CHEMISTRY

# The Newer Metals of Group IV

### "A Classic of Science"

# A Century of Chemical Progress Is in the Contrast of Hafnium's Prediction With the Others' Chance Discovery

#### Zirconium

KLEINE MINERALOGISCHE BEY-TRAEGE (Minor Mineralogical Contributions); vom Hrn. Prof. Klaproth. In Crell's Chemische Annalen für die Freunde der Naturlehre, Arzney-gelahrtheit, Haushaltungskunst und Manufacturen: I. Band, 1789.

THE analysis of zircon has given me almost as much trouble as that of corundum; on the other hand I have been rewarded by repeatedly finding an elemental earth which seems new to me. The complete account of my experiments on this mineral will appear in the next number of the present volume of Schriften der Berlin. Naturf Freunden. In the meantime I have determined the constituents of this kind of gem, in percentages:

Silica 31½; nickeliferous iron oxide ½; unknown earth, which seems new to me, 68. The contituents of corundum, after separation of the fine grains of magnetic iron interspersed with it, are ½3 alumina and ½3 an earth likewise strange to me, which, so long as it was not removed from its natural intimate combination with the alumina, would dissolve, although with difficulty; after accomplishing the separation from alumina, however, it proved entirely insoluble, in acids and in alkaline salts. The new earth from zircon on the contrary is insoluble in alkalies but easily soluble in acids.

My researches on the constitution of other precious stones are not yet complete enough for announcement. I am sorry that my results do not agree with the determinations of Mr. Bergmann and other analysts.

#### Titanium Found in Menakanite

BEOBACHTUNGEN UND VER-SUCHE UBER DEN MENAKANITE, einen in Cornwall gefundenen magnetischen Sand; vom Hrn. William Gregor. (Observations and experiments in a magnetic sand found in Cornwall; by Mr. William McGregor). In Crell's Chemische Annalen . . . I. Band, 1791.

This sand is found in great abundance in a valley in the parish of Menakan in the county of Cornwall. Through this valley flows a brook whose source is in the valleys of Gonhilly. The sand is black, and has externally a resemblance to gunpowder. Its grains are of various sizes and have no definite shape. It is mixed with another dirtywhite sand, whose grains are much finer. The specific gravity of the black sand, separated from the other by a sieve, was to that of distilled water, by the method of Mr. de Lugart,=4.427:1. It is easily reduced to a fine powder, and is magnetic. . . .

[A long account follows of the experiments made upon this mineral. These lead McGregor to the following conclusion.]

I send in this letter scattered facts rather than a completed research. And I do not offer you my theory for the purpose of securing priority of publication; I leave such clever work to sharper philosophers than I.—My friend, Mr John Hawkins, has seen this sand, and has confessed to me that he has never seen a mineral like it. Such an expression from a man so outstanding in mineralogy, combined with the unusual properties of the sand, have led me to think that it contains a new metallic substance. In order to distinguish it from others I have ventured to give it a name suggested by the place where it is found (that is in the parish Menackan), and on that account the metal could also be called Menakanite. The researches of other chemists, may perhaps, by explaining its strange properties, rob it of its novelty. Other matters have hindered me from carrying out further the research from which I have already won this much, onto the sure ground of experience. But the scattered facts which I have laid before you here may help to save much trouble for others who take up the examination of this strange substance.



MARTIN HEINRICH KLAPROTH (1743-1817)

a German apothecary who advanced the methods for chemical analysis of minerals. In addition to his discovery of zirconium as told here, he isolated the metal from "menakanite" and renamed it titanium. Uranium and cerium are also his finds.

#### Thorium

UNTERSUCHUNG EINES NEUEN MINERALS und einer darin enthaltenen zuvor unbekannten Erde. (Examination of a new mineral and a hitherto unknown earth contained in it); von J. J. Berzelius. In Annalen der Physik und Chemie, Jahrgang 1829, Siebentes Stück.

The mineral, the examination of which I am reporting here, occurs on Löv-ön, an island lying in the sea near Brevig in Norway, in syenite. It was itself discovered by Rev. Esmark, a son of the famous professor of mineralogy in the University of Christiana, Jens Esmark, who recently sent me a sample of this mineral for analysis, because, on account of its great specific gravity, he suspected tantalum in it. . . .

This mineral contains a hitherto unknown metallic body, which from its properties belongs to those which comprise the so-called true earths; its oxide is an earth, which is most like the earth of zircon, and which, strangely enough, possesses most of the properties and earmarks which I found for thorium earth in my former description of it. This circumstance at first made me think that thorium earth might possibly not be merely basic yttrium phosphate, as my later researches seem to prove, but a mixture of this and thorium earth. By this I was moved in the beginning of this analysis to let the new earth have the name Thorium earth, and since by a repeated analysis of the remainder of the mineral in which I thought I had found the former thorium earth,1 I could not discover the slightest trace of the new, so I have, and with so much greater right, thought I might retain for the latter the same name, since the former description for the most part fits the new earth, and the name Thorium earth is once more introduced to science. This offers at the same time an opportunity for naming the new mineral; I name it Thorite.

#### Hafnium

ON THE MISSING ELEMENT OF ATOMIC NUMBER 72. Letter from Universitets Institut for teoretisk Fysik, Copenhagen, January 2, by D. Coster and G. Hevesy. In Nature, London, January 20, 1923.

Since Moseley's discovery of the fundamental laws of the X-ray emission, it has become quite clear that the most simple and conclusive characteristic of a chemical element is given by its X-ray spectrum. In addition, Moseley's laws allow us to calculate very accurately the wave-lengths of the X-ray spectral lines for any element in the periodic table, if those of the elements in its neighborhood are known. Taking into account that the presence of a very small pro-

Fifty years ago, Pasteur's contemporary

#### ROBERT KOCH

opened up a new chapter in the history of medicine with his discovery of the

#### Tubercle Bacillus

This paper will be the next CLASSIC OF SCIENCE

portion of a definite element in any chemical substance suffices to give a good X-ray spectrum of this element, it is quite evident that for the eventual discovery of any unknown element X-ray spectroscopy, especially as it has been developed by Siegbahn, represents the most effective method.

In the Comptes rendus of the Paris Academy of Sciences for May 22, 1922, Dauvillier announced the detection by means of X-ray spectroscopy of the element 72 in a mixture of rare-earth metals. This element was identified by Urbain with a rare-earth element, which he called celtium, the presence of which he had previously suspected in the same sample. For different reasons, however, we think that Dauvillier's and Urbain's conclusions are not justified. It appears from Dauvillier's paper that at any rate the quantity of the element 72 in the sample, if present, must have been so small that it seems very improbable that the element 72 should be identical with the element which in former papers Urbain claims to have detected in the same sample by investigation of the optical spectrum and of the magnetic properties. The only lines which Dauvillier claims to have detected are the lines L alpha 1 and L beta 2, both of which he finds to be extremely faint (extrêmement faible). The wave-lengths he gives, however, for these lines are about 4 X.u (1X.u.=10—11 cm.) smaller than those which are obtained by a rational interpolation in the wave-lengths tables of Hjalmar and Coster, for the elements in the neighborhood of 72.

From a theoretical point of view it appears very doubtful that the element 72 should be a rare-earth. It was announced in 1895 by Julius Thomsen from Copenhagen that from general consideration of the laws of the periodic system we must expect between tantalum, which in many compounds possesses five valencies, and the trivalent rare-earths, a tetravalent element homologous to zirconium. The same view has also recently been put forward by Bury on the basis of chemical considerations, and by Bohr on the basis of his theory of atomic structure. It is one of the most striking results of the latter theory, that a rational interpretation of the appearance of the rare-earth metals in the periodic system could be given. For these elements, according to Bohr, we witness the gradual development of the group of 4-quantum electrons from a group con-

ETHNOLOGY

# Seminoles Not Un-Musical But Have Kept Music Secret

A LONG-STANDING mystery regarding the picturesque Seminole Indians of the Everglades has at last been fathomed.

The mystery is why the Seminoles should be so hopelessly un-musical a tribe. The solution, discovered by Miss Frances Densmore, collaborator for the Bureau of American Ethnology, is that the Seminoles are not hopelessly unmusical at all. They have merely kept their music very much to themselves, and so it remained unheard, and unheard of, among their white neighbors.

Miss Densmore, who has had long experience in studying music of Indian tribes, has found the Seminoles friendly and cooperative, despite their reputation for being most uncommunicative.

"People who have lived for years among the Seminoles have insisted that they do not sing, except 'ki-yi' when they are drunk," says Miss Densmore.

"The explanation is that they sing only at the June Corn Dance and the October Hunting Dance, and on those occasions the singing is done mostly by one man. The dancers do not sing."

Learning this important fact, Miss Densmore won an introduction to the head singers of the Big Cypress group and the Cow Creek group of Seminoles and thus found herself at the source of information on Seminole music.

#### Sang for Three Days

The ethnologist stated that she has just finished recording 125 songs from one of the head singers of this "unmusical" tribe. And the singer had not exhausted his supply. He sang one song after another for three days, while the ethnologist made her records. Never before has Miss Densmore found an Indian who knew so many.

Far from being monotonous "ki-yi" singing, the Seminole songs are good music, with pleasing melodies and showing wide variety, she discovered.

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<sup>&#</sup>x27;It seems to me probable that the Eudialite from Greenland might contain thorium earth, particularly since the properties of zirconium at the time of Stromeyer's analysis of Eudialine were not as well known as now, consequently the new earth might possibly have been taken for zirconium earth; I found however, according to the method specified by Stromeyer, only zircon earth present.

taining 18 electrons into a group of 32 electrons, the numbers of electrons in the groups of 5- and 6-quantum electrons remaining unchanged. Bohr was able to conclude that in the element lutecium (71) the group of 4-quantum electrons is complete, and we consequently must expect that in the neutral atom of the next element (72) the number of electrons moving in 5- and 6-quantum orbits must exceed that in the rare-earths by one. The element 72 can therefore not be a rare-earth but must be an homologue of zirconium.

In view of the great theoretical importance of the question we have tried to settle it by an experimental investigation of the X-ray spectrum of extractions of zirconium minerals. We have succeeded in detecting six lines which must be ascribed to the element 72 (in Siegbahn's notation L alpha 1, alpha 2, beta 1, beta 2, beta 3, and gamma 1. The complication was met that the lines L alpha 1 and alpha 2 lie almost exactly in the place corresponding in the spectrum to the zirconium K alpha 1, and alpha 2, lines in the second order. Difficulties which might arise from this fact may easily be avoided by keeping the tension on the tube between the critical tension of the zirconium K-lines (18,000 volts) and that of the L-lines of the missing element (10,000 volts). Besides, the relative intensity of the K alpha lines is so different from that of the two L alpha lines that any ambiguity is already thereby excluded. Not only the L alpha lines but also the lines L beta 1, beta 2, and beta 3 were, as regards their mutual distance and their relative intensity, in exact agreement with the expectation. The values which we obtained for the wave-lengths of the six mentioned lines all agree within one X.u. with those found by interpolation. Between our values for the lines L alpha 1 and L beta 2, and those published by Dauvillier, however, there exists the discrepancy referred to of about 4 X.u. (in general for other elements which have been measured by Dauvillier and by Coster the discrepancy is never more than 2 X.u.). Exposures under different conditions as well as a thorough discussion of the plates showed that the new lines found during our investigation cannot be ascribed to the first or higher order spectrum of any other known element. Our provisional results are, L alpha 1 = 1565.5; alpha 2 = 1576; beta 1 = 1371.4; beta 2 = 1323.7; beta 3 = 1350.2; gamma 1 = 1177 X.u. More accurate and complete data

as well as photographs of the spectrum will soon be published.

In a Norwegian zirconium mineral the new lines were so intense that we estimate the quantity of the element 72 present in it to be at least equal to one per cent. Besides we investigated with low tension on the tube a sample of "pure zirconium oxide." Also with this specimen the L alpha lines were found, but very faint. It seems to be very probable that ordinary zirconium contains at least from 0.01 to 0.1 per cent. of the new element. Especially the latter circumstance proves that the element 72 is chemically homologous to zirconium. Experiments are in progress to isolate the new element and to determine its chemical properties.

For the new element we propose the name Hafnium (Hafniae — Copenhagen).

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MEDICINE

### Skin Color Makes Negroes Get Rickets More Easily

D ISEASES which Negroes may safely be said to have oftener or less often than whites solely because of the racial factor are only those diseases which depend on differences in the skin, Dr. Harry Bakwin of New York University and Bellevue Hospital Medical College has found as a result of studies of the differences between white and Negro infants in health and disease.

For example, rickets-preventing ultraviolet light does not penetrate the Negro skin as readily as the white skin, which explains why rickets and tetany occur more often in Negro than in white children in temperate regions, Dr. Bakwin explains in a report to *Human Biology*.

"A second difference in the Negro skin is its reaction to external heat," Dr. Bakwin pointed out. "When the external temperature is high, body temperature regulation is better in the Negro than the white individual. This explains, in part at least, their greater ability to withstand high external temperatures, e. g. in stoke rooms, and the lower incidence among them of heat-stroke.

Some investigators have found a relation between heat and the incidence of summer diarrhea. If this is true, the Negro's more effective mechanism for withstanding heat may account for the fact that in certain communities the Negro infant death rate from diarrheal diseases is no higher than the white, even though the Negro lives under poorer hygienic conditions, which would

tend to increase the death rate from this disease.

Another property of the skin, which is probably racial, may account for the comparative immunity of the Negro to various skin infections, such as erysipelas and boils, Dr. Bakwin concluded.

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### Yellowstone Elk Have Steam-Heated Dormitory

SMALL BAND of Yellowstone Park elk, through luck or animal instinct, has found for itself a steamheated dormitory in the midst of the park's winter-bound interior.

Park Ranger Curtis K. Skinner, while on patrol one winter day, observed the elk in Midway Geyser Basin, just above the great Excelsior crater. Examination of the spot showed a small plot of level sandy ground which is kept constantly dry and warm throughout the long snowy winter months by steam channels which lie close beneath the surface and which give off their vapor through surrounding vents and pools. Mr. Curtis inserted a small thermometer beneath the surface of the sand and found the temperature to be just about 70 degrees Fahrenheit, the standard room temperature. Experimenting still further, he found by personal experience that one could rest quite comfortably on the ground.

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with the left hand is controlled by the right side of the brain. Speech going on at the same time would naturally come under the same control.

The person begins by copying words and speaking them at the same time. The writing movement is always started before the word is pronounced. Then the words may be spoken more rapidly and only the initial letter written. Finally ordinary conversation is conducted in this manner.

The stutterer finds it much easier to speak when he combines his speech with writing in this manner. Gradually his speech improves until only certain sounds give difficulty. Then he need only write the first letters of those words which cause the trouble.

If you stutter, you will be glad to know that Dr. Travis does not recommend phonetic drills. Forcing a stuttering child to recite frequently in class is condemned as downright harmful.

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