CHEMISTRY

Cerium Group of Rare Earths

"A Classic of Science"

The Puzzle of the Rare Earths Sharpened Chemists' Wits To Devise New Analytical Methods for Separating Them

ACCOUNT OF EXPERIMENTS MADE ON A MINERAL CALLED CERITE, AND ON THE PARTICULAR SUBSTANCE WHICH IT CONTAINS, AND WHICH HAS BEEN CONSIDERED AS A NEW METAL. By M. Vauquelin. In Philosophical Magazine, Vol. XXII, 1805.

Cerium

M. KLAPROTH wrote to me, about eight months ago, that he had discovered, in a mineral of Bastnaes, in Sweden, a new earth to which he had given the name of *ochroit,* on account of the red colour which it assumes by calcination. He even sent me in a letter a small specimen of this substance; and having discovered in it, by several trials, the presence of a considerable quantity of oxide of iron, I stated some doubts, in a note which I read in the Institute, in regard to the colour of that earth. I observed also in the same note, that this substance had as many metallic properties as earthy characters; but that the small quantity of it which I had in my possession did not allow me to give any decisive opinion on this subject.

Some time after, Messrs. Berzelius and Hisinger, having been informed, by their correspondents at Paris, of M. Klaproth's labour, wrote to me to claim a priority, stating that they had sent to M. Klaproth the specimens of that mineral which he had employed for his experiments, and that at the same time they had announced to him that they had found a new metal in it. I can give no opinion on this difference. I shall only observe, that the well known delicacy of M. Klaproth, and the high reputation he has justly acquired by his numerous and important discoveries, render it very improbable that he would appropriate to himself the discovery of another. M. Klaproth must, no doubt, have received from another quarter the mineral in question; and his labour was perhaps terminated before he acquired any information respecting that of the Swedish chemists. What seems to justify this opinion is, that they obtained results entirely different.

Everything, therefore, seems to show that M. Klaproth of Berlin, and Messrs. Berzelius and Hisinger of Stockholm, made experiments at the same time on the same mineral without having any communication with each other; and that each may have had the honour of the discovery.

Lanthanum

LANTAN, A NEW METAL, note in Annalen der Physik und Chemie (Poggendorff), vol. 46, p. 648 (1839).

By repeated experiment with cerite from Bastnäs, the mineral in which 36 years ago cerium was discovered, Mosander has found a new metal.

That which, obtained in the usual manner from cerite, is considered cerium oxide, contains almost two-fifths of its weight of oxide of the new metal, whose properties differ only slightly from those of cerium and as it were conceals itself in it. On that account Mosander has given the new metal the name Lantan.

It is prepared when one ignites lantan nitrate mixed with cerium nitrate. The cerium oxide thus loses its solubility in weak acids, and lantan oxide, which is a very strong base, can be taken up in one part of nitric acid in 100 parts of water.

Lantan oxide is not reduced by potassium, but from lantan chloride it will separate a gray metallic powder, which oxidizes slowly in water, with evolution of hydrogen, and changes into a white hydrate.

Lantan sulphide is obtained by strongly heating the oxide in the vapor of carbon disulphide; it is pale yellow and changes in water, with evolution of hydrogen sulphide, into the hydrate.

Lantan oxide has a brick-red color, which does not appear through the cerium oxide present. In hot water it changes into a white hydrate, which turns red litmus-paper blue. It dissolves quickly in acids, even very dilute; in excess it easily forms basic salts.

The salts have an astringent taste, without an admixture of sweetness. Their crystals are usually rose-red. Potassium sulphate precipitates it only if it contains salts of cerium.

Digested with ammonium salts, the oxide dissolves, gradually setting free ammonia. The atomic weight of lantan is less than that heretofore given for cerium, that is, to the mixture of the two metals.

Didymium

CONCERNING A NEW METAL, DIDYM. In Annalen der Physik und Chemie (Poggendorff), Vol. 56 (1842).

After my lecture given to the chemical section of the Scientific Congress at Stockholm, upon a few recent discoveries, Prof. Mosander took occasion to make to the members of that section present an announcement of the highest interest, of which I shall here repeat the main points in short form (to which Prof. Mosander has given his authorization).

The same material which for many years has been considered cerium oxide, and in which Mosander found lanthan as an ingredient, contains, beside these two metals (cerium and lanthan), still a third, which Mosander has named *"Didym,"* for to a certain degree it seems to be a twin brother of Lanthan, and, as it now appears, unfortunately a very *inseparable* one. It is Didymium oxide which gives to the (so-called) cerium oxide its brown color, and which at the same time is the reason some salts of the Yttrium earth show a more or less strong rose-red or amethyst-red color. Pure cerium oxide and lanthanum oxide seem nearly colorless and might in a pure state appear entirely colorless. Cerium hydroxide is sulphur-yellow. Didymium sulphate has a color which is between rose-red and amethyst-red. When the brown Didymium oxide is subjected to strong heat, it loses its color and becomes a dirty white. At the same time, it seems that its weight is not changed by this. Prof. Mosander added also that from a mixture of cerium oxide and lanthan oxide

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the latter is taken up very imperfectly by dilute nitric acid. A part of the lanthan remains undissolved, and a part of the cerium oxide is dissolved with it. Ignited cerium oxide is entirely insoluble in dilute nitric acid, *but not if it is mixed with lanthanum oxide.* In spite of the fact that Prof. Mosander has already worked for several years on these interesting bodies (he has known Didym for one and a half years), he has not yet succeeded in finding a good method for their complete isolation. But until he has determined the nature of these three metals and their compounds thoroughly, must we await his further reports upon them.

It seems very probable from these facts that the reactions which I formerly quoted, which I ascribed to lanthan oxide, *are due not to it, but to cerium oxide.* Now everything seems to me to be in a very uncertain state. It appears that every colored oxide which accompanies the yttria of gadolinite from Hitteröen, in which I ventured to surmise a new element, is really Didymium oxide.

Prof. Mosander moreover counsels every chemist who takes up research upon compounds containing cerium, lanthanum, and didymium, to content himself for awhile with the sum of these three oxides, until a good method of separation is found. Approximate determinations of the relative mixtures themselves are of no value, and can even mislead to false inference.

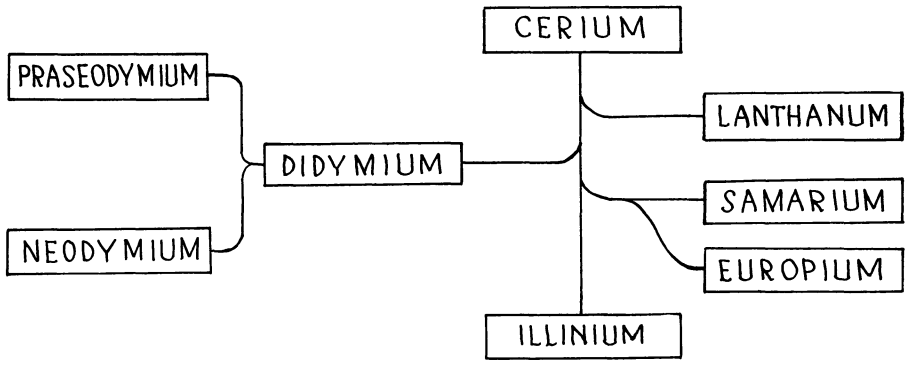
Samarium

NEW SPECTRUM RAYS OBSERVED IN MATERIAL EXTRACTED FROM SAMARSKITE. Note by Lecoq de Boisbaudran. In Comptes Rendus, Vol. 88, p. 322. February 17, 1879.

In examining with the spectroscope, both by absorption and by means of the electric spark, the products of my work upon the mixture of earths from samarskite (rich in didymium), I observed lines or bands not related to any formerly known body and not corresponding to the descriptions of spectrum lines of earths recently announced by Messrs. Delafontaine, L. Smith, Soret and de Marignac.

The new line of emission and those of absorption appear to correspond (at least the principal ones) to a single substance, for they follow similar variations of intensity in the series of products obtained by fractional crystallization. . . .

Awaiting further verification, my two blue absorption bands and my four emission bands seem therefore to indicate the existence of a substance hitherto unknown. I hope soon in a measure to be able to confirm this supposition or to correct certain points in the description of the spectrum of decipium.



FAMILY TREE OF THE CERIUM EARTHS
Including Didymium, which turned out to be two elements.

Praseodymium and Neodymium

SPLITTING DIDYMIUM INTO ITS ELEMENTS, by Carl Auer von Welsbach. In Berichte der Deutschen Chemischen Gesellschaft. 18th year, 3d vol. Berlin: 1885.

The practical method of separation consists in repeating many hundred times the fractional crystallization of ammonium double nitrates of lanthanium and didymium in strong nitric acid solution, by which lanthanum separates first, and finally didymium breaks up into its constituents: Praseodymium (Pr= 143.6) and Neodymium (Nd = 140.8). In the last crystallization the difficultly crystallizable ammonium double salt is converted into the corresponding sodium compound. The absorption spectra of the two new elements are part of the spectrum of didymium: If we mix the two in a definite ratio, the solution color and the original spectrum of didymium appear. The compounds of Praseodymium, which is nearest to Lanthanum, are clear and intense leek-green, those of Neodymium, which makes up the most of the so-called didymium are clear rose or amethyst-colored. The former gives a dark almost blackish brown, the latter a blue oxide, R_2O_3; the former admits also a super-oxide, R_4O_7 (?). The spectrum count of the elements is the same as for the original.

Europium

ON A NEW ELMENT, EUROPIUM. Note by Eugene Demarcay, presented by Henri Moissan. In Comptes Rendus, Vol. 132, p. 1484. June 17, 1901.

In 1885 M. Crookes (Phil. Trans. v. CLXXVI, p. 691), in his beautiful researches on electric fluorescence in a vacuum, reported a band which he attributed to samarium and which, because of its disappearance in the presence of calcium and of some other peculiarities, he called the *anomalous line.* Later he distinguished it with a number of other bands as characterizing apparently some special meta-element. He called the hypothetical meta-element corresponding to the anomalous line S *delta.* M. Lecoq de Boisbaudran, in the course of his important researches on phosphorescence, confirmed the announcements of M. Crookes upon the anomalous line.

In 1892, M. de Boisbaudran described a spectrum of three brilliant blue lines, discovered in the spark spectrum of samarium. These three lines could be strengthened by suitable fractionation. From this he concluded that they correspond to a particular element Z *epsilon.* At the same time he turned his attention to a particular band of the reversal spectrum of samarium which seemed to correspond to the anomalous line and was considerably strengthened in nitric acid solution. M. de Boisbaudran, without stopping for really precise conclusions, was inclined to believe it characteristic of a particular element Z *zeta.*

In 1896, I announced the presence of an element intermediate between gadolinium and samarium, characterized by various strong violet and ultra-violet lines. In 1900, I showed that this new element was identical with Z *epsilon* of M. Lecoq de Boisbaudran, that it was similar to the material to which the anomalous line of M. Crookes was due, the reversal line Z *zeta,* various other reversal lines not (*Please turn page*)

JOSEPH HENRY

The American Co-Discoverer with Faraday of the Way to Get

ELECTRICITY FROM MAGNETISM

Describes his Experiments in

THE NEXT CLASSIC OF SCIENCE

yet described, and, further, a special absorption spectrum unknown until that time. I added that it had not been possible for me to continue the fractionation long enough to affirm positively that all these properties correspond to the same substance. Since then, I have been able, following a considerable number of fractionations of magnesium nitrate, to accumulate a greater quantity of this scarcely abundant element, to fractionate it in turn and to report finally that these different characteristics: line spectrum, spectra of reversal, absorption, electric fluorescence of the sulphate in vacuum (anomalous line); with calcium or gadolinium sulphate, accompany one another very constantly, remain sensibly proportional, and that they evidently characterize the same element.

The apparently contradictory results of MM. Crookes and Boisbaudran are due, I think, to the varying proportion of *Sigma* — Z *epsilon* contained in their material and to the fact that calcium and gadolinium reinforce the spectrum of samarium more than that of the other.

I propose for the new element the name *europium,* with the symbol Eu = 151 (approximately).

Illinium

OBSERVATIONS ON THE RARE EARTHS: XXIII. ELEMENT NO. 61. PARTS ONE AND TWO. By J. Allen Harris with L. F. Yntema and B. Smith Hopkins, in Journal of the American Chemical Society, Vol. 48, June 1926.

Summary:

1. Fractionation of cerium group material as double magnesium nitrate concentrates element No. 61 between neodymium and samarium.

2. All fractions contain so small a proportion of No. 61 that its detection by X-ray analysis is difficult.

3. The absorption bands of Element No. 61 are masked by the broad bands of neodymium and samarium.

4. Fractionation as bromates reverses the order of solubilities interposing gadolinium between No. 61 and samarium and terbium between No. 61 and neodymium. Under these conditions absorption bands probably due to the presence of Element No. 61 become plainly visible. . . .

We base our claim to the discovery of a new element on three different lines of evidence:

1. The presence of lines in the arc spectrum of materials prepared in this laboratory common to both samarium and neodymium and stronger in intermediate fractions. These consist of 130 lines in the red and infra red and five lines toward the violet.

2. The presence in our intermediate fractions of absorption bands which become stronger as the characteristic bands of neodymium and samarium become weaker. The bands at 5816 A. and 5123 A. are especially prominent and their positions confirm the belief that there is a systematic drift in the absorption bands of the rare earth group.

3. The presence of lines in the X-ray emission spectrum corresponding closely to the theoretical position for L *alpha* 1 and L *beta* 1 of Element 61. The mean value obtained for L *alpha* 1 agrees within 0.0004 A. of the value calculated from Siegbahn's precision values. The single reading obtained for L *beta* 1 varies by 0.0040 A. from the calculated value.

Science News Letter, August 29, 1931

ORNITHOLOGY

Duck Shortage Imminent As Breeding Places Dry

DUCK SHOOTING during the coming fall, already shortened by two weeks, may face a still further curtailment as the result of a cooperative survey of the drought situation in the northwestern breeding grounds of the wild fowl, conducted by the United States and Canadian governments. As reported to *Science,* the findings of the field biologists are pessimistic.

Discouraging reports were made of unprecedented drought; of lakes and ponds and marshes turned into dusty barrens with no sign of aquatic life, and of the almost complete absence of water during the period in the great prairie breeding grounds of southwestern Manitoba, southern Saskatchewan as far north as Saskatoon, and Alberta westward to the foothills of the Rocky Mountains and northward to the vicinity of Edmonton.

Science News Letter, August 29, 1931

DR. WILHELMINE E. KEY

Geneticist who checks up on fictionists.

FROM PAGE 135

scribed the daughter born of this unpromising marriage:

"Here is the picture of the 'sport' which is miraculously put forth from this weak, ineffectual family stock. She was beautiful, she was intelligent and ardent. She was admirable and she felt that she was effective; and she had a confidence 'amounting almost to a feeling of power.' She has, too, a wonderful warmth of sympathy and human understanding."

Rosalie, in other words, was a bundle of positive traits, none of which, the author would have us believe, was inherited from her parents. In such an imposing array of characters we would expect some to be dominant, and dominant traits have a way of showing themselves in each generation.

Another stumbling-block which keeps the fiction writer from creating his characters in accordance with scientific laws is the danger of confusing social heredity with physical heredity. Many human lives are ruined, not through any hereditary defect, but through outworn traditions, prejudices, and unfortunate teachings which have been handed down from generation to generation like folk-lore.

The error of blaming physical heredity for the disastrous effects of this social kind of heredity is illustrated, Dr. Key believes, by May Sinclair's "Mary Olivier."

In "The Forsyte Saga," where Galsworthy carries the story of the Forsyte