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A summary of the theories of the origin of the Lake Superior copper ores, with evidences pertaining thereto

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A SUMMARY OF THE THEORIES OF THE ORIGIN OF THE LAKE SUPERIOR COPPER ORES, WITH EVIDENCES PERTAINING THERETO.

T256

by

Eva Endurance Hirdler.

A

T H E S I S

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
D E G R E E O F
BACHELOR OF SCIENCE IN GENERAL SCIENCE

Rolla, Mo.

1911

Approved by *[Signature]*

Assistant Professor of Geology and Mineralogy.

11869

MISSOURI
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C O N T E N T S .

"A Summary of the Theories of the Origin of the Lake Superior Copper Ores, with Evidences pertaining thereto."

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A SUMMARY OF THE THEORIES OF THE ORIGIN OF THE
LAKE SUPERIOR COPPER ORES, WITH EVIDENCES
PERTAINING THERETO.

HISTORY.

The Lake Superior Copper district of Michigan was the first American copper field of importance and is now one of the oldest of the leading copper producing districts of the world, as well as the third in size of output (1909) in the United States.

The Copper ores were first discovered by a race preceding the North American Indians- possibly the Mound-builders.

Benjamin Franklin, having heard of the mineral wealth of Lake Superior took advantage of this knowledge, and when preparing the Treaty of Paris which brought peace between the United States and Great Britain, he deflected his pencil a trifle to the north upon the crude map that was made the basis of delimitation, and thereby secured to the possession of the United States bodies of copper and iron that since have yielded those metals to the value of more than a billion dollars.

The first miners to arrive in this district located in 1843. The location of claims soon became so abundant that they overlapped in many cases, resulting in

confusion which grew worse until the Government adopted the expedient of selling the mineral lands outright. However, actual mining was not begun until the year 1844, and in 1846 the first smelting operations were made which were gradually developed into the improved methods of today.

At the present time this district may not only boast of being one of the leading copper districts of the world, but may also boast of the fact that within its confines is located the deepest shaft in the world- namely Tamerak #3, 5283 feet deep.

STRATIGRAPHY.

Paleozoic- Cambrian - Lake Superior Sandstone

{ Upper Keweenawan- mostly sandstones; little
{ conglomerate; small amount of igneous
{ material

Algonkian { Middle Keweenawan- sandstone and conglomerate
{ about half and half, with considerable
{ igneous material

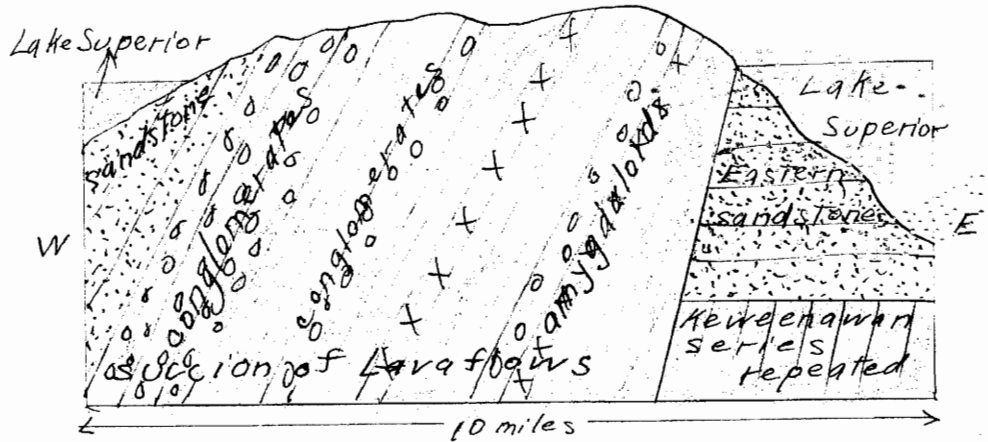
{ Lower Keweenawan- mostly basic lavas, with
{ some conglomerate

Archean - Granites and schists.

The above formations, up to the Cambrian, are pierced considerably by intrusives.

STRUCTURE,

Keweenaw Peninsula. - (Fig. 1.)



The Keweenaw, to which the copper deposits are limited, comprise part of a great synclinorium. In detail the structure of the upper Huronian is far more complex than that of the Keweenaw series, and appears in a series of rolls which apparently have no counterparts in the Keweenaw series. The lower and middle Huronian sediments occupy but limited areas as compared with the other Algonkian rocks. For the most part they are closely folded and have steep dips. Their strikes and dips give evidence that they were complexly folded before the beginning of the earth movements which resulted in the Lake Superior synclinorium. They accord in structure only in that the prevailing strike of bedding, folds, and cleavage is east-northeast, parallel to the axis of the Lake Superior syncline. The same is, of course, true of the Archean. In general, the dips toward the south on the

north shore of Lake Superior are less steep than those towards the north on the south shore.

Correlative with the folding there exists considerable faulting. Definitely recognizable strike and dip faults have been located. The main fault in this district occurs along the southeastern edge of Keweenaw Point, as shown in figure 1.

The central portion of the Keweenaw Peninsula is formed of a succession of extrusive lava beds interbedded with layers of sandstone and conglomerate. The lavas are of two kinds, the prevailing variety being a dark basaltic rock, having the texture of diabase,- commonly called trap- and the other a light-colored lava-quartz porphyry,- corresponding in composition to andesite. The conglomerates are composed of rounded fragments of igneous rocks,- the light colored porphyries predominating.

The upper part of the diabase beds is often scoriaeous, giving rise to the term "ash-bed", and these beds are similar in character to the amygdaloidal lava beds. This amygdaloidal structure is undoubtedly due to the filling of the cavities by primary and secondary minerals according to the theory for such. The epidote, prehnite, etc. are secondary as they are due to the alteration of the rocks themselves, but as^{to} the copper- its source is the

point in question.

The entire series has a thickness of from 25,000 to 30,000 feet, and is flanked on both sides by conglomerates and sandstones. To the west the series appear to be conformable, dipping with the lava beds, but to the east, as illustrated in figure one, there is a fault, and the sandstones at that position assume a nearly horizontal position.

In the uplifting of this great series of rock there has been dislocation, and cross veins have been formed; also veins which cut the bedded series at an acute angle to the dip.

The cross veins, tho frequent, do not extend beyond the limits of the mineralized lava flows and conglomerates.

ORES.

Ores and associated minerals.

Chiefly metallic copper with some malachite, azurite, red oxide of copper (cuprite), and small amounts of chalcocopyrite and chalcocite, etc.

Occurrence of deposits.

The workable deposits of ore occur in two classes-viz. (1) belt or bed deposits, and (2) transverse vein deposits.

The first class includes the cupriferous conglomerates and sandstones, and the cupriferous amygdaloids, and most, if not all, the so-called veins carrying much epidote and coinciding with the bedding of the formation.

The second class includes those veins which traverse the formation in a direction more or less nearly at right angles to the bedding and also parallel to the bedding.

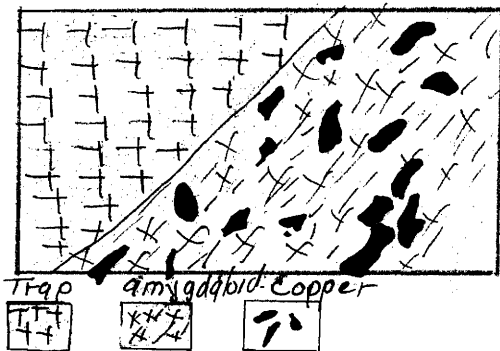
No copper has ever been observed in connection with the acid eruptives of the series, nor have any workable deposits been discovered in the massive non-vesicular beds, except those distinctly subordinate to, and directly connected with the amygdaloidal deposits or epidote courses and always accompanied with an extreme degree of alteration. However, in both the above named occurrences, the copper is found:

(1) As cementing material, and as a replacement of the constituent grains,

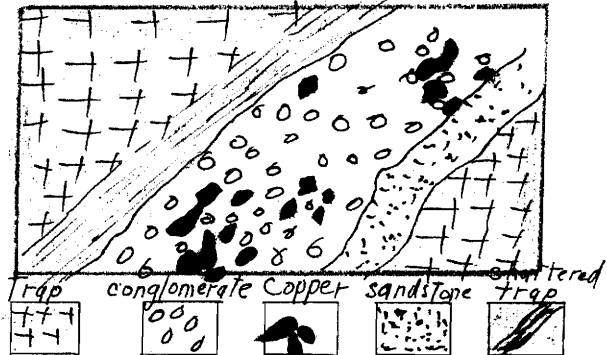
- (2) As replacement of wall rock by copper masses,
- (3) As entirely enveloping pieces of wall rock,
- (4) More or less sparcely disseminated in the compact and less readily changeable formations,
- (5) Richer where the veins traverse the more readily alterable amygdaloids and looser textured diabases.

Character of deposits.

An amygdaloid lode:(fig.2)



A Conglomerate lode:(fig.3)



HISTORICAL RESUME.

The minerals and occurrence of the copper ore of this district are of such a nature that the origin of the ore has been the subject of much discussion but still the genesis remains more or less obscure because no one of the theories so far provided by scientists is absolutely satisfactory.

Raphael Pumpelly.

The first theory for the origin of these ores was advanced in 1873 by Pumpelly, wherein he concluded that the copper was most likely deposited in a sulphuretted form in the Upper Keweenawan and concentrated from the entire thickness of sedimentary members of the group, including thousands of feet of sandstones, conglomerates, and shales which overlie the melaphyrs, as well as the altered melaphyrs themselves. From these formations it was no doubt leached partly as the sulphate, but principally as a carbonate and silicate. In fact, where the metal is found in the sandstones the rocks are stained with copper-carbonate in many places.

Now, thruout these deposits, Pumpelly found that the copper exhibits a decidedly intimate connection with delessite, epidote, and green-earth silicates, containing a considerable percentage of peroxide of iron as a more or less essential constituent. This relation between the precipitation of copper and the peroxidation of the ferrous oxide of the augitic constituents of the basic rocks is so constant as to render irresistible the conclusion that in this ferrous oxide is to be found the precipitating agent of the copper.

As regards the green-earth silicates and the chlorite or delessite associated with the copper, Pumpelly's de-

ductions from his investigations were that the deposition of these immediately follow that of the copper or was contemporaneous with it, and may be considered as having been formed under the influence of this reduction. Where copper is associated with prehnite it is invariably younger than the latter, which is consistent, as it has been found that prehnite undergoes a change to delessite. These pseudomorphs have been found in every stage of the process from the first green discoloration on the cleavage planes to the amygdule of delessite with prehnite structure.

This displacement of pre-existing minerals is most apparent in the cupriferous conglomerates where the copper has displaced the cementing materials.

Now, the fact that copper was deposited in the "trappean" series without the ores of the baser metals, - as lead, zinc, nickel, etc., which are present in the less metamorphosed rocks of the Quebec group in other localities - led Pumpelly to consider this to be due to a greater intensity of chemical action to which the melaphyrs have been subjected; an intensity which may be measured by the extent to which the process of concentration has been carried on.

Now, copper and silver belong to a class distinct

from the baser metals, due to the fact that they have a smaller affinity for oxygen, and are therefore more readily reduced to the metallic state- (the condition of greatest permanence in presence of the usual reagents to which they may be exposed.) If the arresting cause of these metals was their reduction by protoxide of iron, it is a cause which would have been powerless, according to Pumphelly, as regards the salts of the baser metals, and we may suppose these to have continued in solution until they reached some locality where they were precipitated by the aid of organic matter, or of sulphuretted hydrogen, etc.

R. D. Irving.

Irving, in 1883, took up this matter for the United States Geological Survey, and after considerable field work decided that he could not agree altogether with Pumpelly as to the origin of these copper deposits. However, he agreed on the following:

- (1) That a large deposit of metallic copper existed in the Monesuch sandstones, but separated from the nearest trappean flow beneath it by many hundreds of feet of detrital material.
- (2) That the copper exhibits a decidedly intimate connection with delessite, epidote, and green-earth silicates, containing a considerable percentage of peroxide of iron as a more or less essential constituent.
- (3) That the deposition of copper has been a result of a process of displacement of pre-existing minerals.
- (4) That Pumpelly's view as to the cause of arrest of the copper in the places where it is now found is satisfactory.
- (5) That the copper was originally deposited in a sulphuretted condition along with the detrital members of the Upper Keweenawan series, from which it was subsequently leached, partly as a sulphate, but principally as a carbonate and silicate.

Irving considers the "trappean" flows to be the home

of the copper with which it is supposed to have come to the surface when the land was elevated, and therefore objects to Pumpelly's remarks in the following respects:

(1) Objects to the source of the metal being considered the entire thickness of sedimentary members of the group, as Irving's investigations brought out the fact that there was an extreme scarcity of the copper in the upper sandstones of the series to consider that these sandstones was the home of the copper deposits.

(2) As a result of the foregoing objection, Irving cannot consider the presence of the copper in the Nonesuch sandstone as having been leached from overlying sandstones but believes it to have been leached from overlying "trap-pean" beds, and, descending along with the infiltrating carbonated waters, was precipitated upon meeting the rich basic detritus in the Nonesuch.

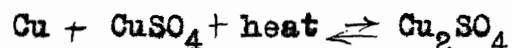
(3) While agreeing that the ferrous oxide was the precipitating agent, Irving claims that it was not only this but also the ferrous oxide of the magnetite and of the "unindividualized magma of the visicular layers" that has also been concerned in this reaction.

H. W. Stokes.

Later, in 1887, Stokes began investigations in this district, but owing to the fact that he was obliged to discontinue his work in the field, he was not able to publish a full account as he had intended. However, his preliminary work was published in its present incomplete form.^(a) His research and also laboratory work led him to conclude that thru "the reversal of certain reactions, by a fall of temperature, solutions carrying ferric or cupric salts, after acting upon certain minerals at a somewhat elevated temperature, may, upon reaching cooler regions, deposit metallic copper, silver, or gold, and that by a similar change of temperature, neutral or acid solution carrying ferrous or cupric salts may yield hematite at one place and metallic copper at another."

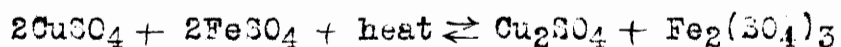
By experiments Stokes proves that metallic copper is deposited by changes in the temperature of the solution-cooling to the proper degree- with many combinations of cupric and other salts, some of which are as follows:

Solution of metallic copper by hot cupric sulphate solution and its redeposition on cooling.

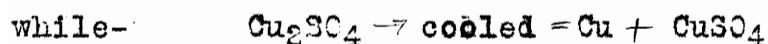


Solution of ferrous sulphate and cupric sulphate-

(a) Econ. Geol. Vol.L, p.644

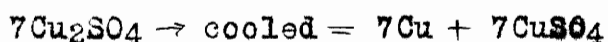
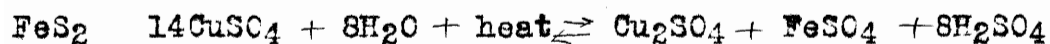


The ferric sulphate undergoes partial hydrolysis to ferric hydrate and H_2SO_4 especially at higher temperatures, at which the ferric hydrate may be deposited as hematite:

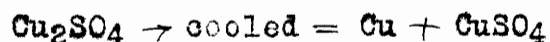
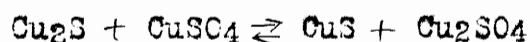


Hence it is possible to get deposition of hematite in the hotter, and metallic copper in the cooler region.

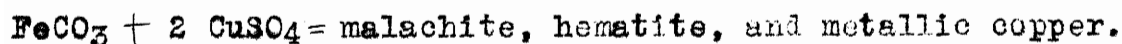
Solution of pyrite and cupric sulphate:



Solution of chalcocite and covellite with cupric sulphate:



Solution of siderite and cupric sulphate:



All the foregoing reactions were based on the actual experiments of Mr. Stokes.

Franz Posépný.

Posépný believed that the copper ore was not deposited with the sedimentary formations or with the eruptives, but that it was brought up by hot springs from great depths, perhaps from a considerable distance, and that these thermal effects occurred long after the lava flows and interbedded sandstones.

This explanation, he considers, is applicable to all the deposits here and also accounts for the presence of the copper in the Nonesuch sandstone, which seems to be a "bone of contention" between Pumpelly and Irving, as previously cited, and which is far away from any eruptive flow.

Posépný, however, does not attempt to explain the manner in which the ores became reduced, claiming that he did not have sufficient data for the formation of an opinion.

Dr. M. E. Wadsworth.

"From the fact^(a) that the copper is generally found most abundantly under the heavy lava flows and associated with minerals evidently the product of the decomposed lavas, it appears probable that the copper was once finely disseminated through the lavas and has since been concentrated by waters percolating through them."

That the copper was deposited from water, with or without electro-chemical action is shown by the following evidences:

(1) It is found enclosed entirely in minerals known to be formed by water only, and also by its enclosing such minerals.

(2) It is found in disconnected or isolated masses in the lavas and elsewhere and is more abundant where the most signs of water action are found.

(3) The presence of spikes of copper and calcite that extend from one bed down into others, with the small end downward, -like an icicle, - indicates that the course of water depositing the copper was generally downward.

(4) Where copper is found uniformly distributed, the largest masses are generally found in the upper portions of the veins.

(5) The copper was deposited after the copper-bearing

(a) Trans. Amer. Inst. Min. Eng., Vol. 27, p. 669

series was complete, as shown by the fact that it is found in fissures extending across the beds that could only have been produced after the beds were in place.

(6) The copper was deposited subsequent to the jointing of the lavas owing to its now being found wrapped around pieces of material broken off in the jointing.

(7) The extension of copper from one flow down into another as a continuous mass.

If the copper had been deposited by igneous agencies, subsequent to the formation of the melaphyrs and conglomerates, Wadsworth says that it would have had a channel or line of passage and would have been continuous along that line, so that all the different masses of copper would have been connected together, unless separated by fractures or faults.

C. R. Van Hise.

Mr. Van Hise agrees with Mr. Pumpelly as to the deposition of the copper of the Lake Superior regions having been the result of reduction by the ferrous compounds, and adds that these conclusions have been confirmed by experimental work. Mr. Biddle's ^(a) experiments, in a thick-walled flask, proved that both cupric and cuprous chlorides were reduced by ferrous chloride in a saturated solution of potassium bicarbonate. More recently Stokes, ^(b) by heating an acidified solution of cupric sulphate and ferrous sulphate in a closed tube, produced metallic copper at the cool end of the tube and pure hematite at the hot end of the tube.

Thus experimental work completely confirms the conclusions that under natural conditions copper may be reduced from its salts by ferrous compounds, and that the metallic copper of Lake Superior region was probably reduced both by ferrous solutions and by the ferrous iron of the solid compounds.

In this connection Van Hise calls attention to the fact that in this district of native copper deposits, abundant ferrous compounds occur, and that magnetite is

(a) Biddle, H.C. "The Deposition of Copper by Solution of Ferrous Salts" Jour. Geol. Vol.9, 1901.

(b) Stokes, unpublished manuscript, after Van Hise.

a very common mineral both in the amygdaloid and conglomerate deposits. As has already been noted in Irving's report, there is an intimate association of native copper and magnetite in the Nonesuch cupriferous sandstones, the copper frequently surrounding grains of magnetite. In this case the native copper and magnetite were evidently both precipitated as the result of the reaction of ferrous salts upon copper salts. According to Stokes' work these would not be simultaneously precipitated at the same place. The magnetite would form where the temperature is higher, and the copper where the temperature is lower. To explain the existence of both at the same place, one is obliged to suppose that the magnetite formed first, and that later, when the temperature was lower, the copper was thrown down. It is notable that in this particular case, in the Nonesuch sandstones, the copper surrounds the grains of magnetite, and this therefore corresponds with Stokes' experimental work.

The Lake Superior copper deposits are believed to be an ideal case of ores deposited from ascending waters, the sources of which are the igneous rocks of the Keweenawan. The copper is not found in paying quantities in all the rocks in this district, but is found in small amounts in all the Keweenawan basic lavas, and according to Van Hise, this is the most conclusive evidence that these la-

was, are the source of the metal.

Van Hise further says that while the copper commonly occurs in many of the igneous rocks in its native state, especially in those which are porous, it is found in the less porous and therefore less altered rocks in minute quantities in the form of a sulphide, and this is thought to be the original form of the metal. At the time the lavas crystallized, the copper probably separated out as the sulphide, or copper-iron-sulphide. When the lavas were upturned by the formation of the Lake Superior syncline, and denudation began truncating them, the segregation of the copper deposits was inaugurated. The descending oxidizing waters transformed the copper sulphides into copper sulphates and took them into solution. The underground water was finally converged into trunk channels, and there met solutions bearing ferrous salts or came into contact with ferrous compounds. At such places reduction and precipitation took place. The greatest deposits of copper, as stated previously, are found in the scoriaceous amygdaloids and conglomerates, unquestionably due to the fact that these rocks offered the least resistance to the passage of ore-bearing solutions.

A. C. Lane.

Lane's theory for the origin of these copper ores differs considerably from all the preceding theories written on this subject, as he claims that the metal was deposited in native form from sea water, where it had been held in solution.

In explaining the position he takes in this regard, Lane refers to the discoveries of Brun^(a) that hydrocarbons or carbides, nitrides, and silico-chlorides are normal constituents of lavas, and that various chlorides, especially ferrous and ferric, and chlorine emanations are found around volcanic vents,- these substances all being powerful reducing agents,- all these conditions having existed possibly contemporaneous with the deposition of the copper, and also cites the fact that abundant salt is found in the deep mines even at the present time.

Lane therefore considers it plausible to suppose that the carbon compounds were originally present in the lavas or sea water. It may be that these compounds, which, in oxidizing, produced the calcite which is the mineral most intimately associated with the copper. However, carbon dioxide and carbonates are almost absent from the lower waters,- altho they are present in the rocks- so it is natural to suppose that the slow oxidation of the hydrocarbons and carbides originally in the beds, has formed the

(a) Lake Superior Min. Inst.Proc. Vol.12, p.97

carbonates and reduced the chlorides, and has been the cause of much of the alteration of the rocks. "The copper may have been in the original lava, the original soluble chlorides, or in the original ocean and have slowly segregated as the water slowly migrated, and considers that the precipitation of this copper is probably due to the chemical and possibly electrolytic reaction of the deeper waters and the rocks in which they are contained."

Some of the evidences substantiating this "sea-water theory" are as follows:

- (1) It has been found that mine waters have deposited copper at the bottom of the Quincy mine, where the waters are **strong** brines, carrying considerable bromine.
- (2) To a depth of 1000 feet the mine waters are soft or slightly hardened by sodium silicate. Below this depth the waters become briney with sodium chloride and calcium chloride, the latter increasing rapidly with depth, while below half a mile the waters contain a few grams of copper chloride per ton, and deposit copper therefrom as opportunity offers. Carbon dioxide is lacking entirely from the deep mine waters of the district. An example of the deposition of native copper under these conditions is demonstrated in New Zealand, where the sulphide ores of a

mine abandoned for forty years were found partly transformed to native copper by the action of the sea which had broken into the workings.

Under these circumstances Lane says that Pumpelly's suggestion, of the co-operation of the change to peroxidation of the ferrous compounds in throwing down the copper, is still applicable.

Hiram Hixon.

In a paper written by Hiram Hixon,^(a) and read by him before an assembly of scientific men in Canada, on "Reduction During Deposition" of native metals, he touched upon the subject of copper of the Lake Superior Region, and brought out the following facts:

"The usual explanation for the occurrence of native gold, silver, copper, platinum, and more rarely iron, is that they have been derived from the baser ores by action of surface waters. All surface waters carry air, carbonic acid, and salt in solution; and thru the oxidizing action of the dissolved air, the sulphide ores are changed to sulphates, oxides, and chlorides. The soluble salts being carried down along the veins encountered unaltered sulphides and the reducing action of the sulphides on the sulphates results in depositing the metals in forms intermediate between the two. -----

"Further, it is a well established fact that various hydrocarbons are discharged from volcanic vents. On this hypothesis it is conceivable that mineralizing solutions could contain them, and their action on solutions containing gold, silver, and copper, would result in precipitating the metals in the metallic state. (which corroborates the statement made by Lane in this regard.)- The presence

(a) Min. & Sci. Press, Vol. 94. p. 593.

of hydrocarbons would be necessary for the precipitation of native metals below the zone of secondary enrichment, and in cases where these metals do not occur it would appear that hydrocarbons were absent during deposition.---

"In the case of the Lake Superior Copper ores, as all the copper is present in the form of metallic copper, this fact precludes the possibility of its being derived from pre-existing sulphides."

However, according to the last statement, Mr. Hixon seems to overlook the fact entirely that sulphide of copper is present in the trappean flows, even at the present time.

H. J. Stevens.

In the 1907, 1908, and 1909 "Handbook of Copper," Stevens states that the most plausible theory for the genesis of the Lake Superior copper ores seem to him to be that of Lane wherein the native copper was deposited from sea-waters from sulphide solution thru chloride reactions.

He also states that this theory is the more commonly accepted due to the fact that synthetic laboratory experiments lend corroborative evidence more to this than to any other theory.

C. K. Leith.

Like Hiram Hixon, Mr. Leith touches upon the subject of Lake Superior copper ores in his report of "The Iron Ores of Canada" wherein he calls attention to certain general features of comparison of Canadian ores with the several types of deposits of the United States,- those in our country having been more fully exploited and studied,- and thus secure a perspective to view the Canadian iron ore situation which could not otherwise be easily obtained.

Mr. Leith states in his report that "it has long been known that the Lake Superior iron ores were concentrates in certain sedimentary iron formations. It was believed that these sedimentary iron formations were derived from the weathering of basic shores containing much basic igneous rocks, usually called greenstone. As a result of further study it has been found necessary to conclude that the iron formations have not only been derived from greenstones by direct weathering, but have actually been contributed by the greenstones directly to the water in magmatic solution and that there are all intermediate stages between the two processes. It begins also to appear that the iron, copper, nickel, and silver ores of the Lake Superior and Lake Huron districts are related in a great metallographic province in which the characteristics

and distribution of the different ores are initially controlled by igneous rocks."

In this connection Mr. Leith's ideas concerning the migration of magma in the earth's crust is that the ores were brought to the surface, either by igneous rocks themselves or by magmatic waters in connection with vulcanism and transferred either directly or indirectly to the ocean. From the ocean the iron silicate was thrown down as a chemical precipitate in conformable succession of sedimentary rocks;- the various eruptives responsible for the introduction of the ores came up presumably largely near the axis of the present Lake Superior basin and probably the Lake Superior copper ores came up from the same source in a later period and that the cobalt ores in Canada were probably a further differentiation product of the same magma. The first vulcanism produced the iron ores; the second period of eruption caused the Keweenawan flows to be given off in which were introduced the copper ores; and the third period of vulcanism afterwards occurred in which we had the cobalt ores formed.

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CONCLUSION WITH REASONS.

In each of the foregoing theories we obtain sound reasoning in connection with many facts. Therefore a correlation of these facts ought to give us enough material to deduct a sound theory.

The most plausible supposition seems to be that all metallic ores are derived ultimately from the interior of the earth,- from a great metallographic province,- whence they are delivered by igneous eruptives near or at the surface.

In this district we find copper sulphides ^(a) distributed in minute quantities in the less altered igneous rocks of the Keweenawan series. This being an original mineral, it seems safe to say that the metallic copper, which is present in the altered igneous rocks of this series, was derived from these sulphides.

The sulphides are believed to have been oxidized during the ordinary processes of weathering to the sulphate, and the sulphate solution carried by meteoric waters, upon coming in contact with the ferrous salts and ferrous compounds, peroxidized the ferrous salts and ferrous compounds, precipitating the metallic copper.

We find, as a means toward this reduction, that the fractured conglomeratic and visicular beds are such as not

(a) Sulphides in the "trappean" flows- Irving, Van Hise, etc.

only to permit of free circulation of water and furnish favorable conditions for concentration, but also ones in and adjacent to which are found adequate precipitating substances.

