simultaneously with, if not before, the formation of the chloride of iron. Hence the conclusion to be drawn as a result of the study of the behavior of marcasite and pyrite with bismuth chloride would be that each mineral contains its iron wholly in the ferrous state. The formula representing them would then have the following configuration: 

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE USE OF SULFUR MONOCHLORIDE IN THE DETERMINATION AND ANALYSIS OF THE RARE EARTH MINERALS.[1]

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Many of the rare earth minerals contain columbium, tantalum and titanium as their acid components. The usual methods of decomposing such minerals are fusion with potassium bisulfate, bifluoride or by treatment with hydrofluoric acid. Each of these methods present difficulties. Fusion with potassium bisulfate is most generally used, but even when one fusion is sufficient to effect the decomposition the resulting mixture containing all the earths is difficult to handle, particularly when a quantitative separation of the metallic acids from the other constituents is desired. On the other hand, the fluoride methods lend themselves to cleaner and more rapid separations but are objectionable because they preclude the use of glass vessels. The present investigation introduces sulfur monochloride as a decomposing agent of such minerals and it is applied in their analysis. Smith,[2] who was the first one to use sulfur monochloride in the decomposition of minerals, showed that many naturally occurring sulfides, as well as rutile, wolframite, scheelite and columbite, were decomposed by this reagent. Oddo and Serra,[3] two Italian chemists, used it in the preparation of anhydrous chlorides of arsenic, antimony and bismuth, while Hall[4] applied it to the preparation of pentachloride of columbium. He also observed that it decomposed such minerals as chromite and columbite and that it converted many oxides into their corresponding chlorides, the notable exceptions being the oxides of boron and silicon. Bourion[5] has used sulfur monochloride in the preparation of anhydrous chlorides in general as well as for the decomposition and analysis of scheelite and wolframite. It, therefore, seemed probable to me that this reagent might decompose such minerals

[1] Details may be found in the author's inaugural thesis, Univ. of Penna., 1911.

[2] THIS JOURNAL, 22, 289 (1898).

[3] *Gaz. chim. ital.*, [2] 29, 355 (1899).

[4] THIS JOURNAL, 26, 1243 (1904).

[5] *Ann. chim. phys.*, 20, 547 (1910).

as fergusonite, eschynite, etc., with the formation of chlorides. Accordingly they were submitted to its action and the extent of their decomposition carefully noted. The rare earths, after the expulsion of the metallic acids, were examined for scandium. This method of decomposition was also used in the analysis of eschynite. At the outstart, samples of these minerals not altogether pure were used, and while the decomposition was apparently complete, it was felt necessary to submit only the purest material, free from all contamination, to the action of the vapors of sulfur monochloride. The result was that fergusonite was completely decomposed—not a trace of the metallic acids remained in the boat and rare earths could not be detected in the volatil portion. Eschynite was readily and completely decomposed and euxenite yielded without the slightest difficulty to the action of the decomposing agent. A picked sample of samarskite (0.6197 gram) left a residue of 0.0078 gram, which meant a decomposition of 98.78 per cent. All of these minerals, in amounts varying from $^1/_2$–25 grams, were placed in porcelain boats in a combustion tube, which was heated on a furnace while the vapors of sulfur monochloride were passed over them. As previously stated the volatil chlorides of the metallic acids passed into the receiver, while the non-volatil chlorides or oxychlorides of the earth metals remained in the boat.

It was in these non-volatil portions of the minerals that search was made for scandium. In the case of fergusonite, 50 grams of the mineral were decomposed. The boat contents were then dissolved in water and filtered from the gang. Nitric acid was added to the filtrate and the solution evaporated to dryness. The residue was taken up in 800 cc. of 1 : 1 hydrochloric acid and to this boiling solution were added gradually 15 grams of sodium silicofluoride.[1] The boiling was continued for $^1/_2$ hour, when a slowly subsiding and slightly colored precipitate appeared. This was filtered and washed by boiling it with dilute hydrochloric acid. It was then converted into sulfate and the solution treated while boiling with ammonium hydroxide. The resulting precipitate was dissolved in hydrochloric acid and the excess of acid removed by evaporation. The concentrated neutral chloride solution was next added to 50 cc of a 20 per cent. sodium carbonate solution. The white precipitate which appeared at once readily dissolved and on boiling the liquid for half an hour there was no trace of precipitation. This would indicate the absence of scandium. The treatment was repeated several times with different samples of the material with the same negative results or scandium. The substance which had been precipitated from a strongly acid solution with sodium silicofluoride and which failed to give a precipitate on boiling with a 20 per cent. sodium carbonate solution was studied further. For

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[1] Meyer, *Z. anorg. Chem.*, 60, 154 (1908).

example, it yielded a white precipitate with oxalic acid, even in strongly acid solutions. It was completely precipitated by sodium thiosulfate from neutral solution and it showed an atomic weight of 224 on ignition of its sulfate to oxide. Further it was found to be radioactive. These behaviors were taken as conclusive evidence that the substance under examination was thorium, which is not generally mentioned as a constituent of fergusonite, where it evidently exists to the amount of between 2 and 3 per cent.

When the residual chlorides from eschynite were taken up in 1 : 1 hydrochloric acid, and the solution treated with an excess of sodium silicofluoride at the boiling temperature, a copious precipitate appeared. It was washed with dilute hydrochloric acid, converted into the sulfate and then back into the chloride. The latter when treated with sodium carbonate yielded a white precipitate after a few minutes' boiling. This precipitate was filtered, washed several times with a sodium carbonate solution, then with water, after which it was dissolved in hydrochloric acid and precipitated with ammonium hydroxide and reprecipitated in order to get rid of the last traces of sodium. 100 grams of the mineral were decomposed and the chloride solution precipitated twice with sodium silicofluoride, once with sodium carbonate and once with oxalic acid. The oxalate was ignited to oxide and weighed 0.0320 gram equivalent to 0.03 per cent. of the mineral. The fact that a precipitate was produced by sodium carbonate was pretty strong indication that eschynite contained scandium, but to test this point farther the spark spectrum of the chloride was studied. A Rowland grating was used and the second order spectrum photographed as a standard of comparison. The iron spectrum was photographed on one-half of the plate and also served as a means of detecting the air lines, because these would show in both halves of the plate. The photographs were made of the portion of the spectrum which contained the strongest scandium lines, that is, from 3,500–5,000, measured in Angstrom units. The wave lengths were then measured by projecting the lines on a screen, containing an accurately divided scale, from such a distance that the wave lengths of different known iron lines would fall on the proper scale divisions. When this was done, the wave lengths sought could be read directly. As a result of this study no scandium lines were detected. There were few strong lines, leaving out those of platinum, but a larger number of dim lines. In general, the latter corresponded very closely to the lines of yttrium and thorium, though it must be stated that some of the stronger yttrium and thorium lines were not noticed. The conclusion is that the substance which had been separated from eschynite by sodium silicofluoride and sodium carbonate was not scandium but a mixture of yttrium and thorium. A similar experiment was conducted with euxenite with like result and scandium was not observed in samarskite.

For the analysis of eschynite some pure crystals, as free as possible from foreign matter, were ground to a fine powder, and then subjected to the action of sulfur monochloride. As the decomposition proceeded, the volatil chlorides and the excess of sulfur monochloride passed into a dilute nitric acid solution and were there decomposed. Much of the sulfur was oxidized and consequently, less free sulfur was precipitated. At the end of the operation, dry hydrochloric acid gas was passed through the combustion tube, and, by means of a free flame, all the volatil portion was driven out. After cooling in a current of hydrochloric acid gas, the tube was cut by scratching with a file and touching with a hot glass rod. The short end of the tube and the glass cover were thoroughly washed into the beaker, which now contained all the columbium, tantalum, titanium, tungsten and most of the iron from the mineral as well as a considerable amount of separated sulfur. This mixture was treated as follows:

The lumps of sulfur were broken up as much as possible by means of a glass rod, a large excess of ammonium hydroxide was added, and then hydrogen sulfide in sufficient quantity to dissolve the sulfur completely. The yellow ammonium sulfide, thus formed, dissolved the tungstic acid, leaving the acid earths and iron in the residue. This was filtered off. By acidifying the filtrate, tungsten sulfide was precipitated along with a large amount of sulfur. After filtering, the precipitate was washed with water, alcohol and carbon disulfide. The precipitate was then evaporated with nitric acid, ignited, and weighed as WO_3.

The residue, containing iron and the acid earths, was digested with hot, dilute sulfuric acid until perfectly white. All the iron and some of the acid earths went into solution, which was decanted through a filter, and the residue washed. Hydrogen sulfide was passed into the filtrate to reduce the iron, and then sodium carbonate was added until the solution became almost neutral. This solution was boiled for an hour, during which time a current of hydrogen sulfide was passed through the solution to prevent the oxidation of the iron. By this means, the acid earths were completely precipitated, while the iron was left in solution. This precipitate was added to that obtained above, ignited, and weighed. No attempt was made to separate columbium, tantalum and titanium.

The non-volatil portion was dissolved in water, to which a few drops of hydrochloric acid had been added. The solution was boiled, and filtered from the gang. The filtrate was treated with hydrogen sulfide to remove the lead and tin. These were separated in the usual way. The filtrate, after removing the lead and tin, was treated with an excess of ammonium chloride and ammonium hydroxide. All the iron and rare earths were precipitated. Calcium was determined in the filtrate. The rare earths were separated from the almost negligible amount of iron by ammonium carbonate and ammonium sulfide.

By an application of this method of procedure, the following results were obtained:

	Per cent.
Cb_2O_5, Ta_2O_5, TiO_2	53.55
ThO_2, Ce_2O_3, La_2O_3, Y_2O_3, etc	41.30
WO_3	0.17
SnO_2	0.04
FeO	0.82
CaO	0.55
PbO	0.91
Gang	0.22
Loss on ignition	2.25
	99.81

The only purpose of this analysis was to show that the sulfur monochloride method of decomposition could be used in the analysis of eschynite. The results obtained above prove this point. Owing to the lack of time neither columbium, tantalum, and titanium, nor the rare earths were separated, yet it is obvious that any of the methods proposed for separating these elements could readily be applied.

The principal advantages of this method are the readiness with which the mineral is decomposed by sulfur monochloride, the simplicity and cheapness of the apparatus required, and the separation of columbium, tantalum, titanium and tungsten from the rare earths during the decomposition. The chief disadvantage that has been encountered in applying the method is the treatment of the volatil portion which consists of the excess of sulfur monochloride mixed with the volatil chlorides. This has been successfully dealt with by allowing the mixture to pass into dilute nitric acid and then removing the precipitated sulfur by adding excess of ammonium hydroxide and hydrogen sulfide.

Since fergusonite, euxenite, and samarskite are completely decomposed by sulfur monochloride with the separation of columbium, tantalum, titanium and tungsten from silica and the rare earths, it is evident that this method of decomposition could, likewise, be used in their analysis. By analogy, we would reason that columbates, tantalates, and titanates in general would be decomposed by sulfur monochloride, and that this method of decomposition would lend itself to their analysis.

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