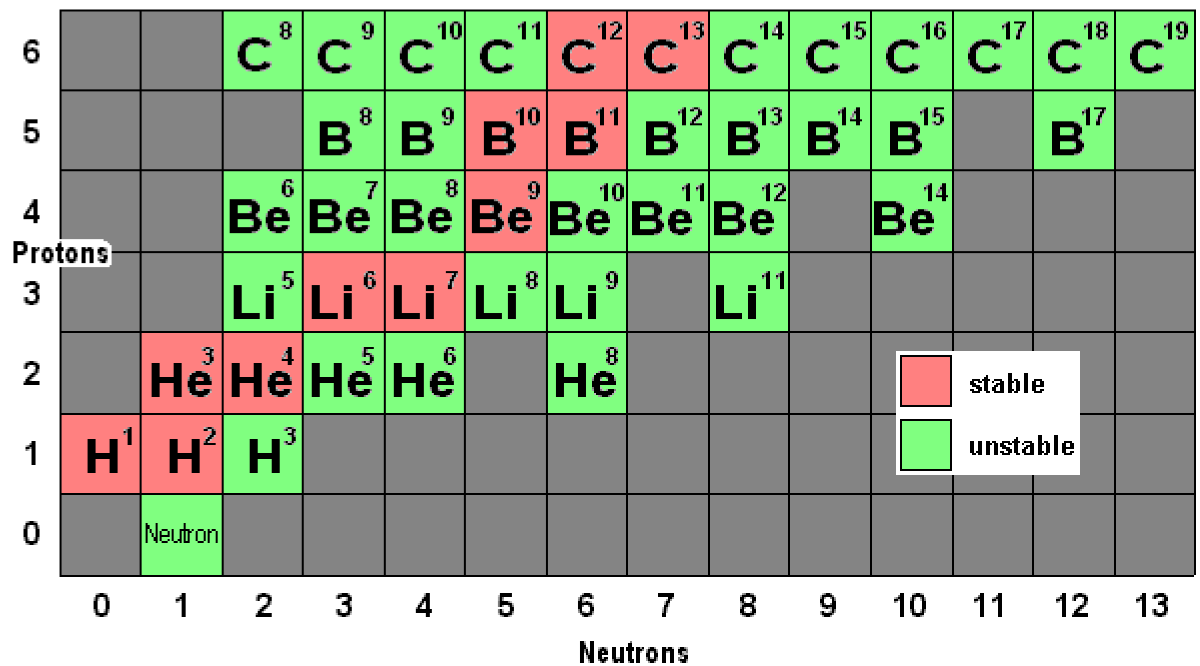
- Preparation: fusion reactions in particle accelerators (Dubna, RIKEN, OakRidge, Hamburg)
- Life times typically less than second
- 1937: first artificially prepared element:

  Technetium (Tc) (Greek *teknetos* = artificial)

ISOTOPES

- Known atoms (273 stable + radioactive) much more than elements (118) → many elements have different atoms → ISOTOPES
- Isotopes of the same element are (MOSTLY) chemically similar but the physical properties may be different
- With increasing atomic number Z the relative number of neutrons increases
- Natural isotope composition nearly constant for stable elements but varies for radioactive elements





ATOMIC WEIGHTS

- Accuracy is continuously increasing

Element	1873–5	1903	1925	1959	1961	1995
H	1	1.008	1.008	1.0080	1.007 97	1.007 94(7)
C	12	12.00	12.000	12.011 15	12.011 15	12.0107(8)
O	16	16.00	16.000	**16**	15.9994	15.9994(3)
P	31	31.0	31.027	30.975	30.9738	30.973 761(2
Ti	50	48.1	48.1	47.90	47.90	47.867(1)
Zn	65	65.4	65.38	65.38	65.37	65.39(2)
Se	79	79.2	79.2	78.96	78.96	78.96(3)
Ag	108	107.93	107.880	107.880	107.870	107.8682(2)
I	127	126.85	126.932	126.91	126.9044	126.90447(3)
Ce	92	140.0	140.25	140.13	140.12	140.116(1)
Pr	—	140.5	140.92	140.92	140.907	140.907 65(2)
Re	—	—	188.7[b]	186.22	186.22	186.207(1)
Hg	200	200.0	200.61	200.61	200.59	200.59(2)

SOURCES OF ERROR IN ATOMIC WEIGHTS

- **accuracy of measurement**
- **natural isotope composition (B, S)**
- **”depleted” elements (in natural Li 7.5% ^{6}Li, commercially only 3.75 %)**
- **enriched elements (from nuclear reactors)**
- **radioactive elements (atomic weight changes as a function of time)**

LITHIUM ISOTOPES

- Lithium has two stable isotopes: ^{6}Li and ^{7}Li (92.5 %)
- Both isotopes have an uncommon property: nuclear fission is possible → Lithium is much less common in the Solar System than expected
- Besides the two natural isotopes, seven unstable Li radioisotopes are known, the most stable being ^{8}Li (half-life of 838 ms)
- The two natural isotopes behave differently in many natural processes, such as mineral formation, metabolism and ion exchange
- For example: ^{6}Li has higher preference for octahedral coordination (than ^{7}Li) → ^{6}Li is enriched when lithium ions substitute for octahedral Mg or Fe in clay minerals
- **^{6}Li** is important for nuclear physics and **nuclear weapons**:
  - absorber of neutrons in nuclear fusion reactions
  - source material for the production of tritium ^{3}H

  → In commercial Li chemicals the ^{6}Li content is often visibly low (7.5 → 3.75 %)
- Nowadays even in nature (e.g. rivers) lower ^{6}Li 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