Art. XXXIV.—*The Precipitation of Manganese from Meteoric Solutions;*[1] by George A. Thiel.

Introduction and Summary.

This paper presents the results of a series of experiments dealing with the relative effectiveness of various rocks and minerals of the Deerwood iron formation of the Cuyuna range, Minnesota, in the precipitation of manganese from solution. Other mineral combinations and solutions are also included for comparative purposes. The experiments indicate that magnesium carbonate is by far the most active precipitant of manganese from cold solutions. Iron carbonate and calcium carbonate produce a partial precipitation from carbonate solutions, but have no effect on sulphate solutions that are associated with organic acids derived from peat bogs. The ferruginous cherts produce very little precipitation from either sulphate or carbonate solutions, whereas the gray-green carbonate slates are most effective. In the latter type of rocks the iron and magnesium carbonates precipitate more manganese than calcite. Magnesium and iron silicates, however, are very inactive, consequently the amphibole magnetite slates play a very minor role in the concentration of the manganese deposits.

The writer wishes to acknowledge the suggestions offered by Dr. W. H. Emmons and Dr. F. F. Grout of the University of Minnesota.

Experiments with Manganese Solutions.

Material used and method of analysis.—Different phases of the ferruginous slates of the Deerwood formation were selected, together with other minerals and rocks that would be of value in making a comparative study. The minerals were ground to 200-mesh in an agate mortar and 5 grams placed in a flask. To each was added 100 cc. of stock manganese solution. After being vigorously agitated the flasks were closed with rubber stoppers and were kept at room temperature.

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[1] Written as a sequel to a paper on "The Manganese Minerals, their Identification and Paragenesis," Econ. Geol., vol. 19, p. 107, 1924.

The following solutions were prepared:

1. Manganese sulphate solution, containing 185 parts per million of manganese.
2. Peat solution containing manganese sulphate, with 185 parts per million of manganese. The peat solution was prepared by treating peat with distilled water for 48 hours and then filtering off the solution. (For a partial analysis of the peat, see Table I.)
3. Manganese bicarbonate solution, prepared by dissolving freshly precipitated manganese carbonate in saturated carbonic acid. The solution contained 32 parts per million of manganese.
4. Manganese bicarbonate in a peat solution, 32 parts per million manganese.
5. A sulphate solution containing approximately 1 gram of ferric sulphate and 1 gram each of ferrous sulphate, and manganous sulphate dissolved in 1000 cc. of N/10 H_2SO_4. To this was added 500 cc. of a saturated manganese bicarbonate solution. The total manganese content was 205 parts per million.

The following rocks and minerals were used:—(For analyses see Table I).

1. Massive hematite chert. Thin sections and polished surfaces show that the rock is composed of very fine-grained quartz with minute needles of hematite, together with small areas of fibrous amphiboles. (1, Table I.)
2. Thin-bedded hematite-limonite slate. A finely laminated rock with some bands entirely replaced by iron oxides, including a few euhedral crystals of martite. Some remnants of carbonate grains are seen in the iron bands. (2, Table I.)
3. Amphibole-magnetite slate. A dark green banded slate. Magnetite is concentrated in the darker bands. Radiating masses and dense fibrous mats of green amphiboles compose the lighter colored bands. Small grains of carbonate accompany the cherty layers. (3, Table I.)
4. Gray-green carbonate rock. Thin sections show that the rock is composed of quartz, carbonate and green fibrous amphiboles. Some phases contain so much calcite that an effervescence with cold acid is easily detected. (4, Table I.)
5. Clastic carbonate rock. Fragmental quartz grains, well rounded and sorted. Cemented by carbonate and iron oxides. (5, Table I.)
6. Calcite. Large rhombs of coarsely crystalline spar.
7. Magnesium carbonate—C. P.
8. Siderite. Large crystals of vein siderite.
9. Springfield clay. A gray thin-bedded clay derived from Cretaceous sediments at Springfield, Minnesota. (9, Table I.)

10. Heron Lake clay. A highly dolomitic clay from the shore of Heron Lake, Minnesota.

11. Kaolinite. A colorless clay from a lense in the Deadwood formation in the Black Hills, South Dakota.

12. Decorah shale. From the lower part of the Decorah formation at the brick yards of West St. Paul, Minnesota. (12, Table I.)

13. Hornblende. Large crystals of vein hornblende.

14. Peat. A lime-deficient peat from Williams bog north of Duluth, Minnesota. (14, Table I.)

15. Iron spring deposit. Solution and precipitate from the basin of an iron spring issuing from a fracture in the Platteville dolomite at Minneapolis, Minnesota.

16. Graphite. Amorphous graphite isolated from a graphite schist by flotation.

Table I. Analyses of rocks used in experiments.

	1[a]	2[a]	3[a]	4[a]	5[a]	12[b]	10[b]	9[b]	14[c]
SiO_2	41.60	47.83	43.24	38.28	30.15	56.35	53.94	63.65	5.66
Al_2O_3	2.18	16.62	1.12	3.20	.40	18.63	11.39	17.27	
Fe_2O_3[d]	31.93	23.93	26.66	22.38	26.61	6.19	3.23	4.75	.012
MnO	5.01	3.60	0.95	6.98	2.53	n. d.			
MgO	.08	.23	2.23	3.03	1.25	2.97	3.47	1.21	.360
CaO	.04	.73	1.12	2.28	4.77	.96	9.80	.06	.510
K_2O		3.24				7.37	.76	2.47	
P_2O_5	.029	.176	1.090	.138	.665				
CO_2					24.65		4.70		

[a] J. H. McCarthy, Analyst. Minn. Sch. Mines Exp. Sta.
[b] F. F. Grout, Analyst. Dept. Geol. University of Minnesota.
[c] J. W. Gruner, Analyst. Dept. Geol. University of Minnesota.
[d] Total Fe.

1. Red hematite chert.
2. Thin-bedded hematite-limonite slate.
3. Amphibole-magnetite slate.
4. Gray-green carbonate slate.
5. Clastic carbonate rock.
12. Decorah shale.
10. Heron Lake clay.
9. Springfield clay.
14. Peat.

In making a determination of the amount of manganese in solution the colorimetric method recommended by the United States Geological Survey[2] was used. The stock solution stood under the same laboratory conditions as the solutions in contact with the rock and mineral powders. At the end of one month 10 cc. were

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[2] Hillebrand, W. F., The analysis of silicate and carbonate rocks: U. S. Geol. Survey, Bull. 700, p. 137, 1919.
Walters, H. E., Chem. News, vol. 84, p. 239, 1901.

drawn from each of the flasks containing the rock samples and their manganese content compared with the original stock solutions. A similar comparison was made at the end of six months.

Relative Effectiveness of Rock Powders.

The results in terms of parts per million of manganese precipitated are shown in Table II.

Magnesium, calcium, and iron carbonates are active precipitants of manganese. Of these three magnesium carbonate is the most effective. Its action is so rapid that all but a few parts per million were precipitated from each of the solutions by the end of one month. Calcite will not precipitate manganese from a manganous sulphate solution, but it is very active in precipitating iron from an acid ferric sulphate solution. Its action on manganese is not as rapid as magnesium carbonate, however, as a trace of manganese remained at the end of six months. Siderite acts slowly, but it is more effective than calcite on manganous sulphate solutions. It also produces a precipitation from both organic and bicarbonate solutions of manganese.

The same basic elements, magnesium, calcium and iron, show no effect on the manganese solutions when combined as silicate minerals.

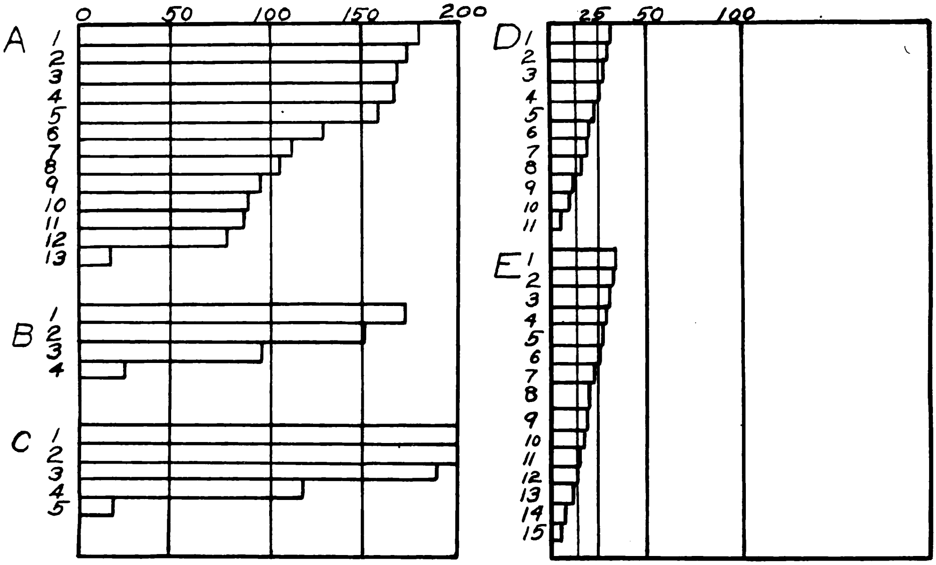
Table II. Showing the relative amount of manganese precipitated by various rock and mineral powders, during a period of six months. Reported in pts. per M. Mn.

A—Manganous sulphate solution. 185 pts. per M. Mn.

1—Magnesium carbonate.
2—Iron spring mud.
3—Heron Lake clay.
4—Peat.
5—Gray-green carbonate slate.
6—Clastic carbonate rock.
7—Siderite.
8—Decorah shale.
9—Springfield clay.
10—Kaolinite.
11—Red hematitic chert.
12—Thin-bedded hematitic slate.
13—Amphibole magnetite slate.
Hornblende and calcite negative.

B—Manganous sulphate in a peat solution. 185 pts. per M. Mn.

1—Magnesium carbonate.
2—Iron spring mud.
3—Peat.
3—Heron Lake clay.
All others negative.



C—Ferric sulphate solution. 205 pts. per M. Mn.

1—Magnesium carbonate.
2—Calcium carbonate.
4—Heron Lake clay.
4—Iron spring mud.
5—Peat.
All others Negative.

D—Carbonate solution. 32 pts. per M. Mn.

1—Magnesium carbonate.
2—Heron Lake clay.
3—Iron spring mud.
4—Gray-green carbonate rock.
5—Clastic carbonate rock.
6—Thin-bedded hematitic slate.
7—Springfield clay.
8—Kaolinite.
9—Amphibole magnetite slate.

10—Peat.
11—Siderite.
All others negative.

E—Carbonate in a peat solution. 32 pts. per M. Mn.
1—Magnesium carbonate.
2—Iron spring mud.
3—Heron Lake clay.
4—Peat.
5—Siderite.
6—Clastic carbonate rock.
7—Gray-green carbonate rock.
8—Amphibole magnetite slate.
9—Decorah shale.
10—Red hematitic chert.
11—Calcite.
12—Kaolinite.
13—Springfield clay.
14—Thin-bedded hematite slate.
15—Hornblende.

The solution in contact with finely powdered ferro-magnesian silicates as hornblende showed no appreciable loss of manganese. If, however, the hornblende is subjected to weathering, the resulting carbonates become active precipitants.

The comparative effects of magnesium and calcium carbonates are further illustrated by the results shown with Heron Lake clay, Springfield clay and Decorah shale. Heron Lake clay is a yellow laminated clay[3] that is highly calcareous, but which also carries nearly 3.5 per cent of magnesium carbonate. (See analysis 10, Table I.) The Decorah shale contains 2.9 per cent MgO and the Springfield[4] clay, which is non-calcareous, contains but one per cent of MgO. Heron Lake clay precipitated more than twice as much manganese as either of the other two. The effect of the high calcite content in the clay from Heron Lake is shown in the precipitation of the acid ferric sulphate solution which resulted in a loss of 200 parts per million of manganese. Neither of the clays with a low lime content showed any appreciable effect on the manganese content of the ferric solution, but each produced a partial precipitation in the bicarbonate solutions.

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[3] Grout, F. F., Clays and shales of Minnesota, U. S. Geol. Survey, Bull. 678, p. 179, 1919.

[4] Grout, F. F., op. cit., p. 132.

The same reactions of the carbonates were found to occur when manganese solutions are brought in contact with rocks that are characteristic of the various phases of a sedimentary iron-bearing formation. Massive hematite chert produces a partial precipitation of a manganese sulphate solution, but has no effect on acid solutions. A few parts per million are extracted from a carbonated peat solution but they may have been adsorbed by organic colloids.[5] Thin-bedded hematitic, limonitic slate produced very similar results.

The ferruginous, dolomitic carbonate rocks are the most active agents of precipitation. The actions of two phases of such rock are shown by the effect of a gray-green carbonate rock and a clastic carbonate rock. (See analyses 4 and 5, Table I.) The former is higher in magnesium than in calcium and it precipitates more manganese from the sulphate solution. The clastic rock contains more lime than magnesia, and it is of interest to note that the presence of 4.77 per cent CaO is sufficient to produce an appreciable precipitation of manganese from the ferric sulphate solutions. Such a reaction serves as a check on the results obtained from calcareous clays and calcite.

Organic mixtures, such as peat and iron spring sediments, precipitate manganese from each of the solutions used in the experiments. A partial analysis of the peat (see Table I) indicates that calcium and magnesium salts played a very minor part in the reduction of the manganese content, but that organic compounds are the chief precipitants. The intensive action of the iron spring sediments on the ferric sulphate solution (see Table II) may be accounted for by the presence of calcium and magnesium bicarbonates in the spring water. A partial analysis of the sediments shows that both calcium and magnesium are present in considerable amounts. Their presence is to be expected as the spring issues from a fracture in the Platteville dolomite. The iron spring sediments, however, extracted more manganese from each of the solutions than peat did. This is undoubtedly due to the presence of fresh organic material in the spring whereas the peat was partially dehydrated and

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[5] Gruner, J. W., Origin of sedimentary iron formations, Econ. Geol., vol. 17, 1922.

decomposed. Living micro-organisms in the spring water may have played a part in the precipitation from a manganous solution, but during a period of six months a sterile solution showed as great a decrease in the manganese content as one in which the organisms were not destroyed. The sterilization was accomplished by heating the flask in an autoclave after the manganese solutions and the sediments had been introduced.

Very few of the rock or mineral powders produced an appreciable decrease of manganese from manganous sulphate dissolved in a peat solution. This is perhaps due to the fact that when manganous sulphate with a strong acid radical comes in contact with some of the natural organic colloids, acid is liberated, which keeps the manganese in solution. That manganese is kept in solution in a strongly acid environment is shown by the negative results obtained by bringing an acid ferric sulphate solution that contains over 200 parts per million of manganese, in contact with the rocks and minerals used in the experiments. (See column 3, Table II.) Only those that possess large amounts of magnesium and calcium carbonates are capable of precipitating any of the manganese.

Bicarbonate Solutions as Precipitants of Manganese.

Bicarbonate solutions of magnesium, calcium and sodium are capable of precipitating manganese from both carbonate and sulphate solutions. A saturated solution of magnesium bicarbonate diluted one to ten precipitated 200 parts per million of manganese from the sulphate solution in 48 hours. Twenty-five parts per million of manganese were precipitated from a saturated bicarbonate solution of manganese during the same length of time.

Calcium bicarbonate is less active than magnesium bicarbonate. A saturated solution diluted one to ten precipitated but ten parts per million from the stock sulphate solution, in 48 hours, and 15 parts per million from a saturated bicarbonate solution of manganese. Sodium carbonate is the most active precipitant. A molecular solution diluted one to ten produces a heavy yellowish brown precipitate in the manganese sulphate solution in a few minutes. Only a trace of manganese remains in solution at the end of 48 hours. In a saturated bicarbonate solution of manganese, a colorless precipitate appears in 48 hours, leaving only a few parts per million of manganese in the solution.

In all of the experiments described above only such solutions were employed as are known to carry manganese under natural conditions. Experimental work has shown that manganese may be transported as a sulphate, chloride, bicarbonate, or by humic acids. The chlorides play a very minor part in the enrichment of sedimentary manganese deposits, and were consequently omitted. The relative importance of the minerals and rocks listed as precipitants of manganese may be more clearly shown by comparing the effects of various agents of weathering on manganese minerals.

The Relative Solubility of Manganese Minerals.

Since nearly all of the deposits of manganese oxides owe their origin to deposition from meteoric waters, a study of the relative solubility of the manganese minerals in solutions that are characteristic of the zone of leaching may help to elucidate the problem of their precipitation and concentration. In the experimental work done by Mr. Carlson[6] the following solutions were employed:

$NaCl$	2% solution.
$NaCl + H_2SO_4$	1% $NaCl$, N/10 H_2SO_4
H_2SO_4	N/10 solution
H_2SO_4	N/50 "
Na_2CO_3	1% "
$CaH_2(CO_3)_2$	1% "
Humic acid (swamp H_2O)	saturated
Carbonic acid	saturated
$FeSO_4.7H_2O$ + N/10.H_2SO_4	equal parts of each
$Fe_2(SO_4)_3.9H_2O + H_2SO_4$	equal parts N/10 of each

The minerals used were psilomelane, pyrolusite, manganite, rhodochrosite, rhodonite, franklinite and alabandite. These minerals were crushed to 200-mesh and one

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[6] The included data on the solubility of manganese minerals were compiled by Mr. Edwin N. Carlson of the University of Minnesota and presented as a thesis in partial fulfillment of the requirements for an Engineer of Mines Degree in Geology. The results are published with his consent.

gram placed in a large test tube. Thirty-five cubic centimeters of one of the solutions were introduced and the test tube stoppered to exclude air. However, in all probability many were not air-tight, as hydrogen sulphide was generated in sufficiently large amounts to remove the corks from some of the tubes.

Because manganese sulphide is more soluble than the oxides, each of the samples of oxides were tested for the presence of sulphide. No manganese sulphide was found in any of the oxides used in the experiment.

The results of the experiments are shown in Table III. Alabandite is noted to go into solution to a greater degree than any of the other minerals. It is followed by the mineral rhodochrosite. The carbonate solutions are very inactive, but saturated carbonic acid is a moderately active solvent. Ferrous sulphate in N/10 H_2SO_4 shows the greatest reaction. It attacks all of the oxides at a comparatively uniform rate, dissolving from 1000 to 1500 parts per million of manganese in 48 days.

Table III. Showing Relative Solubility of Manganese Minerals.

Reagents	Days	Franklinite	Pyrolusite	Psilomelane	Manganite	Rhodonite	Rhodochrosite	Alabandite
NaCl 2%	75	trace	neg.	trace	trace	neg.	neg.	50
NaCl 2%	120	trace	trace	trace	trace	trace	trace	
NaCl+H_2SO_4	70	1600	1080	1000	780	1300		7600
(1% (N/10)	115	1860	1395	1315	1000	1300	1550	
H_2SO_4N/10	70	780	780	620	530	620	3250	6000
H_2SO_4N/10	115	1400	815	800	800	950		6100
H_2SO_4N/50	75	150	310	400	155	370	1200	2000
H_2SO_4N/50	120	200	500	600	295	525	1300	2400
Na_2CO_3 1%	72	trace	trace	trace	trace	trace	trace	10
Na_2CO_3 1%	177	trace	trace	trace	trace	trace	25	28
$CaH_2(CO_3)_2$	62	trace	trace	trace	trace	trace	trace	20
(1%)	107	trace	trace	trace	trace	trace	50	70
Carbonic Acid	70	40	trace	trace	20	40	40	110
(Saturated)	119	28	trace	17	22	25	35	300
Humic Acid	74	10	50	31	40	36	36	50
(Swamp H_2O)	115	70	85	60	70	62	66	150
$FeSo_4+H_2SO_4$ N/10	48	1550	1860	1775	1400	1200	4950	7400
$Fe_2(So_4)_3+H_2SO_4$N/10	48	800	600	500	380	630	4960	4500

The minerals were crushed to 200 mesh and one gram added to 35 cc. of solution, at laboratory temperature.

Manganese indicated in parts per million as determined by the calorimetric method.

An appreciable amount of manganese is dissolved by humic acid (swamp water) without the addition of any mineral acids. Its action is not rapid, but the results indicate a considerable increase in the manganese content of the solution with an extension of time.

Pyrolusite is more soluble in the mineral acids when in an oxidizing atmosphere. This was determined by comparing the results shown for pyrolusite in Table III with a similar series with open tubes that were frequently agitated.

Comparison of Solvents with Precipitants.

Mineral acids are the most active solvents of the common manganese minerals, and when carried in such solutions manganese is precipitated only by the rocks that are high in magnesium and calcium carbonate. Organic material may play a part, but where the solution is but feebly acid, as a manganous sulphate solution in swamp water, only small amounts are precipitated. The action of magnesium and calcium as precipitants is further illustrated by the negative action of a calcium bicarbonate solution as a solvent. (See Table III.) Rhodochrosite and alabandite are the only minerals that yield more than a trace of manganese.

Carbonic acid, although a universal leaching agent that attacks all of the manganese minerals, readily gives up manganese when brought in contact with various rocks and rock-forming minerals. (See Table II.) The most noteworthy exception is the action of calcite as compared with magnesite. Although calcite is particularly active in the precipitation of a ferric sulphate solution, its effect on the other solutions is negligible..

The Relative Solubility of Iron and Manganese Minerals.

A comparative study of the results of experimental work dealing with various minerals of maganese and iron indicates that in some solutions iron is more soluble than manganese, whereas in others the opposite relation exists. Table IV is a compilation of data showing the effect of carbonic acid and peat solutions on the carbonates and oxides of the two metals. The reaction with alkaline earth carbonates is also indicated.

Table IV. The solubility of iron and manganese minerals. Reported in parts per million.

Mineral	Peat solution 70 da.	Saturated carbonic acid 50 da.	CaH_2CO_3 60 da.
Siderite	94	19	none[b]
Rhodochrosite[a]	36	40	trace
Magnetite	31[c]	28[c]	10[b]
Limonite[c]	14		
Hematite[c]	25		
Pyrolusite[a]	50	trace	trace
Manganite[a]	40	20	trace
Psilomelane[a]	31	trace	trace

[a]Determined by E. N. Carlson, op. cit.
[b]Determined by J. W. Gruner, op. cit.
[c]Determined by H. L. Henkel, unpublished thesis, University of Minnesota.

In a peat solution iron carbonate is more readily dissolved than manganese carbonate. However, carbonic acid attacks rhodochrosite more rapidly than siderite. The results of the latter reaction are corroborated by the findings of Sullivan who subjected crushed porphyry that contained 0.8 per cent iron and 0.033 per cent manganese to the action of saturated carbonic acid. At the end of several hours the solution contained 0.03 parts per million manganese and no iron.[7]

The alkaline earth carbonates are readily soluble in carbonic acid, but their solutions have very little effect on the leaching of iron and manganese minerals. In fact experimental work indicates that the presence of magnesium salts retards the solution of iron, but accelerates the solution of silica.[8] The same is true of its reaction with manganese-bearing minerals.

Comparison of Precipitation of Iron and Manganese.

As was shown above, calcite is an active agent in the precipitation of manganese from acid ferric sulphate solutions that carry manganese, but its effect on man-

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[7] Emmons, W. H., Manganese and gold enrichment; Am. Inst. Min. Eng., Trans., vol. 42, p. 38, 1911.

[8] Gruner, J. W., loc. cit.

Lovering, T. S., The leaching of iron protores, Econ, Geol., vol. 18, p. 523, 1923.

ganous sulphate solutions is very slight. Ferrous iron is, however, readily precipitated from a mixture of ferrous and manganous sulphates.[9] It is thus evident that limestone may play an active part in the separation of iron and manganese from slightly acid or neutral sulphate solutions. Furthermore, calcite precipitates iron from a peat solution[10] but has little or no effect on manganese sulphate or carbonate in similar organic solutions. Magnesite precipitates iron much more rapidly than calcite, and it is the only alkaline earth carbonate that produces extensive precipitation of manganese from the organic acid solutions. However, neither manganese nor iron is completely precipitated from such solutions; from one to eight parts per million remain for an indefinite period. More remains in the carbonate than in the sulphate solution. The inorganic sulphate and carbonate solutions give up their manganese more readily; by the end of six months no traces remain in the solutions in contact with $MgCO_3$.

Certain Geologic Applications.

The results of the experimental work on the relative solubility and precipitation of manganese minerals have a direct bearing on the deposition of manganese ores. They may be applied to a limited extent to the primary deposition of high temperature veins rich in manganese, but they have a wide application in the transportation and precipitation of primary sediments that carry manganese, and in the enrichment or lateritic deposits or concretionary deposits in residual clays, or replacements in carbonate sediments.

High Temperature Veins.—In the veins deposited by thermal solutions, manganese in the form of carbonates or silicates is generally associated with the sulphides of silver, copper, lead or zinc, or other metalliferous sulphides. Its deposition is accomplished by the intermingling of hot alkaline solutions. The above experiments were not designed to simulate high temperature conditions, but meteoric solutions are instrumental in the concentration and enrichment of such vein deposits.

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[9] Emmons, W. H., op. cit.

[10] Gruner, J. W., op. cit., p. 438.

Manganiferous Sediments.—Surface waters are the chief agents for transporting the manganese that is a primary constituent of sedimentary rocks. In such waters manganese may be carried as a chloride, sulphate, bicarbonate or by humic acids. Where manganese is carried great distances, organic solutions aid in preventing precipitation. Exposure to air or an intermingling with waters containing various other electrolites is not sufficient to produce complete precipitation. Living organisms may be instrumental in producing the final precipitation, as their action on manganous solutions indicates.[11] Thus the intimate association of iron and manganese carbonates in the protores of the Lake Superior region is perhaps due to the protective action of humus colloids on both iron and manganese solutions that accumulated in the Huronian seas of that area.

Concentrations and Replacements.—In the formation of lateritic manganese deposits by the weathering of crystalline schist, magnesium salts play an important role. Where magnesium solutions are present, the solution of manganese is retarded but the leaching of silica is enhanced. Thus manganese-bearing silicates would lose silica more readily than manganese, and the small amount of manganese that might go into solution would again be precipitated. Analyses of rocks and ores from the lateritic deposits of Brazil[12] indicate such reactions.

In the extensive deposits of manganese associated with residual clay in the southern Appalachian region, most of the clays are derived from dolomitic limestone.[13] Of these the Shady dolomite of Cambrian age is most productive. The manganese solutions were concentrated in the troughs of the Erwin quartzite and were precipitated in the dolomite and dolomitic clays.

Analyses of carbonate ores and wall rock from East

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[11] Beijernick, M. W., Centr. Biochem. Biophys., vol. **16**, p. 277, 1914.

[12] Scott, H. K., The manganese ores of Brazil, Jour. Iron and Steel Inst., No. 1, p. 179, 1900.

Derby, O. A., On the original type of manganese ore deposits of the Queluz district, Brazil, this Journal, March 1908, p. 213.

[13] Stose, G. W., Miser, H. D., Katz, F. J., and Hewett, D. F., Manganese deposits of the West Foot of the Blue Ridge, Va.; Va. Geol. Survey Bull. **17**, 1919.

Stose, G. W., and Schrader, F. C., Manganese deposits of East Tennessee: U. S. Geol. Survey, Bull. **737**, 1923.

Fork, Tenn.,[14] and from Bromide, Okla.,[15] show that magnesium carbonate is also intimately associated with the ores of those regions.

In the Batesville district, Ark., much of the marketable ore is associated with the Cason shale, which is also high in magnesia.[16] In fact nearly all of the so-called "button ore" is found at that horizon.

In the Philipsburg[17] district many of the smaller concentrations of manganese are in the dolomitic members of the Hasmark formation. In the manganese deposits of Langban, Sweden, much of the ore is in the dolomite and skarn.

On the Cuyuna Range much of the manganese was originally precipitated with the carbonates of the Deerwood formation. The gray-green carbonate slates of this formation contain as much as 3 per cent of manganese. Replacements and concentrations in the carbonate rocks have produced the highest grade manganese ore on that range.

Undoubtedly carbonic acid, sulphuric acid, and humic acids played a part in the concentration of the ore. Carbonic acid is universally active and locally sufficient pyrite is presented in the Deerwood slates to produce sulphate solutions. Peat bogs are numerous in the region of the manganiferous ores, in fact such ore-bodies as the Sagamore and several in the region of Mahnomen Lake are located below bogs or depressions in the topography. Thus organic solutions have been active during all of post-glacial time, but undoubtedly most of the concentration is pre-glacial.

In the carbonate horizons, magnesium, calcium, and iron carbonates and bicarbonates acted as the chief precipitating agents. Analyses of these rocks show that they are highly dolomitic. (See Table I.) Consequently magnesia was instrumental in producing much of the local enrichment.

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[14] Stose and Schrader, loc. cit.

[15] Hewett, D. F., Manganese deposits near Bromide, Okla., U. S. Geol. Survey, Bull. 725, 1921.

[16] Miser, H. D., Deposits of manganese ore in the Batesville district, Ark., U. S. Geol. Survey, Bull. 734, p. 139, 1922.

[17] Pardee, J. T., Deposits of manganese ore in Montana, Utah, Oregon, and Washington: U. S. Geol. Survey, Bull. 725, p. 157, 1921.

Most of the concretionary ore occurs in limonitic slates. The limonite owes its origin to the oxidation of slaty sediments high in ferro-magnesium minerals. Therefore, magnesium-bearing solutions were produced by the weathering of the slates. These solutions aided in the precipitation of the concretions of psilomelane and manganite. The hematitic ores derived from hematitic chert contain very little manganese.[18]

Cold Water Veins.—In numerous regions manganese oxides are present as cement in brecciated zones or as a fracture-filling where but slight replacement of the wall rock is evident. In such occurrences the precipitation was accomplished probably by an intermingling of solutions. The above experiments indicate that sodium, magnesium, and calcium bicarbonates will precipitate manganese from either a sulphate or a bicarbonate solution. Thus vein deposits in limestone, such as the manganese oxides in the New World area near Cooke City, Mont.,[19] or the botryoidal psilomelane in the brecciated porphyry near the Hidden Fortune mine in the Black Hills, may be precipitated without the wall-rock serving as a precipitating agent. On the Cuyuna range most of the manganite in the quartz manganite veins was deposited in a similar manner.

Department of Geology,
University of Minnesota,
Minneapolis, Minn.

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[18] Thiel, Geo. A., The Manganese Minerals, their Identification and Paragenesis, Econ. Geol., vol. 19, p. 107, 1924.

[19] Personal communication.