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Ore Deposition at Franklin Furnace, New Jersey

By J. E. Spurr and J. Volney Lewis

orebodies.

Grenville sediments are of Huronian age.

[illegible]

[illegible]

[illegible]

pegmatite forming a limestone dike, which in contact

planation is in accordance with Spencer's view. But no trace of the fault plane or fault zone has been found; exhibited by the various Pre-Cambrian rock contacts

to oxides and silicate, with distillation of sulphur and

limestone (Kittatinny) were laid down upon the ver-

neous with the pegmatite in part

Franklin Furnace.

N. E. of New Jersey. Zn ores, mined for many years.

Rocks - Granite gneiss, crystalline ls., granite (cuts 1,2) both cut by dikes. The ore occurs in a bedded deposit in the (Pal. or Arch.) ls.

Ores.

1. Red Zincite. 92-4% ZnO, 6-8% MnO.

Gangue calcite 2. Willemite 68% ZnO 5-10% MnO.

3. Franklinite. 56-7% FeO

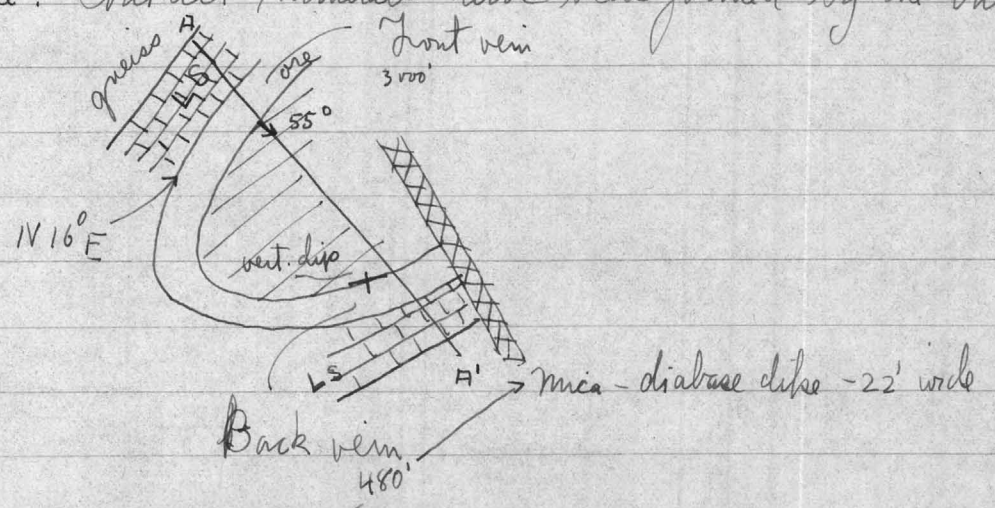
4-16% MnO

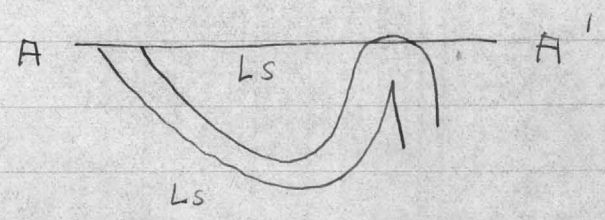
7-23% ZnO

10-16% Mn_2O. [3/2/17]

The Zn ores are underlain by magnetite.

The granite cuts the ores so that the ores are older than the granite. Contact minerals have been formed by the intrusion.





Genesis - Obscure.

The minerals in the ore-body are not primary (no ZnS) but are gossan ores. They are bedded deposits. The Ls. is highly metamorphosed. Oxidation & 2nd enrichment occurred in the Ls. before metamorphism.

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THE GEOCHEMISTRY OF THE ORES OF FRANKLIN, NEW JERSEY.*

JOHN DREW RIDGE.

ABSTRACT.

It is suggested that the ores at Franklin and Sterling are pyrometasomatic deposits formed in the Franklin Limestone, at some distance from the unknown igneous source of the ore-forming fluid. The general classes of skarn minerals developed by contact metamorphism (contact metasomatism in Barrell's sense of the term)—spinels, garnets, pyroxenes, epidotes, micas, olivines, and melilites—all are present in the deposits. These minerals are, however, unique in their high content of Mn^{+2} and Zn^{+2} and their relatively small amounts of Fe^{+2} and Mg^{+2}. The explanation advanced for this peculiar situation is that, in the source magma of the ore-forming fluid involved, an unusual abundance of Mn^{+3} resulted in the oxidation of most of the Fe^{+2}, which normally would have entered the ore fluid in that form, to Fe^{+3} and the concomitant reduction of much Mn^{+3} to Mn^{+2}. This oxidation of ferrous to ferric ion resulted in an uncommonly high acceptance of magnesium ion in the dark silicates of the crystallizing source magma and almost entirely eliminated Mg^{+2} from the ore fluid. The unusual scarcity of ferrous and magnesium ions in the ore fluid forced Zn^{+2} and Mn^{+2} to neutralize in large part those various contact mineral anions which are found in normal contact deposits combined with Fe^{+2} and Mg^{+2}. The lack of Cu^{+2} is thought to have been caused by its proxying for ferrous iron in the minerals of the original source magma and the paucity of Pb^{+2} by the difficulty of the large lead ion in entering and neutralizing any of the variety of anions available.

INTRODUCTION.

THE ore deposits at Franklin and Sterling in Sussex County, New Jersey first attracted attention before 1730 (1, p. 14).[1] Through the 200-odd years since their mineral worth was first suspected, countless mineralogists and geologists have visited the deposits, collected specimens of the unique mineral assemblage, and written and published discussions of the origin of the ore bodies, the printed length of which often varied inversely with the duration of the visit. It is, therefore, with some hesitancy that I enter the arena as my actual acquaintance with Franklin is slight, but such unique deposits almost certainly must have a unique explanation and what follows has that virtue at least.

In Palache's (1, pp. 2–14 and 130) monumental work on Franklin-Sterling mineralogy, he lists 289 titles in a bibliography running from 1810–1935, inclusive. From this impressive background of ideas, Palache summarized (1, pp. 23–24) five hypotheses which had been advanced by various authors,

* "Contribution of the Divisions of Geology and Mineral Economics, The Pennsylvania State College."

[1] Numbers in parentheses refer to Bibliography at end of paper.

including himself, and concludes that his own, calling for the metamorphism of a mixed deposit of oxidized ores of zinc, iron, and manganese, is most logical. Since that time Pinger (2, pp. 84–87) has advanced cogent arguments against Palache's theory and has discussed further the various other hypotheses mentioned by Palache. Pinger concludes that "the only hypothesis of origin that fulfills the observed conditions is a replacement of favorable horizons in the folded structures by a primary oxide ore." Pinger declines to speculate on the chemistry and mechanics of transportation and emplacement which is much to be regretted for no geologist has had more or better opportunity to observe the Franklin-Sterling ores and none is more capable of a sound contribution to the problem.

THE FRANKLIN ORES—A PYROMETASOMATIC DEPOSIT.

Pinger's concept of the Franklin deposits as primary oxide ore, however, is a distinct contribution to the solving of the problem of their genesis and in this paper I shall attempt to build from that foundation. If these ores are primary as Pinger contends (and what I have seen of them certainly convinces me that they are) they must, from the assemblage of high temperature ore and gangue minerals developed, have been formed under conditions of high temperature and pressure, at least several thousand feet beneath the then existing surface. The deposits were classified by Lindgren (3, pp. 737–739) as pyrometasomatic[2] and if it is kept in mind that the deposits are not at or near any known igneous contact, such a classification is satisfactory. As Loughlin and Behre (4, p. 47) pointed out, the distinction between hypothermal and pyrometasomatic (contact metamorphic) deposits is in the rocks in which they are formed; the solutions from which the two types of deposits are derived are essentially similar. The Franklin deposits, then, can be strictly termed "hypothermal in calcareous rocks" or "pyrometasomatic not at an igneous contact" without doing violence to the Lindgren scheme of classification.

The justice of classing the Franklin ores as pyrometasomatic is further demonstrated by comparing them, for example, to the deposits at French Creek in Eastern Pennsylvania (5). The French Creek ores are in a Precambrian white marble similar to, if not the same as, the Franklin (or White) Limestone at Franklin. There is, of course, a great diversity in the mineral suites but the general setting and the occurrence of the ore minerals is essentially the same in the two deposits. French Creek is a normal magnetite contact-metamorphic ore body—normal in its silicate and ore mineral content and in its relation to the igneous rock from which the ore-forming fluids were derived. Franklin is an unusual contact-metamorphic deposit—unusual in its mineral suite and in its position definitely away from contact with any possible source rock for the ore solutions.

[2] In this paper I have used "pyrometasomatic" and "contact metamorphic" interchangeably as adjectives to modify such terms as "ore body" or "mineral deposit" but have qualified both by indicating whether the deposit is truly at an igneous contact or away from it. Actually, in the strict sense of Barrell and Bateman, essentially all the deposits and minerals discussed are "contact metasomatic."

Ideally it would be desirable to explain both of the anomalous conditions that obtain at Franklin—lack of immediately adjacent igneous source rock and the strange mineral suite. As to the first peculiarity I have little to contribute except to remark that the igneous source rocks cannot have been the pegmatites because pegmatite is lacking at Sterling and often is considerably removed from ore at Franklin. I am in agreement with Pinger that the ores are later than the pegmatites and I do not believe that they were in anyway responsible for the ore. While I think that some of the unique Franklin minerals are the result of the reaction of the ore-forming fluid with pegmatitic skarn, much of the skarn is found around ore which is not spatially associated with pegmatite at all. In other words, much, if not most, of the skarn and the peculiar minerals it contains was the result of the reaction between the White Limestone (and what relatively few impurities it may have contained) and the ore-forming fluid and of nothing else. That the pegmatites were related to the ore-forming fluid in their ultimate source, however, is indicated by the notable amounts of manganese in pegmatite skarn well removed from any appreciable quantity of ore.

Even granting that a number of the mineral species at Franklin were developed by alteration of pegmatite skarn minerals by the ore fluid, the three principal ore minerals, willemite, franklinite, and zincite, and many of the gangue minerals have been produced without any contribution from the pegmatites and represent a definite, though peculiar, type of pyrometasomatism of the Franklin Limestone. The problem posed by these strange contact-metamorphic minerals is to explain why such unusual spinels, silicates, and simple oxides formed instead of the normal contact spinels, silicates, and oxides of pyrometasomatic deposits such as that at French Creek.

As Ries and Bowen (6, p. 552) demonstrated, the order of deposition of the ore minerals at Franklin was first the silicates tephroite and willemite, which were introduced contemporaneously or nearly so, followed by the spinel, franklinite, which replaced mainly the limestone but also the silicates slightly as well. The oxide zincite was somewhat later than franklinite and replaced calcite and silicates and filled fractures in franklinite (which fractures probably contained calcite before the zincite was emplaced). This is the general order of formation of silicate gangue and spinel and oxide ore minerals in the average contact deposit and fits (allowance being made for the abnormal composition of these minerals) with the classification given the ores by Lindgren. The paragenesis of the less common and less well studied silicates at Franklin has never been worked out in detail but apparently varies somewhat from one area of the mine to another. Actually the sequence of emplacement may not be too complicated because the relations of the gangue silicates to each other and to the ore minerals have been considerably obscured by the insistance of the earlier workers, principally Palache and Ries and Bowen, that the pegmatites came in after the ore minerals and that all of the non-ore silicates not in hydrothermal veins were the result of the interaction of solutions given off by the crystallizing pegmatites and the already emplaced ore minerals. The disproving of this theory

by Pinger and his colleagues at Franklin has made possible a much more reasonable interpretation of the reasons for the development of the Franklin mineral assemblage. Instead it now appears that the bulk of the skarn is the result of the reaction of the ore-forming fluid with the calcite of the White Limestone and that locally an even more complex skarn was developed when the ore fluids encountered the skarn around the earlier pegmatites.

THE PYROMETASOMATIC MINERALS AT FRANKLIN.

Spinels.—If Franklin is an unusual pyrometasomatic deposit, then it is important to indicate exactly how it differs from a normal deposit of the class. The main difference and the one I believe to be the ultimate cause of all the peculiar minerals developed is the relative abundance of manganic ion and the concomitant paucity of ferrous iron in the deposit and, presumably, in the ore fluid from which it was formed. While ferrous iron is minor in amount in the Franklin minerals, iron in the ferric state is the principal cation in franklinite, a spinel, which is the dominant ore mineral—43% of the average ore according to Palache (1, p. 17). In a normal pyrometasomatic deposit, the $Fe_2O_4^{-2}$ anion is in balance with Fe^{+2} and ferrous ferrite (magnetite) is present. At Franklin, however, the ore-forming fluid was relatively poor in Fe^{+2} and the $Fe_2O_4^{-2}$ was neutralized in large part by Zn^{+2} and Mn^{+2}, and to a lesser extent by Fe^{+2} to give a mineral that is actually a solid solution of various amounts of magnetite, franklinite, and jacobsite, with $Mn_2O_4^{-2}$ substituted in small part for $Fe_2O_4^{-2}$ (7, p. 698).[3]

The spinel group is also represented at Franklin by gahnite, $ZnAl_2O_4$. The usual representative of the non-iron bearing members of the spinel groups in contact-metamorphic deposits is spinel proper, $MgAl_2O_4$, and its absence at Franklin is indicative of a low Mg^{+2} content in the ore fluid just as the presence of franklinite, instead of magnetite, is suggestive of a low Fe^{+2} content.

Olivines.—A low Fe^{+2} content of the ore fluid is also indicated by the silicates present. As Neuman (8, p. 578) has suggested, the 4-coordination and homopolar bonding of the zinc atom with oxygen prevents its complete substitution for Fe^{+2} or Mg^{+2} in the olivine lattice despite its similar ionic radius (0.79Å).[4] So instead of olivine, the phenacite-type mineral, willemite (Zn_2SiO_4), was formed at Franklin because the ore fluid was poor in Fe^{+2} and Mg^{+2} as well.[5]

[3] The absence of hausmannite, $MnMn_2O_4$, at Franklin is probably due to the low concentration of $Mn_2O_4^{-2}$ in the ore fluid which seems to have been sufficient only to allow $Mn_2O_4^{-2}$ to proxy for $Fe_2O_4^{-2}$ to a limited extent in franklinite but never was abundant enough to cause the formation of hausmannite as a distinct mineral.

[4] All ionic radii used in this paper are taken from Dana (7, pp. 4–5) with the exception of Cu^{+2} which is not given in Dana. Nockolds and Mitchell (9, p. 543) give Cu^{+2} as equal in radius to Fe^{+2} and it is so considered here despite the slight difference (0.04Å) between the Dana value and that given by Nockolds and Mitchell.

[5] The lack of appreciable Mg^{+2} in the Franklin ore fluid, as witnessed by its rarity in the gangue minerals (including the recrystallized calcite), also was an important control over the minerals formed and would make it likely that the ore fluid came from a silicic rather than a basic source magma, although this is not certain because the unusually complete oxidation of Fe^{+2} to Fe^{+3} (if it took place in the magma) would have increased greatly the need in the primary magma for 6-coordination Mg^{+2} to neutralize the various silicate anions. This point will be touched on further on pp. 187–188.

of garnets in pegmatite skarn and in ore skarn and in the areas where the two overlap must be charged to a similarity of source and composition (high Mn^{+2} and Fe^{+3} and low Fe^{+2}) of the ore fluids and the pegmatitic fusions. The lack of alamandite and pyrope is a tribute, again, to the low Fe^{+2} and Mg^{+2} content of the ore fluid and to the high concentration of Mn^{+2}. The presence of much more Fe^{+3} than Al^{+3} in the garnets is unusual and emphasizes the abundance of Fe^{+3} in the ore fluid.

Micas.—Manganophyllite, probably $K_2(Mn)_{6-x}(Mg,Fe)_x(OH)_4(Si,Al)_8O_{20}$, is the representative of the biotite group in the Franklin skarn and its composition indicates the low Fe^{+2} and Mg^{+2} concentrations of the ore fluid and the high Mn^{+2}. It is unique in being the only fairly common mineral at Franklin (outside the pegmatites) to contain potassium. This also brings out the lack of sodium-bearing minerals except for those in the pegmatites.

SUMMARY OF THE PYROMETASOMATIC CHARACTERISTICS OF THE FRANKLIN ORES.

From the preceding discussion, it is apparent that the typical gangue minerals of a contact-metamorphic deposit—garnet, spinel, diopside, wollastonite, epidote, biotite, olivine, and vesuvianite—are all present, in rather unusual chemical character it is true, in the Franklin skarn. It is also evident that the main ore mineral—franklinite—is only a variant of the spinel mineral, magnetite, that the other important ore mineral—willemite—is a phenacite-type mineral which, had Fe^{+2} or Mg^{+2} been available in quantity, probably would have been an olivine. The minor ore minerals—zincite and tephroite—are respectively a variant of periclase (MgO) and an unusual olivine, both not unlikely in a contact deposit.

Of the gangue minerals, the most common are the variants of garnet, wollastonite, diopside, and biotite—a normal contact-metamorphic assemblage. It seems probable then that the deposit at Franklin is a contact metamorphic one, not actually at an igneous contact, containing unusual ore and gangue varieties of common contact minerals because the ore solutions were abnormally low in Fe^{+2} and Mg^{+2} and probably in S^{-2} and Cu^{+2}, high in Mn^{+3} and well, though perhaps no more than normally, supplied with Zn^{+2} and probably with Pb^{+2}. Why such a set of conditions has obtained poses questions that I will attempt in part to answer in the following section of this paper.

THE FRANKLIN ORE-FORMING FLUID.

Iron in Igneous Magmas and Contact Deposits.—Wickman (10, pp. 380–381) points out that, as the average magma crystallizes, Fe^{+3} in the diminishing, still-fluid portion increases in relation to Fe^{+2}. He considers that this phenomenon can be explained as the result of two processes, each of which tends to concentrate Fe^{+3} over Fe^{+2} in the remaining liquid. The first of these is the greater acceptance of Fe^{+2} as compared with Fe^{+3} in dark silicates. The second is the simultaneous oxidation of Fe^{+2} to Fe^{+3}. In other words, Fe^{+2} is being removed from the melt at a faster rate than Fe^{+3} and at the same time a part of the Fe^{+2} still in the molten phase is being converted

to Fe^{+3}.[7] An examination of the average analyses of various igneous rocks, ranging from dunites to granites (11, p. 166), shows that an increase in the ratio Fe^{+3}/Fe^{+2} is to be noted from basic to acid rocks and probably reflects a similar enrichment of Fe^{+3} in the primordial earth magma to that which Wickman mentions for derivative magmas of later origin. Despite these variations in Fe^{+3}/Fe^{+2} ratio, no contact-metamorphic or *hydrothermal* iron deposits contain franklinite except Franklin-Sterling although several are related spatially, and probably genetically, to intermediate and even to acid rocks (Lyon Mountain). In short, in normal magmas under normal conditions of crystallization, there is always enough Fe^{+2} left in the late stages of the cycle to assure the presence in the ore fluid of enough Fe^{+2} to balance the $Fe_2O_4^{-2}$ anions it contains.

Franklin and Iron Springs.—Iron Springs, Utah (13, 14) is a rather peculiar contact-metamorphic deposit in which the large bulk of the iron is Fe^{+3} in hematite. This hematite, however, is not the original iron mineral in the important replacement ore bodies but is the result of the high temperature hydrothermal replacement of magnetite (13, p. 487) which last was deposited with its normal quota of Fe^{+2} ions. At Franklin, it must be remembered that the franklinite was deposited as such and is not the result of the replacement of magnetite. In other words, at Franklin the oxidation of Fe^{+2} took place before, and at Iron Springs after, magnetite deposition. Thus, though Franklin and Iron Springs are both unusual contact deposits, they are different and are probably due to different causes. This is indicated not only by the time of Fe^{+2} oxidation but also by the large Mn^{+2} content at Franklin as opposed to its essential lack at Iron Springs.

Having used Iron Springs to emphasize that the Franklin zinc ferrite is a primary ore mineral and not a replacement of a previously formed ferrous ferrite and that Mn^{+2} is lacking at Iron Springs and not abundant as at Franklin, it is necessary to concentrate on Franklin and leave the problem of the Iron Springs oxidation to some one else.

Iron, Manganese, and Magnesium at Franklin.—It seems that the low concentration of Fe^{+2} and the unusual abundance of Mn^{+2} in the Franklin ore fluid must have had a direct connection. This connection is not, of course, hard to discover for the half reactions:

$$Fe^{+2} = Fe^{+3} + e^{-1} = -0.77 \text{ volts}$$
$$Mn^{+2} = Mn^{+3} + e^{-1} = -1.51 \text{ volts}$$

indicate that the reaction

$$Fe^{+2} + Mn^{+3} = Mn^{+2} + Fe^{+3}$$

will go to the right, under standard conditions, with an emf of +0.74 volts (15, p. 526). This means that, either in the original magma or in the ore-forming fluid developed from it, there was enough Mn^{+3} to convert most of the Fe^{+2} available, i.e., not accepted into dark silicates, to Fe^{+3} while, at the same time, being itself converted to Mn^{+2}. This is confirmed by the lack

[7] The enrichment of Fe^{+2} relative to Mg^{+2}, which also is going on in the melt, is "somewhat obscured" by the oxidation of Fe^{+2} to Fe^{+3} but still is quite apparent (12, p. 229, et. seq.).

of really important amounts of Fe^{+2} or Mn^{+3} in the Franklin ore and gangue minerals.

In the normal ore deposits of hydrothermal origin it will be remembered that the manganese is in the manganous state while the much more abundant iron is in both ferric and ferrous states, indicating that there was not enough Mn^{+3} even when completely reduced to Mn^{+2} to oxidize more than a fraction of the Fe^{+2}.

If this oxidation of Fe^{+2} occurred largely in the main part of the cycle of magma crystallization rather than in the ore fluid, the amount of Mg^{+2} which would have been used up in the dark silicates would have been much more than in a magma in which Fe^{+2} oxidized to the customary much lesser degree. This excessive incorporation of Mg^{+2} in the dark silicates would have reduced the quantity available for the late-stage ore fluid considerably. That Mg^{+2} probably was present in the Franklin ore fluid only in small amount is indicated by the lack of dolomitization of the White Limestone and the rarity of magnesium-bearing ore and skarn minerals. Certainly, had Mg^{+2} been present in quantity, zincite, gahnite, and hardystonite would not have developed, instead periclase, spinel proper, and åkermanite, respectively, would have been formed.

The fact that the percent of Mn^{+2} in the Franklin ore is not equal to that of Fe^{+3} (as it should approximately be if the bulk of the oxidation of Fe^{+2} had been produced by the reduction of Mn^{+3}) suggests that, in the parent magma chamber, Mn^{+2} (ionic radius = 0.91Å) proxied for unavailable Fe^{+2} in the dark silicates and reduced by a considerable amount the Mn^{+2} which could go into the Franklin ore fluid. This further strengthens the possibility that the bulk of the oxidation of Fe^{+2} took place in the magma rather than in the ore-forming solutions.

Sulfur at Franklin.—The absence of sulfides in any appreciable quantity at Franklin is not particularly surprising as the amount of sulfide ore in typical magnetite contact deposits is not large. The amount of pyrite in the ore, however, certainly is less than in the average pyrometasomatic ore body, another indication of the scarcity of ferrous iron. The small quantities of sulfate minerals at Franklin indicate that there probably was no abnormally large oxidation of S^{-2} to the S^{+6} of SO_4^{-2}. This suggests that the generally later and lower temperature solutions which deposited the sulfides (sphalerite not unreasonably is the most common) did not contain any large quantities of Mn^{+3}. Had there been such, the S^{-2} would have been oxidized to, or close to, the limit set by the Mn^{+3} available. This is true because the oxidation potentials of the half reactions involved are such that the three steps of the reaction

$$S^{-2} + 8Mn^{+3} = S^{+6} + 8Mn^{+2}$$

all go easily to the right in acid or alkaline solutions (15, p. 526). This again suggests that the oxidation of Fe^{+2} to Fe^{+3} took place in the magma chamber and not in the upward moving ore fluid. This poses the problem of why all of the S^{-2} in the magma chamber was not oxidized to S^{+6} by Mn^{+3} because this reaction should proceed preferentially to the oxidation of Fe^{+2}

to Fe^{+3} by the same cation. The answer probably has been suggested by Weyl (16, p. 39) who points out that the zinc in silicate melts forms a tetrahedral structure with sulfur which is analogous to the silicon-oxygen tetrahedron. So long as the sulfur is locked up in this homopolar combination with zinc, the oxidation of S^{-2} by Mn^{+3} is inhibited and the sulfur remains in solution in the silicate magma until the development of the water-rich fluid provides a medium in which the zinc-sulfur complex anion is more soluble than in the silicate melt. This leaves the cations Fe^{+2} and Mn^{+3} free to react with each other approximately to the limit of their ability to do so.

Copper at Franklin.—Another problem posed by the Franklin deposit is the essential absence of copper which, as was mentioned previously, is unlikely had the ore-forming fluid carried copper in quantities of the same general order of magnitude as those of zinc. Had such an abundance of copper been present in the ore fluid it is difficult to see how the minerals formed would not have been copper-rich spinels, oxides, and silicates rather than those zinc-rich ones which actually occur. This follows because of the similarity in size, type, and field strength of Cu^{+2} (17, p. 221)[8] to Fe^{+2}. Had Cu^{+2} been available in quantity, it would have been much more likely to proxy for Fe^{+2} than Zn^{+2} which last has a greater preference for homopolar bonding and 4-coordination than Cu^{+2}. It might be put forward that copper was in the Franklin ore-fluid as Cu^{+1} which would not proxy for Fe^{+2} but against this it must be argued that Cu^{+1} would have oxidized to Cu^{+2} in the presence of Mn^{+3} in the parent magma chamber even more readily than Fe^{+2} to Fe^{+3} (15, p. 526). It is possible, of course, that the lack of copper in the ore fluid simply may reflect a lack of that element in the parent magma itself. The neighboring Paleozoic zinc deposits at Friedensville in Pennsylvania and the even closer zinc-lead ore bodies in the Shawangunk of southeastern New York also are lacking in copper and these occurrences may reflect an unusual deficiency in copper in the earth's crust of this general region. There is also the possibility, however, that copper was present in the magma and was prevented from concentrating in the ore-forming fluid for one or combination of both of two reasons. These are: (1) that the large bulk of the copper, oxidized to Cu^{+2} by Mn^{+3}, was accepted in the dark silicates crystallizing from the parent magma and essentially none was left over for incorporation in the ore fluid and (2) that much of the copper was incorporated in an immiscible sulfide melt developed early in the magma's cooling history. As to the first possibility, Nockolds and Mitchell (9) have shown that copper (as Cu^{+2}) is appreciably acceptable in the dark silicates which are basically iron-magnesium silicates. With a marked decrease in Fe^{+2}, due to the unusually large Mn^{+3} content in the Franklin-Sterling source magma, the opportunity for Cu^{+2} to enter the femic minerals would have been greatly increased and the copper left in the late stages of crystallization for incorporation in the water-rich ore fluid might well have been essentially nil. In connection with the second possibility, Rankama and Sahama (11,

[8] Neither Osborn nor his source (Dietzel) gives the field strength of copper but for Cu^{+2} in 6-coordination it is the same as for Fe^{+2} in 6-coordination. For Cu^{+2} in 4-coordination the field strength is the same as Zn^{+2} but Cu^{+2} has a greater tendency to form ionic bonds than does Zn^{+2}.

p. 969) point out that copper has a greater affinity for sulfur than iron or nickel. This indicates that in a basic magma rich enough in sulfur to cause the separation of an immiscible sulfide phase on cooling of the combined melt, the concentration of copper in the sulfide melt would greatly reduce the amount left in the molten silicates.[9] Obviously, both of these tendencies would operate in the same direction—the reduction or complete elimination of copper in the water-rich ore fluid when that phase developed.

The Non-Existence of Natural Copper Silicates and Spinels.—The lack of minerals at Franklin in which copper is the principal cation is, therefore, susceptible of explanation. It may be asked, however, why there are no copper-dominant silicates or spinels in other contact deposits in which the content of copper in the ore fluid must have been much higher than it is presumed to have been at Franklin. The answer to this probably is that, in the formation of such normal contact deposits, the ratio of Fe^{+2} to Cu^{+2} in the ore fluid was large and the Cu^{+2} concentration was continuously being reduced by its substitution (to a minor extent) for Fe^{+2} in the iron-rich contact minerals and never reached the value necessary to exceed the solubility products of any possible copper-dominant minerals. On the other hand, the minor development of such zinc-dominant minerals as willemite and tephroite, in certain high temperature deposits other than Franklin, can be explained by the difficulty of proxying Zn^{+2} for Fe^{+2} when the latter is abundant. This failure of Zn^{+2} to be subtracted from the ore-forming fluid, under normal conditions of contact metamorphism, locally may result in building up the Zn^{+2} concentration to the amount required to exceed the solubility product constant of one or more zinc silicates. Thus, it is possible that zinc-dominant silicates can form occasionally in a normal contact deposit but those of copper cannot. Only if an ore-forming fluid low in iron and rich in copper were to form a contact deposit could copper silicates, spinels, and simple oxides be developed and then only if the ore fluid were rich in the necessary anions and either poor in sulfide ions or above the temperature at which sulfides could precipitate. It is unlikely, moreover, that such an ore fluid often would be produced because, as has been suggested, the excessive oxidation of ferrous to ferric ion in the parent magma would force an unusually large proportion of the copper in that magma into the femic silicates and would, thereby, lower markedly the copper available for the ore fluid.

A Basic Source Magma for the Franklin Ore Fluid?—The inference is inescapable, that, if the copper content of the parent magma of the Franklin ores was reduced wholly or in part by the separation of a sulfide melt, the magma in question was a basic one. This follows from two lines of reasoning: (1) that ore bodies, such as Sudbury or Lancaster Gap, which formed at least in part from the solidification of sulfide melts, are closely associated spatially and genetically with basic rocks, and (2) that only basic rocks of

[9] It should be noted that Rankama and Sahama say that manganese has an even higher affinity for sulfur than copper but this has been determined mainly by slag studies and cannot apply to natural magmas and sulfide melts of magmatic origin in which alabandite is an uncommon mineral.

the primary outer shell of the earth could contain enough sulfides to form, on melting, a magma from which, on cooling, a sulfide melt would separate. So far as I know, the suggestion has never been put forward that the Franklin ore fluid derived from a basic magma and there are a good many arguments against it. For example, there are no basic rocks, except those much later in time, associated with the Franklin ores. In addition there is no extensive dolomitization or serpentinization of the host rock—Franklin Limestone—and of the silicate minerals developed in it as might have been expected had the source magma been basic. Of course, the paucity of Fe^{+2} in the parent magma would have reduced the amount of Mg^{+2} in the ore fluid considerably but, if that fluid had come from a basic magma, there still should have been much more Mg^{+2} in the Franklin minerals than there is. Finally, the pegmatites at Franklin, while pre-ore, are rich in manganese, if not in zinc, as is witnessed by the Mn^{+2}-rich garnet and manganiferous calcite contact skarns developed around them even at considerable distances from ore. This argues a common or similar parent for ore fluid and pegmatitic fusion. Although the variety of pegmatites at Franklin is wide (there are none at Sterling), they all are definitely of acid magma parentage and have produced by contact metamorphism many of the minerals so formed by the ore fluids.

Thus, as things stand now, it is unlikely that the Franklin ore fluid came from a basic magma. The probably low Fe^{+2} content of the magma seems to me to obviate the need for the removal of copper in a sulfide melt—it probably was all used up in neutralizing a fraction of the dark silicate anions crystallizing from the parent magma.

A Basic Source for Other Zinc-Lead Ore Fluids?—In a more normal deposit of zinc and lead, however, in which the copper content is low and the manganese content normal, I would suggest serious consideration be given to the possibility of the ore fluids in such cases having come from basic magmas from which the copper had been largely eliminated through the separation of an immiscible sulfide melt. The alternative to this mechanism is, of course, that the parent magma of the ore fluid in question was quite low in copper. The problem well may be resolved in those zinc-lead deposits low in copper, the time of emplacement of which can be established with a fair degree of certainty. In these, age determinations based on the ratio of lead isotopes (18, p. 1448) should give much older ages if the deposits were of basic rather than of intermediate or acid origin because of the much smaller content of radio-active elements in basic than in acid rocks. Presumably this is one of the possibilities Cannon had in mind when he wrote: "They (Nier's isotope determinations of ore leads) reaffirm the likelihood that lead ores originate from diverse sources."

CONCLUSIONS.

From the considerations presented in the course of this paper, it seems probable that the deposits at Franklin and Sterling are pyrometasomatic deposits whose unique mineral suite can be explained almost entirely as a consequence of an unusually high manganic ion content in the parent magma

of the ore fluid. Essentially all of the peculiarities of the deposit stem from this cause—the lack of lead is less directly related to this cause; lead is largely missing because it would not fit in the lattices of the minerals being formed. It only remains to explain the cause of the remarkable abundance of Mn^{+3} in the parent magma and anticlimatically I have no suggestion to offer but the heterogeneity of the primary earth. This is, of course, unsatisfying in the extreme but an attempt to explain the heterogeneity, were I competent to make it, would be far beyond the scope of this paper.

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