THE MINERALOGY OF HAFNIUM*

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Although it has been but a scant five years since the advent of hafnium (1), the missing element of atomic number 72, a considerable literature has accumulated, one of the most complete accounts of the element being embodied in the recent monograph by the discoverer, Georg v. Hevesy (44). The papers published, however, have dealt almost exclusively with the chemistry and physics of the metal, and little has been said about the minerals in which it is found. As there are indications that hafnium is emerging from the laboratory to the ranks of the commercial rarer metals, some account of this rather neglected phase of the subject is of general interest and may be of assistance in making the metal more accessible. Inasmuch as elements closely related chemically are often coupled in minerals, as, for example, copper and silver, zinc and cadmium, gallium and indium, germanium and tin, columbium and tantalum, molybdenum and tungsten, and the rare earths, it will be instructive briefly to review the salient facts which led to the association of hafnium with zirconium and its discovery therewith.

THE RARE EARTHS AND THEIR RELATION TO HAFNIA

Ever since Mendelejeff and Lothar Meyer conceived their periodic arrangement of the elements, certain discrepancies were known but ignored for the sake of the more fundamental harmony. The magnetic triad of iron, cobalt and nickel, and the noble ones of the platinum metals were disturbing, but even more so were that significant group of numerous metals follow-

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* Based on a paper presented to the New York Section of the American Chemical Society, December 10, 1926.

ing barium, known collectively as the rare earths. So far as then known, other triads could follow and new rare earths might

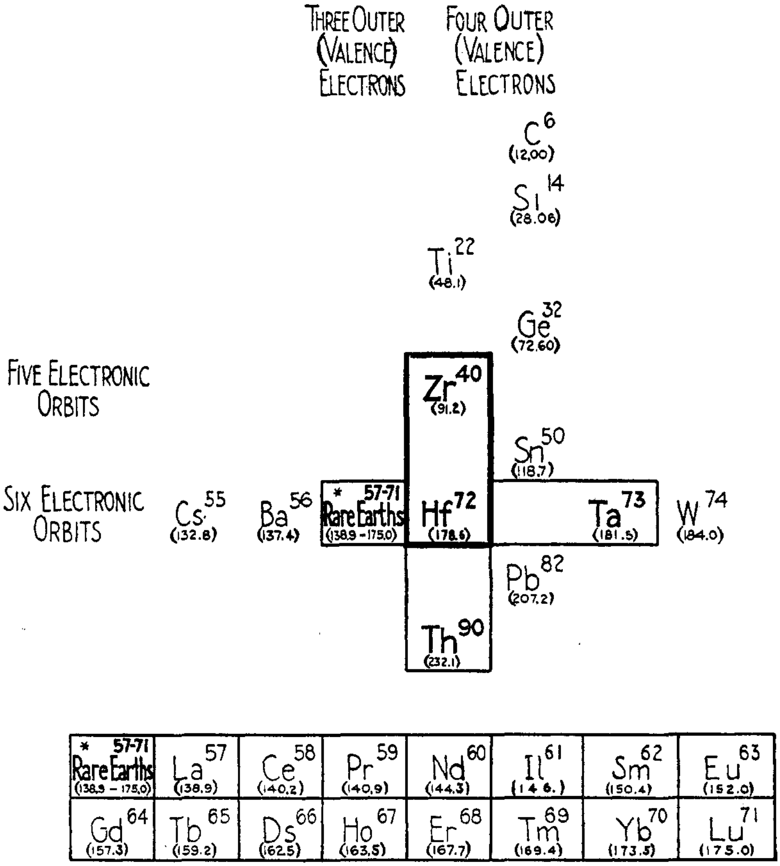

FIG. 1. HAFNIUM AND RELATED ELEMENTS ARRANGED ACCORDING TO MOSELEY'S LAW OF ATOMIC NUMBERS[1]
(Atomic weights[2] given in parentheses)

be sought; in a word, no valid limitation could be placed on the number of elements possible, and it might even be greater

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[1] After H. D. Hubbard, U. S. Bureau of Standards, Periodic Chart of the Atoms, Pub. W. M. Welch Mfg. Co., Chicago, Ill., 1926.

[2] Berichte **60**, 1; 1 (1927), Il excepted.

than could be accommodated by the periodic system. Mendelejeff estimated the rare earths as numbering twenty. But Moseley's concept of atomic numbers has demonstrated that there is room for but fifteen, all now known since Hopkins' discovery (2) of element number 61, illinium.

Of the fourteen rare earths known at the time of Moseley's postulation, those with atomic number 70 and 71 were the last discovered. In 1878, Marignac isolated a new earth from the old erbia, slightly more basic, and which was named ytterbium. In 1905, Welsbach found that ytterbium was a mixture of two elements, and in 1907 named them aldebaranium and cassiopeium, and they have since been identified as elements number 70 and 71. Urbain, however, had already confirmed their entity and named them neoytterbium and lutecium, and the names finally adopted in 1914 were ytterbium and lutecium. It was suspected by both Welsbach and Urbain that Marignac's ytterbium contained yet a third element, and both investigators carefully searched for it. Welsbach failed to find any, but Urbain was more successful, and in 1911 announced the discovery of this new rare earth which he called celtium. In 1922, Dauvillier stated that Urbain's preparation showed faint traces of elements number 69 and 72 in addition, indicating in 1923 that element 72 was present in the proportion of about 1:10,000. Meanwhile, Hevesy had taken up the question, and in 1922, by virtue of the quantum theory of atomic structure (3) asserted that element 72 should indeed be a constituent of an "old element," but of "zirconium" and not of "ytterbium" (fig. 1).

PROBABLE ABUNDANCE OF THE MISSING ELEMENT, AND RESEMBLANCE TO ZIRCONIUM

It could not be foretold by the pioneer investigators whether element No. 72 was abundant enough in a mineral to be recognized in the specimens to be examined, but there was good reason to believe that the element sought was not rare. For instance, it was known that elements with odd atomic numbers, such as gallium, 31, indium, 49, and thallium, 81, are much more scarce than those with even, such as germanium, 32, tin, 50, and lead, 82. A study of the relative abundance of silica, titanium, zirconium and thorium in the lithosphere was also reassuring on this point, their oxides being found in the earth's crust in the percentages respectively of 59.09, 1.05, 0.04 and 0.002.

Bohr's theory of atomic structure (3) demanded that element 72 must differ entirely in its outer structure from that possessed by the rare earths which precede it, so that the difference between lutecium and element 72 is greater than that of any two of the rare earths. In addition, its atomic structure shows a very marked analogy to that of element number 40, zirconium. The simultaneous addition of another electron with one more in the outer ring causes element 72 to be quadrivalent. All these considerations gave weight to the belief that element 72 must be analogous to zirconium and therefore likely to be found with it, thus leading to the examination of zirconium minerals and preparations in which the new element was soon identified and isolated.[3] This association is so characteristic that as yet hafnium has not been found other than with the older element discovered by Klaproth in 1789.

The chemical similarity of the two metals is so great that their separation is attended with difficulty, for *hafnium and zirconium exhibit the same chemical reactions.* The fractionation of the hexafluorides makes possible a separation which, while much more difficult than that of columbium and tantalum, is nevertheless easier than most rare earth separations (4).

SUGGESTED USE OF CLERICI SOLUTION FOR THE CONTROL OF HIGHER FRACTIONATION

In connection with the resolution of the fluorides of hafnium and zirconium, it occurred to the writer that the little known Clerici solution (5) (6) (7) (8), a molecular mixture of thallium malonate and thallium formate, might be used for testing the

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[3] A small sample of the first metallic hafnium ever made, presented by G. Hevesy, the discoverer, is on permanent exhibition at the American Museum of Natural History, New York, in the Element Collection being compiled by G. F. Kunz, Curator of Research.

ammonium hafnium-zirconium hexafluoride crystals with densities too high to float on even fortified methylene iodide, if not soluble or incompatible.

Through the generosity of C. Palache of the Department of Mineralogy, Harvard University, some Clerici solution was placed at the author's disposal, and it was ascertained that ammonium hexafluozirconate floats readily in the diluted solution without sensible solution or decomposition. The only ammonium fluohafniate available appeared in tetragonal instead of monoclinic form, and was possibly heptafluoride. However, it sank in methylene iodide but less readily in the dilute Clerici solution. The finer crystals slowly dissolved, but the coarser ones remained a long time, ample for observation, so that it is believed that this mineralogical reagent should prove useful in advanced hafnium fractionation.

THE OCCURRENCE OF HAFNIUM IN NATURE

It will be recalled that in the case of chlorine, no matter from what source it may have been derived, the atomic weight is always the same in spite of the fact that it is a mixture of two isotopes of atomic weights 35 and 37. All the chemical vicissitudes of eons have not disturbed the ratio which was presumably present in the primeval homogeneous mixture. On the other hand, since zirconium and hafnium are chemically separable, some change should have taken place in their original ratio, reflecting in various minerals different geochemical processes in the earth's history. It has been demonstrated that this difference in the ratio of HfO_2 to ZrO_2 is a reality, and ranges from 0.007 for the bean-like favas of Brazil to 0.5 for the rare scandium mineral "befanamite" of Madagascar. In general, minerals of granitic origin exhibit a decidedly higher ratio, but the ratios are never so marked as those of less dissimilar elements occurring in pairs such as columbium and tantalum or molybdenum and tungsten. The association of Hf and Zr and other paired elements finds an adequate explanation in the studies of Goldschmidt (9) which support his belief that the geochemical distribution of the elements is conditioned by the electron shell.

TABLE 1

List of zirconium minerals known to contain hafnium

(Specific paired analyses are italicized)

NAME	FORMULA	Per cent ZrO_2	Per cent HfO_2
Baddeleyite (distinct crystals)	ZrO_2	96.5–*97.7*–98.9	*1.2*
Syn. Brazilite (fibrous, botryoidal, columnar)	ZrO_2	71–93	
Syn. var. (rock) Jacupirangite (crystallized)	ZrO_2		
Zirconia ore: 1. Favas (alluvial pebbles)	ZrO_2	*59–74–92.4*	*0.5–0.5–0.7*
2. "Zirkite" (mixture): Brazilite	ZrO_2	71–93	
Zircon	$ZrO_2 \cdot SiO_2$	67	
		80–85	
Unnamed Zr silicate (orvillite?)	?	75	
Catapleite	$(Na_2, Ca)O \cdot ZrO_2 \cdot 3SiO_2 \cdot 2H_2O$	*31.53*	*0.3*
Elpidite	$Na_2O \cdot ZrO_2 \cdot 6SiO_2 \cdot 3H_2O$	*20.28*	*0.2*
Eudialyte	$Na_{13}(CaFe)_6Cl(SiZr)_{20}O_{52}$	*12.20–14.32*	0.1–*0.2–0.17*
Var. Eucolite	$Na_{13}(CaFe)_6Cl(SiZr)_{20}O_{52}$	*12.21*	*0.2*
Polymignite	$5RTiO_3 \cdot 5RZrO_3 \cdot R(NbTa)_2O_6$ (R = Ce, Fe, Ca)	*29.11*	*0.6*
Pyrochlore	$CaNb_2O_6 \cdot NaF$	*2.90*	*tr.*
Rosenbuschite	$6CaSiO_3 \cdot 2Na_2ZrO_2F_2Ti(SiO_3)(TiO_3)$	*19.80*	*0.3*
Thortveitite	$(ScYt)_2Si_2O_7$	*2*	*0.5*
Var. "Befanamite"	$Sc_2Si_2O_7$	*1.3*	*1.0*
Wöhlerite	$13(CaNa_2)O \cdot 9SiO_2 \cdot 3ZrO_2 \cdot Nb_2O_5$	*15.61*	*0.5*
Zircon	$ZrO_2 \cdot SiO_2$	64.23	0.98*
Var. Hyacinth	$ZrO_2 \cdot SiO_2$	*64.83*	*1.2*
Alt. Alvite	$(Zr, Hf, Th, Be)O_2 \cdot SiO_2 \cdot nH_2O$	*41.98*	*4.6*
Cyrtolite	$R_3Y_2(Zr, Hf)(SiO_4)_{12}$	*52.4*	*5.5*
Malacon	$3(SiO_2 \cdot Zr, HfO_2) \cdot H_2O$	*53.2–65.18*	*3.4–2.6*
Naëgite	$ZrO_2 \cdot SiO_2$ with Yt, Th, Nb and Ta	*49.8*	*3.5*
Zirkelite	$(CaFe)O \cdot 2(ZrTiTh)O_2$	*51.89*	*1*

* Mean value from six analyses.

The hafnium content of virtually every known type of zirconium mineral has been determined, and it has developed that *in the case of zircons, the amount of hafnium is roughly proportional to the radioactivity* (10). The reason for this relation is interesting. The radioactivity is due to uranium and thorium, and hafnium is isomorphous with these elements (11). E. and G. Urbain (12) have discussed the presence of both hafnium and the yttrium elements in some zirconium minerals, and find that the more hafnium is present the larger the proportion of rare earths. Strangely enough, however, hafnium has not been found in any thorium mineral such as thorite or thorianite, nor in titanium minerals like rutile and ilmenite.

THE HAFNIUM CONTENT OF THE EARTH'S CRUST

If the average hafnium content of zirconium is assumed to be 3 per cent, the hafnium content of the earth's crust works out to be 1:100,000. Fortunately, nature has made the search easier by segregating the element in certain minerals, among which may be mentioned the following species, varieties and alterations in which hafnium has actually been determined (table 1).

Although numerous zirconium minerals have been investigated for their hafnium content, the field is by no means exhausted inasmuch as the species and varieties enumerated in table 2 are not specifically mentioned as having been tested. Most of these are very rare, and the status of some, such as the varieties of zircon, is not well defined; nevertheless it is of interest and value to test doubtful and even discredited species and varieties as an additional means of checking their validity.

THE OCCURRENCE OF HAFNIUM MINERALS IN THE UNITED STATES

Only two zirconium minerals have ever been systemmatically mined, the ortho silicate, zircon, and in more recent years, the native oxide, brazilite. Only the former occurs in this country and in commercial quantity in but three localities. Zircon was mined intermittently in western North Carolina from 1869 to 1911 (13), as much as 26 tons having been taken out in 1883 by

TABLE 2

List of zirconium minerals not reported investigated for hafnium

NAME	FORMULA	PER CENT OF ZrO_2
Astrophyllite	$(KNaH)_9(FeMnCaMg)_9(FeAl)[(TiZr)\cdot(OF_2)]_3[SiO_4]_9$	1.21–4.97
Beckelite	$Ca_3(YtCeLaNdPr)_4(SiZr)_3O_{15}$	2.5
Chalcolamprite	$R^{II}Nb_2O_6F_2\cdot R^{II}SiO_3$(R = Ce, Na, Zr and Ca) (allied to pyrochlore)	5.71
Endeiolite	$R^{II}Nb_2O_6(OH)_2R^{III}SiO_3$($R^{II}$ = Na_2, Ca; R^{III} = Ce)	3.78
Guarinite } identical?	$3CaSiO_3(Ca(FOH))NaZrO_3$	19.70
Hiortdahlite }	$6(Ca_2Si_2O_6)\cdot 2[(Na_2CaH_2)_2Zr_2F_4O_4]2/3[Ca(MgFeMn)(ZrTiSi)_2O_6]$	21.48
Johnstrupite	$Na_3Ca_8Ce_2(FOH)_7(SiO_3)_9$	2.84
Låvenite	$Na[ZrOF](MnCaFe)(SiO_3)_2$	28.79–28.90
Leucosphenite	$BaSi_4O_9\cdot 2Na_2(TiZr)Si_3O_9$	3.5
Loranskite (var. wiikite)	Tantalate of Yt, Ce, Zr, Fe, etc.	20.00
Lorenzenite (ramsayite)	$Na_2(TiZr)_4O_9\cdot Na_2Si_4O_9$	11.92
Mosandrite	Very near johnstrupite	7.43
Nohlite (var. samarskite)	Hydrated niobate of U, Yt and Fe	2.96
Oliveiraite (alt. euxenite)	$3ZrO_2\cdot 2TiO_2\cdot 2H_2O$	63.36
Orvillite (in zircon in "caldasite")	$8ZrO_2\cdot 6SiO_2\cdot 5H_2O$	68.04
Riebeckite (arfvedsonite)	$4Na_2SiO_3\cdot 5FeSiO_3\cdot 5Fe_2Si_3O_9$	0.75–4.7
Soda-catapleite (var. catapleite)	$Na_2O\cdot ZrO_2\cdot 3SiO_2\cdot 2H_2O$	30.80
Uhligite	$3\cdot 3Ca(TiZr)_2O_5\cdot Al_2TiO_5$	21.95
Zircon	$ZrO_2\cdot SiO_2$	
Alt. Auerbachite		38–61.53–69
Var. "Hagatalite"		42.0
Var. "Oyamalite"		40.9

W. E. Hidden (14). More recently, the Pablo Beach deposit of rare minerals on the East Coast of Florida has yielded 2 per cent of zircon sand as an adjunct to the electromagnetic separation of garnet, monazite, rutile and ilmenite. The zircon is stated to swell greatly when ground, disengaging large quantities of helium (15). The occurrence of a rich zirconiferous sandstone near Ashland, Va., has also been described (16). Unfortunately unaltered zircon does not appear to be a promising source of hafnium as the content is usually less than two per cent of HfO_2, although a specimen from Henderson County, N. C., is stated to contain more (17). Of the altered zircons, cyrtolite is by far the most common and widely distributed, having been reported from at least seven states—Mt. Antero, Colorado, Branchville, Conn., Rockport, Mass., Mitchell and Henderson Counties, N. C. (three localities) (18), Westchester County, N. Y., Pennsylvania (five localities) (19) and Llano County, Texas, and the Massachusetts and New York minerals have already been shown to be among the richest hafnium minerals known. In addition, a hydrated zircon from Amherst County, Virginia, first described by Mallett (20) is under examination.

The cyrtolite from Texas does not appear to have been analyzed for hafnium as yet, but since it is known to have given "good radiographs after twenty-four hours exposure" (21) it is a fair presumption that the mineral should prove a rich source of hafnia. Hidden and Mackintosh (22) state that it was abundant at the famous Baringer Hill locality during the mining of the yttria minerals, many hundred pounds having been found in a great variety of form and color, but this mine is no longer operated.

The cyrtolite from Rockport, Mass., is high in hafnia (9 to 17 per cent (?)), but very rare, and that from Connecticut and Colorado is also very sparing in occurrence, but the radioactive cyrtolite from Westchester County, New York, has twice been authenticated as high in hafnia and is fully as abundant as the Texas deposit.

THE OCCURRENCE OF HAFNIUM NEAR NEW YORK CITY

Up in the hills of Westchester County, near the historic village of Bedford, is a large feldspar mine which has long been a Mecca for mineralogists from the metropolitan district, since the great pegmatite vein to which the quarry owes its origin, is a prolific and unfailing source of a variety of those minerals which delight the collector. Among these may be mentioned asteriated rose quartz, beryl, columbite, garnet and black tourmaline.

Early in the history of the mine when the workings were not so deep, an unusual, heavy, dark brownish-black mineral of adamantine luster altering to brownish-red or chocolate color of duller aspect, was noticed. It occurred in pockets or isolated vugs in contact with both smoky quartz and orthoclase, intimately associated with yellowish secondary uranium minerals, one identified as autunite. The presence of these, coupled with the black color, unusual weight and pitchy luster, and tests for uranium, led to the mineral being mistaken for pitchblende or uraninite, then attracting considerable interest because of the recent discovery of radium.

FIG. 2. CYRTOLITE (ALTERED ZIRCON) RICH IN HAFNIA, FROM NEAR BEDFORD, WESTCHESTER COUNTY, NEW YORK

Characteristic curved tetragonal pyramidal crystals are shown penetrating feldspar. This mineral was used by C. James of the University of New Hampshire as the source of the first hafnium and pure zirconium salts prepared in this country (1924). Hafnia: 5.5 per cent (9.5 per cent of $ZrO_2 + HfO_2$). Zirconia: 52.4 per cent. Natural size.

L. V. Case of Tarrytown, N. Y., the original finder, submitted specimens to the department of mineralogy of Columbia University, New York, and Luquer (23) published a paper showing that the strange mineral was not pitchblende, but the altered zircon known as cyrtolite. It is characterized and named because of the curved form of its crystals, which are tetragonal pyramids not infrequently resembling rhombic dodecahedrons (fig. 2). The unaltered black portions of higher density were found to contain minute lacunae of uraninite, thus accounting for the uranium tests and alteration products, one of which was identified as uraconite, a mineral new to this locality. Striking radiographs are easily made with it (fig. 3), a fact of especial practical significance to the prospector and mining engineer. A rough analysis of the cyrtolite showed 27.24 per cent of silica, 53.56 per cent of zirconium oxide, and 1.14 to 4.35 per cent of uranium oxide, together with traces of copper, calcium, manganese, *"and probably of yttrium."* An exact analysis was not considered advisable because of the altered character of the mineral.

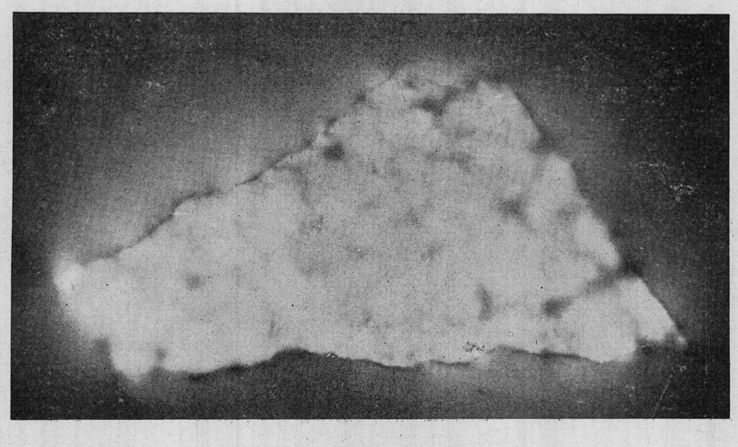

FIG. 3. RADIOGRAPH OF HIGHLY HAFNIFEROUS CYRTOLITE, NEAR BEDFORD, WESTCHESTER COUNTY, NEW YORK

Hafnia: 5.5 per cent (9.5 per cent of $ZrO_2 + HfO_2$). Zirconia: 52.4 per cent. Exposure: 22 days on bare plate. Courtesy of T. I. Miller, Newark Mineralogical Society, Newark, N. J.

About four years ago, the author recalling the statement italisized above, suggested to C. James of the University of New

Hampshire, that the suspected yttria might warrant detailed study, a fifteen pound sample of the mineral subsequently being forwarded. An investigation by him revealed that the presence of yttria, erbia, thulia, etc. was transcended by a notable percentage of the new element hafnium, approximately 10 per cent of hafnium oxide being present in the mixed $HfO_2 + ZrO_2$ as obtained from the mineral (24). In a later letter from Hevesy (25), James' original analysis was confirmed in that a preliminary analysis "very near to the final value" showed 9.5 per cent of hafnium oxide in the mixed zirconium-hafnium oxides which total 52.44 per cent. Unlike the Norwegian alvite, this unusual percentage of the New York mineral appears to be rather consistently maintained, although the yttrium earths are very variable, and a large

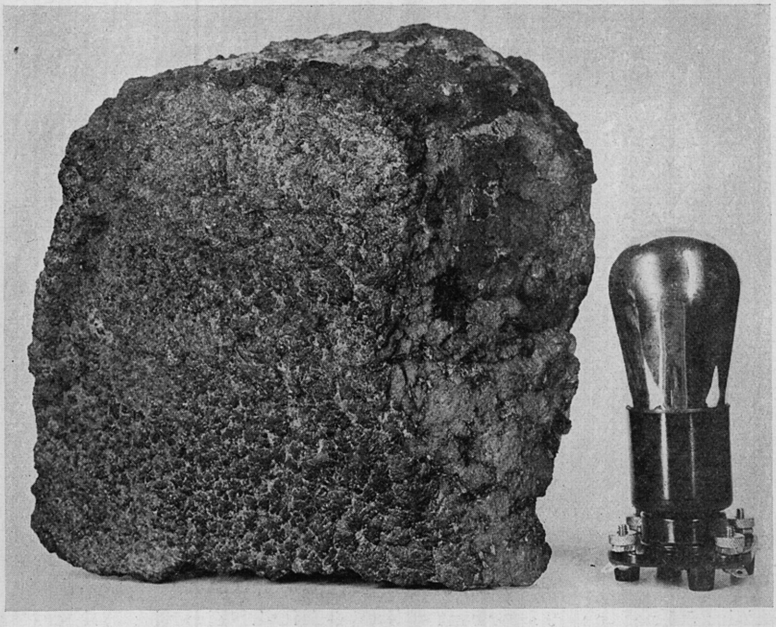

FIG. 4. LARGE SPECIMEN OF HIGHLY HAFNIFEROUS CYRTOLITE, NEAR BEDFORD, WESTCHESTER COUNTY, NEW YORK

Weight: 7.5 kgm. (16.5 pounds). Hafnia: 0.41 kgm. (0.91 pounds). (A standard radio tube is shown for comparison.)

quantity was afterwards successfully worked up by James for hafnium and the concomitant zirconium. This is believed to have constituted the first production of these elements in this country.[4] With the possible exception of the Rockport cyrtolite[5] the mineral occurring at Bedford is apparently the richest ore of hafnium yet reported (44). Although the deposit is of limited extent, specimens weighing ten or twelve pounds are not uncommon, and one is illustrated which perhaps contains more hafnium for its size than any other extant (fig. 4).

FOREIGN DEPOSITS OF HAFNIUM

Abroad, the principal commercial occurrences of zircon are in the monazite sands of Travancore, India, and of Brazil, and in the pegmatites of Southern Norway, but the mineral has largely lost its former importance as a source of zirconia because of the discovery of the native oxide, baddeleyite. The pure crystallized mineral has been known for thirty-five years, and has been reported from Ceylon, Italy, Sweden and Montana, but it remained for the Brazilian states of Minas Geraes and São Paulo to disclose to the world in 1915, zirconia ore in unprecedented quantity (26). The ore (fig. 5) outcrops on a mountainous plateau, and the methods of mining and transportation employed are very primitive owing to the distance from railroads and the rugged character of the region. Isolated boulders have been found weighing as much as 27¼ milliers (thirty tons), so that such a "specimen" would presumably contain from 136 to 190 kgm. (300 to 420 pounds) of hafnium oxide.

A third hafnium mineral of considerable interest is the com-

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[4] Specimens from G. Hevesy of the first hafnium and pure zirconium salts ever isolated, and of the first made in America, from C. James, may be seen in the Chandler Chemical Museum of Columbia University, New York, with related exhibits of historic interest, including Bedford cyrtolite from which the American salts were produced, and a cast lead dish used in their fractionation.

[5] A reprint of "Recherches sur les propriétés du hafnium" (København, 1925) received by the author from G. Hevesy contained the marginal annotation against the hafnia content of 17 per cent reported for analysis 23 (Cyrtolite, Rockport, Mass., U. S. A.), "Uncertain! Must be repeated." This is the same mineral previously reported (G. Hevesy and V. T. Jantzen, J. Chem. Soc. **123**, 3218 (1923), analysis 20) as giving 9 per cent of HfO_2.

plex eudialyte (and var. eucolite) reported in the United States only from Arkansas (27) and whose occurrence in Hibina-Toundra and Lujavr-urt in the Kola Peninsula of Russian Lapland was recently described by Fersman (28).

In spite of the trying nature of the district—1200 meters above sea level, covered with forests and swamps, infested with insects, devoid of roads, paths or habitations, with snow falling as early as August 9th—the Mineralogical Museum of the Academy of Sciences of the USSR, and the Research Institute of the North have sent six expeditions to this inhospitable country to collect the rare and unique minerals found there in profusion. Over five tons of specimens have been collected and are now in part displayed in Leningrad. Among them are about a dozen of the rarer zirconium minerals. Only the eudialyte has been analyzed for hafnium as yet so that this field is a virgin one.

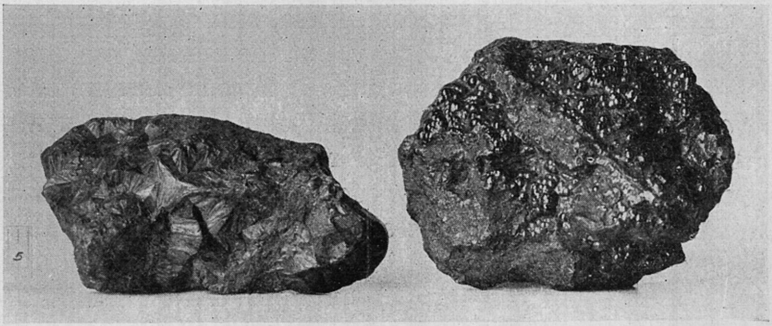

FIG. 5. LOW GRADE HAFNIA ORE ABUNDANT IN BRAZIL. FIBROUS AND BOTRYOIDAL BRAZILITE (BADDELEYITE), CALDAS REGION, STATES OF MINAS GERAES AND SÃO PAULO

Hafnia: 0.5–1.2 per cent. Zirconia: 71–93 per cent. Natural size

Gordon (29), however, in his description of the noted cryolite mine at Ivigtut, Greenland, notes that eudialyte is of common occurrence in the alkaline syenites about the Tunugdliarfik and Kangerdluarsuk fiords of the Julianehaab district; and 55 tons were collected for technical purposes according to K. J. V. Steenstrup (30). It occurs disseminated in the rock as well as in veins, and Gordon remarks, perhaps prophetically, that "this district should become an important producer of this mineral if a use for it is ever discovered." A typical specimen of this rare species from this remote locality is illustrated in Figure 6.

It is unfortunate that all of the three minerals aforementioned which are known to be abundant at favored but inaccessible localities, should be so lean in hafnia, even zircon seldom exceeding 1.2 per cent. In this connection, it is well to remember that James (31) has pointed out that *so long as one has a use for pure zirconium material, zirconia of very low hafnia concentration can be utilized.* From a strictly scientific viewpoint, the properties of pure zirconium, contaminated as it was for one hundred and thirty-four years, should claim equal attention with those of the offending hafnium, known for only five. Nevertheless, since commercial and historical zirconium preparations examined by Hevesy and others contained only small percentages of hafnium, the general properties already chronicled for the older element do not exhibit marked divergences from those found for

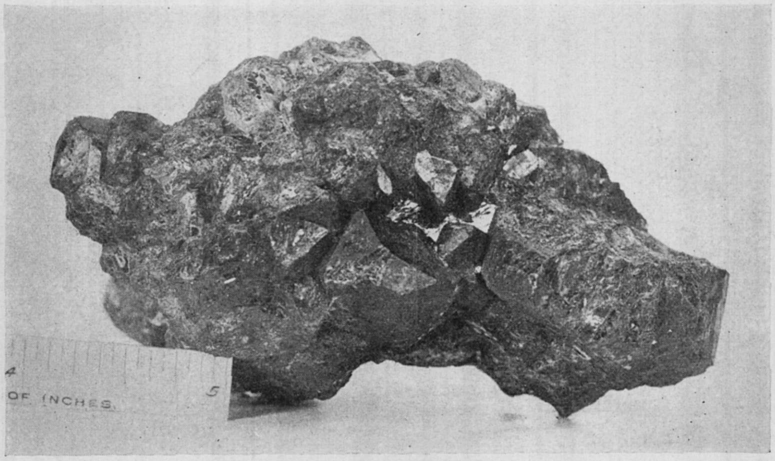

FIG. 6. A RARE AND COMPLEX HAFNIUM MINERAL COMMON IN SOUTHERN GREENLAND. TYPICAL CRYSTALLIZED EUDIALYTE FROM KANGERDLUARSUK
Hafnia. 0.17 per cent. Zirconia: 14.3 per cent. Natural size

TABLE 3

The occurrence of hafnium minerals by countries

LOCALITY	MINERAL	ZrO_2	HfO_2
Africa:			
Diego Suarez	Zircon		0.8
Madagascar	Zircon		0.9
Madagascar	Grey zircon		0.8
Madagascar, Befanamo	"Befanamite" (thortveitite)	1.3	1.0
Madagascar	Malacon (alt. zircon)	53.2	4.
Asia:			
Ceylon	Beccarite (var. zircon)		2.1
Ceylon	Reddish-brown zircon		2.7
Ceylon	Zirkelite	51.89	1.
India (Travancore?)	Zircon from monazite	64.0	1.2
Japan, Mino	Naëgite	48.30	7.
Japan, Naegi	Naëgite	49.8	3.5
Siam, Province of Chantaboon	Zircon (transparent blue)		4.?
Australia: No minerals have yet been definitely reported from the continent as containing hafnium			
Tasmania	Zircon		*
Tasmania	Greyish brown zircon		1.1
Europe:			
Austria, Carinthia	Zircon (transparent white)		4.?
France, Espailly (Le Puy)	Zircon (var. hyacinth; transparent red)	64.83	1.2
France, Espailly (Le Puy)	Zircon (var. hyacinth; transparent red)		0.7
France, Espailly (Le Puy)	Zircon (transparent green)		1.1
Italy, Lonedo	Zircon (yellow)		0.7
Italy, Lonedo	Zircon (red)		0.7

Italy, Vicenza	Zircon (transparent green)		0.8
Italy, Vesuvius	Zircon		0.7
Norway, Barkevik	Eudialyte (var. eucolite)	14.47	0.7
Norway, Barkevik	Eudialyte (var. eucolite)	12.21	0.2
Norway, Barkevik	Wöhlerite	15.61	0.5
Norway, Brevik	Zircon		1.0
Norway, Brevik	Reddish-brown zircon	63.2	1.0
Norway, Frederiksvärn	Polymignite	29.11	0.6
Norway, Frederiksvärn	Brown zircon	65.2	1.0
Norway, Gjersted	Alvite (alt. zircon)		9.
Norway, Iveland	Thortveitite	2	0.5
Norway, Hitterö	Malacon (alt. zircon)	65.18	2.6
Norway, Kragerö	Alvite (alt. zircon)	41.98	4.6
Norway, Kragerö	Alvite (alt. zircon)		3.
Norway, Kragerö	Alvite (alt. zircon)		8.
Norway, Kragerö	Alvite (alt. zircon)		15.
Norway,	Catapleite	31.52	0.3
Norway, Langesund	Brown zircon		1.7
Norway, Langesund	Rosenbuschite	19.80	0.3
Norway, Larvik	Greyish brown zircon		6.
Norway, Risör	Alvite (alt. Zircon)		10.
Norway	Grey syenite (rock)		3.8
Norway, Unneland	Thortveitite	0.8	1.1
Sweden, Alno	Pyrochlore	2.90	tr.
Russia, Miask	Greyish brown zircon	64.22	1.1
Russia, Rojkow Kliutsch, Ural	Brown zircon		0.5
Russia, Kola	Eudialyte (red)		0.1
North America:			
Canada, Eganville, Ont	Brown zircon		1.2
Canada, Renfrew County, Ont	Zircon		0.6

TABLE 3—*Continued*

LOCALITY	MINERAL	ZrO_2	HfO_2
North America—Continued:			
Greenland	Zircon		0.8
Greenland	Catapleite	31.53	0.3
Greenland, Narsarsuk	Elpidite	20.28	0.2
Greenland, Narsarsuk	Reddish-brown zircon		0.8
Greenland, Narsarsuk	Eudialyte (red)	12.20	0.2
Greenland, Narsarsuk	Eudialyte (brown)	12–16	0.6
Greenland, Kangerdluarsuk	Eudialyte	14.32	0.17
United States, Connecticut	Zircon		1.0
United States, Rockport, Massachusetts	Cyrtolite (alt. zircon)	40.	9.
United States, Rockport, Massachusetts	Cyrtolite (alt. zircon)	44.	17. (?)
United States, Bedford, New York	Cyrtolite (alt. zircon)	52.4	5.5
United States, North Carolina	Grey zircon		4. (?)
United States, North Carolina	Brown zircon		1.3
United States, North Carolina, Henderson County	Zircon		4.0(?)
Oceania: No minerals have yet been reported definitely as containing hafnium.			
South America:			
Brazil	Baddeleyite	97.7	1.2
Brazil	Fava	92.42	0.7
Brazil	Fava (shell)	59.	0.5
Brazil	Fava (nucleus)	74.	0.5
Brazil	Zircon separated from monazite sand	64.	0.4
Brazil, Caldas	Zircon		1.8
Brazil, Minas Geraes	Zircon		1.0

* "Very considerable."

hafnium-free zirconium preparations. On the other hand, the properties of hafnium are very remarkably different from those of zirconium, so that interest has naturally centered in the newer element and the minerals richest in it.

Of the altered zircons, cyrtolite is known in India, Madagascar, Italy, Sweden and Hybla, Ontario, and Norwegian alvite has been useful to the early investigators of hafnium, but does not seem to be a common mineral.

For the guidance of those interested, table 3 presents the distribution of zirconium minerals whose hafnium content has been definitely determined (32) but the list can ultimately be made far more comprehensive as more analyses accumulate.

It is to be feared that the prospector and the mining engineer will be compelled for some time to come to rely on well equipped chemists of skill and experience for authentic information concerning the actual hafnium content of suspected minerals and ores. Meanwhile, it may be useful to point out that since the various types of altered zircon which have proven richest in the new element, are pseudomorphic after zircon, it is not difficult to become accustomed to recognizing their square pyramidal form, particularly if specimens of the various alterations of zircon are studied. If such a mineral is identified and found to be in addition markedly radioactive, it is reasonably certain that the mineral under examination will prove to contain an appreciable percentage of hafnia.

CONCLUSION

In conclusion, it must not be forgotten that the discovery of hafnium has necessitated the revision and correction of all the data on zirconium so painfully acquired over the course of a century and a third. The International Critical Tables warns that "All zirconium salts (are) probably contaminated with 1–5 per cent of hafnium" (33). So far as hafnium is concerned, it is somewhat early to ask for what practical purpose it may ultimately prove singularly appropriate, for the process of accumulating and studying facts about it is still actively engaging the attention of many chemists and physicists. An excellent summary of the commercial uses of zirconium set forth by Meyer (34) will be found very suggestive, however, to those of a pragmatic turn of mind. It may be of interest also, to note that the close similarity of metallic hafnium to thorium coupled with its high melting point and electronic emissivity (35), have already led to patents being taken out for its use in lamp filaments, particularly those used in radio tubes (36).

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