

50 YEARS OF CURRENT SCIENCE—GLEANINGS

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 inner shell 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 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

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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 was 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-ray. 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 Boggild, 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 a_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, a_2 , β , γ and so on, and finally to endeavour to change the intensity of the a_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*.

Our next aim was to elucidate the optical spectrum of the new element. We hoped to obtain both the arc and the spark spectrum from the mother liquor of a double fluoride crystallisation of the mineral in which hafnium was first found. Hansen and Werner, who photographed the spectrum found; however, only a very intense niobium spectrum free of tantalum lines. This result, which discouraged them at first, was due to the fact that the double fluoride of the oxyniobate is a very soluble compound, much more soluble than the soluble fluoride of tantalum, zirconium, or even hafnium, so that niobium concentrated in the most soluble fraction. The present writer did not share that discouragement but thought the next best fraction must contain a hafnium concentrate, and this was found to be actually the case. The elaborate work of Meggers identified several thousand lines of the hafnium spectrum, and he showed too that 26 of these lines are to be found among those ascribed by Exner and Haschek to zirconium. On the other hand in the arc spectrum of zirconium measured by Rowland only one hafnium line occurs. By noticing this discrepancy in the zirconium spectrum given by Exner and Haschek and by Rowland it should have been possible to have discovered hafnium many years ago. Accurate atomic weight determinations carried out on zirconium of different origin might also have led to the discovery of the element, but the methods used in early days, which were based on the analysis of the sulphate, selenide, or oxychloride were not trustworthy and yielded mostly values too low, the error being, however, to a large extent compensated by the presence of an appreciable amount of hafnium in the preparations investigated. Venable and Bell, on the other hand, who were the first to use the modern methods of determining the atomic weight of zirconium, namely, the analysis of the tetrachloride, found in spite of very careful work, too high a value, due, as the present writer was able to ascertain, to the presence of 0.7 to 1.0 per cent. hafnium oxide in the zirconium used. While an early discovery of element 72 might have been achieved by comparing the optical spectrum, the atomic weight, or the density of zircon extracted from different minerals, one can hardly

imagine that this element could have been discovered by following up the chemical reactions of zirconium compounds of different origin. The chemical similarity between the compounds of zirconium and hafnium is as close as, or closer than, that between any other pair of elements in the Periodic Table. We were very fortunate when we embarked on the separation of hafnium from zirconium, to hit straightaway on just the two compounds which are most suitable for making the separation desired. These are the phosphates and the potassium (or ammonium) hexafluorides. The hafnium compounds prepared on a semi-commercial scale by the "Auer-Gesellschaft" in Berlin are obtained by crystallisation of the fluorides. Van Arkel, de Boer and their associates in the laboratory of the Philips Lamp Works, in preparing single crystals of hafnium metal by a very ingenious method, obtained a separation by precipitation of the phosphates. The close chemical relationship between the compounds of zirconium and hafnium is also shown by the fact that no chemical reaction is known which would be shown by one of these elements and not the other, and also that zirconium never occurs in minerals without hafnium and *vice versa*. This close similarity was not expected by us when we started our search for missing element 72; although, as was shown a few years later by the present writer, such similarity is to be expected on the basis of the quantum theory of atomic structure.

The chemical character of an element is defined, according to Bohr's views, by the charge on the nucleus of the atom and the attraction exerted by the charge on the electrons of the outermost shell. An increase in the nuclear charge without a change in the arrangement of the electrons has the effect of binding the outer electrons more tightly and the atom becomes less basic. In the vertical groups of the Mendeleeff system such an increase in charge takes place from the lower to the higher elements, but at the same time the valency electrons are displaced further and further from the nucleus into quantum orbits of higher quantum number. On account of this fact the increased attraction—which is an effect of the increase in the nuclear charge—is actually overcompensated by the greater distance of the outer electrons from the nucleus and the higher members become more basic than the lower. Barium has a nuclear charge 18 units higher than strontium and yet it is the more basic element. In comparing hafnium with zirconium we find difference in nuclear charge of 32 units, much more than in the case of barium and strontium, while the difference in the quantum number of the orbits is the same in the two cases. In comparing barium and strontium with zirconium and hafnium we have in both cases the same difference in the quantum number of the valency electrons, but in the latter case the much greater difference in nuclear charge, 32 units, can no

longer be compensated by the increase in the quantum number of the valency electrons and hafnium is therefore but inappreciably more basic than zirconium. We can always imagine two atoms of very different nuclear charge showing practically the same chemical behaviour provided that the quantum numbers of the valency electrons differ sufficiently to compensate exactly for the difference in nuclear charge.

The next question which occurs is: why has hafnium a nuclear charge so much larger than zirconium? The difference is due to the presence of the 14 rare earth elements before hafnium. That the appearance of the rare earth elements is responsible for the extreme similarity between zirconium and hafnium becomes apparent when we try to draw up a fictitious periodic table containing no rare earth elements and deduce the properties of the element that would follow lanthanum in such a table. After lanthanum there would be a "pseudo-hafnium", a "pseudo-tantalum," a "pseudo-tungsten" and so on. These pseudo-elements would all be more reactive than the genuine one because their valency electrons would be less tightly bound. "Pseudo-hafnium", would have a density of 9 instead of 13, "pseudo-tantalum" 14 instead of 17, "pseudo-tungsten" 15 instead of 19. Although these pseudo-metals are a mere fiction their compounds are not fictitious. The quadrivalent compounds of "pseudo-hafnium" are known and in fact are identical with the ceric compounds. This is obvious from a single inspection of the electronic grouping shown in the following table.

TABLE.
*Electronic Arrangement showing the Identity Cerium⁺
and Pseudohafnium⁺⁺⁺*

Hafnium			Hafnium ⁺⁺⁺		
N	Q	P	N	Q	P
s p d f	s p d	s	s p d f	s p d	s
2 6 10 14	2 6 2	2	2 6 10 14	2 6 -	-
Pseudo-hafnium			Pseudo-hafnium ⁺⁺⁺		
N	O	P	N	O	P
s p d f	s p d	s	s p d f	s p d	s
2 6 10 -	2 6 2	2	2 6 10 -	2 6 -	-
Cerium			Cerium ⁺⁺⁺		
N	O	P	N	O	P
s p d f	s p d	s	s p d f	s p d	s
2 6 10 1	2 6 1	2	2 6 10 -	2 6 -	-

As is to be expected, the anomalous behaviour of the ionic sizes of the oxides disappears if we replace the hafnium ion by the ceric ion. This observation is not without interest in connection with the earlier, apparently insuperable, difficulty of deciding whether to place cerium in the third or in the fourth group of the Periodic Table. The cerium atom and the cerous ion are not directly related to zirconium, but the ceric ion is the pseudo-homologue of the zirconium ion. Similarly the quinquevalent praseodymium ion would be the pseudo-homologue of the niobium ion.

The investigation of a very large number of zirconium minerals and also of rock samples led to the

result that hafnium always accompanies zirconium in nature. Zirconium is chiefly found as zircon and in most cases the hafnium oxide content of zircon is 1.5 to 2.5 gm. hafnium oxide in 100 gm. $ZrO_2 + HfO_2$. From the above figures and also from analysis of the hafnium-zirconium ratio in meteoric stones, it follows that in the fluid-gaseous stage of our solar system a zirconium-hafnium ratio of about 60:1 prevailed throughout and, on account of their similarity, the same ratio is found in present lithosphere. About 1/200,000 part of the earth crust is built up of hafnium, the terrestrial abundance of the latter being as large as that of arsenic, molybdenum or tin.

ANNOUNCEMENT

COAL SCIENTISTS AWARD FOR 1981 - CENTRAL FUEL RESEARCH INSTITUTE DHANBAD

Ministry of Energy and Coal (Department of Coal) has instituted two annual awards for meritorious research in the fields of application oriented basic research or development research in Coal Science and Technology. The Awards will be of two categories, a "Senior Coal Scientist Award" open to all research, development and technological personnel connected with coal science and its utilisation and the other "Junior Scientist Award" restricted to similar personnel but below the age of 40 on first January of the year for which the Award is made.

Organisational aspects of the awards will be by Central Fuel Research Institute, Dhanbad. The awards will carry a cash prize of Rs. 5,000/- and Rs. 3,000/- respectively besides a Gold Medal.

Nominations are invited for Awards for the year 1981 on or before 31.5.82. Applications and rules and regulations regarding the awards are given by the above Institution.

Nominations for the awards can be made by Directors of IITs, CSIR National Laboratories and other Research Institutions, Deans of Science, Engineering and Technology, Deans of Faculties and

Head of Institutions of Universities, Learned and Professional Societies/Organisations. Managing Director/General Managers of Coal-based industry, N.R.D.C., N.P.C. etc. and all relevant organisations concerned with coal in any way could also recommend persons. Individuals can also apply for the Awards through the Heads of their organizations who should vouchsafe for the statements made by the applicants.

Each nominations (in 10 copies) should accompanied by a detailed statement of work and attainment of the nominee and a critical assessment in not more than 500 words bringing out the importance of the significant research and development contributions of the nominee made during 5 years preceding the year of the Award.

Nominations should be sent in sealed cover marked to the Director, Central Fuel Research Institute, P.O. FRI 828 108, Dist. Dhanbad (Bihar). The selected Awardees will be informed of the results directly, and also through various media of information.

Further details can be obtained from Samir Sen, Information and Liaison Officer, Central Fuel Research Institute, P.O. FRI Dist. Dhanbad, (Bihar).
