THE DISTRIBUTION OF IRON, MANGANESE, NICKEL, AND COBALT BETWEEN CO-EXISTING PYRITE AND BIOTITE IN WALLROCK ALTERATION[1]

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Abstract

Pyrite and biotite samples from a schist body enclosing scheelite veins have been analyzed spectrographically. Cobalt and iron in the biotite show a distinct decrease in the areas where pyrite has been developed, indicating that the metallic constituents of the pyrite have probably been derived from the wallrock minerals.

The ratios of the cobalt, nickel, and manganese contents in pyrite to those in biotite can be considered to be a measure of the sulphophile characters of these elements. On this basis, cobalt is the most sulphophile, followed by nickel and manganese, in that order.

The writer recently had an opportunity to study a scheelite deposit in the Michipicoten district of Ontario. The deposit is in the form of irregular quartz-scheelite veins with some molybdenite and calcite. There is abundant pyrite in the wallrock near the mineralized veins and in zones parallel to the veins. Where the pyrite is developed the wallrock appears to be lighter in color than some distance away; this feature is particularly evident in remnants of schist in the quartz veins.

The quartz-scheelite veins lie conformably in the central portion of a narrow schist body. The schist consists largely of quartz, calcite, albitic plagioclase, biotite, hornblende, and chlorite, with minor epidote. There is a general correlation between the type of ferromagnesian mineral and the development of pyrite. Where there is pyrite, biotite is commonly the only ferromagnesian mineral present; where there is no pyrite, chlorite and hornblende are usually present, sometimes to the exclusion of biotite. Because of the close association between biotite and pyrite, the distribution of elements between these two minerals is considered to be of particular interest. The interrelations between the silicates is discussed in a separate paper (Nickel, 1954).

Analytical Methods

The biotite analyses were carried out spectrographically as outlined briefly in the paper preceding this (p. 486). The minor elements in pyrite were also determined spectrographically using a D.C. arc source. The arcing was preceded by pre-heating to drive off the sulphur. Iron was used as internal standard.

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Thirty-four samples of biotite were analyzed, and sixteen of pyrite. The minor elements analyzed in pyrite are cobalt, nickel, and manganese; their values are listed in Table 1. Other elements, present as traces in some of the specimens but not determined quantitatively, include copper, titanium, and zinc.

TABLE 1. MANGANESE, NICKEL, AND COBALT IN PYRITE

Sample	Manganese Weight %	Nickel Weight %	Cobalt Weight %
S-133-30	0.0014	0.13	0.40
S-133-37	.0021	.140	.38
S-133-42	.0013	.125	.50
S-133-47	.0024	.085	.37
S-133-64	.0028	.097	.240
S-133-90	.0008	.113	.133
S-133-94	.0020	.095	.248
S-133-125	.0024	.084	.315
S-133-131	.0036	.144	.240
S-133-135	.0028	.12	.76
Tl-10E	.0011	.14	.265
T1-20E	.0036	.125	.217
T1-40E	.0025	.11	.16
T1-60E	.0009	.082	.32
T1-70E	.0016	.11	.230
T1-80E	.0007	.115	.265

In Table 2 are given the amounts of cobalt, nickel, manganese, and iron in the biotite samples analyzed. Other major and minor elements were determined as well, but since they were not detected in pyrite, these are not of much significance for the present study. The more complete biotite analyses are to be found in Nickel (1953).

VARIATIONS IN THE COMPOSITION OF BIOTITE AS RELATED TO THE DEVELOPMENT OF PYRITE

It is necessary to consider whether the pyrite, at the time of its formation, was in physico-chemical equilibrium with the wallrock minerals or, more specifically, with the biotite. If there is no genetic relationship between the two, then the major and minor elements in the two minerals should bear no consistent relationship to each other. If, however, there was an exchange of ions between these two phases, then the presence or absence of pyrite should, under certain circumstances, be reflected by appropriate changes of composition in the biotite.

The most obvious element to consider in this respect is iron, since it

Table 2. Iron, Manganese, Nickel, and Cobalt in Biotite

Sample	Iron Weight %	Manganese Weight %	Nickel Weight %	Cobalt Weight %
S-133-30	10.6	.118	.0873	.0052
S-133-42	11.2	.120	.0786	.0026
S-133-47	10.0	.118	.0660	.0016
S-133-64	9.7	.197	.0802	.0014
S-133-67	8.1	.142	.0841	.0032
S-133-79	5.3	.154	.0774	—
S-133-90	6.4	.137	.0653	—
S-133-94	9.5	.156	.0653	.0030
S-133-99	12.0	.130	.0825	.0066
S-133-102	12.5	.148	.0762	.0061
S-133-108	10.4	.128	.0896	.0090
S-133-113	10.2	.132	.119	.0111
S-133-121	9.7	.123	.0660	.0072
S-133-125	9.3	.118	.0720	.0006
S-133-131	9.0	.121	.0621	.0007
S-133-135	10.0	.118	.0790	.0025
S-133-142	9.3	.118	.0943	.0065
S-133-147	9.5	.128	.0692	.0053
T1-50W	11.5	.128	.0848	.0070
T1-40W	10.6	.115	.0865	.0069
T1-30W	9.9	.118	.0778	.0072
T1-20W	10.2	.126	.0660	.0070
T1-10W	12.1	.122	.0928	.0090
T1-0	10.7	.138	.0825	.0065
T1-10E	7.9	.157	.0510	—
T1-20E	5.7	.142	.0700	—
T1-30E	10.6	.127	.0865	.0075
T1-40E	8.1	.131	.0802	.0064
T1-50E	10.7	.131	.0849	.0077
T1-60E	7.9	.120	.0928	.0055
T1-70E	7.9	.131	.0542	—
T1-80E	7.7	.135	.0786	—
T1-90E	10.3	.132	.0943	.0097
T4-50W	10.4	.139	.0833	.0074

is a major constituent in both pyrite and biotite. Of the minor constituents, cobalt is probably the most suitable because of the high cobalt content of pyrite, and its relatively low concentration in biotite. This latter condition is necessary because the proportion of pyrite to biotite is rather small, and if a minor element is abundant in the silicate, then the amount taken into the few pyrite crystals formed would not significantly affect the content of this element in the biotite. For this reason nickel is less suitable than cobalt in determining whether an exchange between the sulphide and silicate has taken place.

Figures 1 and 2 show the variation of the iron and cobalt content in the biotite of samples from two sections taken at right angles to the strike of the foliation of the schist. The T-1 samples (Figure 1) were taken from a trench across schist and orebody made to expose bedrock. The S-133 samples (Figure 2) were taken from a diamond drill core dipping at forty-five degrees, also cutting schist and orebody.

These diagrams clearly show a decrease in the iron and cobalt content of the biotite in the neighborhood of pyrite. This suggests very strongly that there was some sort of cation transfer between the biotite and pyrite, and that the distribution of elements between these two minerals represents at least an approach to equilibrium at the time of formation of the pyrite.

SULPHOPHILE CHARACTER OF COBALT, NICKEL, AND MANGANESE

Assuming that a state of equilibrium exists, or existed, it is interesting to inquire into the distribution of elements between the pyrite and biotite. Cobalt, nickel, and manganese can be considered in this respect. Iron cannot properly be discussed in this way because it is a major constituent whose content, in the pyrite at least, is fixed.

TABLE 3. RATIO OF MINOR ELEMENT CONTENT IN PYRITE TO THAT IN BIOTITE

Sample	% Metal in Pyrite/% Metal in Biotite		
	Cobalt	Nickel	Manganese
S-133-30	78	1.49	.0119
S-133-42	194	1.59	.0108
S-133-47	236	1.28	.0203
S-133-64	169	1.21	.0142
S-133-90	>600	1.20	.0058
S-133-94	83	1.45	.0128
S-133-121	33	1.73	.0292
S-133-125	573	1.16	.0203
S-133-135	316	1.53	.0237
T1-10E	>600	2.75	.0070
T1-20E	>600	1.78	.0254
T1-40E	25	1.50	.0191
T1-60E	59	0.89	.0075
T1-70E	>600	2.04	.0122
T1-80E	>600	1.47	.0052

Table 3 shows the ratios of cobalt, nickel, and manganese in pyrite to that in biotite. It should be noted here that the cobalt ratios show considerable fluctuations. These are mainly due to variations in the biotite, and in general reflect the amount of pyrite developed, the highest ratios

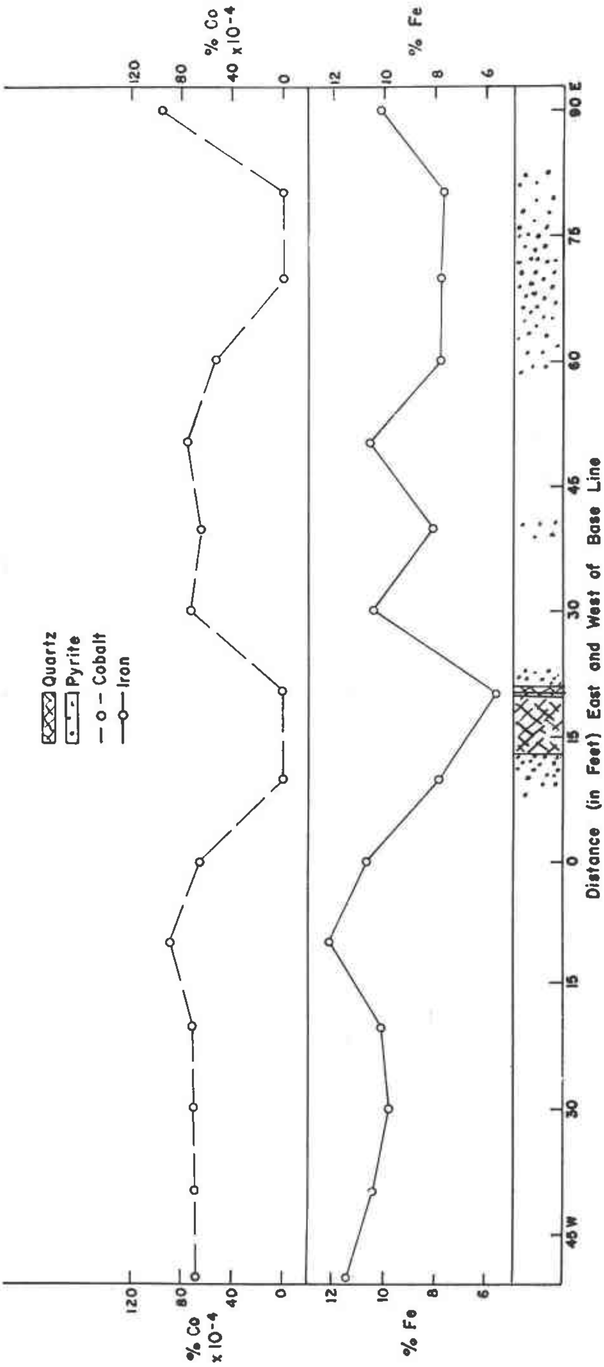

FIG. 1. Variations in the content of cobalt and iron in biotite from samples of trench 1 (T-1).

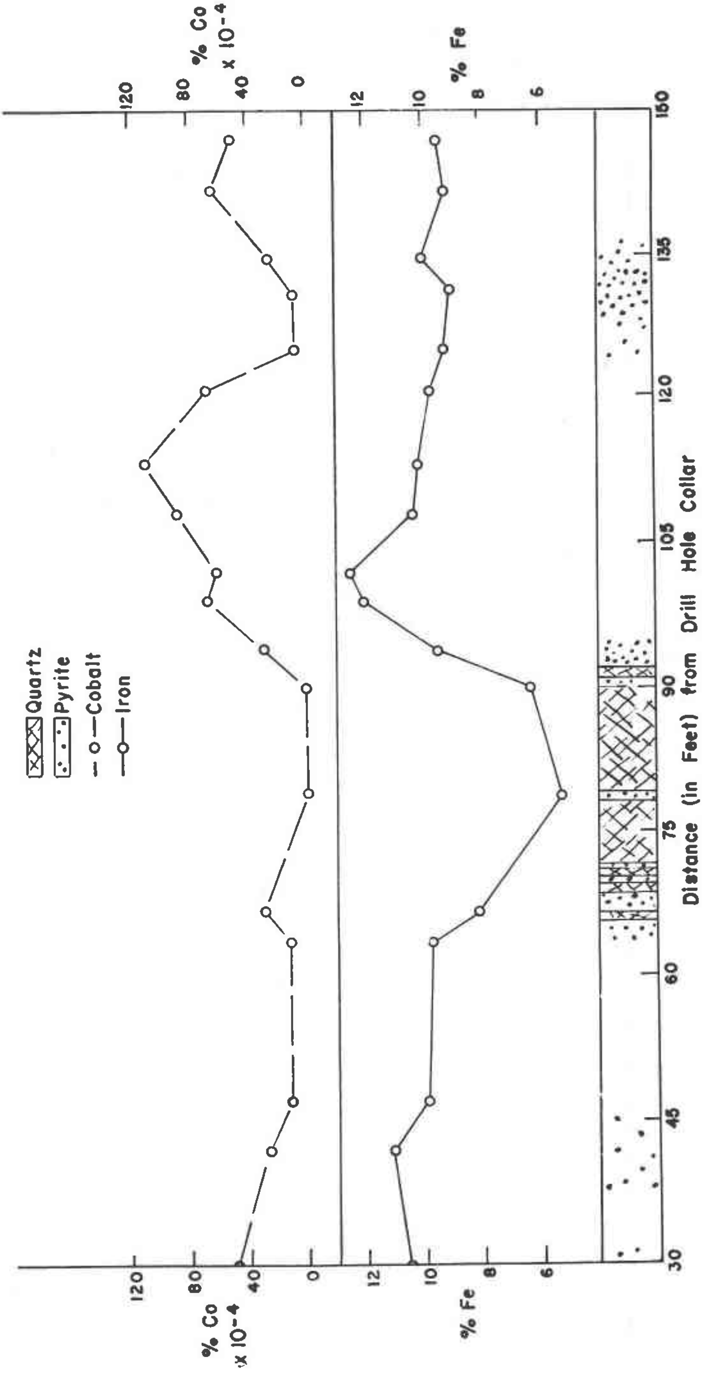

FIG. 2. Variations in the content of cobalt and iron in biotite from samples of diamond drill core no. S-133.

associated with the heaviest sulphide mineralization. This suggests that the highest ratios probably represent the closest approach to equilibrium distribution of the cobalt.

As can be seen, there is a large difference between the ratios of cobalt, nickel and manganese. This can be taken as a measure of the sulphophile nature of these elements or, in other words, the relative tendencies of these metals to form sulphides as opposed to silicates. This statement requires several qualifications. In the first place, any tendencies shown must be considered as applicable chiefly to the physico-chemical conditions existing in this instance, unless further evidence extends this observation over a wider range. Secondly, the only sulphide considered here is pyrite, so the tendencies exhibited must be restricted to only this sulphide until, again, further observations support a more general view.

With these qualifications in mind it can be stated, then, that of the three elements here considered, cobalt is the most sulphophile, nickel less so, and manganese is the least sulphophile of all. This same order of metal affinity for sulphur relative to silicate anions appears to be true for the monosulphides, as well, on the basis of thermochemical data (Ramberg, 1953).

It is probable that the polarizing power of the metals will influence their distribution between silicate and sulphide phases because of the difference in polarizability of sulphur and oxygen. Sulphur, more easily polarized than oxygen, should have the greatest attraction for the cation showing the greatest polarizing power. An idea of the degree of polarization can be obtained from the metal-sulphur distances in cobalt, nickel, and manganese disulphides having the pyrite structure. These are: CoS_2—2.33; NiS_2—2.42; and MnS_2—2.59 (Haraldsen, 1947, p. 6).

Cobalt, it will be noted, has the smallest metal-sulphur distance, although its normal ionic radius is greater than that of nickel. This suggests that the cobalt-sulphur bond is more covalent than the bonds in nickel and manganese disulphides, indicating a greater polarizing power for cobalt. Similarly, nickel and manganese have respectively decreasing polarizing powers. Thus the sulphophile natures of cobalt, nickel, and manganese can be explained on the basis of their relative polarizing abilities.

Significance of Pyrite-Silicate Relationships in Regard to Theories of Ore Genesis

The major and minor element relationships in biotite and pyrite discussed above make it evident that there is probably some genetic connection between these two phases. The conventional interpretation of wallrock alteration is that the "solutions" carrying the ore materials effect changes in the mineralogical and chemical composition of the host rock. To apply this reasoning here would require that those elements necessary for the formation of the sulphide minerals have been removed from the wallrock and carried away. Apart from the improbability of such a coincidence it can hardly be expected that the conditions favoring the deposition of certain elements would at the same time and at the same place cause the removal of these self-same elements. A more reasonable assumption, or so it appears to the author, is that *the metallic constituents of the pyrite have at least in part been derived from the wallrock silicates.*

Numerous examples of the "bleaching" of wallrock silicates close to hydrothermal deposits have been cited in geological literature. Perhaps the best known districts in which this has been noted include the Butte area (Sales, 1914) and the East Tintic District, Utah (Lovering, 1949). Sales suggests that the iron silicates were broken down to form the pyrite of the altered zones (p. 32). Lindgren (1933, p. 534) has invoked the same process to explain the development of pyrite in the alteration zones of mesothermal gold-quartz veins.

The close spatial relationship between biotite and pyrite has been mentioned earlier, as well as the general lack of chlorite and hornblende with pyrite. This association can be explained in one of several ways: The mineralogical differences may represent varying compositions of the original sediment and the introduced sulphur reacted only with the biotite to form pyrite; or the introduction of sulphur into certain positions in a compositionally homogeneous rock caused the mineral assemblage to break down into largely biotite and pyrite.

Considering the possibility that sulphur moved evenly through a rock complex of varying mineralogy, it is structurally improbable that volatiles would move more or less evenly through a rock of varying composition; it is much more reasonable that movement would take place along more or less well-defined low pressure areas. Also, it has been observed in many studies of wallrock alteration that minerals relatively high in Bowen's Reaction Series are transformed into minerals lower in the scale during ore deposition. A number of examples have been summarized by Butler (1932). One would assume, then, if sulphur had complete access to the hornblende in the schist, the hornblende would have been destroyed.

The other possibility—namely, that certain changing physico-chemical conditions, including the introduction of sulphur, have caused the change in the silicate mineral assemblage—will now be considered. This could be regarded as a more or less closed system except for the sulphur, and would require that the bulk chemical composition of the rock remain relatively uniform. Strict uniformity would, of course, be impossible because of material is obviously necessary to form even one pyrite crystal from neighboring constituents. Bulk chemical analyses have not been made in this study, so at this time no information is available on the quantitative distribution of the various elements through the rock as a whole. But speculation suggests that breakdown of a mineral assemblage into biotite, pyrite, and non-ferromagnesian minerals is possible.

To form an equivalent volume of biotite from hornblende with the approximate composition of the hornblende analyzed would involve a loss of calcium and silicon, and an increase in potassium, iron, aluminum, and water. The abundant calcite and quartz in the schist and in the orebody could account for the calcium and silicon freed. The potash required in biotite may have come from potash feldspars. In this connection, refractive index determinations of the schist feldspars indicate that all the feldspar associated with biotite, and most of that associated with chlorite and hornblende is a sodic plagioclase. In one specimen, however, only microcline was found. The sole ferromagnesian mineral in this specimen was chlorite; biotite was characteristically absent.

Is it not possible, then, that a mineral assemblage including potash feldspar and an iron-rich aluminous hornblende could have been altered by the action of sulphur, water, and probably heat to an assemblage consisting of biotite, talc, pyrite, quartz, and a hornblende of a different composition? A feature observed in thin-section from a specimen about 1200 feet from the orebody lends partial support to this theory. The hornblende there commonly contains a core of a much darker, highly altered hornblende which may represent the original mineral.

Whether the other ore minerals—scheelite and molybdenite—can be considered to have a similar origin to that suggested for the pyrite must remain, in this study at least, an unanswerable question. The close spatial relationship between ore and pyrite suggests a genetic relationship. Yet none of the analyses of the silicates show even a trace of tungsten or molybdenum. This could be explained in a number of ways. The scheelite and molybdenite may, indeed, have been introduced into their present positions from a considerable distance and from an unknown source. A second possibility is that the schist minerals contain tungsten and molybdenum but that they are present in amounts too small to be detected. This explanation might appear reasonable for tungsten since the spectrographic method used has rather a low sensitivity for tungsten; but molybdenum, if present in amounts greater than one part per million, should have been detected.

Still a third possibility, although one that has no direct supporting evidence, is that the original minerals in this sedimentary complex contained both tungsten and molybdenum but that these have been released by metamorphism and have migrated to the central ore zone, or out of the area of immediate observation. That they have completed their migration and that pyrite has not, could be due to the tungsten and molybdenum being released earlier than the iron. In this connection, paragenetic studies of numerous ores containing these elements have shown that in practically all cases tungsten and molybdenum minerals are deposited earlier than pyrite (Edwards, 1947, p. 114). If an origin by metamorphic differentiation (Ramberg, 1952, pp. 265, 266) can be ascribed to this deposit, the process could be considered as having been arrested at a stage where tungsten and molybdenum have completed their migration to a stable area, whereas pyrite is still more or less where is was formed.

Conclusions

Variations in the iron and cobalt content of biotite have been observed and can be correlated with the development of pyrite in the schist. This indicates that the metallic elements in the pyrite have likely been derived from the wallrock minerals—in this case biotite. No tungsten or molybdenum were detected in the wallrock silicates.

The distribution of cobalt, nickel, and manganese in co-existing biotite and pyrite indicate their relative sulphophile characters. Cobalt is the most sulphophile of these elements, followed by nickel and manganese, in that order.

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