THE CONSTITUTION OF NICKELIFEROUS PYRRHOTITE.

By Dr. S. H. EMMENS.

It is the custom of mineralogists to speak of many mineral varieties as formed by one metal "replacing" another to a greater or less extent in certain chemical combinations. This is, I think I may say, the invariable account given in the text books respecting nickeliferous pyrrhotite, a mineral described as consisting of an iron sulphide in which "part of the iron is replaced by nickel." The object of the present paper is to enquire whether the account in question is a correct representation of the facts of the case, or whether the constitution of nickeliferous pyrrhotite differs from the description given in the text books.

The general formula of pyrrhotite is $Fe_n S_{n+1}$. This is sometimes written n (Fe S). $Fe S_2$ or n (Fe S). Fe_2S_3; though probably, for reasons analogous to those recently set forth, (Journal of Analytical and Applied Chemistry, Vol. VI., No. 10, October, 1892), the more correct view is to regard the typical compound, Fe_3S_4 as being a homogeneous body, and not as being composed of a mixture of sulphides. This question, however, is comparatively unimportant in the present discussion; as, whatever may be the precise arrangement of the molecules, their number will not be changed, and pyrrhotite will still be defined as an iron sulphide composed of n molecules of Fe and $n+1$ molecules of S. And, on the "replacement" theory, nickeliferous pyrrhotite will be a sulphide composed of x molecules of Ni, $n-x$ molecules of Fe and $n+1$ molecules of S. Let us test this numerical theory by the actual results of analysis.

At p. 74 of the 6th edition of Dana's *Mineralogy* is a table of analyses of various specimens of pyrrhotite. From this I will select the following for discussion, namely :

		S.	Fe.	Ni.
No. 14.	Brewster, N. Y.	37.98	61.84	0.25=100.07
" 15.	Putnam Co., N. Y.	39.28	60.03	0.78=100.09
" 15a.	" "	38.99	60.04	1.02=100.05
" 15b.	" "	39.85	58.73	1.53=100.11
" 20.	Frigido	39.65	58.18	2.17=100.
" 18.	Hilsen	40.27	56.57	3.16=100.
" 17,	Sudbury	38.91	56.39	4.66= 99.96
" 19.	Gap Mine, Pa	38.59	55.82	5.59=100.

Now it is obvious that any replacement of iron by nickel must take place by whole molecules weighing respectively 58.6 for Ni and 55.9 for Fe. Hence for every Ni molecule in mineral No. 14 of the above list there must be $\frac{58.6}{.25} \times \frac{61.84}{55.9} = 258.9$ molecules of Fe; and, in like manner, there must also be $\frac{58.6}{.25} \times \frac{37.98}{32} = 278.2$ molecules of S; or, in view of the analytical total being a little in excess of 100, we may regard the mineral as consisting of $Ni\ Fe_{259}\ S_{278}$ instead of $Ni\ Fe_{259}\ S_{261}$, as called for by the pyrrhotite theory.

Similar calculations in the other cases give the following results :

No. 15 ....$Ni\ Fe_{80.68}\ S_{92.22}$ showing an excess of $S_{9.54}$

" 15a....$Ni\ Fe_{61.71}\ S_{70.00}$ " " $S_{6.29}$

" 15b....$Ni\ Fe_{40.24}\ S_{46.62}$ " " $S_{4.38}$

" 20 ....$Ni\ Fe_{28.11}\ S_{33.46}$ " " $S_{3.35}$

" 18 ....$Ni\ Fe_{18.77}\ S_{23.34}$ " " $S_{2.57}$

" 17 ....$Ni\ Fe_{12.685}\ S_{15.29}$ " " $S_{0.605}$

" 19 ....$Ni\ Fe_{10.468}\ S_{12.642}$ " " $S_{0.174}$

In none of these minerals does the formula (Fe Ni) $_n$ S_{n+1} hold good; and we therefore have reasonable ground for declaring that the constitution of nickeliferous pyrrhotite is *not* represented by this time-honored but somewhat superficial generalization.

It will be noticed that the excess of sulphur bears some relation to the percentage of nickel; the lower the nickel contents the greater being the surplus of sulphur, and *vice versa*. This necessarily follows from the great size of the compound molecule when the percentage of nickel is small. If, however, we investigate the proportion borne by the sulphur to the total metal, we shall find a tendency to constancy rather than to variation, as is shown in the following Table :

Per Centage of Nickel.	PROPORTION OF S MOLECULES IN EXCESS OF $n+1$ TO		
	Ni Molecules.	Fe Molecules.	Ni+Fe Molecules.
0.25	17.3	.0667	.0666
0.78	9.54	.1182	.1168
1.02	6.29	.1019	.1003
1.53	4.38	.1088	.1062
2.17	3.35	.1192	.1152
3.16	2.57	.1369	.1300
4.66	0.605	.0477	.04421
5.59	0.174	.0166	.01517

This suggests that the constitution of nickeliferous pyrrhotite is polymeric; an inference which is also supported by the fact that Nos. 17 and 19, containing the high nickel percentages of 4.66 and 5.59, show less than 1 complete molecule of sulphur in excess, and therefore require a multiplication of their several figures. Taken as a whole, however, the results of analysis are opposed to any assumption of homogeneity of structure.

Coming now to physical investigation, we are at once met by a feature that is conclusive against the hypotheses of "replacement" and homogeneity. I allude to the fact that nickeliferous pyrrhotite may be divided into two portions, one of which is magnetic while the other is non-magnetic. This fact has long been known to chemists. In 1879 Habermehl effected a separation of the magnetic from the non-magnetic portions of pyrrhotite for the purpose of obtaining a pure mineral for analysis. In 1890 T. J. McTighe applied magnetic separation in the treatment of the nickeliferous pyrrhotite of Canada; and in July of this year T. A. Edison applied for a U. S. Patent, in respect of virtually the same invention, and filed a specification containing the following statement:

"I have discovered that where magnetic pyrites, called "pyrrhotite" is nickeliferous, as it usually is to a more or less extent, the nickel is not distributed generally throughout the whole body of the pyrrhotite, but certain crystals are pure pyrrhotite or magnetic pyrites, while other crystals have some of the iron replaced by nickel and sometimes by cobalt, and that the crystals containing the nickel or cobalt are considerably less magnetic than the pure pyrrhotite."

Any statement made by Mr. Edison is deserving of respectful attention; but I believe that gentleman has frequently disclaimed anything beyond a rudimentary knowledge of chemistry and is therefore presumably open to correction in matters belonging to that department of science. Be this, however, as it may, I am safe in saying that pyrrhotite is rarely found in a crystalline form, and that crystals of nickeliferous pyrrhotite are as yet unrecorded as having been observed. Mr. Edison's mention of "crystals" is probably only a loose way of describing the minute fragments, particles or grains into which the massive pyrrhotite is divided by comminution.

Again, Mr. Edison speaks of the strongly magnetic particles as being "pure pyrrhotite," meaning thereby a non-nickeliferous iron sulphide of the general form $Fe_n S_{n+1}$. My own observations do not confirm the statement that nickeliferous pyrrhotite can be magnetically separated into nickeliferous and non-nickeliferous portions. A separation into two very distinct minerals or mineral mixtures is possible, and these contain very distinct percentages of nickel; but both are nickeliferous. The following results obtained by Mr. C. T. Mixer at the laboratory of the Emmens Metal Company will illustrate this.

Two samples of nickeliferous pyrrhotite were taken, one from the Gap mine, Lancaster Co., Pa., and the other from a mine near Sudbury, Ontario. These were very finely powdered and then each sample was carefully separated by means of a magnet into three grades, namely, "magnetic," "feebly magnetic" and "non-magnetic." The "magnetic" and "non-magnetic" grades were then analyzed and resulted as follows, after deduction of gangue :

	Ni.	Fe.	S.
Gap *magnetic*....	0.35 %	59.97 %	39.68 %
" non-mag....	15.59 "	43.00 "	41.41 "
Sudbury magnetic	1.30 "	58.27 "	40.43 "
" non-mag.	23.16 "	33.92 "	42.92 "

Treating these figures in the same way as those of the analyses recorded by Dana, we have :

1. Molecular Constitution.

Gap mag......... $Ni\,Fe_{46.99}\,S_{56.95}$ showing an excess of $S_{7.96}$
" non-mag.... $Ni\,Fe_{1,535}\,S_{3.394}$ " a deficiency of $S_{0.141}$
Sudbury mag .... $Ni\,Fe_{179.6}\,S_{207.6}$ " an excess of S_{26}
" non-mag- $Ni\,Fe_{2.891}\,S_{4.864}$ " a deficiency of $S_{0.027}$

2. Proportion of Excess S to Metal.

Percentage of Nickel.	Proportion of S molecules in excess of $n + 1$ to Ni molecules.	Fe molecules.	Ni + Fe molecules.
0.35	26.00	.1448	.1440
1.30	7.96	.1694	.1659
15.59	Slight deficiency of S.		
23.16	" " "		

A comparison of the results here obtained with those from Dana shows conclusively that the magnetic minerals are of the pyrrhotite type, but that the non-magnetic concentrates are of a quite dissimilar constitution ; and as the latter are much higher in nickel than the former it is also clear that the nickel is *not* present as an element replacing iron in pyrrhotite. It is also apparent that the minerals Nos. 17 and 19 of Dana are mixtures of the magnetic and non-magnetic minerals found in the Gap and Sudbury samples examined by Mr. Mixer.

Much additional investigation is needed to determine the true constitution of pyrrhotite and its allied nickel compound. It may be that experiments as to the solvent action of molten ferrous sulphide upon iron disulphide and nickel sulphide will throw the needed light upon the subject. Many geologists are of opinion that the massive pyrrhotites of Canada and other places are the cooled remains of a molten mass; and every parcel of matter produced from a smelter is an object lesson respecting the varying mixtures that are possible under such conditions. Provisionally, therefore, we may regard the constitution of the minerals under discussion as represented by the following formulæ:

Crystalline pyrrhotite.. $n\ (Fe_3S_4)$
Amorphous do .. $n\ (FeS).\ x\ (FeS_2)$
Nickeliferous do .. $n\ (FeS).\ x\ (FeS_2).\ y\ (NiS)$

In conclusion it may be well to say a word as to the practical problem of the magnetic concentration of nickeliferous pyrrhotite. The two samples above referred to as examined by Mr. Mixer gave the following results:

1. Division of the total sample:

	Gap.	Sudbury.
Magnetic portion.........	58.66 per cent.	92.95 per cent.
Feebly magnetic portion..	6.67 "	2.09 "
Non- " " ..	34.67 "	4.96 "

2. Division of the total nickel contents:

	Gap.	Sudbury.
Magnetic portion.........	16.25 per cent.	58.01 per cent.
Feebly magnetic portion..	19.96 "	7.60 "
Non- " " ..	63.79 "	34.39 "

3. Total gangue in sample:

Gap	41.28 per cent.
Sudbury	10.7 "

4. Division of the total gangue:

	Gap.	Sudbury.
Magnetic portion.........	25.85 per cent.	75.51 per cent.
Feebly magnetic portion..	7.12 "	9.07 "
Non- " " ..	67.03 "	15.42 "

5. Percentages of gangue in the portions:

	Gap.	Sudbury.
Magnetic portion.........	18.20 per cent.	8.70 per cent.
Feebly magnetic portion..	44.00 "	46.60 "
Non- " " ..	79.80 "	33.20 "

The practical inferences from these figures are as follows:

1. Magnetic separation will give a rich nickel concentrate.
2. An ore with considerable gangue will yield more of its nickel as "concentrate" than will be the case with cleaner ore.
3. The concentrate from clean ore will be of a higher grade than that from ore carrying much gangue.
4. The nickeliferous portion of the mineral is attached to the gangue more firmly than is the non-nickeliferous portion.
5. The nickel is *possibly an essential constituent of the gangue instead of being a constituent of the pyrrhotite.*

This last inference is so opposed to the generally received teachings that I have instituted a fresh series of investigations with a view to determine its correctness or the reverse. The results shall in due course be communicated to the Society; and, in the meantime, all I can say is that at present they seem to favor the supposition of the gangue being nickeliferous.