Rediscovery of the Elements

The Rare Earths–The Last Member

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Figure 2. The Kaiser Wilhelm Institute is now the Freie Institute, located in Berlin-Dahlem, Thielallee 63—N52° 26.85 E13° 17.11. This is the Hahn-Meitner-Bau (Building): Institut für Biochemie, the laboratory where the splitting of the atom was first observed.

The final rare earth to be discovered. In the previous "Rediscovery" article,[1c] we saw how Henry Gwyn Jeffreys Moseley (1887–1915) in 1914 through X-ray analysis formulated the concept of atomic numbers; and how he concluded that there was one rare earth yet to be discovered—number 61. This element had actually been "predicted" a decade earlier—Bohuslav Brauner (1855–1935), professor of chemistry at the University of Prague, Czechoslovakia, in 1902 announced, on the basis of an anomalous atomic weight gap between the two elements, that an element should exist between neodymium (60) and samarium (62).[2d]

Chemists promptly began to search in crude preparations of these two elements, hoping to find element 61 as an impurity, but during the next two decades nothing definitive was reported.[2d] In 1921 Charles James (1880–1928), the co-discoverer of lutetium in 1907 and professor at the University of New Hampshire and member of ΑΧΣ (*Mu* '11), suggested in 1921 that solubility trends of the rare earth carbonates indicated such an element existed between neodymium and samarium.[3] However, in spite of his expertise in the separation of the rare earths[1c]—he is credited with preparing the purest sample of lutetium, the last rare earth discovered in 1907—he was silent on the matter of actually isolating the intermediate element.

Figure 1. B. Smith Hopkins of the University of Illinois, is the only ΑΧΣ member whose announced element—illinium—appears on the Mendeleev Wall Periodic Table of the Elements in St. Petersburg, Russia (see Figure 11 on page 10).

The discovery of illinium. Five years later "illinium" was announced in the *Journal of the American Chemical Society* by B. Smith Hopkins (Figure 1) (1873–1952; ΑΧΣ, *Zeta* '13) of the University of Illinois.[4] Hopkins had not isolated the element, but he reported that new absorption lines appeared common to the intermediate crystallization fractions of neodymium and samarium. He reported that he also was able to observe faint X-ray lines whose frequency agreed with the predicted values of element 61.

Among the myriad of spectral lines appearing for neodymium, samarium, and contaminants of other rare earths and heavy metals, a few were confirmed by German chemists[5] – and also by Charles James.[6] Both James and Hopkins had been simultaneously working on this problem, but each was unaware of the other's research.[7] James had obtained similar data several years previously,[7] but elected not to publish until he obtained more definite results. Ironically, James had been asked to referee Hopkins' announcement publication on illinium! A true gentleman,[8] James did not demand shared honors, but instead promptly endorsed Hopkins' publication. This example of "moral integrity" has been lauded by the authors of the

Figure 3. Plaques on the Hahn-Meitner Building. LEFT: "In this building of the Dahlem Kaiser Wilhelm Institute for Chemistry, the splitting of the uranium atom was discovered by Otto Hahn and Fritz Strassman." RIGHT: "In this building Lise Meitner worked 1913–1938, the co-discoverer of the splitting of the atom, and Max Delbrück, pioneer of molecular genetics, who worked with Frau Meitner 1932–1937." Max Delbrück, who migrated to the U.S., received a Nobel Prize in 1969 for discoveries concerning "the replication mechanism and genetics structure of viruses."

recent *The Lost Elements: The Periodic Table's Shadow Side*,[2] citing this as scientific professionalism at its highest: "Real integrity is doing the right thing, knowing that nobody's going to know whether you did it or not."[2d] Upon Hopkins' announcement of illinium, James quietly published his results in a less prominent journal,[6] confirming Hopkins' observations.[7]

An independent discovery—florentium. Meanwhile, across the Atlantic Ocean another claim for element 61 was made.[2d] An independent observation of the same absorption and X-ray spectra was made by Luigi Rolla (1882–1960) of the Royal University of Florence. He called his element *florencium*, later *florentium*.[2d,9] Rolla claimed he had actually performed his research two years previously, and he proved it by providing a packet of documentation he had sealed at that time—he wanted more time to prepare a sample of the element before publishing.[2d]

A contentious trans-Atlantic debate ensued as to the priority of "illinium" or "florentium."[2d] A race ensued as to who could isolate an authentic sample of element 61, but no one was able to perform the deed. Even Walter Noddack (1893–1960) and Ida Tacke Noddack (1896–1978), the geological chemistry experts who had just discovered rhenium in 1925,[1b] tried their hand at isolating element 61—but were unsuccessful. Ida Tacke Noddack, who had ingeniously prophesied nuclear fission years before Otto Hahn observed it in Berlin,[1b] suggested element 61 might be gaseous and radioactive[2d] (she turned out to be half correct—*vide infra*).

Was illinium/florentium authentic or spurious? The evidence for element 61 was very thin indeed. The X-ray lines that were "proof" of element with an atomic number of 61 appeared only as faint traces, sometimes lost in the forest of the main spectral lines, in the fractions of neodymium and/or samarium. Since an actual sample of element 61 could not be prepared, many scientists began to doubt its presence. One such person was Wilhelm Antonin Alexander Prandtl (1878–1956), at that time at the Wilhelm-Institut für Physikalische Chemie und Elektrochemie in Berlin (where Fritz Haber had been conducting research on poison gases during World War I). Prandtl, who in 1926 was simultaneously heavily criticizing the claims[2c] by the Noddacks for "discovery" of element 43 (masurium),[1b] rejected the claim of discovery for illinium.[10] Prandtl reported he could produce the "illinium" lines in the absorption spectra by simply changing the proportions of neodymium and samarium in the sample to be analyzed; furthermore he claimed the very faint X-ray lines could be produced by contaminants of barium, bromine, chromium, and platinum.

Mattauch's rule of isobars (1934). Meanwhile, theoretical considerations bore on the issue regarding element 61. Josef Mattauch (1895–1976), a researcher in mass spectrometry who succeeded Lise Meitner (1878–1968) as head of the physics department at Kaiser Wilhelm Institute for Chemistry (Figures 2,3), after she fled Germany in 1938, formulated his "Isobarenregel" (Rule of Isobars) in 1934.[11] This Rule was an empirically derived law which defined the possible combinations of stable or unstable nuclei for isobars (nuclides with the same atomic mass but different atomic numbers, e.g., ${}_1H^3$ and ${}_2He^3$). The rule states that for isobars differing by only one atomic number, if one nucleus is stable, then the other one must be radioactive. Examples: Since ${}_7N^{14}$ is stable, then ${}_6C^{14}$ must be radioactive; since ${}_6C^{13}$ is stable, ${}_7N^{13}$ must be radioactive. This rule, after 80 years, still holds true with only two minor exceptions, and has been refined and quantified on the basis of the liquid drop model of the nucleus.[12]

In his 1934 article,[11] Mattauch applied his rule to element 61, for which he predicted all isotopes would be radioactive. This conclusion follows for 61 because the elements both immediately before and after 61—neodymium and samarium—have stable isotopes for the range of the masses of isotopes of 61. Specifically, for the mass range of element 61 (centered between Nd=144.2 and Sm=150.4), either Nd or Sm has a stable isotope—neodymium has stable isotopes 142–146 and 148 and samarium has stable isotopes 147–150 and 152, thus excluding stable isotopes 142–150 of element 61. (In Mattauch's article, a similar argument is given for Noddacks' masurium, element 43,[1b] taking into account the stabilities of isotopes of its surrounding elements molybdenum and ruthenium).

Some in the scientific community of the 1930s took heed of Mattauch's rule and began to make the obvious conclusion: perhaps element 61 (as well as masurium) had not been found in nature, because it didn't *exist* in nature.[13] Even the Chair of the Chemistry Department at Illinois, William Albert Noyes (1857–1941; ΑΧΣ *Zeta* 1912), who had been championing Hopkins' claim for illinium, was beginning to have "doubts about the experimental evidence" and in 1928 asked Charles James—whom he actually previously attempted to lure to Illinois[7]—to collaborate to resolve the uncertainty of the claim of the element.[7] Regrettably, James was terminally ill and died that same year.

The status of element 61 before World War II. With no definite sample of element 61 in hand, its status was uncertain. Hopkins believed in illinium without reservation; he wholeheartedly believed that the element was there, if only in trace quantities.[7] Slowly the scientific community began to consider that since technetium had been artificially produced in 1937 and was shown to be radioactive,[1b] perhaps promethium could be artificially prepared as well. However, the situation as described by Mary Elvira Weeks stood perhaps as a convenient best guess—in the 1939 edition of *Discovery of the Elements* she reported that, "Element number 61, illinium, the last of the rare earths, [finally] took its place in the periodic table.”[9]

The Manhattan Project. World War II, with the development of the atomic bomb, created the opportunity for the artificial synthesis of element 61. A complete city—Oak Ridge, Tennessee—was built from scratch to develop fissionable and trigger materials for the Manhattan Project. The fissile materials for the bomb were the 235 isotope of uranium (U-235) and plutonium. Constituting 0.7% of the natural abundance of uranium, U-235 was separated at three facilities known as K-25 (which used the gaseous diffusion method, using different diffusion rates of UF6), S-50 (liquid thermal diffusion), and Y-12 (using calutrons, essentially huge mass spectrometers). A pilot plant for the production of plutonium was named X-10, or the Graphite Reactor (Figure 4). This was the second nuclear reactor, the first being the atomic pile at the University of Chicago (the “Fermi” pile). The Graphite Reactor went into operation on November 4, 1943. Natural neutron production in the uranium rods transformed uranium-238 into plutonium-239 (Figures 5–7). This process involved slow neutrons (decelerated while passing through graphite) which were absorbed by uranium-238, which then experienced two beta-decays to produce plutonium-239.

Other nuclear events occurred simultaneously. To understand all of these processes at X-10, fission products of uranium needed to be analyzed. Georges Urbain (1872–1938), the co-discoverer of lutetium, had once said that fractional crystallizations was the only method of merit in the search for new elements.[2b] However, now a much more efficient method of separation was needed. Fortunately, such a technique—ion-exchange chromatography—was developed by Frank Harold Spedding (1902–1984)[14] (Figure 8) using an Amberlite support and a citrate eluant with a carefully controlled pH. Ion-exchange chromatography was particularly applicable to rare earths because of the dynamic equilibrium of rare earth ions with ligands, which causes significantly different retention times of different rare elements on the specialized substrate. With this method, clean separation of the rare earths was realized.

Figure 4. X-10, Code name for the Graphite Reactor (Building 3001), was built to produce fissionable plutonium.; Hillside Drive—N35° 55.68 W84° 19.06. The X-10 Graphite Reactor has been designated a historical landmark by the American Society for Metals (dedicated 1973) and the National Park Service (1966). Also, the American Chemical Society has designated the Oak Ridge National Laboratories as a National Landmark.

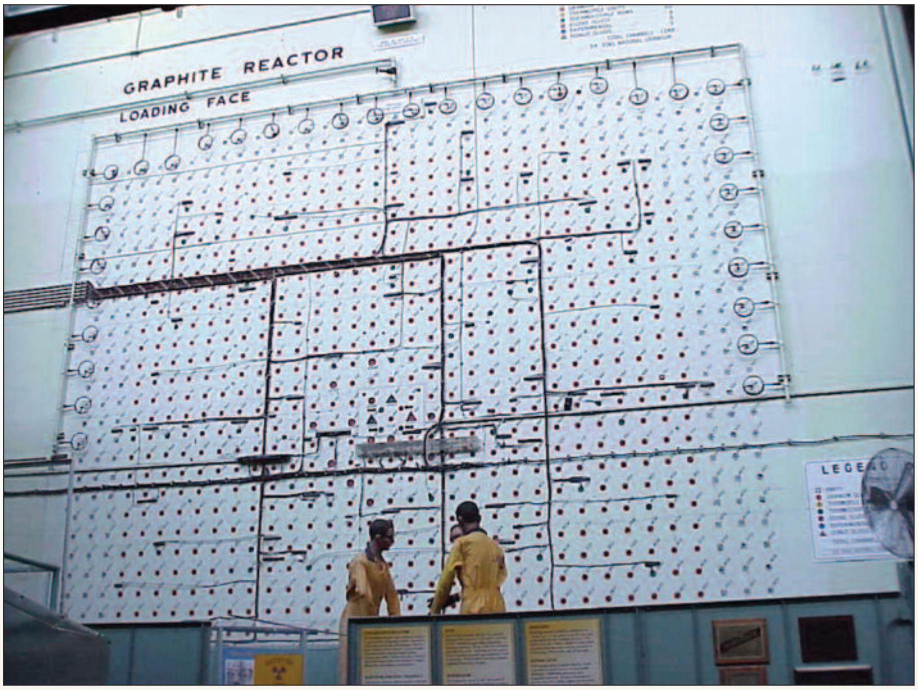
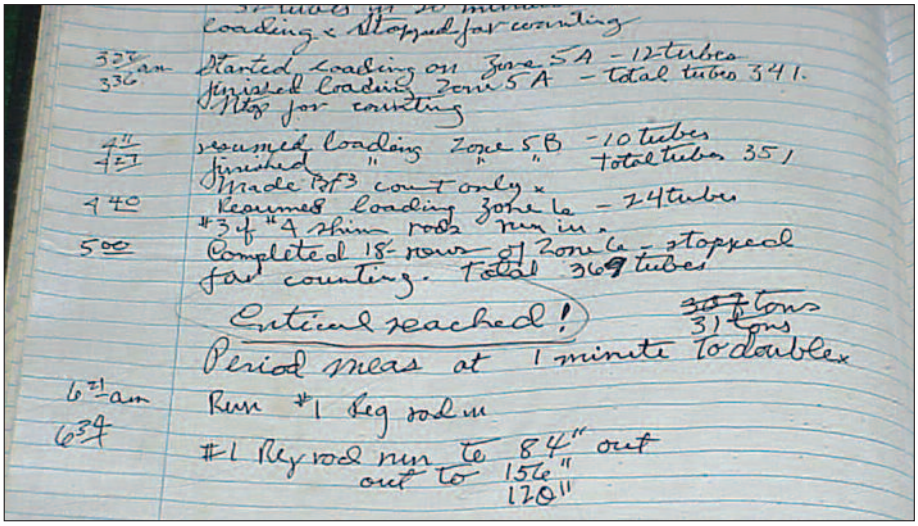


Figure 5. Inside X-10, Graphite Reactor, where promethium was produced in the atomic pile. This is the “loading face” where 54 tons of uranium rods had been inserted, with model mannequins at the bottom. After reaction, the uranium slugs were pushed into a canal of water 20 feet deep, and then were transferred to the Chemical Separations Building.

The analysis of the rare earths was performed in a neighboring laboratory (Figure 9) by the team of Jacob Akiba Marinsky (1918–2005), Lawrence Elgin Glendenin (1918–2008), and Charles DuBois Coryell (1912–1971). They followed the travel of various fractions by tracing their radioactivity, using the pioneering method of the Curies[1a] for radium and polonium. They isolated a fraction which proved to be the new element,[15] a “long-lived” isotope (half-life of 2.6 years) which they eventually proved by mass spectrometry to have a mass of 147.[16] They went on to discover another isotope, Pm-149 (half-life 53 hours).[16,17]

It soon became clear that all isotopes of promethium were radioactive (the longest-lived isotope is promethium-145 with a half-life of 17.7 years), and claims by earlier researchers to have observed it in nature were



Loading & Stopped for counting

3 27 am Started Loading on Zone 5A - 12 tubes

3 36 Finished Loading Zone 5A - total tubes 341.

Stop for counting

4 11 resumed loading Zone 5B - 10 tubes

4 21 finished " " " total tubes 351

Made BF3 count only x

4 40 Resumed loading zone 6 - 24 tubes

#3 & #4 shim rods run in.

5 00 Completed 18 rows of Zone 6 - stopped for counting. Total 369 tubes

Critical reached!

~~30½ tons~~

31 tons

Period meas at 1 minute to double x

6 21 am Run #1 Reg rod in

6 34 #1 Reg rod run to 84" out

out to 156"

120"

Figure 6. The Graphite Reactor was designed and built in 10 months. Notebook on display: "Critical reached" on November 3, 1943, 5am, at which time the nuclear chain reaction was self-sustaining. The reactor went into production the following day.

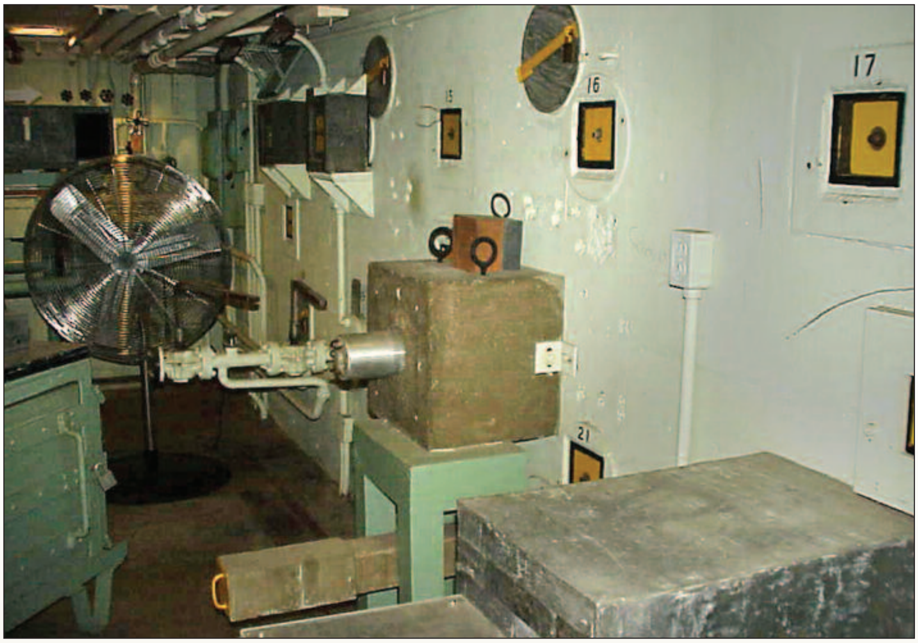


Figure 7. Upper room, where radioisotopes were prepared, after 1945. Radioisotopes were produced by bombarding chemical elements with neutrons from the nuclear chain reactions or fissioning—that occur inside a nuclear reactor. Radioisotopes are used in various applications for medical, industrial, agricultural, military, space, and scientific research. Prepared radioisotopes inclulde iodine-131, phosphorus-32, and carbon-14. The reactor stopped operation in 1963.

Figure 8. Frank Spedding pioneered the method of ion-exchange chromatography for the separation of materials.[14] *He was "universally acknowledged as one of the world's foremost experts on the identification and separation of rare earths."*[21] *He developed methods for producing large quantities of high purity uranium critical to the Manhattan project.*[21] Photo courtesy of University of Iowa archives.

thus shown to be erroneous.[17] The (extremely faint) X-ray lines claimed to belong to a new element by Hopkins and others now were known to have been due to impurities which could never be completely removed in those days before ion exchange chromatography (unfortunately, the original analyzed samples are no longer available,[7] and the exact composition of these is not known).

Owing to security concerns, the announcement[17] of the discovery of promethium was delayed until 1947 (Figure 10). The formal announcement[15] itself was made at the 112th national meeting of the American Chemical Society, New York City, September, 1947.[16] (Ironically, W. A. Noyes was then president of the American Chemical Society, and presided over the General Meeting). Afterwards a press conference was held where Hopkins, Harris, and Yntena attended to make a futile plea for "illinium," as well as Lawrence Larkin Quill (1901–1989) and M. L. Pool (1900–1982) of Ohio State University, who had performed some inconclusive cyclotron studies (bombarding samarium with deuterium) and were suggesting "cyclonium" for the name of the element 61.[2d] The adopted name of "promethium" was made the following year.[18] The suggested name, promethium, was made by Coryell's wife Grace Mary.[16] "The name refers to Prometheus, the Titan in Greek mythology, who stole fire from heaven for the use of mankind. It not only symbolizes the dramatic way in which the element is produced as a result of harnessing of the energy of nuclear fission, but also warns of the danger of punishment by the vulture of war." In 1949 the name promethium was officially adopted by the IUPAC.[16]

The fate of illinium. After the discovery of promethium, all isotopes of which had short half-lives, it became clear that it was impossible for promethium to have been observed in ordinary rare earth minerals. Rolla himself retracted the claim of his discovery of element 61, as if he wanted Hopkins to own completely the "credit of failure."[2d] Rolla's successor at Florence, Giorgio Piccardi (1895–1972), who was heavily involved in Rolla's rare earth research, when later asked what he thought of all the florentium work, was heard to state philosophically, …"the great Poincaré defined science as the cemetery of hypotheses; if in it our own is buried, I will be honored."[2d]

Promethium in nature. Intense searches have actually shown that promethium has been observed in nature "in trace amounts in uranium ores, as a product of uranium fission."[7] A sample of African pitchblende was found to contain 4×10^{-15} grams of Pm-147 per kilogram of ore.[19] The 147Pm/U ratio in the pitchblende was 3×10^{-4} disintegrations per second per gram of uranium. The observed 147Pm/U ratio in the pitchblende was in agreement with the 147Pm/U equilibrium ratio in non-irradiated natural uranium. The results indicate that the

Figure 9. Chemical Analysis Building, Oak Ridge, TN, where promethium was isolated (originally the west wing of the building complex; then building #706, now building #3550, Central Ave.—N35° 55.61 W84° 18.99). The actual laboratory where the separation of promethium was done is at the far end, where now a modern brick building stands (visible behind the wooden structure).

Figure 10. Dr. Ellison Hall Taylor (1913–2008) was interested in preserving the legacy of ORNL (Oak Ridge National Laboratory) since its inception. He was director of the Chemical Division 1954–1974. In this photo taken in 2002, Dr. Ellison holds the original internal memorandum describing the isolation of promethium, dated June 27, 1947, while the actual work itself was performed three years earlier and was kept classified during WWII. The formal publication appeared in the Journal of the American Chemical Society *five months later.*[15] *In the 1950s Dr. Taylor was part of the team which pioneered molecular beam chemistry at Oak Ridge.*

147Pm in African pitchblende was produced predominantly by U-238 spontaneous fission – just as it was produced at the X-10 Graphite Reactor. Apparently, billions of years ago, when the concentration of U-235 was higher, there *was* such a natural reactor—the Oklo Reactor[17]—a site in Gabon, Africa, ca. 2 billion years ago. Analysis of the product shows an anomalously large concentration of samarium-147 (a beta-decay product of Pm-147), indicating that the concentration of Pm-147 was once higher at this site (but no longer).

The ultimate fate of illinium. Although Rolla had conceded the obvious, Hopkins campaigned the rest of his life for the cause of illinium, never wavering in his claim, even when he saw Marinsky's preparations at a regional American Chemical Society Meeting (Syracuse, New York) in 1948.[2d] The announcement read: "The first exhibition to the public of compounds of elements 43 and 61 took place at the closing session of the symposium held by the Division of Physical and Inorganic Chemistry of the American Chemical Society at Syracuse University, June 28–30. Three milligrams each of the yellow chloride and the rose nitrate of element 61 were shown as well. . . ."[20] Promethium had definitely replaced illinium.

And yet the memory of illinium lives on in St. Petersburg, Russia! On the "Wall Periodic Table" erected in 1936 at the Metrology Institute (where Mendeleev was employed his later years), illinium still stands (Figure 11)—a ghost reminding us of the thousands and thousands of hours of crystallizations necessary to deliver a handful of new elements to the chemist's laboratory shelves. This element—albeit spurious—is the only one on this Mendeleev wall which was "discovered" by a member of ΑΧΣ.

Figure 11. The "Wall" Periodic Table in St. Petersburg, at the Metrology Institute, 19 Moskovsky Pr., St. Petersburg, Russia (N59° 55.08 E30° 19.05), constructed in 1935.[22] *Two of the original elements included in this table—illinium and masurium— were eventually discredited. However, illinium ("Jl") remains, while masurium (which was originally assigned for element 43; directly above the "Jl," between "Mo" and "Ru") has been scraped off, probably for political reasons, rising from painful memories of World War I battles in the Masurian region.*[1b]

It is a tribute to the professionalism of chemistry that the relationship between Hopkins and James, albeit competitive, was always cordial. In the end, although both achieved great success in their research of rare earths, neither had ever actually understood that they never had in hand any sample containing element 61. The discovery of this element had to await the nuclear age with its new methods and technology. This is a story that reminds us of the philosophical words of Roald Hoffmann that the "voyagers of discovery" should lead us not into "false condescension" of criticism, but instead through the joyful travel "into lovely meandering paths, leading to an understanding of how chemistry really works."[2a] ⬡

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In addition, discussions with Marco Fontani and Mary Virginia Orna (authors of reference 2) were extremely valuable, furnishing details regarding the history of illinium and florentium (aka promethium).

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