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## Mendeleev's "Family:" The Actinides

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**Abstract.** When Dmitri Mendeleev laid out his ordered grid of the then-known elements in 1869, he could not have predicted the overwhelming and all-encompassing effect that his idea would have on scientific theory for the next 150 years. Nevertheless, he knew, presciently and from the start that he had conceived and laid claim to a powerful predictive tool that would bring some kind of order to a seemingly random set of fundamental substances. It is not within the scope of this paper to detail how the thought currents of his day were converging, little by little, on the realization that the universe was an intrinsically ordered one, nor is it our purpose to award to Mendeleev the title of sole "discoverer" of the periodic system. We wish merely to point out that he now occupies a well-deserved place within the system under the title of "mendelevium," element 101, and that, by this attribution, he belongs to a special "family," the actinides. How this family was uncovered, grew, and developed is the topic of this essay.

**Keywords.** Discovery, Fission, Intergroup Accommodation, Priority, Radioactivity.

### INTRODUCTION

One glance at any modern periodic table (Figure 1) will superficially show that the actinides belong to a group of elements, from atomic numbers 89 to 103, that occupy the "southern plateau" offset from the main body of the periodic table and directly under the rare earths. How and why this "geography" came about is a tale to be told, fraught with both theoretical and experimental implications.

The first caveat is that this form of the table is one that Mendeleev himself never saw, nor even dreamed of. His table<sup>1</sup> took form from a set of cards on which Mendeleev had written the names and properties of all 63 of the then-known elements. Arranging them in order of increasing atomic weight, many of which were erroneous, he began nevertheless to see a pattern.<sup>2</sup> The genius of the arrangement was (1) spaces were presciently left open for presumed missing elements based upon obvious large gaps in atomic weights and physical properties; (2) anomalous pairs that threw the atomic weights out of order were retained in groups with similar valences instead; (3) as an afterthought, Mendeleev flipped his chart 90 degrees to the right, giving us

**Periodic Table of the Elements**

1 IA 1A																	18 VIIIA 8A		
1 H Hydrogen 1.008																	2 He Helium 4.003		
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180		
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 III B 3B	4 IV B 4B	5 V B 5B	6 VI B 6B	7 VII B 7B	8 VIII 8			9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	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	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798		
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294		
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018		
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]		
		57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967			
		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]			

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Figure 1. The standard medium-long form of the periodic table.

the arrangement that persists to this day. By acknowledging an implied motif known only to Nature, he conferred a predictive quality on his table that bore fruit in the discovery of three of the missing elements within the following 20 years. His acceptance of the anomalous order of some elements left wiggle room for attempts to determine more accurate atomic weights and at the same time to allow this mystery to unfold into the discovery of isotopes many years later. His 90-degree “flip” eventually made the elemental groupings and trends in their properties more visible. Since this first table appeared, more than 700 others have found their way into print.<sup>3</sup>

The table shown in Figure 1 has headings with group numbers. Group numbers have been a bone of contention for years, leading to confusion for both practicing chemists and for students. In 1983, the American Chemical Society decreed the now-familiar 18-column numbered sequence version<sup>4</sup> and in 1988 the International Union of Pure and Applied Chemistry (IUPAC) followed suit, acknowledging that the system actually had been proposed as long ago as 1956 by Stockholm chemistry professor Arne Ölander (1902-1984).<sup>5</sup>

Over the course of the sixty years following Mendeleev’s attempt,<sup>6</sup> a series of discoveries were made that began to reveal the modern picture of the structure of the atom. In chronological order these were cathode

rays, emission spectra, canal rays, X-rays, radioactivity, the electron,  $\alpha$ ,  $\beta$ , and  $\gamma$  rays, Planck’s Law, the photoelectric effect, the atomic nucleus, isotopes, Bohr model of atomic structure, atomic number, and the neutron. It gradually became clear that the number of nuclear protons equaled the nuclear charge and conferred on each atom its unique identity. This allowed scientists to determine how many elements existed in nature, theoretically 92. It also allowed them to devise experiments to push the envelope beyond 92 – to actually create new elements by bombarding and combining existing atomic nuclei, thus expanding the original periodic table to 118 elements. The impact of these discoveries has changed the course of history. The story of Debierne’s discovery, actinium, and the fourteen elements that follow it are the subject of this article.

#### WHAT ARE THE ACTINIDES?

“Discovery is new beginning. It is the origin of new rules that supplement, or even supplant, the old...Were there rules for discovery, then discoveries would be mere conclusions.”<sup>7</sup> The history of the discovery of the actinides, the 15 elements that comprise the second f-block row of the present periodic table of the elements, is pep-

pered with rules: new rules, old rules transformed, new rules broken and remade – not necessarily by those doing the research, but often by Nature itself. Furthermore, if we consider the ways in which discoveries are made, they often fall into the categories of planned research, trial and error, or accidental discovery. Add to this a creative and observing mind<sup>8</sup> and you can encompass virtually all of the discoveries, and the methods used to further understand and gain more information about how the discovery can be exploited. It would be useful to analyze the following story for these characteristics for this is the discovery that set in motion the train of events that would expand and change the periodic table forever. As our exploration continues, we will discover that the actinides themselves, just like any family, have their share of rugged individuals, lawlessness, disruptive behavior, problem children, nonconformists, and law-abiding citizens.

In 1896, Henri Becquerel (1852-1908) reported that the double sulfate of potassium and uranium, formulated by him as  $[\text{SO}^4(\text{UO})\text{K}\cdot\text{H}^2\text{O}]$  using the superscript notation common at the time, emitted radiation capable of penetrating light-opaque paper to expose silver salts. He realized that the so-called phosphorescent material was emitting this radiation by its very nature and not because of becoming phosphorescent by exposure to light.<sup>9,10</sup> Subsequent work showed that the radiation could also penetrate thin sheets of aluminum and copper. Becquerel realized at this stage that the radiation was analogous to the newly-discovered Roentgen rays.<sup>11</sup> Five additional notes in the same volume of the journal follow the course of his further experiments to show, beyond doubt, that the radiation was spontaneous and due to the uranium component of the salt. This conclusion is succinctly summarized in Becquerel's Nobel Lecture:

*The phenomenon could be ascribed to a transformation of solar energy, like phosphorescence, but I soon recognized that the emission was independent of any familiar source of excitation...We were thus faced with a spontaneous phenomenon of a new order...[My experiments] showed that all uranium salts, whatever their origin, emitted radiation of the same type, [and] that this property was an atomic property connected with the element uranium.<sup>12</sup>*

It was Marie Curie (1867-1934) who eventually named the new phenomenon "radioactivity."

Radioactivity, discovered in a uranium salt, was to dominate the scientific, political, economic, and social scenes of the first half of the 20<sup>th</sup> century. And during that century, all the rest of the actinides were to be discovered.

Using radioactivity as the signature by which radioactive atoms could be detected, scientists began to bombard targets with particles such as  $\alpha$ -particles and neutrons as they became available, and then to identify the products of these reactions. They gradually surpassed the limit of atomic number 92 imposed by nature to venture onto an unknown sea, not knowing where it would lead. So far, the journey has led to the discovery of 26 elements beyond uranium, completing the seventh row of the periodic table. This has involved massive amounts of funding, dedicated and persevering work on the part of genius-level individuals, and a surprising degree of international cooperation even during the Cold War. It has led to spectacular discoveries, overturned assumptions and theories, and given glimpses of a Nature full of unexpected surprises.

A simple definition of the actinides is: the elements beginning with actinium, with atomic number 89, and ending with lawrencium, element number 103. None of these elements possesses a stable isotope; every actinide is radioactive with half-lives that vary from billions of years, like thorium, <sup>232</sup>Th, with a half-life of  $1.41 \times 10^{10}$  y, to microseconds, like polonium, <sup>214</sup>Po, with a half-life of  $1.62 \times 10^{-4}$  s. The electronic structures of the actinide elements are complicated and still a subject of both theoretical and experimental research, although the latter is hindered due to the nature and scarcity of the atoms being studied. They are thought to all have a  $7s^2$  outer electronic configuration, with variable and irregular occupancy of the 5f and 6d subshells. Table 1 lists these 15 elements (occupying about 12.7% of the periodic table) in order of atomic number. However, the chronology of discovery does not follow from this order.

The first actinide to be discovered, in 1789 by Martin Heinrich Klaproth (1743-1817), was uranium; a century later it was, as well, the first element recognized to be radioactive. Klaproth's alertness to detail accompanied by his pure love of science<sup>13</sup> no doubt prepared him to recognize a new substance when he dissolved the mineral pitchblende in nitric acid, and then neutralized the solution with a strong base and observed the formation of a yellow precipitate. Using the tried and true method of heating the precipitate in the presence of a reducing agent, he obtained a black powder that he took for the element, which he named uranium in honor of the newly-discovered planet, Uranus.<sup>14</sup>

A glance at Table 1 is quite informative regarding discovery. The first three actinides to be discovered were "lone wolf" affairs: a single discoverer is named, and that brings us to the end of the 19<sup>th</sup> century. It is an entirely different matter for the entire 20<sup>th</sup> century: discovery is a team affair, often with long lists of multi-

**Table 1.** Discovery of the Actinides.

Atomic Number	Symbol	Name/Symbol	Discoverer	Date of Discovery	Place of Discovery
89	Ac	Actinium	A. Debierne	1899	Paris, France
90	Th	Thorium	J. J. Berzelius	1829	Stockholm, Sweden
91	Pa	Protactinium	O. Hahn, L. Meitner, K. Fajans F. Soddy, J. A. Cranston, A. Fleck	1917	Berlin, Germany Karlsruhe Glasgow, Scotland
92	U	Uranium	M. H. Klaproth	1789	Berlin, Germany
93	Np	Neptunium	E. McMillan, P. Abelson	1940	LBL*, USA
94	Pu	Plutonium	G. T. Seaborg, A. C. Wahl, J. W. Kennedy	1940	LBL, USA
95	Am	Americium	G. T. Seaborg, L. O. Morgan, R. A. James, A. Ghiorso	1944	LBL, USA
96	Cm	Curium	G. T. Seaborg, R. A. James, A. Ghiorso	1944	LBL, USA
97	Bk	Berkelium	S. G. Thompson, A. Ghiorso, G. T. Seaborg	1949	LBL, USA
98	Cf	Californium	S. G. Thompson, K. Street, Jr., A. Ghiorso, G. T. Seaborg	1950	LBL, USA
99	Es	Einsteinium	G. Choppin, S. G. Thompson, A. Ghiorso, B. G. Harvey	1952	LBL, USA
100	Fm	Fermium	G. Choppin, S. G. Thompson, A. Ghiorso, B. G. Harvey	1952	LBL, USA
101	Md	Mendelevium	G. Choppin, S. G. Thompson, A. Ghiorso, B. G. Harvey, G. T. Seaborg	1955	LBL, USA
102	No	Nobelium	G. Flerov & others	1958	JINR*, Russia
103	Lr	Lawrencium	A. Ghiorso, A. E. Larsh, T. Sikkeland, R. M. Latimer	1961	LBL, USA JINR, Russia

\*LBL = Lawrence Berkeley National Laboratory; JINR = Joint Institute for Nuclear Research.

ple authors: we have entered the age of “big chemistry,” characterized by specialized and expensive equipment in a national laboratory. It is easy to see that the Lawrence Berkeley National Laboratory (LBL) exercised a monopoly on actinide discoveries, completing the list with element number 103, lawrencium, in 1961.

#### THE PLACE OF THE ACTINIDES IN THE PERIODIC TABLE

The modern periodic table is a grid consisting of seven rows (periods) and eighteen columns (groups). Periods 6 and 7 exceed the 18-column model with thirty-two groups each in the long form, and two offset rows of fifteen elements each in the traditional, or medium-long, configuration, used for convenience so that the table will fit on a normal printed page, as shown in Figure 1.

The grid, originally arranged in order of increasing atomic weights of the elements, is now arranged in order of increasing atomic number (the number of protons in the nucleus of an atom, often abbreviated  $Z$ ) in one dimension, and in order of similar chemical properties in the second dimension to form the groups. This grid actually defines the way electrons arrange themselves in atoms in terms of principal energy levels and sublevels

that they occupy, the so-called s, p, d, and f blocks. Not only has it brought order out of the chaos of so many elements with so many different properties, but it also functions as a theoretical tool, a “marvelous map of the whole geography of the elements.”<sup>15</sup>

The two rows offset as “footnotes” from the main body of the periodic table each consists of fifteen elements. The top row, from lanthanum ( $Z = 57$ ) to lutetium ( $Z = 71$ ), along with two elements in the main body of the table, scandium and yttrium, are termed the “rare earths.” The fifteen rare earths in the offset sit below yttrium with properties so similar to one another that the Czech chemist, Bohuslav Brauner (1855-1935), once proposed that they should all occupy the same space.<sup>16</sup>

Today, we take the placement of the actinides in the table for granted. However, initially, the first-discovered members of this group were placed in the main body of the table with actinium in the yttrium group, thorium under hafnium, protactinium under tantalum, and uranium under tungsten. Any transuranium elements to be yet discovered were expected to fall into place to complete period 6, with the last element in the row,  $Z = 104$ , fitting under radon.

The differences in chemical properties between, say, tungsten and uranium, soon made this assumption untenable. It was Alfred Werner (1866-1919) who first suggested that the heavier elements beyond ura-

nium might need an intergroup accommodation similar to that of the rare earths.<sup>17</sup> Decades later, in 1940, when Edwin McMillan (1907-91) and Philip Abelson (1913-2004) discovered element 93, and shortly afterward, Glenn Seaborg (1912-99) and his team discovered element 94, they had a surprise waiting. Chemical tests revealed that the properties of both new elements were more similar to those of uranium than to their supposed homologs, rhenium and osmium.<sup>18</sup> At this point in the group's struggle to place the new elements in the periodic table, its extreme utility became spectacularly evident as both a flexible and predictive theoretical tool: Seaborg took up Werner's old idea and made it his own:

*"I began to believe it was correct to propose a second lanthanide-style series of elements ...[starting]...with element number 89, actinium, the element directly below lanthanum in the periodic table. Perhaps there was another inner electron shell being filled. This would make the series directly analogous to the lanthanides, which would make sense, but it would require a radical change in the periodic table...[I was told] that such an outlandish proposal would ruin my scientific reputation. Fortunately, that was no deterrent because at the time I had no scientific reputation to lose."<sup>19</sup>*

So the initial stages of discovery of the transuranium elements gave rise to a reconfiguration of the periodic table. The two new elements were appropriately named neptunium and plutonium after the two planets that lay beyond Uranus in the solar system. The rest of the actinides, as they were discovered, fell right into place under their rare earth homologs, and the transactinides, from atomic numbers 104 to 118 populated period 7 to its completion. It remains to be seen how the future treats the super-actinides beginning with atomic number 121.

#### THE PRE-URANIUM ACTINIDES: ACTINIUM, PROTACTINIUM, AND THORIUM

##### *The Discovery of Thorium*

Element number 90, thorium, was the first of this trio to be discovered in 1829. One of the most famous chemists of the time, Jöns Jacob Berzelius (1779-1848), Professor at the Karolinska University, Stockholm, in examining a curious mineral sent to him by Jens Esmark (1763-1839), a Norwegian mineralogist, thought he could discern the presence of a new element. He isolated the impure metal by reducing its fluoride salt with elemental potassium, and named it thorium, after the Scandinavian god, Thor. The mineral subsequently was called thorite.<sup>20</sup> In 1898, working independently, Marie Curie and Ger-

hard C. Schmidt (1865-1949) reported almost simultaneously that thorium, like uranium, was radioactive.<sup>21,22</sup>

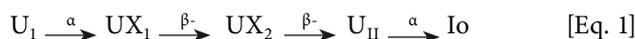
##### *The Discovery of Actinium*

Seventy years were to pass before the announcement of the discovery of actinium ( $Z = 89$ ), the element that gives its name to the entire actinide series.<sup>23</sup> Parisian André-Louis Debierne (1874-1949) began his studies at the École de Physique et de Chemie and began to study mineral chemistry following the death of his mentor, Charles Friedel (1832-99). Welcomed into the Curies' laboratory, he began to treat the enormous quantities of pitchblende they supplied to him until he soon discovered a new element; he was one of the youngest chemists ever to do so.<sup>24</sup> He called it actinium from the Ancient Greek word, *aktinos*, meaning beam or ray.

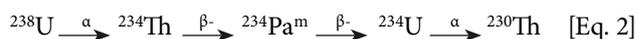
The year 1913 was a landmark one for science: in that year H. G. J. Moseley (1887-1915) conferred a number and identity on every atom by reason of its number of nuclear protons, and Frederick Soddy (1877-1956) discovered isotopes, atoms with differing neutron numbers in atoms with like atomic numbers. He also formulated the law of chemical displacement:  $\alpha$ -emitters produce a daughter product two atomic numbers lower and  $\beta$ -emitters one atomic number higher. Moseley's work defined the list of elements still missing in the periodic table, namely elements 43, 61, 72, 75, 85, 87, and 91.<sup>25</sup> Soddy's work solved the puzzle of the myriad of new "elements" spawned by radioactive decay and his chemical displacement law had predictive properties. All of these facts figured weightily in the discovery of protactinium over the period from 1913 to 1917.

##### *The Discovery of Protactinium*

The hunt was now on for the missing element 91. Kasimir Fajans (1887-1975) and Ostwald Helmuth Göhring (1889-1915?) took up the challenge. Fajans was the first to succeed in deciphering the radioactive decay cascade of  $^{238}\text{U}$  as the following:



which translates in modern terminology to:



They found that the substance  $\text{UX}_2$ , a  $\beta$ -emitter with a very short half-life of about one minute, did not correspond to any radioisotope already known, realizing that

it should occupy a vacant space in the periodic table. Due to its short half-life, they named this new element *brevium*.

Soon after Fajans's announcement, Otto Hahn (1879-1968) and Lise Meitner (1878-1968), working in Berlin, began to search for longer-lived isotopes of this same element. Hampered by the outbreak of World War I, especially by Hahn's conscription, Meitner carried on alone with a miniscule sample (21 g) of pitchblende, doing preliminary separations. It was only a year later that she received a kilogram sample of radioactive salts from which she was able to isolate an isotope of element  $^{231}\text{91}$  with a half-life of about 32,700 y.<sup>26</sup> They named it protoactinium (later changed to protactinium by IUPAC in 1949), recognizing it as the mother substance of actinium.

In June of that same year, Frederick Soddy and his young student, John Arnold Cranston (1891-1972), published the results<sup>27</sup> of their heat treatments of pitchblende that yielded small sublimated amounts of protactinium for which they were unable to characterize the decay scheme. Obviously, the case of protactinium, with multiple publications claiming priority over a period of several years, was a complicated one. Eventually the priority was awarded, by custom, to the team that had discovered the isotope with the longest half-life, Hahn and Meitner,<sup>28</sup> but not without dealing delicately with the aggressive character and imperious temperament of Kasimir Fajans, who eventually withdrew his claim.<sup>29</sup> Cranston and Soddy, having published their papers three months after those of Hahn and Meitner, immediately recognized their priority.<sup>30,31</sup>

While it is beyond the scope of this paper to single out one element on which to discourse on chemical properties, we beg this little exception. Because protactinium's electron configuration is such that an energy crossover between its 6d and 5f orbitals results in nearly degenerate states, its bonding characteristics deviate drastically from its neighboring actinides. For this reason, protactinium's chemistry has been described as puzzling, peculiar, mysterious, and even smacking of witchcraft!<sup>32</sup>

This little protactinium story was told at some length because it presages the multiple contentious priority disputes to follow: who gets the recognition for the discovery, and who gets to name the new element? The naming, in the end, came to be the most controversial issue, for as paleobotanist Hope Jahren (b. 1969) observes:

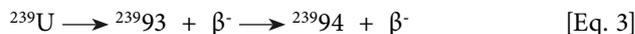
*The scientific rights to naming a new species, a new mineral, a new atomic particle, a new compound, or a new galaxy are considered the highest honor and the grandest task to which any scientist may aspire.*<sup>33</sup>

## DISCOVERY OF URANIUM FISSION

### *Enrico Fermi's Neutron Bombardment Experiments*

The facts that uranium was discovered in 1789 and its radioactivity was recognized in 1896 seem almost trivial in light of the shattering discovery of its most important, and most all-encompassing property: its ability to undergo nuclear fission with the consequent release of immense amounts of energy. This property was undreamed of, and in fact dismissed, when Enrico Fermi (1901-54) and his team, the legendary "Ragazzi di via Panisperna," began to bombard uranium with neutrons. Fermi, convinced that knowledge of the atom was in large part complete, decided to investigate the properties of the atomic nucleus. He was one of the first to recognize the tremendous importance of artificial radioactivity, discovered by Frédéric Joliot (1900-58) and Irène Joliot-Curie (1897-1956), and for which they received the Nobel Prize in Chemistry in 1935.<sup>34</sup> Not possessing a cyclotron, and therefore lacking sufficient irradiated material, he decided to attack the atom with neutrons, discovered only two years previously by James Chadwick (1891-1974), instead of with  $\alpha$ -particles. Since neutrons had no electric charge, Fermi reasoned, they would not be repulsed by the nuclear charge and might easily penetrate the nucleus itself. But since neutrons are not spontaneously emitted by radioactive isotopes, he had to obtain them by bombarding lighter elements, like beryllium, with  $\alpha$ -particles emitted by natural substances, like radium. The neutron yield was low: just one per every 100,000  $\alpha$ -particles emitted, but undeterred, Fermi personally built the detectors necessary for counting atomic disintegrations. Success only came when, after bombarding all the lighter elements, fluorine and aluminum exhibited neutron-induced radiation.<sup>35</sup> After that, the list of nuclei susceptible to neutron irradiation grew.<sup>36, 37, 38</sup> Seven months later, in October, Fermi announced a second crucial discovery: the braking effect of hydrogenous substances, like water, on the radioactivity induced by neutrons. This amounted to the first step towards the utilization of nuclear energy.

Meanwhile at Rome, Fermi procured a very precious treasure, 1.6 grams of radium chloride from which he could extract *emanation* (or radon) that would be necessary for the production of neutrons. Further work by Fermi and his team led to seemingly two new elements with atomic numbers 93 and 94<sup>39</sup> due to neutron absorption by  $^{238}\text{U}$ , and subsequent double- $\beta$ -emission according to the following schemes:



Radiochemical tests showed that the activity of  $^{239}\text{U}$  produced particles with properties that did not belong to any elements that preceded them in the periodic table. Believed to be eka-rhenium and eka-iridium, they were placed in period 7 of the table.

#### *Criticism of the Fermi Group's Interpretation of Results*

The Fermi group's announcement raised sharp criticism in scientific circles. In addition to the two "transuranic elements" they thought they had identified, they had found a good half-dozen others with a variety of chemical properties difficult to place in the periodic table since they had to be untangled from uranium's ongoing normal decay producing its own short-lived daughter products.<sup>40</sup> In fact, a chemist at the University of Fribourg, Ida Tacke Noddack (1896-1978), criticized Fermi's experimental judgment in only searching for elements in the neighborhood of element 92. She said that all elements should be searched for, even lighter ones. She did not hesitate to declare that she strongly doubted that the products Fermi identified were transuranium elements, but suggested nuclear fission instead.<sup>41</sup> This idea was unacceptable in the physics world, deemed highly speculative and lacking a theoretical basis. "Everyone knew" that atoms just did not fly apart in such a manner!

Things remained unresolved. A year later, Otto Hahn and Lise Meitner repeated Fermi's experiments using better facilities and they confirmed Fermi's results. Furthermore, according to them, they were also able to observe traces of elements 95, 96 and 97 that they provisionally called *eka-iridium*, *eka-platinum*, and *eka-aurum*.<sup>42</sup> However, as time went on, Irène Joliot-Curie and her Yugoslavian co-worker, Pavle Savić (1909-1994), published some papers documenting their concentration on only one of the products of neutron irradiation, that with a half-life of 3.5 hours, and after a few false starts conclusively stated that the product in question strangely resembled lanthanum, an already known element lodged in the middle of the periodic table. However, they never declared that they had actually found lanthanum, only a possible transuranic element that resembled lanthanum!<sup>43, 44</sup> They could not imagine that they actually had lanthanum. Reality was hidden in plain sight!

#### *Fission at Last!*

The last of these papers made Hahn sit up and take notice: perhaps the almost forgotten suggestion by Ida Noddack was right after all. So later in 1938, after more

experimentation and re-thinking, Hahn and his colleague Fritz Strassmann (1902-80) finally admitted that, as chemists, they realized they were dealing with radio-barium and radiolanthanum, but as physicists they added, "we cannot bring ourselves to take such a drastic step, which goes against all previous laws (a word that Hahn later changed to "experiences") of nuclear physics."<sup>45</sup>

Hahn communicated his conclusions by letter to Lise Meitner who was in exile in Sweden, fleeing the Nazi racial persecution, and she, with her nephew Otto Frisch (1904-79), in their famous walk in the woods, worked out a theory whereby the positive charge of the uranium nucleus was large enough to overcome the effect of the nuclear surface tension almost completely, allowing the nucleus to fall apart at the slightest provocation. They also worked out the fact that the mass loss on nuclear division would be about one-fifth the mass of a proton, exactly equivalent to the correct and enormous energy predicted by Albert Einstein's (1879-1955) relationship,  $E = mc^2$ .<sup>46, 47</sup>

Meanwhile, Enrico Fermi had already received his Nobel Prize in Physics for 1938, awarded

*for his demonstrations of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons.*<sup>48</sup>

The citation is very cautious in using the words "new radioactive elements," initially interpreted erroneously by Fermi as transuranium elements. But in the light of subsequent interpretations, he had actually discovered nuclear fission without knowing it, and actually produced new radioactive isotopes of elements previously known!

#### *The Impact of Uranium Fission on the Modern World*

By the irony of fate (or, some would say, of blindness), Enrico Fermi, in looking for transuranium elements, found nuclear fission. At the about the same time, physicist Paul Scherrer (1890-1969), working in Zurich, had an even closer encounter with fission.

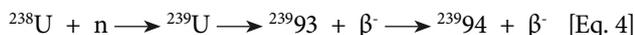
*He bombarded thorium...with neutrons and saw the fission fragments that Meitner and Frisch had identified. But Scherrer wouldn't believe his eyes. He thought his Geiger counter was malfunctioning. What wasn't expected wasn't seen.*<sup>49</sup>

Fermi, working in Fascist Rome in 1933, or Scherrer working in Switzerland, could have handed (or have seized from them) the information the Nazis would need

to build a super-weapon six years earlier than the actual recognition of fission and its potential had they realized the evidence that was right before their eyes. Their “slight oversights” had a profound and beneficial effect on the rest of the world.

When word of the reality of nuclear fission broke upon the world, Niels Bohr (1885-1962) in Copenhagen struck his head with his fist and exclaimed. “Oh, what fools we were that we did not see this before.”<sup>50</sup> And in Paris, Irène Joliot-Curie cried out, “What fools we were!”<sup>51</sup>

In 1941, just two years after the discovery of fission, Hans von Halban (1908-64) and Lew Kowarski (1907-79), two French exiles from the Curie Institute working in Cambridge but under the mentorship of Frédéric Joliot in France, were the first to establish that it was possible to sustain a chain reaction starting with uranium.<sup>52</sup> Simultaneously, two other Cambridge physicists, Norman Feather (1904-78) and Egon Bretscher (1901-73), hypothesized that the chain reaction could have military applications. By now it was recognized that the fissionable nucleus was the  $^{235}\text{U}$  isotope of element 92, only seven parts in 1,000 in naturally occurring uranium. They also hypothesized that the more abundant isotope,  $^{238}\text{U}$ , could be transmuted by neutron absorption into a new, hitherto unknown, element which would not only be fissionable, but would also have a long half-life according to a pathway almost identical to Eq. 3:



What would follow from these discoveries was an international race for the ultimate weapon carried on in wartime under the shroud of utmost secrecy. Although research on the peaceful uses of atomic energy was also on the docket, it had low priority when it came to building the atom bomb. Heavy water, deemed essential for the propagation of a chain reaction due to its moderating (slowing down) properties on neutrons, was in short supply. The largest production plant, Norsk Hydro, was in the hands of Nazi Germany. Although many top scientists abhorred the idea of such a weapon, the Allied governments knew that they could not allow Germany to beat them in the race and use this weapon for world domination. As Frederick Soddy remarked presciently in 1904:

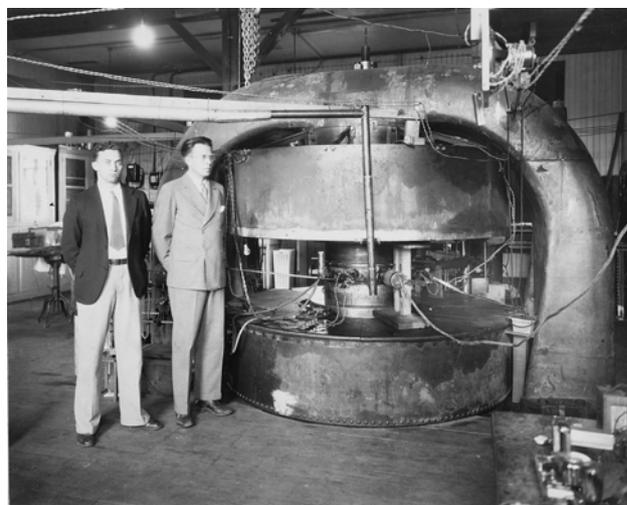
*The man who put his hand on the lever by which a parsimonious nature regulates so jealously the output of this store of energy would possess a weapon by which he could destroy the earth if he chose.*<sup>53</sup>

## THE BERKELEY HEGEMONY

To understand how the University of California at Berkeley eventually became the epicenter of discovery of the transuranium elements, it is necessary to describe some institutional facilities and historical events that came together to form a collaborative whole which led to the completion of the actinide series at this single and unique location.

### *The Invention of the Cyclotron*

It is often said that the three landmark scientific inventions that gave the impetus to discovery of new elements, in chronological order, were the voltaic pile, the spectroscope, and the cyclotron. The voltaic pile, devised by Alessandro Volta (1745-1827), began the age of electricity, the energy source that drives the modern world, as well as the disciplines of electrodynamics and electromagnetism.<sup>54</sup> Its use by Humphry Davy (1778-1829) led to the discovery of numerous elements such as sodium, potassium, magnesium, calcium, strontium, barium, and boron. Similarly, the spectroscope, invented by Gustav Kirchhoff (1824-87) and Robert Bunsen (1811-99), changed the face of analytical chemistry, making possible the myriad instruments available today for purposes as varied as archaeological characterizations and medical diagnoses.<sup>55</sup> It also was the instrumental method in the discovery of thallium, indium, rubidium, and cesium. Perhaps the cyclotron (see Figure 2), invented in 1929 by Ernest Orlando Lawrence (1901-58) and



**Figure 2.** M. Stanley Livingston (L) and Ernest O. Lawrence in front of the 27-inch cyclotron at the old Radiation Laboratory at the University of California, Berkeley.

M. Stanley Livingston (1905-86), was the most prolific invention of all in terms of element discovery: 25 new elements and still counting!

With his ever-larger and more powerful cyclotrons, Lawrence pioneered what is now known as "Big Science," an approach that required large and expensive instrumentation, teams of researchers, interdisciplinary (chemistry, medicine, engineering, physics) collaboration, and consequently, a rather complex bureaucracy. He not only probed and illuminated some of the darkest mysteries held by Nature but also invented a new approach to the problem of studying Nature.

When Lawrence traveled to the centers of science in Europe during a belated "*Studienreise*," he was astounded at the groundbreaking discoveries European scientists, such as Marie Curie and Ernest Rutherford (1871-1937), were making with the most rudimentary equipment. He did not realize that high quality research and solid theoretical reasoning were the key to scientific advances – not necessarily glitzy equipment. As if to give the lie to the "small science" approach he had witnessed, Lawrence experienced a seminal moment in 1929 when he read an article in the obscure *Archiv für Elektrotechnik* which outlined a general approach on how to accelerate ions. By 1930 he was up and running, empirical trial and error running ahead of theory as well, until he discovered the two fundamental principles that would make his ideas work: the "cyclotron principle," as particles gain speed their paths spiral wider, and the "resonance principle," that protons keep time with the oscillator even as they accelerate. Putting these principles together accompanied by lots of hard work with prototypes eventually led to success.<sup>56</sup>

Eventually, with his cyclotrons running around the clock, Lawrence was a sort of overseer of workers, each one focused on bombarding only one element's nucleus to see what secrets it would reveal. He attracted great talent and enormous funding with a panache that would soon attract a Nobel Prize, for physics, in 1939 with the citation:

*for the invention and development of the cyclotron and for results obtained with it, especially with regard to artificial radioactive elements.*<sup>57</sup>

#### *World-Class Theoreticians and Experimentalists*

In 1912, Gilbert Newton (G. N.) Lewis (1875-1946) moved from M.I.T. to take up the chairmanship of the chemistry department at Berkeley, at that time viewed by the eastern establishment as a scientific backwater.

Of the five chemistry faculty in the department, Lewis retained three and managed adroitly to purge the other two. He then began to populate the department with people of his choice beginning with Joel Hildebrand (1881-1983), Kenneth Pitzer (1914-97), and Wendell Latimer (1893-1955). Some of his recruits went on to win Nobel Prizes, such as William Giauque (1895-1982), Willard Libby (1908-80), Melvin Calvin (1911-97), and Glenn Seaborg. Lewis imprinted his educational philosophy on his faculty: educate for chemical understanding and not rote learning. He required every faculty member to run undergraduate labs as part of their departmental duties; he promoted research, especially in physical chemistry, and eventually in nuclear chemistry. Much of Lewis's own work, especially on thermodynamics, and acids and bases, is still taught in undergraduate courses today.<sup>58</sup> Gilman Hall, the seat of Berkeley's chemistry department, was named a National Historic Chemical Landmark by the American Chemical Society in 1997.

Across the road in the physics department, a similar trajectory was in progress: game-changing research, pioneer scientists, and world-class students. In addition to Ernest Lawrence, recruited from Yale to run the Radiation Laboratory, such notables as Emilio Segrè (1905-89), Owen Chamberlain (1920-2006), J. Robert Oppenheimer (1904-67), Charles Townes (1915-2015), and Luis Alvarez (1911-88) were changing the world as we know it by their historic discoveries.

#### *What Motivated the Research?*

In addition to scientific curiosity and national pride, there were three other reasons for pursuing heavy ion research with a view to extending the periodic table. The first was to verify the validity of the periodic table itself as a theoretical tool. By forming elements of higher atomic number one by one and by examining their chemical properties, one could see examples of the trends predicted for the naturally occurring elements among the artificial ones. The second reason was to reach the theoretically predicted "Magic Island of Stability" in which, in the contest between half-life and spontaneous fission, half-life wins out. The third reason, which took pride of place during the years of World War II, was military and commercial exploitation of atomic energy.

THE FIRST TRANSURANICS: NEPTUNIUM,  
PLUTONIUM, AMERICIUM, CURIUM, BERKELIUM,  
AND CALIFORNIUM

### Neptunium

Although it turned out to be upstaged by its long-lived and fissile daughter, plutonium, neptunium remains the first synthetic transuranium element. It is somewhat ironic that it was discovered accidentally during an experiment to study nuclear fission. Working with Berkeley's 37-inch cyclotron, Edwin McMillan bombarded uranium with neutrons and began to examine what he thought were the fission products. He detected two interesting ones, the first with a half-life of 2.3 d and the other with a half-life of 23 m. He was able to identify the latter as  $^{239}\text{U}$ , but the longer-lived product was puzzling. McMillan, working later in partnership with Philip Abelson, realized that the isotope did not resemble any known element and that it had chemical properties similar to those of uranium. This was the first definitive proof that the new element, and presumably those to follow, would behave like the rare earths rather than its supposed homolog, rhenium, in the main body of the periodic table. Theoretically interpreted, there was an inner 5f electron shell that was being filled in, with the outer shells remaining the same, thus explaining the similar chemical properties. They published their results immediately, but only later named it neptunium, after the next planet out in the solar system. Since McMillan and Abelson were the only discoverers, there was no controversy over either the discovery or the name.<sup>59</sup> Element 94, about to make its debut, turned out to be completely unique. To appreciate its uniqueness, it is important to digress on two additional topics: a theoretical model of the atomic nucleus and the criteria for the discovery of new chemical elements.

### The Liquid Drop Model

Ever since people began to believe in the existence of atoms, prior to Dalton, as a matter of fact, the idea of an atom was that of an impenetrable, hard sphere. Newton, in his treatise *Opticks* expressed this model of the atom in this way: "It seems probable to me that God, in the beginning, form'd matter in solid, massy, impenetrable particles...even so hard as never to wear or to break into pieces, no ordinary power being able to divide what God Himself made one."<sup>60</sup> With this model fixed in mind for centuries, it was a great break with tradition when, in the late 1920s, the theoretical physicist, George Gamow (1904-68) advanced a simplified

liquid-drop model of the nucleus; it was extended in the mid-1930s by Wilfrid Wefelmeier (1909-1945), a student at Berlin-Dahlem, who proposed the idea of a non-spherical lump, or *Kernwurst*, with more exposed surface area to allow for the ejection of nuclear particles.<sup>61</sup> Otto Frisch found this model helpful in determining the parameters of fissile (fissionable) nuclei, especially the concept of nuclear surface energy,  $E_s$ , as a stabilizing force which was crucial to understanding it. There are two antithetical forces that determine the conditions under which an atomic nucleus will be fissile: the Coulomb energy,  $E_{\text{Coul}}$  and the surface energy,  $E_s$ . The model predicts that when  $E_{\text{Coul}}$  exceeds twice the value of  $E_s$ , a nucleus will undergo fission. When a liquid drop is perturbed by a little energy, it will just jiggle; there is a threshold energy that will engender a split between roughly two equal halves of the drop to give a bi-lobar, or dumbbell-shaped drop; applying the critical energy,  $E_c$ , exceeds the threshold energy and results in fission.  $E_c$  is directly proportional to the product of the atomic numbers of the separating nuclei, and inversely proportional to the sum of their radii. A potential energy vs. reaction coordinate diagram similar to those used to track ordinary chemical reactions (Figure 3) can be used to illustrate this effect.

As the mass number and atomic number increase,  $E_c$  generally decreases, but since this is a complex term, other factors such as odd or even numbers of nucleons, also determine the value. Table 2 illustrates this with some selected nuclei. Since the isotope  $^{235}\text{U}$  is known to be fissile, any nuclides with  $E_c$  values lower than 6.5 MeV would also be fissile.

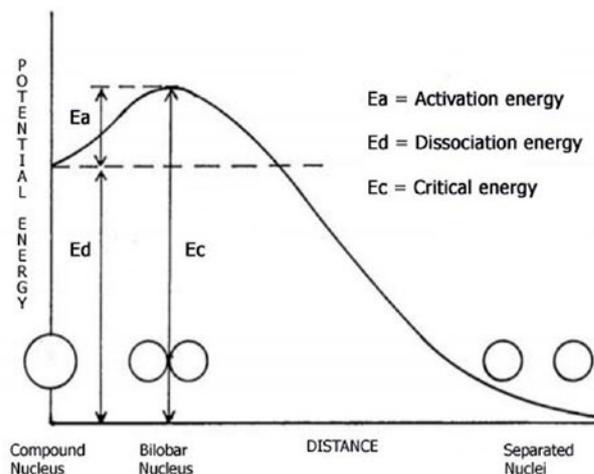


Figure 3. Model Illustrating Conditions for Nuclear Fission.<sup>62</sup>

**Table 2.** Critical Energies of Some Representative Nuclei.

Nucleus	<sup>232</sup> Th	<sup>238</sup> U	<sup>235</sup> U	<sup>233</sup> U	<sup>239</sup> Pu
E <sub>C</sub>	7.5 MeV	7.0 MeV	6.5 MeV	6.0 MeV	5.0 MeV

### Criteria for the Discovery of New Chemical Elements

Now that it is evident that the periodic table can undergo expansion, it becomes necessary to define what forms of experimental proof must be offered to establish one's claim to having discovered a new element. An international group of scientists identified these criteria in a 1979 paper drawing upon the experience of many members of the group.<sup>63</sup> The most important criterion for asserting discovery is to confirm, without doubt, that the element possesses a unique atomic number, *Z*, different from all other elements known. At the same time, it is not necessary to establish the mass number unless evidence for it is directly related to the means by which the atomic number was determined. Establishing *Z* can be done in a variety of ways, and preferably using multiple ways: chemical identification, which is an ideal proof if the chemical procedure is appropriate, such as ion-exchange adsorption and elution; identification of characteristic X-rays that accompany the new element's decay, determination of the half-life, and measurement of the precise, unique energies of the emitted α-particles; or proof of a genetic decay relationship through an α-particle decay chain in which the isotope of the new element is identified by the observation of previously known decay products.

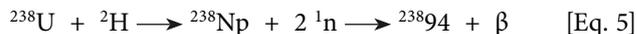
These criteria would prove to be extremely important in adjudicating competing claims in the decades that followed. These criteria, despite the claim by Neil Rowley that physicists alone were responsible for expanding the periodic table beyond element 92,<sup>64</sup> left room for either chemists or physicists to establish the identity of a new element.

### Plutonium

The creation of neptunium turned out to be the stepping-stone to plutonium. The team involved did not include Abelson, who was only temporarily working at Berkeley, nor McMillan, who was called away for "war work," although he received co-authorship on the first paper announcing the discovery.

This time, using the Radiation Laboratory's 60-inch cyclotron (referring to the diameter of the poles of the electromagnet), Glenn Seaborg, Joseph W. Kennedy

(1916-57), and Arthur C. Wahl (1917-2006) bombarded uranium with deuterons (<sup>2</sup>H) and succeeded in replacing one of uranium's neutrons with a proton to yield neptunium which in turn decayed by β-emission to yield an isotope of element 94 with a half-life of about 90 y:



This work was done in 1941, but was not published until 1946<sup>65</sup> due to wartime secrecy, in force at the time. The content of the paper is much understated since the researchers did not feel that they had sufficient proof to say they had discovered a new element.

Chemical characterization proved to be the most difficult part because the element was not susceptible to the ordinary oxidizing agents. They finally used the strongest oxidizing agent known, peroxydisulfate with a silver ion catalyst, and finally obtained proof that the material they had made was different from all other known elements.<sup>66</sup>

The isotope signaling the existence of plutonium for the first time, not yet named, was <sup>238</sup>Pu, which, due to its even number of protons and neutrons, was not fissile. The isotope of interest in this regard was <sup>239</sup>Pu which was identified and characterized as a nuclear energy source in the spring of 1941 – cloaked in secrecy due to the military potential of fission. However, microgram quantities, invisible and almost immeasurable, were all that could be produced after weeks of bombardment of a uranium target in the cyclotron. Glenn Seaborg estimated that at that rate, it would take 20,000 years to produce a kilogram of plutonium! On August 20, 1942, a several-microgram sample of plutonium was isolated and for the first time, a synthetic element was visible to the human eye. It was up to the physicists to figure out how to do a billion-fold scale-up, a task that got an excellent start by Enrico Fermi when he built the first atomic "pile" with 400 tons of graphite, 6 tons of elemental uranium, and 50 tons of uranium oxide. And it was up to the chemists to separate out purified plutonium from the many other products in the mix – a very daunting task that required not only perseverance but creativity and clever ideas in dealing with problems never encountered before.

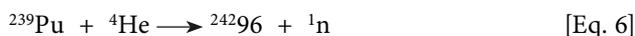
After U.S. scientists succeeded in producing enough <sup>235</sup>U and <sup>239</sup>Pu to make the bombs that would eventually be dropped on Hiroshima and Nagasaki respectively, the world as a whole fell into a period of horror mixed with anger, recrimination, and reflection. Russia stepped up its nuclear program and had a working bomb within a few years; other countries wanted to join the nuclear club immediately. It soon became apparent that this ter-

rible weapon of mass destruction was here to stay and everyone wanted it, if only to use it as a deterrent against aggression. It had “drastically reordered the global hierarchy after World War II and continued to amplify some of the darker pulls of humanity: greed, vanity, xenophobia, arrogance, and a certain suicidal glee.”<sup>67</sup> Eventually terrorist groups and rogue states discovered that one did not need to do years of research to develop explosive fissile material – one only needed the black market to obtain some grams of uranium, perhaps slightly enriched in <sup>235</sup>U, but not necessarily, to create a “dirty” bomb – one with the impact of an ordinary bomb that would scatter long-lived radioactive material over a wide area, rendering it uninhabitable for years, or perhaps centuries. No matter how this two-edged sword would be used in the future, it was clear that there was no turning back. Actinide discoveries changed the course of history forever.

#### *Americium and Curium*

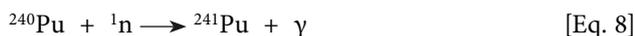
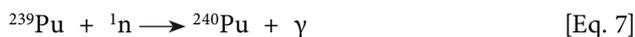
Once the Berkeley scientists had learned the trick of producing elements 93 and 94, they felt that numbers 95 and 96 would soon follow – but such was not the case. The working assumption was that these elements should behave chemically like plutonium, but it took two years of work for the team to realize that their assumptions were off base. Any new element in the series, unlike plutonium, had a stable +3 oxidation state and could not be oxidized further.

The breakthrough occurred in midsummer, 1944, when <sup>239</sup>Pu was bombarded with 32-MeV helium ions:



The new element, 96, an  $\alpha$ -emitter, was identified by detecting its decay daughter, <sup>238</sup>Pu with a half-life of 162.9 d.

Element 95 followed shortly thereafter, in late 1944 and early 1945, when the transplanted Berkeley team, now working in Chicago as part of the war effort, produced it by successive bombardment and neutron capture by <sup>239</sup>Pu,



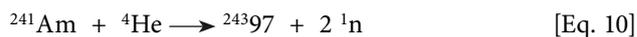
followed by  $\beta^-$  decay to yield element 95 with a half-life of 432.7 y:



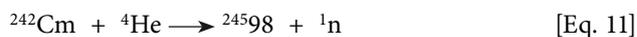
Subsequent characterization of both elements determined that they chemically resembled their rare earth homologs, europium and gadolinium, named respectively in honor of the European continent and of the pioneer chemist, Johan Gadolin (1760-1852), who discovered the first rare earth element. So it was only deemed fitting that the two new elements be named americium, in honor of the American continents, and curium, in honor of Marie and Pierre Curie, the pioneers of radioactivity.<sup>68</sup> The existence of both of these elements was “published” informally in a most unusual way: in a question-and-answer session between Glenn Seaborg and a young participant on the nationally broadcast radio show, “The Quiz Kids.”

#### *Berkelium and Californium*

Production of the next two elements was simple enough, although this depended upon a supply of fairly large amounts of americium and curium to use as targets. Element 97 showed up in late 1949 as the product of  $\alpha$ -particle bombardment of <sup>241</sup>Am:



Then in early 1950, bombardment of a few micrograms of <sup>242</sup>Cm with high-energy  $\alpha$ -particles yielded element 98:



What makes these two elements unusual is that there was so little of them, estimated at under 10,000 atoms and with very short half-lives, that classical chemical means of identification could not be used. In each case, separation and detection methods had to be vastly improved, work that took years to develop. Eventually, both elements were detected by ion-exchange techniques, a first in transuranium element methodology.

Naming these elements proceeded along the logical lines of naming americium and curium. Element 97’s rare earth homolog was terbium, one of four elements named after the Swedish hamlet near the Ytterby mine, where the rare earth ores were first extracted. Although by this time, Berkeley was not exactly a hamlet, it seemed appropriate to name 97 after a town, and hence it became berkelium. The homolog for element 98, dysprosium, presented some difficulties. The name, meaning “difficult to get” in Greek, was certainly also appropriate for 98. So in deciding to call element 98 californium, the researchers pointed out “that the searchers for another element (Au) a century ago found it difficult to get to California.”<sup>69, 70</sup>

In 1950, a challenge from a Russian group headed by A. P. Znoyko (1907-1988) and V. I. Semishin signaled that the LBNL was not alone in claiming discoveries among the actinides. The Soviets claimed that they had the right to name element 97 on the basis of their prediction of its radioactive decay products, and proposed calling it mendeleevium in honor of the father of the periodic table.<sup>71</sup> Although their "discovery by speculation" was rejected as having no merit, the Americans realized that they were no longer the only players in the field.

#### *Einsteinium and Fermium: Children of a Blast*

Elements 99 and 100 burst on the scene "full blown from the head of Zeus," so to speak.<sup>72</sup> Both were unexpectedly found in debris from a thermonuclear blast that took place at the Eniwetok atoll in the Pacific in late 1952. This incredible unplanned event<sup>73</sup> revealed that uranium was capable of absorbing numerous neutrons when subjected to a high enough neutron flux. Scientists immediately began searching the debris for transcalifornium elements and immediately found element 99, <sup>253</sup>99, an  $\alpha$ -emitter with a half-life of 20 d. A few weeks later, element 100 appeared in the coral that had been mined from the test site in sufficient quantity to identify such a short-lived isotope: <sup>255</sup>100, an  $\alpha$ -emitter with a half-life of 22 h. The method of identification once again was ion-exchange.<sup>74 75</sup>

Subsequent to the initial discoveries, it was clear that the amounts found in the bomb debris were not sufficient, so scientists mined tons of coral reefs that surrounded the explosion site in a pilot-plant operation. Credit for all this work goes to scientists participating in a large cooperative project at LBNL, Argonne National Laboratory (ANL), and Los Alamos National Laboratory (LANL).

When it came time to name the elements, for element 99, the groups suggested the name einsteinium in honor of Albert Einstein, whose famous equation supplied the theory behind nuclear power. Enrico Fermi's turn came and appropriately so since he had ushered in the atomic age. When he was on his deathbed suffering with stomach cancer, Al Ghiorso (1915-2010) failed to communicate directly his intention to name element 100 after him. In April, 1955, five months after Fermi's death, he wrote a letter to Mrs. Fermi conveying the good news.<sup>76</sup> The two names were also a symbol of the openness of the research groups: any number of American scientists could have been chosen to be honored. Although Einstein and Fermi were both American citizens, both had been naturalized from countries that

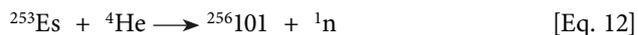
were at war with the United States. In addition, these names did not come without a certain amount of discord. The LANL people pushed hard for recognition by suggesting the name *losalium* (after Los Alamos), among many others, and the Argonne group proposed the name *anlium* (after their acronym, ANL). Many other suggestions came from other sites, even from places and publications that had nothing to do with the initial discoveries. A great deal of mediation was required to settle the matter, a premonition of the naming rights and priority disputes that would occur with virtually every other element soon to be discovered. The halcyon days of LBNL would soon be over.

Another ending of consequence was the fact that fermium would be the last element that it was possible to synthesize by utilizing neutron capture reactions. It was also clear that if fermium could only be produced in the amount of about 200 atoms; the heavier elements soon to come would require much more than large neutron fluxes or small particle bombardment of a given target. It would soon be necessary to devise reactions using heavier bombarding particles and to produce larger quantities of target material in order to move beyond the necessity of characterizing newer elements one atom at a time. And ever more powerful accelerators!

#### THE FIRST TRANSFERMIUM ELEMENTS OR THE LAST OF THE ACTINIDES: MENDELEVIUM, NOBELIUM, AND LAWRENCIUM

##### *Mendelevium*

A first for mendeleevium, element 101, was its production and identification one atom at a time. The exciting story is told in the first person by the discovery team of Albert Ghiorso, Bernard G. Harvey (1919-2016), Gregory R. Choppin (1927-2015), and Stanley G. Thompson (1912-76). They started out by bombarding element 99, einsteinium, with helium nuclei, producing element 101 plus a neutron:



The target was very small, not more than about  $3 \times 10^9$  atoms, and any atoms of element 101 formed were caught on a gold foil placed directly behind the target. Once caught, a relay race of sorts took place: to first separate the one or two atoms of element 101 from the billions of atoms of einsteinium, and then to record the pulse of current from the detector as the atom decayed – all within about a half-hour, which was the estimated half-life of the isotope. The team remarked,

*It is typical of these elusive heavy elements that we cannot positively identify an atom until the moment that it ceases to be that element and disintegrates into something else. It's rather like the man who only counts his money as he spends it.*

They continued,

*In the first experiment, we waited more than an hour before the pen shot to mid-scale and dropped back, marking a line that meant the disintegration of the first known atom of mendelevium. Since this was quite an event...we connected a fire bell in the hallway to the counters so that the alarm would go off every time an atom of element 101 disintegrated. This was a most effective way of signaling the occurrence of a nuclear event, but quieter means of communication were soon substituted, following a suggestion put forth by the fire department. We found only about one atom of mendelevium in each of our first experiments, We repeated the experiment perhaps a dozen times, and our grand total was seventeen atoms of the new element.<sup>77</sup>*

We think Mendeleev himself would have approved of the fire bell.

Surprisingly, mendelevium was a maverick in a group of well-behaved newcomers to the periodic table (also a Mendeleev characteristic?). It exhibited electron capture, a process intuited by Al Ghiorso, and subsequently verified, which enabled the group to identify it by its fissile daughter,  $^{256}\text{Fm}$ :



In naming the new element mendelevium, the discoverers had obviously revisited the reasons put forth by the Russians five years earlier, but also proved to be very open and accommodating given the fact of the Cold War. Selecting a Russian to be honored certainly went against the grain of conventional attitudes at the time, but it brought unexpected political capital as well. At the September 1958 Atoms for Peace Conference in Geneva, the French chemist Moïse Haïssinsky (1898-1976), who had often had combative disagreements with Glenn Seaborg, pulled him aside and confided in him that his choice of the name mendelevium did more for international relations than everything that the U.S. Secretary of State had done in his entire career.<sup>78</sup>

### *The Convoluted History of Nobelium*

By 1956, in order to overcome the barrier presented by the small masses of bombarding particles used up to this time, only three particle accelerators able to

accelerate heavy ions existed: LBNL, Kurchatov Institute in Moscow (later JINR), and the Nobel Institute for Physics, Stockholm. All three were hard at work, and in that same year, a team in Moscow led by Georgy Nikolayevich Flerov (1913-90) produced element 102 by bombarding  $^{241}\text{Pu}$  with  $^{16}\text{O}$ . They proposed naming the element *joliotium* after Irène Joliot-Curie, although Flerov himself noted that the data were inconclusive and thus not widely disseminated. Then, in the following year, the Nobel Institute for Physics, in collaboration with ANL and the Atomic Energy Research Establishment, Harwell, UK, announced the production of either  $^{251}\text{102}$  or  $^{253}\text{102}$  (they were not sure) by bombarding  $^{244}\text{Cm}$  with  $^{13}\text{C}$ .<sup>79</sup> They immediately proposed the name nobelium in honor of the great Swedish philanthropist, Alfred Nobel (1833-96), and the name stuck because it received immediate approval by IUPAC. However, within the year, the group at LBNL were able to show that the Swedish claim was erroneous and in new experiments reported success by fusing  $^{244}\text{Cm}$  and  $^{12}\text{C}$  to produce  $^{254}\text{102}$ .<sup>80</sup>

Now it was the Soviets' turn to disparage the LBNL results, claiming that they had erred in their half-life and isotope assignments, and therefore could not have produced element 102. And they continued to insist on their choice of name, *joliotium*. Spurred by the criticism, the LBNL group re-examined their data and realized their errors. Their revised analysis supported the data from the Soviet group, but continued to agitate for "naming rights" even though they allowed that they would be satisfied with the name nobelium.<sup>81</sup> The Soviets ignored all the claims made and continued to insist on their rights.

It should at this point be recognized that everyone involved in heavy ion nuclear research was feeling their way along a path that they were creating themselves.

*It is important to remember that the methods used for nuclear identification at this time were still being developed so that it was not unusual for mistakes of interpretation to be made by all groups working in the field.<sup>82</sup>*

This standoff lasted for decades, prompted IUPAC to finally re-evaluate the discovery of all transfermium elements to date, and finally, in 1993, they attributed priority to the Flerov group at JINR,<sup>83, 84</sup> which had in the meanwhile published their own version of events.<sup>85</sup> Flerov and his group insisted that the expenditure of material and personal resources in the discovery of elements should result in the group's right to name the discovery. They also criticized the make-up of the IUPAC committee, peopled with persons without the expertise to judge the validity of claims. They cited as well a lack

of objectivity in developing the criteria for judging the claims.<sup>86</sup> LBNL stubbornly rejected the JINR objections and the IUPAC decision, but the Berkeley hegemony was finally over.

In retrospect, Berkeley repeated the Stockholm method for producing number 102 ( $^{244}\text{Cm} + ^{13}\text{C}$ ), using an identical reaction, and yet each group came up with different half-lives for what was presumably the same isotope. Add to this mystery the fact that the Stockholm group was assuming that 102 exhibited a preferred 3+ oxidation state, whereas in reality, it is more thermodynamically stable as the 2+ ion, so they would have missed it in their ion-exchange elution protocol.<sup>87</sup>

Despite all the controversy, the one fixed fact is that the name nobelium is here to stay: in 1997, the IUPAC confirmed the name nobelium with the symbol No.

### *Lawrencium*

In 1958, LBNL lost its Director and founder, Ernest Orlando Lawrence, following a brief illness. It fell to Glenn Seaborg, who, by now, was Chancellor of the University of California at Berkeley, to select a new Director. Luis Alvarez pre-empted Seaborg's choice by first, indicating that he was not a candidate, and secondly, that he would highly recommend Edwin McMillan for the post. Seaborg happily accepted Alvarez's intervention, and McMillan took over soon afterwards.

A few years later, in 1961, element 103 was identified in the following fashion: about 3  $\mu\text{g}$  of a mix of californium isotopes were bombarded with heavy ion beams of  $^{10}\text{B}$  and  $^{11}\text{B}$  at the Berkeley HILAC. An  $\alpha$ -emitter with a half-life of 4.3 s due to  $^{258}\text{103}$  was detected, and immediately named it lawrencium in the title of the publication announcing the discovery.<sup>88</sup> The new element, given the symbol Lw (later changed to Lr by IUPAC), honored the inventor of the cyclotron, the machine that had led to the discovery of so many new elements. Although the Berkeley team was acknowledged as the discoverers, in 1965 the JINR at Dubna identified the longest lived isotope,  $^{256}\text{Lr}$  with a half-life of 28s, and established the genetic decay sequence as well. In its review of the decade-long efforts of both groups, and their substantial contributions to the correct identification and the properties of element 103, the Transfermium Working Group (TWG), in 1992, recommended that the two groups share credit for the discovery. It also reconfirmed the name, lawrencium, and the symbol, Lr.

## SOME CHARACTERISTICS AND USES OF THE ACTINIDES

### *Electronic Structure of the Actinide Elements*

Due to the radioactivity, toxicity, and lack of large numbers of sample atoms for many of these elements, theoretical calculations of atomic characteristics play an important role. However, due to spin-orbit and scalar relativistic effects, open-shell electronic structures, and likely covalent bonding of the 5f shells, among other considerations, ordinary crystal field calculations are unsuitable. The relativistic effects, particularly, are most important because the velocity of the electrons is directly proportional to increasing atomic number; these effects, in fact, overshadow the periodic trends that are characteristic of the lighter elements. *Ab initio* quantum chemical calculations utilizing relativistic multireference wavefunctions can help enormously in understanding the actinide elements' complicated electronic structures.<sup>89</sup>

### *Actinides in Medicine*

The use of radioactivity in medicine got its start when Henri Becquerel realized that uranium was capable of producing images on a photographic film. This discovery was almost simultaneous with the discovery of X-rays by Wilhelm Conrad Röntgen (1845-1923) who, with them, produced an image of his wife's left hand. Thus, diagnostic imaging with high energy electromagnetic radiation became the first application of actinides in medicine. Radiotherapy came next, both external, and internal by brachytherapy and targeted radionuclide therapy (TRNT). The chief actinides in use were naturally occurring uranium and thorium and reactor-generated isotopes of actinium, thorium, and uranium, useful as radionuclide generators for the production of lighter elements such as  $^{99\text{m}}\text{Tc}$ . Cost and availability of the actinides severely limit development of their use in clinical applications.<sup>90</sup>

### *Actinides in Catalysis*

Developments in organoactinide chemistry have spurred the use of these compounds as potential catalysts in areas calling for chemoselectivity on sterically demanding substrates. Most catalytic studies have centered on  $\text{Th}^{4+}$  and  $\text{U}^{4+}$ , but  $\text{U}^{6+}$  has recently come into the limelight. One feature of organoactinides is the possibility of forming high coordination number complexes

due to the large ionic radii of the actinides' 5f orbitals. Determination of bond disruption enthalpies to understand the thermodynamic factors responsible for catalytic turnover utilizing organoactinides has been found useful. This is a rapidly developing field.<sup>91</sup>

## CONCLUSION

We can comfortably assert that the actinides and the rare earths share some similarities, both chemical and historical, but there are also some significant differences between the two groups. They are both set apart from the main body of the periodic table, chiefly for spatial convenience in accommodating their 4f and 5f orbital representations. They both take their group names, lanthanides and actinides, from the name of the first member of each group. Four of the actinides, Am, Cm, Bk, and Cf, received names analogous to those of their lanthanide homologs, Eu, Gd, Tb, and Dy. Discovery stories for both groups are peppered with priority disputes and contention over naming rights. However, we cannot discern many other points of likeness. It took almost 150 years to discover all of the rare earths; if we exclude uranium and thorium, the completion of "Mendeleev's family" took only 40 years of purpose-driven research.

Historically, we observe that the American contribution to lanthanide discoveries was marginal, as in the case Charles James (1880-1928),<sup>92,93</sup> and if not even fallacious, as in the case of John Lawrence Smith (1818-1883).<sup>94</sup> On the contrary, with respect to the actinides, the American laboratories exercised a hegemony for several decades that was not easily challenged. Using the enormous resources of their federal budget, they invented new ways of producing and identifying radioisotopes, resulting in almost routine new element discovery every couple of years. Eventually, their absolute domination of the field crumbled in the face of Russian, Swedish, Japanese and German expertise, ushering in a new age of collaboration, rather than of competition.

For Mendeleev, a scientist who formed the nexus between ancient Greek philosophy and the new 19<sup>th</sup> century discoveries, his periodic arrangement was a Kantian "categorical imperative." He was constrained to dismiss Julius Lothar Meyer's (1830-1895) notion of the unity of matter wherein all the elements were multiples of hydrogen (or possibly of some simpler entity) as simply a relic of classical thought.<sup>95</sup> Mendeleev based his own table on the idea of the "plurality of matter," by which all the elements are different, and yet are connected. He recognized "the existence of multiple elements as the basis of material reality. He never accepted

the idea of "prime matter" maintained by Prout, and the possibility of reducing all the elements to a single element, hydrogen."<sup>96</sup> In his 1976 analysis of Mendeleev's thought,<sup>97</sup> Yuri Solov'ev makes it clear that the exact formulation of the periodic law did not spring forth suddenly from Mendeleev's head (as from the "head of Zeus"), but only after he had processed and clarified the fundamental concept of his system of the elements.<sup>98</sup> He says that there can be no doubt that the fundamental content of the law (the principle of periodicity) was quite clear to Mendeleev from February 17, 1869, and that it served as a guide to expand upon the system of the elements. By 1871, two fundamental concepts on the theory of periodicity had been definitively established and announced by Mendeleev. He emphasized that "every natural law gains its particular scientific significance when it is possible to derive practical consequences from it, that is, logical conclusions that explain what has not yet been explained, pointing out phenomena unknown from the beginning, and above all by the possibility of carrying out controllable predictions by experiment." The results of particular significance in the promulgation of the law was the prediction of the existence of "eka-aluminum" (gallium, discovered by Boisbaudran in 1875), "eka-boron" (scandium, Nilson, 1879) and "eka-silicon" (germanium, Winkler, 1885). The discoveries of these elements, and first of all that of gallium, decisively changed the attitude of the scientific world with respect to the periodic system of the elements. In 1879, in his letter to G.A. Quesneville,<sup>99</sup> Mendeleev had every right to affirm: "It is now evident that the periodic law leads to consequences that preceding systems did not dare to predict. At first there was only a scheme, a grouping according to determined facts, while the periodic law renders the facts subsidiary to itself as the principle, and aims at understanding more deeply the philosophical principle that governs the mysterious nature of the elements." Mendeleev states further "This trend is in the same category Prout's Law, but with this essential difference: that Prout's Law relies on mere numbers, whereas the periodic law draws its authority from a series of mechanical and philosophical laws which constitute the character and brilliance of the present impetus of the exact sciences."

He later stated that the periodic law is a direct outcome of a collection of experimental data and that experiment must take precedence above all else, seemingly a categorical dismissal of the idea of the unity of matter, an idea that comes not from experiment but from speculation.<sup>100</sup>

As Mendeleev's work marks the beginning of the modern chemical world, so the actinides mark the start-

ing point for the expansion of periodic table chemistry, whose end, even up to today, it seems impossible to fix with any certainty.<sup>101</sup> This is a trajectory that doubly fascinates chemists: firstly as scientists, and secondly for the iconic meaning that the periodic table represents for them.

As we have already demonstrated, the early actinides are a subgroup unique among the elements. All radioactive, some naturally occurring, and in great abundance, and many fissionable, they have been the backbone of the nuclear energy industry, both in war and in peace. But, as far as their chemistry is concerned, actinide research fell into the doldrums in the late 20<sup>th</sup> century. A surprisingly recent resurgence of interest in actinide chemistry can be attributed to the realization that nuclear power can help to curtail carbon emissions and understanding actinide chemistry is vital in dealing with nuclear waste. In addition, the lighter actinides are increasingly being scrutinized, as noted above, for possible catalytic and medical applications, especially in terms of indirectly delivering hard-to-get radioisotopes as part of their decay chain. The mid-actinides pose another problem: availability. Unless more than a few milligrams of these cyclotron-produced elements can be available long enough for studies, let alone for commercial or medical use, they will remain in the backwater. But progress is being made: a research team in Japan has recently succeeded in measuring lawrencium's ionization potential. We should see much more activity in this area in the coming decades.<sup>102</sup>

In 1869, Dmitri Mendeleev literally started a family of elements. Now he is an honored part of it.

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