Celebrating 150 years Periodic Table

*Historical remarks and current situation*

Heinz W. Gäggeler

Department of Chemistry & Biochemistry,
University of Bern, Switzerland

*and*

Paul Scherrer Institut, Villigen, Switzerland
D.I. Mendeleev
Outline

- Few comments on the CV of D.I. Mendeleev
- The first periodic table and its consequences
- Noble gases: a new group of elements
- The uranium decay products: birth of radiochemistry
- Seaborgs suggestion: the actinides
- The nuclear weapons elements
- The failure of chemists to discover new elements beyond atomic number 101 (Md)
- How physicists discovered the elements above atomic number 101 (Md) up to 118 (Og)
- How chemists study elements at a few atom level
- Whats next?
Dimitry Ivanovich Mendeleev (8.2.1834 - 2.2.1907)

- Born in Tobolsk (Siberia)
- Elementary schools in Tobolsk followed by studies at Main Pedagogical Institute St. Petersburg
- 1859 - 1861: Leave to Western Europe [Heidelberg, Bonn, Paris]
- 1861 : 1\textsuperscript{st} Int. Chemical Congress in Karlsruhe
- 1867: Full Professor of General Chemistry at St. Petersburg University. Start writing a freshman chemistry course textbook
- 17. Feb. 1869: «An attempt at a system of the elements based on their atomic weight and chemical analogues»
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ESSAI D’UNE SYSTÈME DES ÉLÉMENTS
D’APRÈS LEURS POIDS ATOMIQUES ET FONCTIONS CHIMIQUES.

par D. Mendeleeff,
profes. de l’Univers. à S.-Pétersbourg.

$H = 1$
$Cu = 63,4$  $Ag = 108$  $Hg = 200$
$Be = 9,4$  $Mg = 24$  $Zn = 65,3$  $Cd = 112$
$B = 11$  $Al = 27,4$  $? = 68$  $Ur = 116$  $Au = 197$
$C = 12$  $Si = 28$  $? = 70$  $Sn = 118$
$N = 14$  $P = 31$  $As = 75$  $Sb = 122$  $Bi = 210$
$O = 16$  $S = 32$  $Se = 79,4$  $Te = 128$
$F = 19$  $Cl = 35,5$  $Br = 80$  $I = 127$
$Li = 7$  $Na = 23$  $K = 39$  $Rb = 85,4$  $Cs = 133$  $Tl = 204$
$Ca = 40$  $Sr = 87,6$  $Ba = 137$  $Pb = 207$
$? = 45$  $Ce = 92$
$Er = 56$  $La = 94$
$Yb = 60$  $Dy = 95$
$Th = 118$

$18_{\text{II}}69$
Second Periodic Table from 1871

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<thead>
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<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
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<td>Bk</td>
<td>Cf</td>
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Note: This table is a reproduction of the periodic table created by Dmitri Mendeleev in 1871.
Predictions by Mendeleev in 1871 lead to the following discoveries

- Eka-Al: Discovered by P.E. Lecoq de Boisbaudran in 1875, named Ga
- Eka-B: Discovered by L.F. Nilson in 1879, named Sc
- Eka-Si: Discovered by C. Winkler in 1886, named Ge
- The two Swiss elements:
  - Yb (1878) & Gd (1880): Discovered by J-Ch G. de Marignac in Geneva
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- 1868: Jules Janssen discovered a new line at 587.49 nm in the solar spectrum which he assigned to a «solar metal». Suggested name Helium (Helios for sun and -ium for a metal). Assumption: this new element exists only on the sun.

- 1882: Luigi Palmieri identified this line also in lava from Vesuv.

- 1895: William Ramsey identified He as gas emanating from an uranium mineral treated with sulfuric acid.

- 1894-1898: William Ramsey & colleagues discovered Ne, Ar, Kr and Xe from fractionated destillation of air.


- 1899: Ernest Rutherford discovered emanating gas from uranium and thorium minerals. Later called Radon (Rn)
- 1999: Viktor Ninov and colleagues announced discovery eka-Rn at LBNL (PRL publication). 2002: retracted due to falsified data!

- 2006: Yuri Ts. Oganessian and colleagues claimed to have discovered eka-Rn at FLNR in Dubna in a heavy ion fusion reaction. On 30 Dec. 2015 officially accepted by IUPAC. On 8 June 2016 IUPAC announces the name Oganesson (Og) for this currently heaviest element.

- **General rule**: Names for noble gase elements end with –on. 
  Exception: helium for historical reasons
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Marie Curie’s observation: pure uranium is less radioactive than pitchblende with an equivalent amount of uranium. Which elements are hidden in pitchblende?

- **1898**: discovery of polonium and shortly afterwards radium by P. & M. Curie
- **1899**: discovery of radon by Rutherford
- **1902**: discovery of Ac by Giesel
- **1917**: discovery of protactinium by Hahn and Meitner and independently by Soddy and Cranston
- **1939**: discovery of francium by Perey
- **1940**: discovery of astatine by Corso, McKenzie and Segre
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Periodic Table 1934

Seaborg’s failure to discover Pu as eka-Os after bombarding U with deuterons & neutrons. Seaborg’s suggestion for an actinide series (1945)

![Periodic table](image)

**Fig. 11.** Periodic table published by Seaborg in 1945, showing the heaviest elements as members of an actinide series.
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Idea

• Is neutron flux in an hydronuclear bomb sufficiently high to produce heavy elements via capture of many neutrons by $^{238}\text{U}$ followed by a $\beta$-decay chain?

• 1st thermonuclear explosion IVY/MIKE on 1 Nov. 1952

• $^{238}\text{U} (15n;7\beta)^{253}\text{Es}$ &

• $^{238}\text{U}(17n;8\beta)^{255}\text{Fm}$

• discovered in bomb debris after chemical separation ($\alpha$-HIB separation on CIX column)
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The heaviest element discovered purely by chemical means: Mendelevium (1955)

→ Synthesis: bombardment of $^{253}\text{Es}$ with $\alpha$-particles.
→ Collection of products in a foil.
→ Separation of products after dissolution of foil on a cation exchange column with $\alpha$-HIB
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Shell stabilisation

Courtesy: S. Hofmann
Stability against spontaneous fission

Figure 4.12 Comparison of the measured spontaneous fission half lives (●) for e-e nuclei with those expected in a simple droplet model approach (○). (Pat 89)
Two types of heavy ion fusion reactions to produce No and heavier elements

⇒ **Cold fusion:** the success story at GSI to discover elements 107 (bohrium, Bh) through 112 (copernicium, Cn).
- **Target:** $^{82}$Pb or $^{83}$Bi; **Projectile:** $^{25}$Mn - $^{30}$Zn
- (Minimum excitation energy at fusion barrier: \(\approx 10 - 20 \text{ MeV}\))

⇒ **Hot fusion:** discovery of No (102) – Sg (106) and Nh (113) – Og (118)
- **Target:** $^{94}$Pu – $^{98}$Cf; **Projectile:** $^{11}$B, $^{12}$C, $^{22}$Ne; $^{48}$Ca
- (Minimum excitation energy at fusion barrier: \(\approx 30 - 40 \text{ MeV}\))
How physicists separate new elements and how they identify single atoms

On-Line separators at an accelerator

Two types:

- Wien filter vacuum separators
- Gas filled magnetic separators

Identification of separated atoms (ions)

Position sensitive silicon detectors to assay \( \alpha \)-decay chains
SHIP @ GSI-Darmstadt

Velocity filter

• Electric field: \( F_\rho = \frac{mv^2}{q} \)

• Magnetic field: \( B_\rho = \frac{mv}{q} \)

• Total: \( v = \frac{F}{B} \)

• \( F \): Electric field strength  
  \( B \): Magnetic flux density  
  \( q \): charge
Velocity filter SHIP: the device used to discover elements 107 (bohrium) through element 112
Gas-filled magnetic separators @
LBNL(Berkeley), FLNR (Dubna), GSI (Darmstadt) and RIKEN (Japan)

- $B_\rho = 0.0227 \text{ A } v/v_0 \ q^{-1}$
- $q_{\text{ave}} = v/v_0 \ Z^{1/3}$

$\rightarrow B_\rho = 0.0027 \text{ A } Z^{1/3}$

- Hence $B_\rho$ is independent of initial charge state and velocity distribution
How to identify single atoms of a new elements

Example: $^{208}\text{Pb}(^{70}\text{Zn},1\text{n})^{277}\text{Cn}$

Current detection limit: approx. one atom per year

Courtesy Sigurd Hofmann, GSI
Excitation functions for production of isotopes of element 114 (Fl) in \(^{242,244}\text{Pu}^{48}\text{Ca}\) reactions

![Excitation functions graph](image-url)
Why are production rates so low?

$^{248}\text{Cm}(^{26}\text{Mg}, \, 5n)^{269}\text{Hs} \, (Z=108)$

$^{26}\text{Mg}$  $^{248}\text{Cm}$  FUSION  $^{274}\text{Hs}^*$  $^{269}\text{Hs}$

10 hours 1 mg/cm$^2$ beam

1 billion 1 surviving atom

Courtesy: A. Türler
Riken and Dubna discoveries during last 20 years using $^{70}\text{Zn}$ & $^{48}\text{Ca}$ induced fusion reactions

$^{70}\text{Zn} + ^{209}\text{Bi} \rightarrow ^{278}\text{Nh}$ (Nh) (world record, 1-2 atoms/year!)

$^{48}\text{Ca} + ^{242,244}\text{Pu} \rightarrow ^{288,290}\text{Fl}$ (Fl)

$^{48}\text{Ca} + ^{243}\text{Am} \rightarrow ^{288}\text{Mc}$ (Mc)

$^{48}\text{Ca} + ^{248}\text{Cm} \rightarrow ^{293}\text{Lv}$ (Lv)

$^{48}\text{Ca} + ^{249}\text{Bk} \rightarrow ^{294}\text{Ts}$ (Ts)

$^{48}\text{Ca} + ^{249}\text{Cf} \rightarrow ^{294}\text{Og}$ (Og)

$^{249}\text{Cf}$ is the heaviest target available in mg amounts
Transactinide nuclei (status 2019)

Courtesy Robert Eichler
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Single atom studies of heavy elements

• All elements heavier than Fm are available only at a single atom level. No macrochemical properties but only microchemical properties can be determined.

• Gas phase separation techniques: able to isolate products and deposit them continuously on surfaces kept at different temperatures within about one second
Reactions used and number of atoms found in the „first ever chemical studies“ for $Z \geq 106$ (Sg)

Seaborgium ($Z=106$); (GSI Darmstadt; IC)
$^{248}\text{Cm}(^{22}\text{Ne}; 5n)^{265}\text{Sg}$ ($T_{1/2} = 7\ s$); 7 atoms (M. Schädel et al., Nature, 388, 55 (1997)) (a)

Bohrium ($Z=107$); (PSI Villigen; IC)
$^{249}\text{Bk}(^{22}\text{Ne}; 4n)^{267}\text{Bh}$ ($T_{1/2} = 17\ s$); 6 atoms (R. Eichler et al., Nature, 407, 64 (2000))

Hassium ($Z=108$); (GSI Darmstadt; TC)
$^{248}\text{Cm}(^{26}\text{Mg}; 5n)^{269}\text{Hs}$ ($T_{1/2} = 15\ s$); 7 atoms (C.E. Düllmann et al., Nature, 418, 860 (2002)) (a)

Copernicium ($Z=112$); (FLNR/JINR Dubna, TC)
$^{242}\text{Pu}(^{48}\text{Ca}, 3n)^{287}\text{Fl}$ ($T_{1/2} = 0.5\ s$) $\rightarrow^{283}\text{Cn}$ ($T_{1/2} = 4\ s$); 2 atoms (R. Eichler, Nature, 447, 72 (2007)) (a)

Nihonium ($Z=113$); (FLNR/JINR Dubna, TC)
$^{243}\text{Am}(^{48}\text{Ca}; 2,3n)^{288,289}\text{Mc} \rightarrow^{284,285}\text{Nh}$; 5 atoms (S.N. Dmitriev et al., Mendel. Comm., 24, 253 (2014)

Flerovium ($Z=114$); (FLNR/JINR Dubna; TC)
$^{242,244}\text{Pu}(^{48}\text{Ca}; 3,4n)^{287,288}\text{Fl}$ ($T_{1/2} = 0.5\ s; 0.8s$); 3 atoms (R. Eichler et al., Radiochim. Acta. 98, 133 (2010) (a)

(a) Confirmed in independant experiments though sometimes with different chemical compounds
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Relativistic effects

\[ m = m_0 / \sqrt{1 - (v/c)^2} \]

scale as \( \sim Z^2 \)

- contraction and stabilization of \( s \) and \( p_{1/2} \) orbitals (direct rel. effect)
- expansion and destabilization of \( p_{3/2}, d \) and \( f \) orbitals (indirect rel. effect)
- SO splitting of \( p, d, f \) orbitals
  \[ j = l \pm s \]
Influence of relativistic effects on calculated cohesive (sublimation) energies for group 14 elements

Left black arrow: without spin-orbit splitting
Right black arrow: with spin-orbit splitting

A. Hermann, P. Schwerdtfeger, H.W. Gääggeler et al. 2010

- Eka Radon – Oganesson is a semiconductor!
- J.-M. Mewes, O. Rosette, P. Jerabek, & P. Schwerdtfeger
- Angew. Chem, Int. Ed. (in print) [10.1002/anie.201908327]
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**Periodic Table today**

![Periodic Table Image](image-url)
Outlook

- Experiments planned to produce element 120 at FLNR (reaction $^{50}\text{Ti}+^{249}\text{Cf}$) and started at RIKEN ($^{54}\text{Cr}+^{248}\text{Cm}$)

- How to reach the real center of the island of superheavy elements

- What is the heaviest element that can be chemically investigated?
Reaction of Synthesis of the Heaviest Nuclei

208Pb - target
208 70Pb + Zn

Neutron number
Proton number
100 110 120 130 140 150 160 170 180 190
120
110
100
90
80
70

LogT (sec)
1/2
14
-2
-6
6
10

Reaction of Synthesis of the Heaviest Nuclei

248Cm + 48Ca

ΔN=8

208Pb + 70Zn

248Cm - target

208Pb - target

Courtesy Yu.Ts.Oganessian
<table>
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**Periodic Table tomorrow**