Celebrating 150 years Periodic Table
Historical remarks and current situation

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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) *(1)*

- 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 : 1st 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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First Periodic Table from 1869

ESSAI D'UNE SYSTÈME DES ÉLÉMENTS

D'APRES LEURS POIDS ATOMIQUES ET FONCTIONS CHIMIQUES,

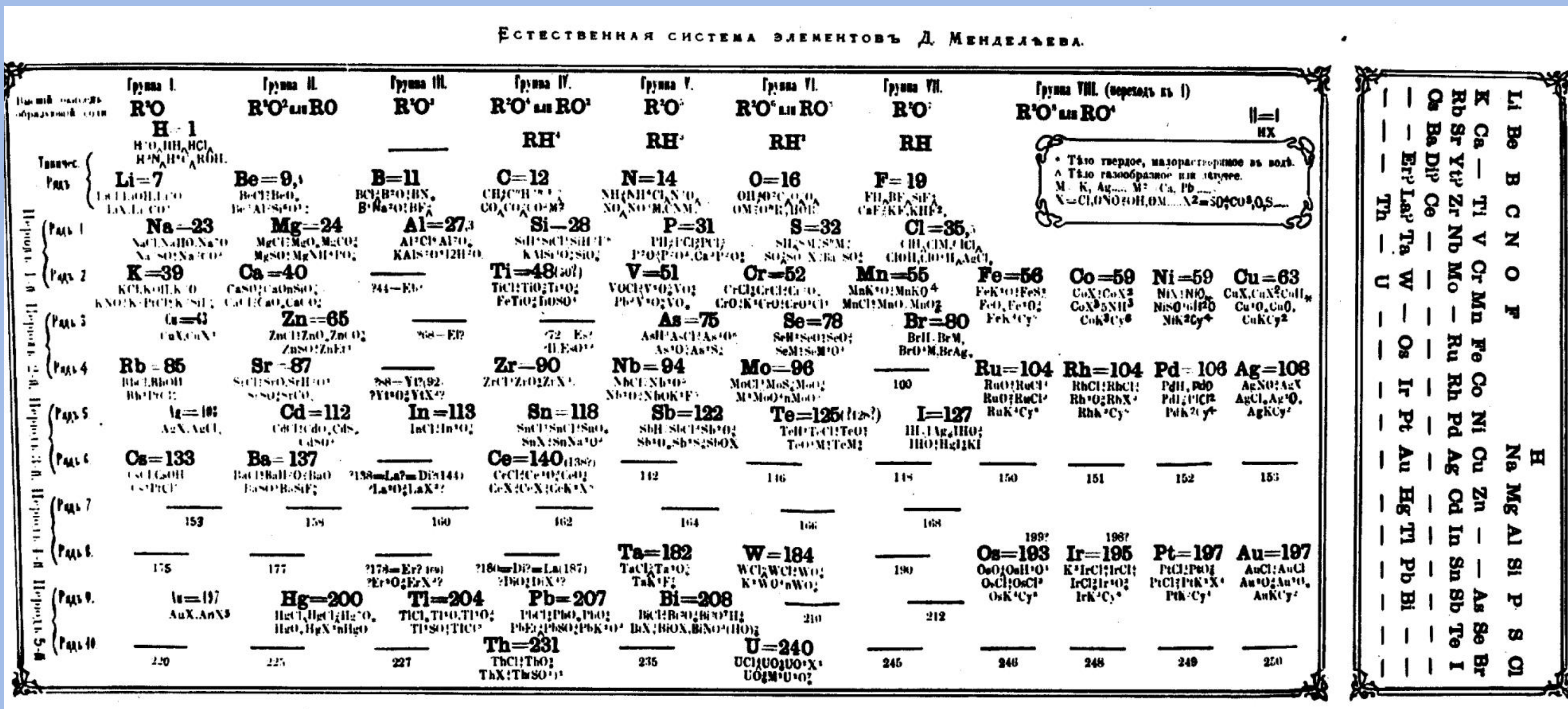
par D. Mendeleeff,

profess. de l'Univers. à S-Pétersbourg.

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182
			Cr=52	Mo=96	W=186
			Mn=55	Rh=104,4	Pt=197
			Fe=56	Ru=104,4	Ir=198
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200
	Be=9,4	Mg=24	Zn=65,2	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		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

$18\frac{III}{I}69$

Second Periodic Table from 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
- <u>The two Swiss elements</u>:
- Yb (1878) & Gd (1880): Discovered by J-Ch G. de Marignac in Geneva

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Discovery of noble gases (1)

-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.

- *1904: William Ramsey receives noble prize for discovery of noble gases*

- 1899: Ernest Rutherford discovered emanating gas from uranium and thorium minerals. Later called Radon (**Rn**)

Discovery of noble gases (2)

- 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?

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UNIVERSITÄT BERN

- **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

H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84		Rn 86
	Ra 88	Ac 89	Th 90	Pa 91	U 92												

LANTHANIDES	La 57	Ce 58	Pr 59	Nd 60		Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

from G. Herrmann, Radiochimica Acta, **70/71**, 52 (1995)

Seaborg’s failure to discover Pu as eka-Os after bombarding U with deuterons & neutrons.

Seaborg’s suggestion for an actinide series (1945)

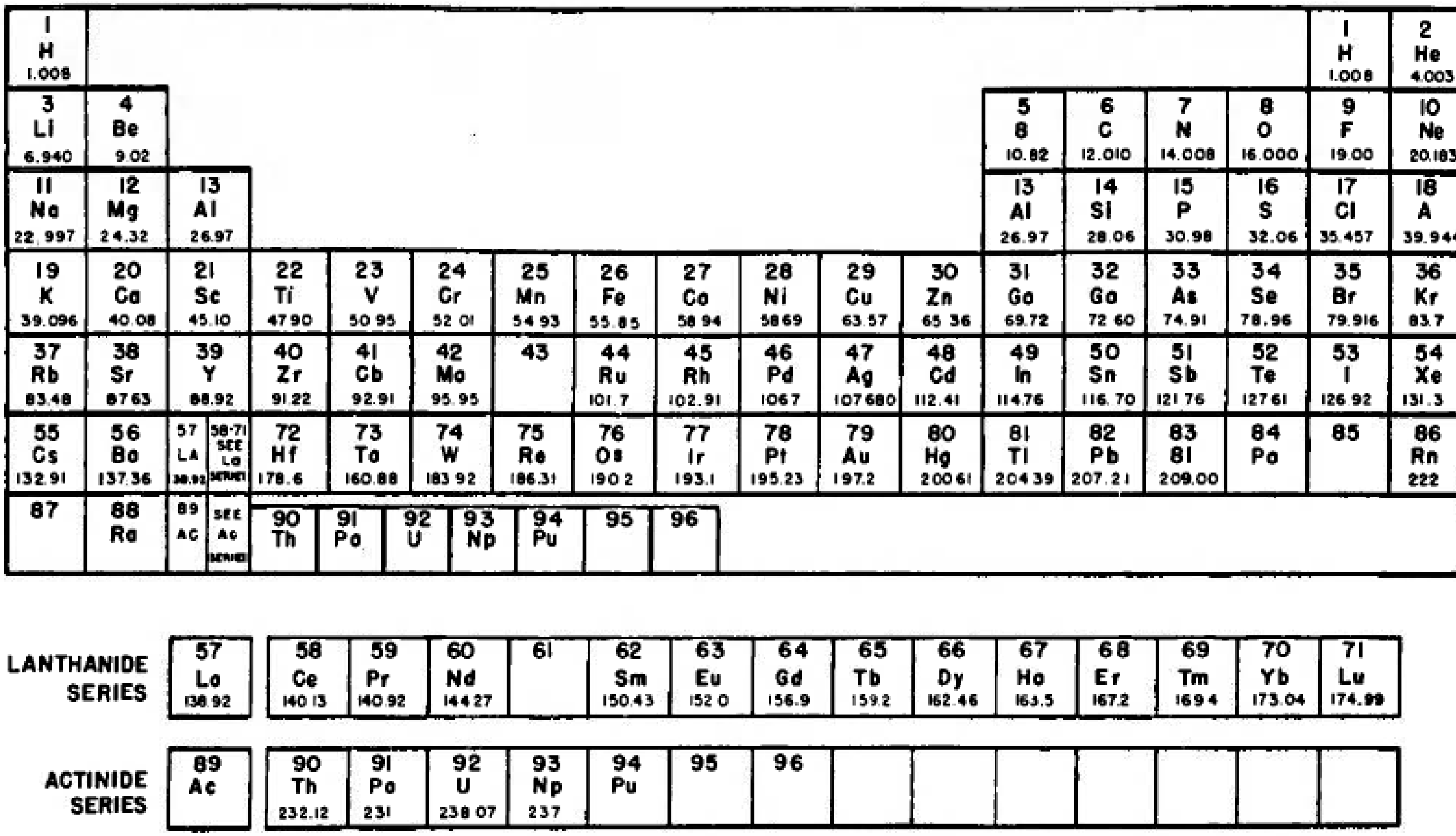

Fig. 11. Periodic table published by Seaborg in 1945, showing the heaviest elements as members of an actinide series.

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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}U followed by a β-decay chain?
- 1st thermonuclear explosion IVY/MIKE on 1 Nov. 1952
- ^{238}U (15n;7β)^{253}**Es** &
- ^{238}U(17n;8β)^{255}**Fm**
- *discovered in bomb debris after chemical separation (α-HIB separation on CIX column)*

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The heaviest element discovered purely by chemical means: Mendelevium (1955)

→ Synthesis: bombardment of ^{253}Es with α-particles.

→ Collection of products in a foil.

→ Separation of products after dissolution of foil on a cation exchange column with α-HIB

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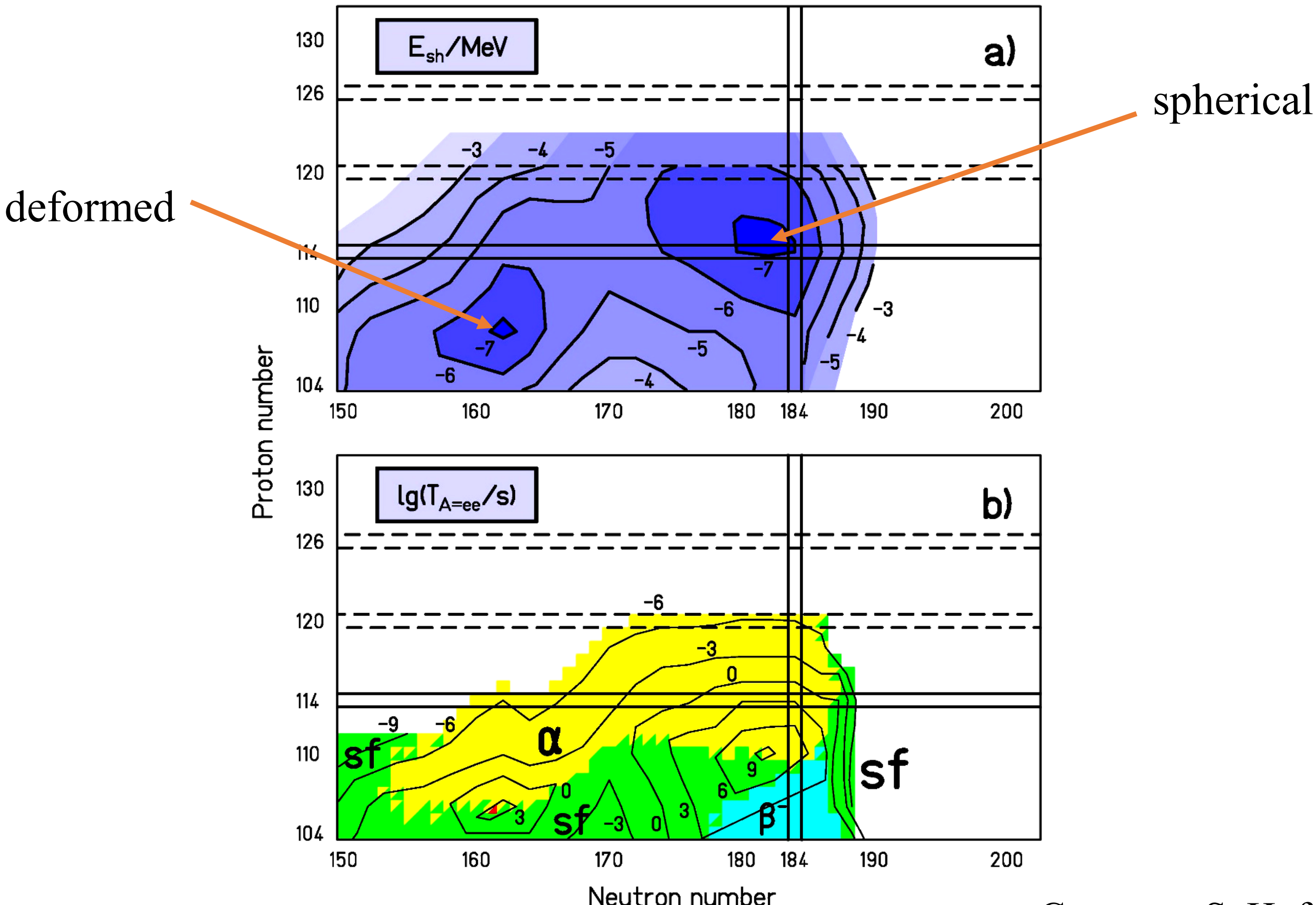
Shell stabilisation



Courtesy: S. Hofmann

Stability against spontaneous fission

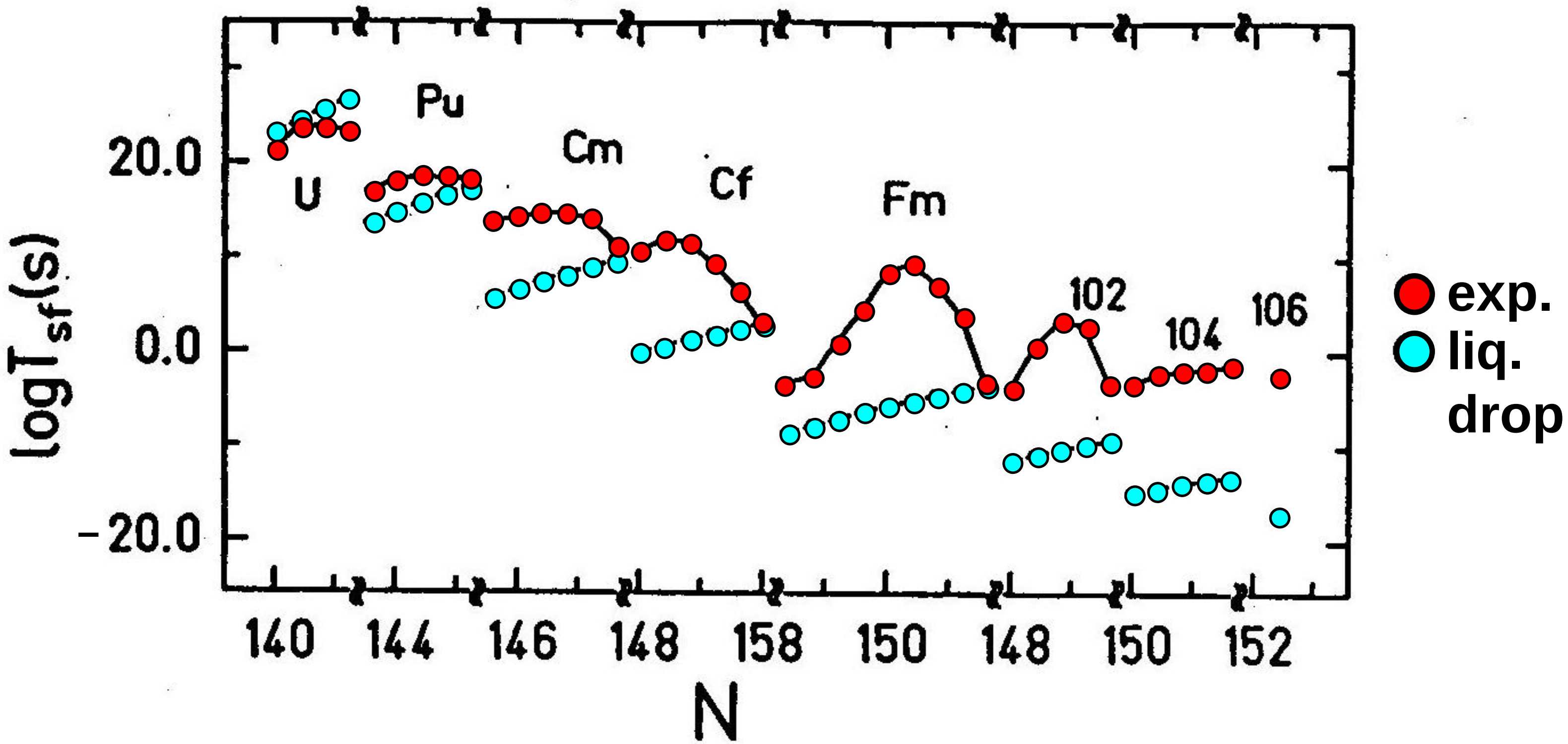


Figure 4.12 Comparison of the measured spontaneous fission half lives (●) for e-e nuclei with those expected in a simple droplet model approach (●). (Pat 89)

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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@fusion barrier: ≈ 10 – 20 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: ≈ 30 - 40 MeV)

How physicists separate new elements and how they identify single atoms

<u>On-Line separators at an accelerator</u>

Two types:

- \- Wien filter vacuum separators
- \- Gas filled magnetic separators

<u>Identification of separated atoms (ions)</u>

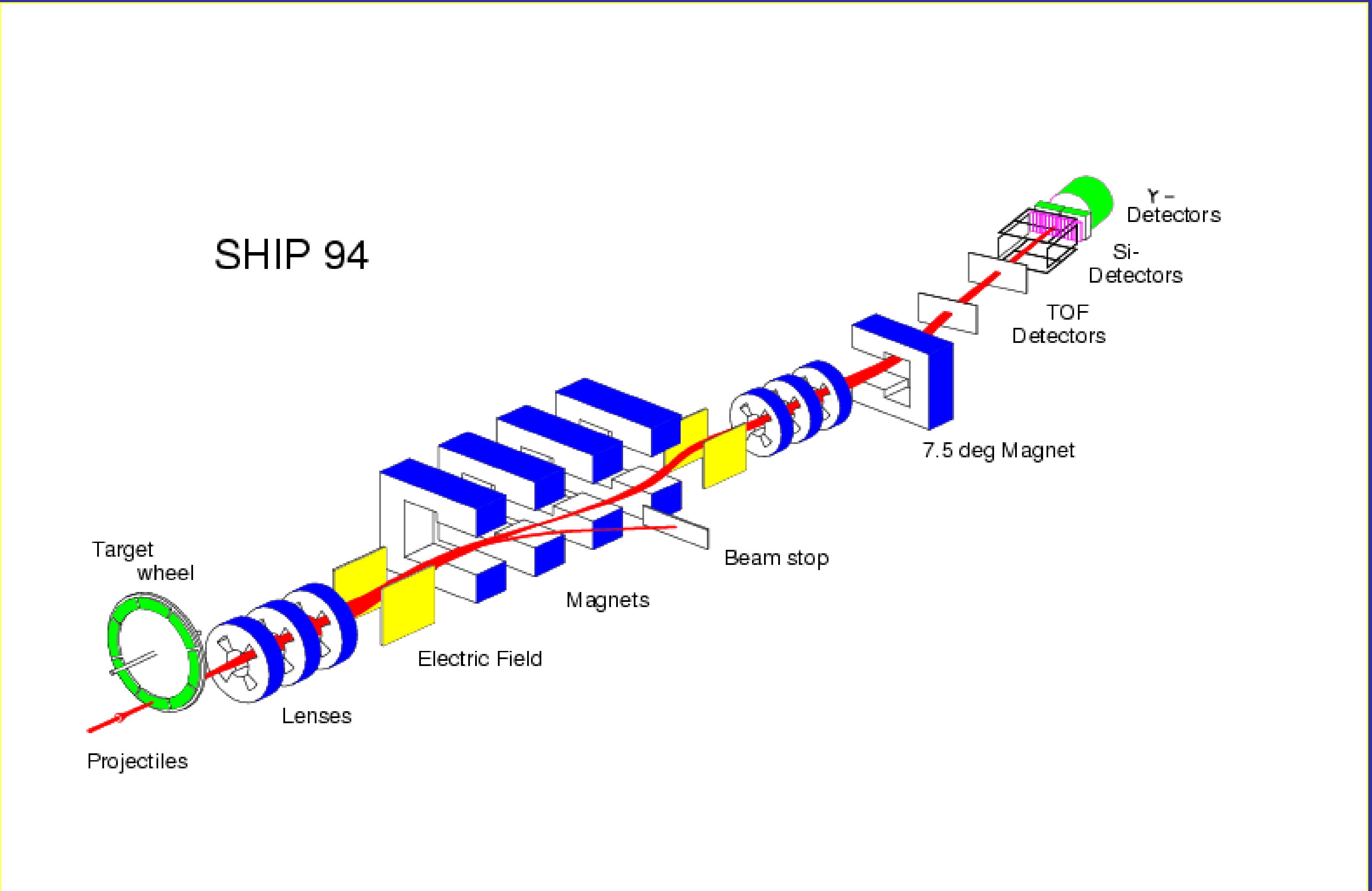
Position sensitive silicon detectors to assay α-decay chains

SHIP @ GSI-Darmstadt

Velocity filter

- Electric field: $F\rho = mv^2/q$
- Magnetic field: $B\rho = mv/q$
- Total: $v = F/B$
- 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 @

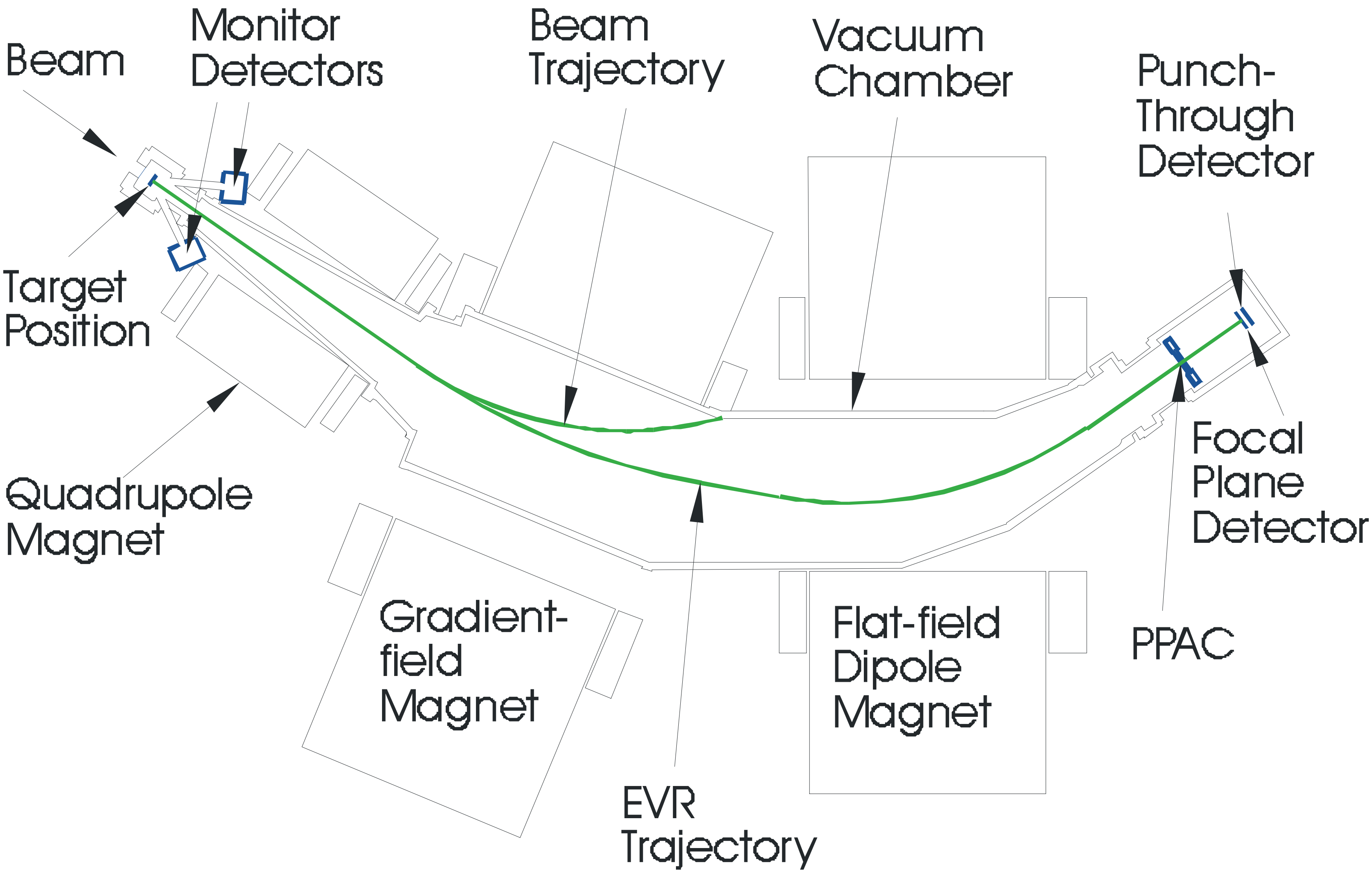
LBNL(Berkeley), FLNR (Dubna), GSI (Darmstadt) and RIKEN (Japan)

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

- $\rightarrow B\rho = 0.0027\ A\ Z^{1/3}$

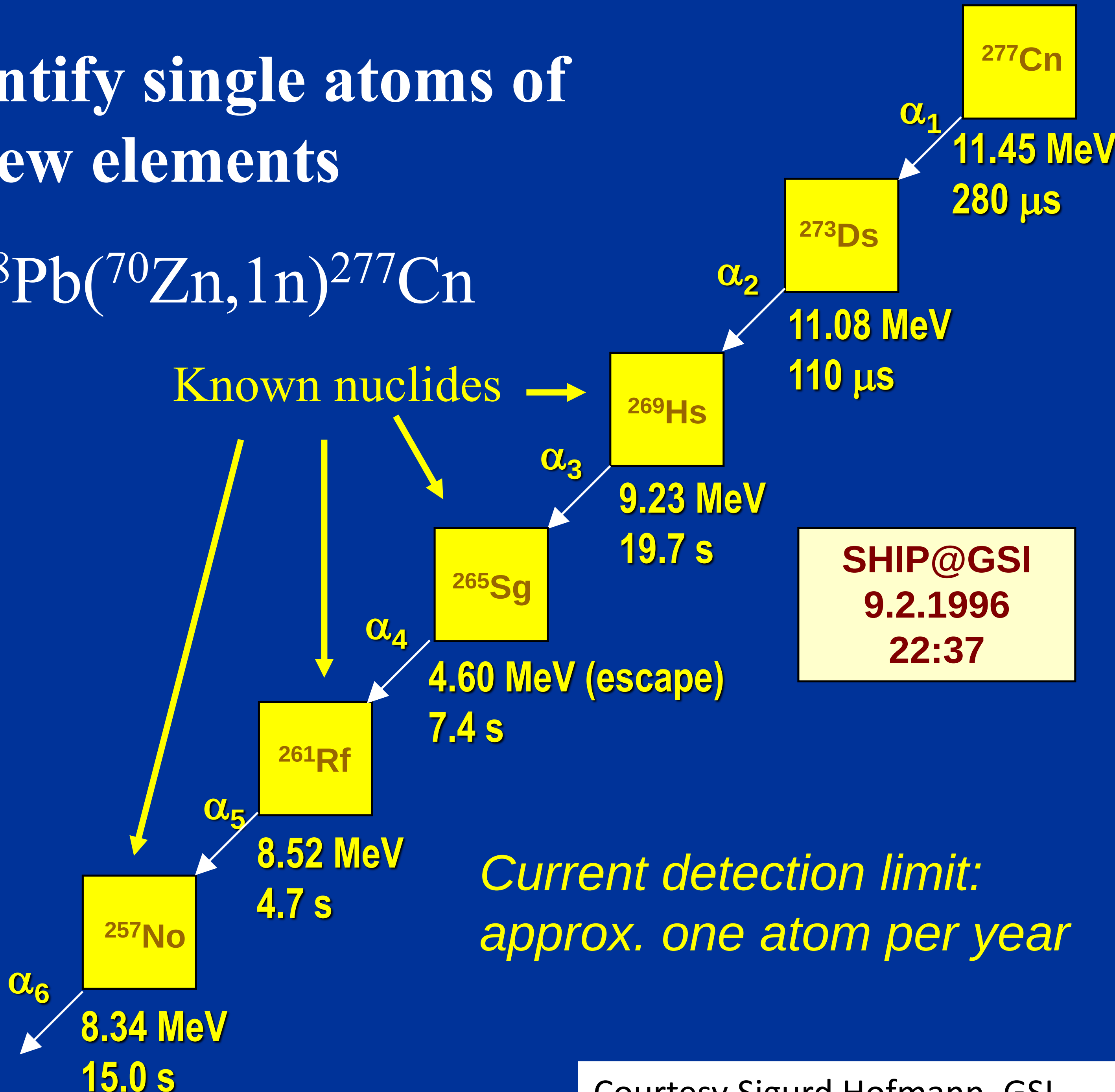
- Hence $B\rho$ is independent of initial charge state and velocity distribution

BGS Schematic



How to identify single atoms of a new elements

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

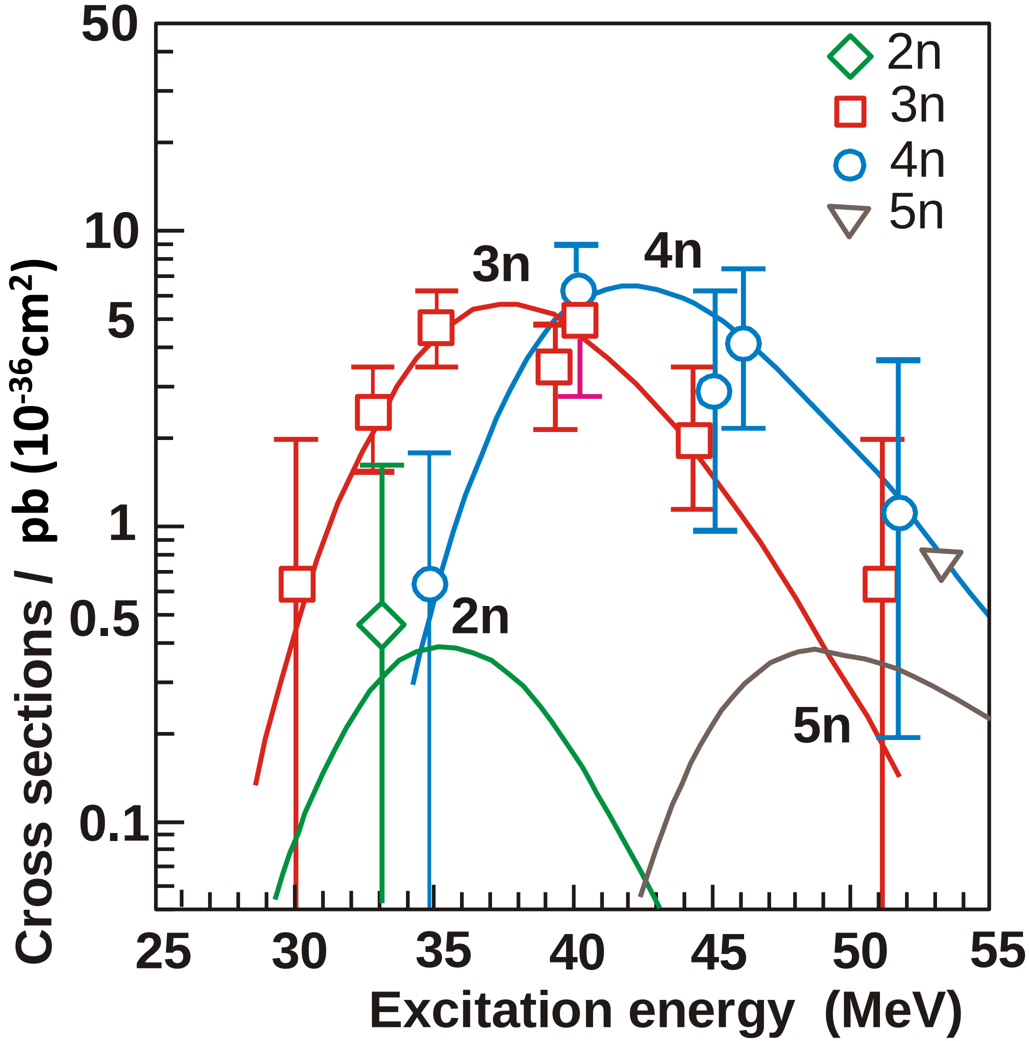


SHIP@GSI
9.2.1996
22:37

Current detection limit: approx. one atom per year

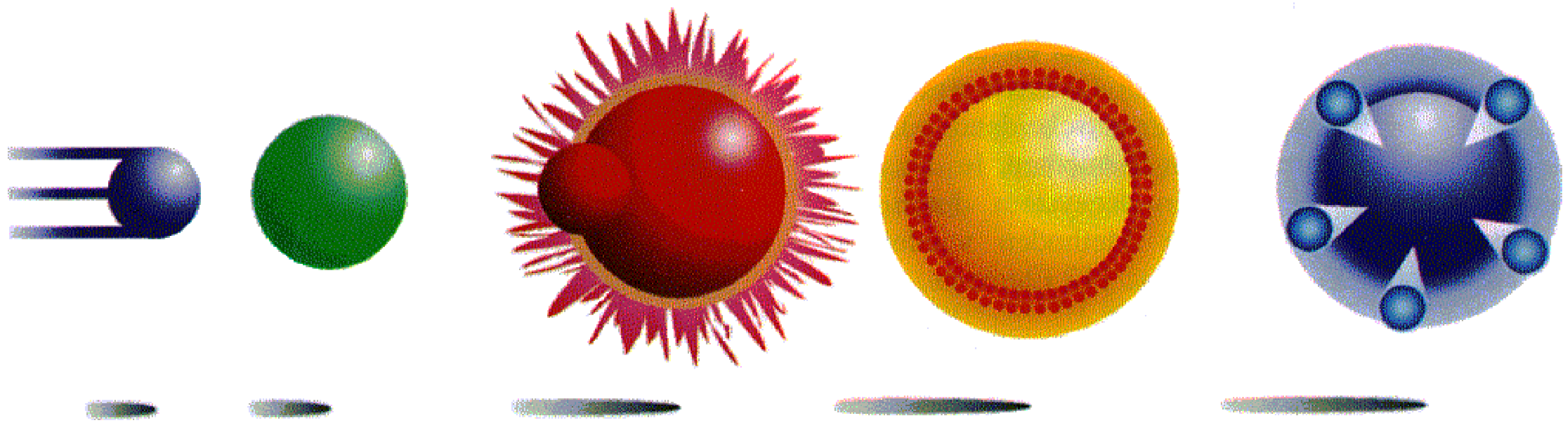
Courtesy Sigurd Hofmann, GSI

Excitation functions for production of isotopes of element 114 (Fl) in $^{242,244}Pu+^{48}Ca$ reactions



Why are production rates so low?

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



Courtesy: A. Türler

Riken and Dubna discoveries during last 20 years using ^{70}Zn & ^{48}Ca induced fusion reactions

$^{70}Zn + ^{209}Bi \rightarrow ^{278}113$ (Nh) (world record, 1-2 atoms/year!)

$^{48}Ca + ^{242,244}Pu \rightarrow ^{288,290}114$ (Fl)

$^{48}Ca + ^{243}Am \rightarrow ^{288}115$ (Mc)

$^{48}Ca + ^{248}Cm \rightarrow ^{293}116$ (Lv)

$^{48}Ca + ^{249}Bk \rightarrow ^{294}117$ (Ts)

$^{48}Ca + ^{249}Cf \rightarrow ^{294}118$ (Og)

^{249}Cf is the heaviest target available in mg amounts

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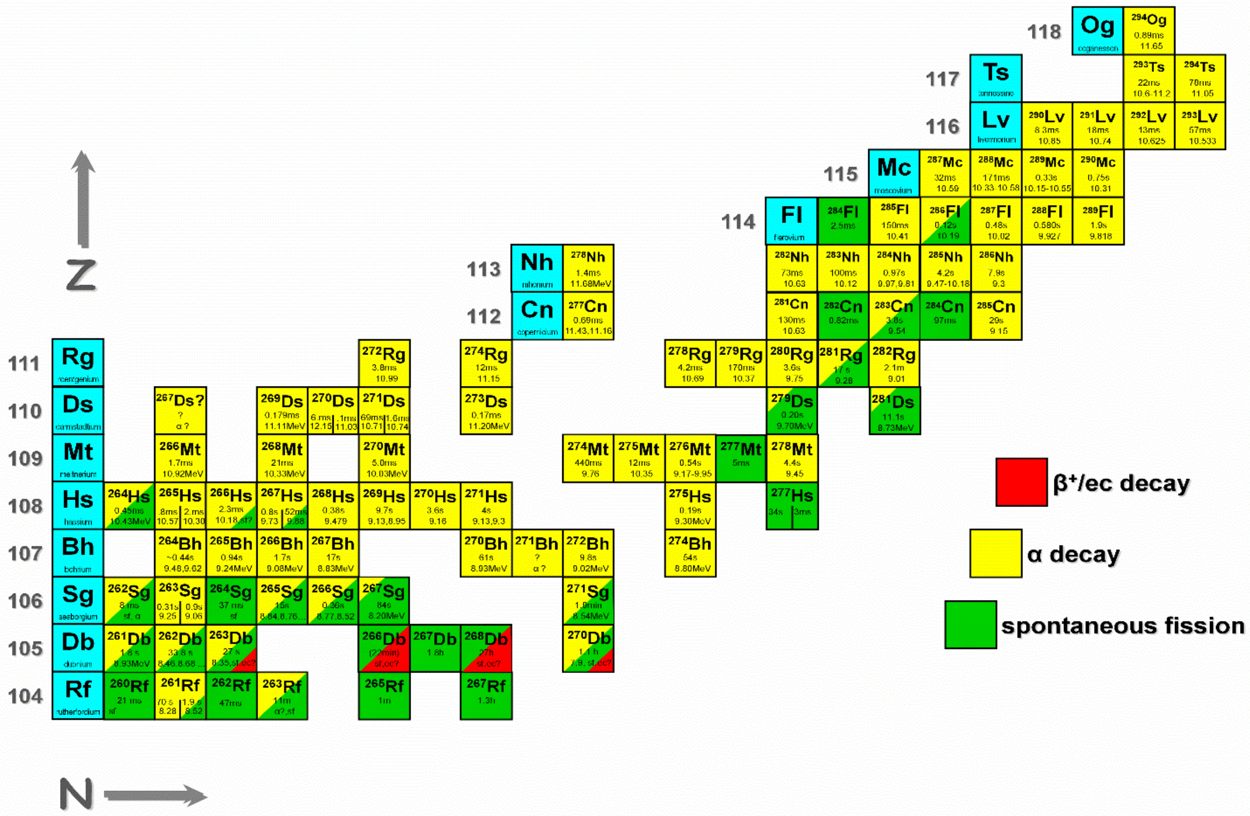
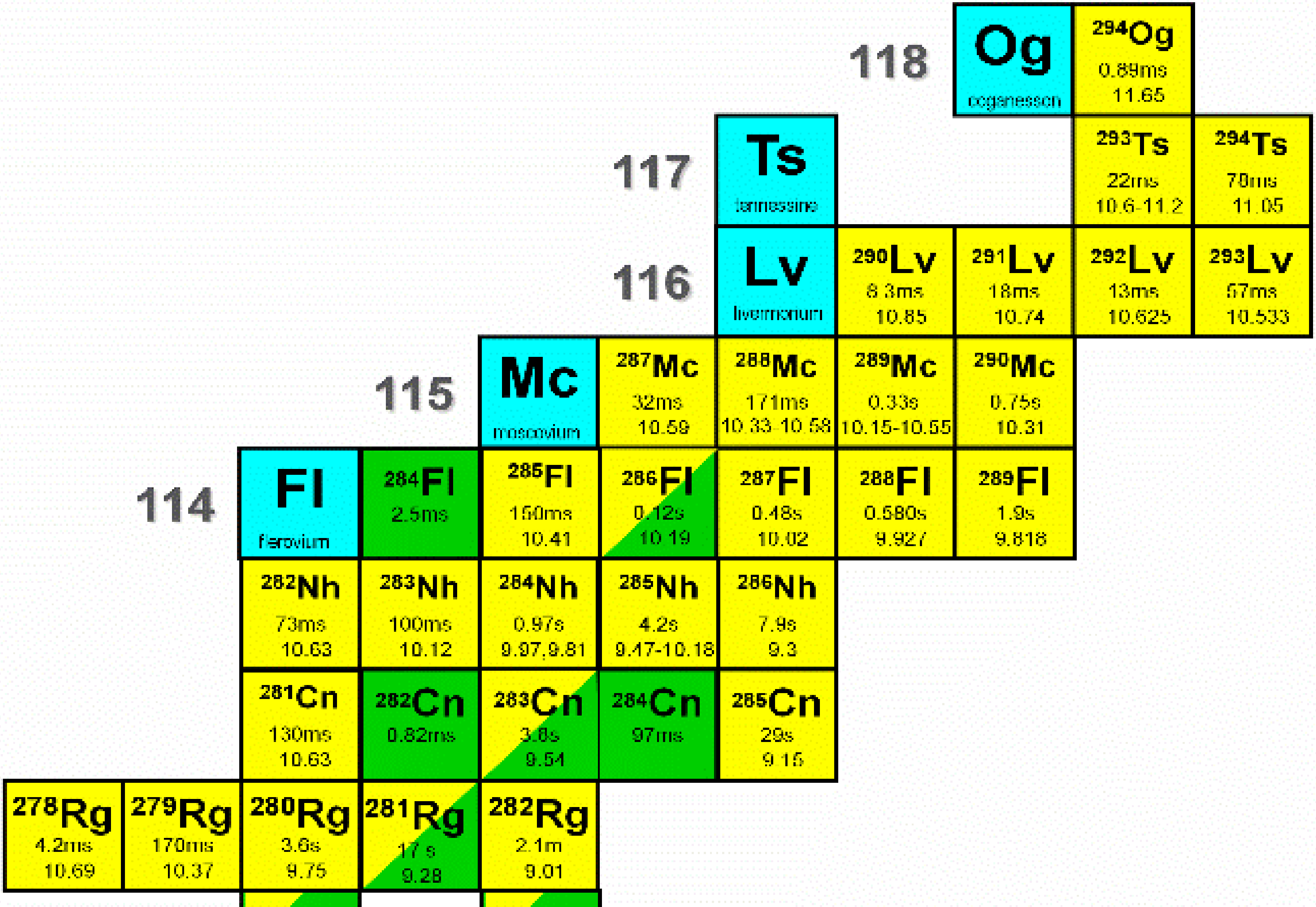
Transactinide nuclei (status 2019)



Courtesy Robert Eichler


118
Og
oganesson
294Og
0.89ms
11.65
117
Ts
tennessine
293Ts
22ms
10.6-11.2
294Ts
78ms
11.05
116
Lv
livermorium
290Lv
8.3ms
10.85
291Lv
18ms
10.74
292Lv
13ms
10.625
293Lv
57ms
10.533
115
Mc
moscovium
287Mc
32ms
10.59
288Mc
171ms
10.33-10.58
289Mc
0.33s
10.15-10.55
290Mc
0.75s
10.31
114
Fl
flerovium
284Fl
2.5ms
285Fl
150ms
10.41
286Fl
0.12s
10.19
287Fl
0.48s
10.02
288Fl
0.680s
9.927
289Fl
1.9s
9.816
282Nh
73ms
10.63
283Nh
100ms
10.12
284Nh
0.97s
9.97,9.81
285Nh
4.2s
9.47-10.18
286Nh
7.9s
9.3
281Cn
130ms
10.63
282Cn
0.82ms
283Cn
3.8s
9.54
284Cn
97ms
285Cn
29s
9.15
278Rg
4.2ms
10.69
279Rg
170ms
10.37
280Rg
3.6s
9.75
281Rg
17 s
9.28
282Rg
2.1m
9.01

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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

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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}Cm(^{22}Ne;5n)$^{\mathbf{265}}$**Sg** ($T_{1/2}$ = 7 s); 7 atoms (M. Schädel et al., Nature, **388**, 55 (1997)) (a)

Bohrium (Z=107); (PSI Villigen; IC)

^{249}Bk(^{22}Ne;4n)$^{\mathbf{267}}$**Bh** ($T_{1/2}$ = 17 s); 6 atoms (R. Eichler et al., Nature, **407**, 64 (2000))

Hassium (Z=108); (GSI Darmstadt; TC)

^{248}Cm(^{26}Mg;5n)$^{\mathbf{269}}$**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}Pu(^{48}Ca,3n)^{287}Fl ($T_{1/2}$ = 0.5 s)$\rightarrow$$^{\mathbf{283}}$**Cn** ($T_{1/2}$ = 4 s); 2 atoms (R. Eichler, Nature, **447**, 72 (2007)) (a)

Nihonium (Z=113); (FLNR/JINR Dubna, TC)

^{243}Am(^{48}Ca; 2,3n) ^{288,289}Mc $\rightarrow$ ^{284,285}**Nh**; 5 atoms (S.N. Dmitriev et al., Mendel. Comm., **24**, 253 (2014)

Flerovium (Z=114): (FLNR/JINR Dubna; TC)

^{242,244}Pu(^{48}Ca; 3,4n)$^{\mathbf{287,288}}$**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

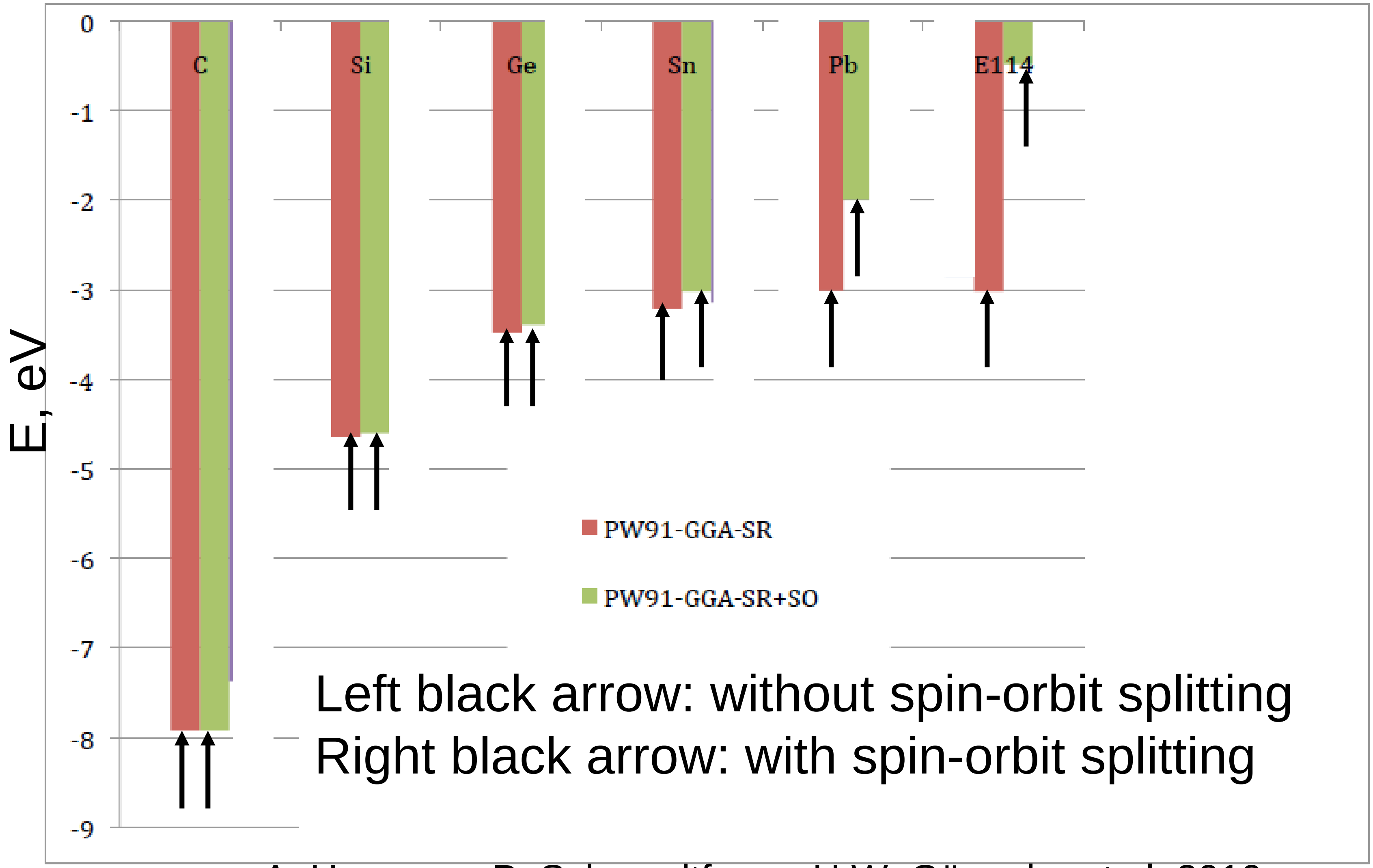
$$m = m_0 / \sqrt{(1-(v/c)^2}$$

scale as ~ 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



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

News from TAN 2019, Wilhelmshaven (25.-30.8.2019)

- 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

IUPAC Periodic Table of the Elements

Key: atomic number / **Symbol** / name / conventional atomic weight / standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

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For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.

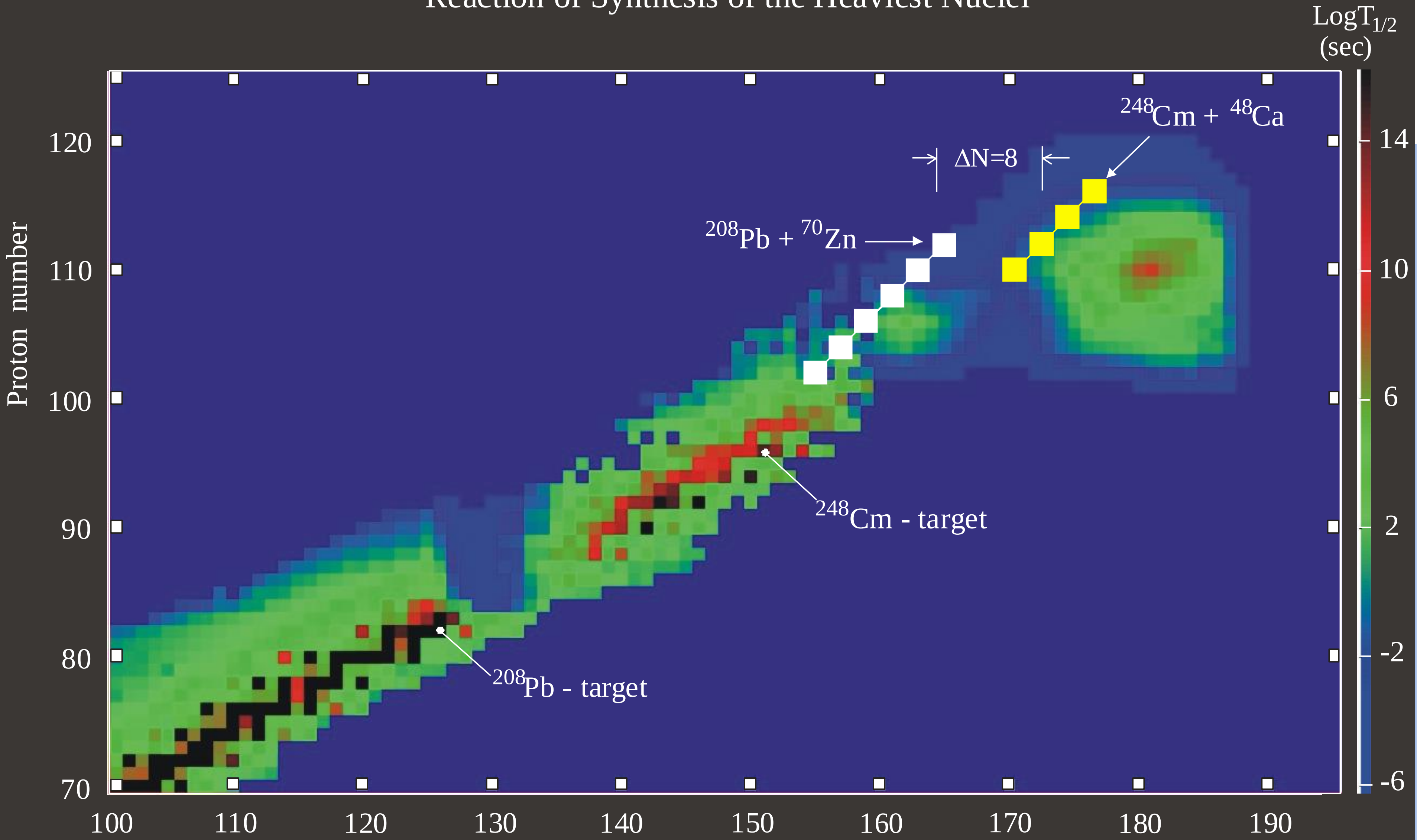
Outlook

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

- 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



Courtesy Yu.Ts.Oganessian

Periodic Table tomorrow

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Orbitals
1	1 H																	2 He	1s
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p
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	4s3d4p
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	5s4d5p
6	55 Cs	56 Ba	57-71	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	6s5d6p
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118	7s6d7p
8	119	120	121-	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p
9	165	166											167	168					9s9p

6	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	4f
7	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	5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	6f

8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g

Pekka Pyykkö, Chem. Phys. Phys. Chem, **13**, 161 (2011)