5 / Intermezzo: The Search for Element 72[1]

ALTHOUGH THE ENUNCIATION of the Periodic Law of the Elements by D. I. Mendeleev (1834–1907) in 1869 brought system to the arrangement of the chemical elements and enabled the prediction of some yet to be discovered, it could not define the total number, largely because of the unknown number of rare earth elements falling between barium (atomic weight 137.33) and tantalum (atomic weight 180.95). Since barium is bivalent, the rare earths trivalent, and tantalum pentavalent, hindsight predicts that a quadrivalent element should exist between the rare earths and tantalum, but this does not seem to have been recognized.

The problem of the total number of elements was solved by H. G. J. Moseley (1888–1915). After graduation from Oxford in 1910 he joined Rutherford's research group at the University of Manchester. Work there was concentrated on problems of radioactivity and atomic structure, but the discovery of the diffraction of X–rays by crystals by Max von Laue in 1912 turned Moseley's attention to this new field. He used the diffraction technique to determine the wave lengths of X–rays produced by bombarding targets of specific elements with electrons. The results were published in two papers in the *Philosophical Magazine*, in December 1913 and May 1914. The second paper contained a listing of the elements from aluminum with atomic number (AN) 13 through gold (AN 79), and he stated "Every element from aluminum to gold is characterized by an integer N which determines its X–ray spectrum; this integer is the atomic number of the element." He identified three gaps in the sequence of elements, at atomic numbers 43, 61, and 75.

At that time it was believed that element 72 had been discovered in 1911 by Georges Urbain (1872–1938), a French chemist who spent many years separating and characterizing rare earth elements; he named it celtium. Urbain was impressed by Moseley's discovery and visited him in June 1914, bringing with him the precious separates supposedly containing celtium. In two days Moseley produced the

X–ray spectrum. Alas, the spectrum showed only the lines characteristic of ytterbium (AN 70) and lutetium (AN 71). Element 72 was still missing.

This was Moseley's last scientific work. Shortly thereafter he sailed for Australia to attend a meeting of the British Association for the Advancement of Science in Melbourne. World War I broke out during the meeting; Moseley hurried back to England to enlist and was posted to the Royal Engineers. Rutherford deplored the acceptance of such scientific talent into the armed forces and tried to have Moseley transferred to the National Physical Laboratory. The transfer was approved but not soon enough. Moseley had been sent to Gallipoli, where a Turkish bullet ended his life on August 10, 1915.

World War I and its aftermath largely suspended scientific research not directly related to the war effort. The search for element 72 was taken up again in 1922, this time in Copenhagen and in Oslo. The Danish physicist Niels Bohr (1885–1962), on the basis of his theory of atomic structure, predicted that this element could not be a rare earth, but must be quadrivalent and an analog of titanium and zirconium. During the summer of 1922 George de Hevesy, working in his institute, became interested in geochemistry and decided to look for this elusive element in zirconium minerals.

Hevesy had been a researcher in Rutherford's institute at the same time as Moseley, and they had become good friends. Indeed, Moseley invited Hevesy to join him in the summer of 1914 and work together on X–ray spectroscopy, an invitation postponed by his trip to Australia and terminated by the outbreak of war. Now Hevesy teamed up with Dirk Coster, a Dutch physicist who came to Bohr's institute in September 1922 to build an X–ray spectrograph. Hevesy obtained specimens of zirconium minerals from the Mineralogical Museum in Copenhagen. He treated the mineral zircon ($ZrSiO_4$) with boiling acid to remove the soluble constituents; the insoluble residue containing zirconium, and perhaps element 72, was fixed on the copper anticathode of the spectrograph. The first exposure taken by Coster showed spectral lines in the positions predicted for the missing element! Hevesy commented:[2] "The appliances at our disposal at that time were very primitive and it took us several weeks to secure conclusive evidence of the discovery of the element." In a letter to *Nature* dated January 2, 1923 and published in the January 20 issue Coster and Hevesy announced the discovery of element 72 in zircon and named it hafnium, from the Latin name for Copenhagen.

In 1922 Goldschmidt and Thomassen were using their newly built X–ray spectrograph for geochemical research, and were also looking for element 72. In the first issue of *Norsk Geologisk Tidsskrift* for 1923 they published an article dated January 31, 1923 entitled "Das Vorkommen [occurrence] des Elementes No. 72 [Hafnium] im Malacon und Alvit" (malacon and alvite are varieties of zircon).

Being beaten to the publication of the discovery of element 72 by only 29 days was a great disappointment to Goldschmidt. For years thereafter he devoted much time and effort in the search for the then unknown element 61. Since it is one of the rare earth elements, he analysed any new rare earth mineral received by the museum. By the 1930's, however, he decided that this element probably had no stable isotope and did not occur naturally. This was confirmed in the 1940's, when the element was identified as one of the products of the fission of uranium, and named promethium (Prometheus, according to mythology, stole fire from heaven); several isotopes are known, the longest–lived having a half–life of 17.7 years.

Goldschmidt sent a sample of his alvite to Hevesy, who confirmed its high hafnium content (16% HfO_2, whereas in most zircons HfO_2 ranged from 1.3 to 6%). Hevesy included this result among others in an invited lecture at the 1923 annual meeting of the German Chemical Society in Berlin. When Goldschmidt learned from Norwegian colleagues present at the meeting that Hevesy had omitted reference to his gift of this particular specimen, he, as Hevesy says, "cut off all connection." Friendly relations, however, were restored when proper reference appeared in the published proceedings. Sensitivity on professional issues, however, remained; a new incident occurred in 1925. This is suggested by the following letter from Goldschmidt, presumably provoked by a complaint from Hevesy about institutional priority distortions apparent from a Danish newspaper account of a lecture given by Goldschmidt:[3]

> "Dear Colleague, Through Prof. Størmer I just received the Danish "Nationaltidende" [Copenhagen newspaper] of February 3. On page 6 is a note about the lecture which I have given, and which can give the erroneous impression that I have ascribed to myself results which are due to others, especially also to your Institute. I have self–evidently in my lecture drawn full attention to the fact that the quantitative X–ray spectral analysis has been used first in Copenhagen, and this is also expressly indicated in the sole Norwegian newspaper report. As you will see from this report, which I permit myself to attach, I have in no way tried to ascribe to myself results that are due to other institutions. That "Aftenposten" [Oslo newspaper] has brought some unfortunate superlatives also in connection with my person is of course to be regretted, but I will under any circumstances place great value on your seeing the article so that the impression shall not be made in Copenhagen that I will steal well deserved fame from Bohr's Institute. If you would regard it as necessary or desirable, I wish to ask you to present the Aftenposten article in original to the Nationaltidende. I assume that the Nationaltidende note must concern a misinterpreted review of the article by cable or telephone. The lecture which I gave was in reality concerned especially with quantitative spectral

analysis and determination of the variability of sensitivity in different spectral regions, and a review of Thomassen's experiences in qualitative X-ray spectrography. Further I also showed the first spectrograms which were taken with diamond crystals. If you are interested, alvite can perhaps now be obtained with 7–8% hafnium oxide from a new deposit which has been found this winter. With best regards, Yours sincerely, V. M. Goldschmidt."

Despite its late discovery, hafnium is not an exceedingly rare element.[4] In the Earth's crust it is more abundant than the familiar elements arsenic and tin. Goldschmidt referred to it as a *camouflaged element,* which because of its great similarity to a more abundant element forms no minerals of its own, but is always dispersed in small amounts in the minerals of the more abundant element.

In March 1940 I had the privilege of meeting Hevesy over dinner in Goldschmidt's home, where he was staying as a house guest. He spoke fascinatingly of the work he was doing on the use of radioactive tracers in biological research, and when I expressed interest he invited me to be a guest at his institute in Copenhagen during the summer. In April, however, the Germans invaded Denmark and Norway, effectively negating that attractive invitation!