
CURRENT SCIENCE — 50 YEARS AGO

The Discovery of Hafnium*

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INTRODUCTION

THE discovery of about four-fifths of the chemical elements without any guidance from the theoretical side and without the aid of the powerful tool provided by spectroscopy, is an outstanding and everlasting monument of the skill, industry, and genius of the experimental chemist. It is with great admiration and deep reverence that we read the papers of the pioneers who succeeded with the primitive tools and methods of their time in discovering and isolating the large majority of the elements. The work of the discoverers of the elements was immensely facilitated later by the introduction of the spectrograph into chemical analysis and by the generalisation put forward by Mendeleeff. It was the guidance offered by the latter which led to the discovery of scandium, gallium, germanium, and recently of rhenium. The periodic classification, so far-reaching in its basic conception and in its applications, failed nevertheless to explain the existence and to limit the realm of the groups of triads and of the large family of rare earth elements. From Moseley's work we could conclude that no more triads are to be expected and that the rare earth group (incl. lanthanum) is limited to a maximum of 16 elements. But the significance of the groups of triads and of the rare earth group was still unexplained and the exact size of the latter still unknown. An explanation was hardly to be expected without a deeper insight into the nature of the periodic classification. Niels Bohr gained such an insight in the course of his classical studies on the building up of the atoms of the chemical elements from nuclei and electrons.

One of the most important points in Bohr's electronic arrangement is that on passing from one element to the next one the number of electrons increases by one, the new electron usually being added to an outermost electronic shell. As the chemical behaviour of the atom depends chiefly on

the outermost shell, neighbouring elements in the periodic table will, in most cases, be chemically very different; but in some cases the electronic arrangements might differ in such a way as to give successive elements similar properties. The newly added electron tries to find as stable a configuration as possible and it may happen that an innershell successfully competes with the outermost one in capturing the electron. Such an event is first encountered in the case of scandium, but the most conspicuous one is that of cerium. In the latter case the preference for the new electron is not given to the outermost *P* shell, nor even to the next one *O*, but is given to the inner shell *N*. After cerium come a number of elements all characterised by the binding of the newly coming electron in the deep *N* shell and it is clear that in this group of elements, all having the same configuration in their outermost shell and differing only in an inner one, the individual members will not differ very distinctly in chemical properties.

In the light of these considerations the existence of the so-called "rare earth" group is no longer an unexplained anomaly of the periodic system but a natural consequence of its development. As the *N* group has 32 electrons and 18 were already present in xenon and the preceding elements, the number of rare earth elements cannot exceed 14 including cerium. Cerium being of atomic number 58, the last rare earth element must have an atomic number 71; element 72 must belong to the titanium and 73 to the vanadium group. In conflict with this conclusion, the literature records the existence of 15 rare earth elements, including cerium and the missing element 61. These 15 elements include also number 72 which, however, according to Bohr's theory, should belong to the titanium group. Besides giving a deep insight into the nature of the periodic classification of the element Bohr's considerations thus supplied an effective guidance in searching for element 72 in the same sort of way that Mendeleeff's generalisation guided the discoverer of scandium, gallium, germanium, and rhenium. I have been asked by the Editor

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of *Current Science* to describe the discovery of hafnium and it is with great pleasure that I write the contribution requested by this high-standing periodical.

DISCOVERY OF HAFNIUM

Bohr's theory of the arrangement of the electrons in the different chemical elements was the impetus for the search for a missing member of the titanium group in exactly the same way as Mendeleeff's generalisation induced the search for other missing members of the periodic system. It is of interest to note that in Bohr's famous paper, so far-reaching in its interpretation of the phenomena of optical and X-ray spectroscopy, magnetism, and chemistry, the suggestion that, contrary to the claim of Urbain and his followers, element 72 is not a trivalent element of the rare earth group but a tetravalent of the titanium group, has had to content itself with a modest footnote. It is not too much to say that only in a very few cases has the following up of the suggestions given in the footnotes of scientific publications led to such striking results as in the present instance. But the impetus given, however important, was far from being sufficient and the discovery of the element 72 as due to the happy coincidence of several different events. Six months after the publication of Bohr's famous paper the present writer embarked on the study of geochemical papers including the first publication of Goldschmidt on the distribution of the chemical elements, a paper which was later followed by a long series of most illuminating and unrivalled papers by the famous Norwegian scientist. The study of geochemistry led my interest to the problem of missing elements including element 72. It seemed, however, very doubtful whether the concentration of the element in question would be sufficient to detect it; nor was it clear at the time whether element 72 should be looked for in thorium or in zirconium minerals. I decided to search for the element when a suitable opportunity presented

itself. It happened that Coster, who was even then an authority on X-ray spectroscopy, joined the Bohr institute. We made plans for a joint investigation of the effect of very intense and hard X-ray radiation on the rate of radioactive disintegration of radio-lead, by measuring the β -activity of a radio-lead plate before and after irradiation with X-rays. While we were waiting for the necessary equipment, I suggested to Dr Coster that we might look for element 72. We did not know at the time whether this element would be found associated with thorium or with zirconium but considered the latter the more probable. Professor Böggild, Director of the Mineralogical Museum of Copenhagen, kindly supplied me with samples of Norwegian and of Greenland Zircon, and after treating them with boiling acids to remove the soluble constituents, the pulverised sample was fixed on to a copper anticathode. The first exposure taken by Dr Coster, revealed at once the presence of the element looked for. We then tried to identify the hafnium α_1 line in other zirconium-minerals and also in commercial zirconium preparations, and were successful in every case. The next step was to try to identify other X-ray lines, α_2 , β , γ , and so on, and finally to endeavour to change the intensity of the α_1 line by chemical treatment of the mineral. I was much impressed in those days by Marignac's beautiful researches on zirconium double fluorides and this led us to extract potassium-zirconium-fluorides from zircon and to crystallise that compound repeatedly. As the solubility of K_2ZrF_6 is fairly pronounced, while that of the thorium salt is very slight, we expected the corresponding compound of element 72 to concentrate in the crystals. The hafnium line obtained from the crystals was, however, much weaker than the line given by the original minerals whereas the mother liquor showed a very marked increase in its hafnium content. It was after we had successfully separated hafnium from zirconium by chemical means that Coster and the present writer announced the discovery of the new element, proposing for it the Latin name of Copenhagen, *Hafnium*.

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