THE CONCRETIONS FOUND IN THE SOILS OF LATIMER COUNTY, OKLAHOMA

By

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I. INTRODUCTION

This paper concerns the concretions which occur in the soils of Latimer County, Oklahoma. An investigation of the occurrence and some of the properties of these concretions was undertaken because of the interest attached to their process of formation.

The natives of Latimer County call these soils containing concretions "shot soils." (Some of the concretions are perfect enough in structure and hard enough to be used for BB shot or in shot gun shells.) Concretions of all shapes and sizes can be seen along livestock trails. These concretions have been washed from the soil by erosion. Where road cuts of soil are exposed, concretions are also evident.

Throughout the course of this investigation the writer had a threefold objective, namely: (1) To study the physical properties of the concretions in the different horizons of the soil; (2) To determine the chemical composition of these concretions and that of the surrounding soil; and (3) To ascertain the origin of the concretions.

II. REVIEW OF LITERATURE

Physical Properties of Concretions

The typical ferromanganiferous concretions found in the solum of the podzolic soils in Illinois were reddish-brown to nearly black and varied in diameter from less than 0.05 mm. to more than 10 mm. Their form was usually spherical, though the surface was often roughened or irregular.

Most specimens showed concentric fracture when broken, thus giving evidence of a layered structure. Hardness was variable, but those specimens with the best developed fracture were usually the hardest. Not all the ferromanganiferous accumulations in the soil were coherent and hard enough to maintain their form when handled. The brownish splotches and the soft, easily pulverized bodies both of which were of rather general occurrence, were of the incoherent type. When ground for analysis, the concretions yielded a powder that varied from very dark brown for those high in manganese, to buff or yellow for those low in manganese. (14)

Wheeting (13) found that the "shot soils" of western Washington contained concretions of varying sizes. The sizes ranged from 0.05 to 19 mm. in diameter for the soils examined. The concretions were spheroidal in shape.

In a detailed study of one Dayton profile, Drosdoff and Nikiforoff (2) noted that of the concretions greater than 2 mm, the largest ones in the A_1 horizon were about 5 mm. in diameter, with most of them being 2 to 3 mm. In the upper portion of the A_2 layer, the largest ones were approximately

7 mm. with the majority of them being 2 to 3 mm., however, there was a greater percentage of concretions larger than 3 mm. as compared to the A_1 layer. In the central and lower sections of A_2 horizons more than half of the concretions greater than 2 mm. in diameter were over 5 mm. The largest ones were from 10 to 15 mm. Concretions larger than 2 to 3 mm. in diameter apparently did not form below the A_2 and even those which were 2 mm. in diameter were few. Most of the concretions in the central part of the B horizon ranged between 0.5 to 1.5 mm., whereas in the lower portion of the B horizon and in the upper part of C, very few concretions larger than 1 mm. in diameter were found. This general distribution of concretions of the varying sizes was observed in several profiles of the Dayton soil.

Wheeting's (13) results showed that there was no definite zone in all profiles where the greatest formation of "shot" took place, although in three glacial soils the maximum development occurred in the region from 8 to 20 inches.

Drosdoff and Nikiforoff (2) found that the A_2 horizon contained the greatest number and the largest concretions.

Occurrence

Winters (14) reported that ferromanganiferous accumulations seem to be present in the solum of most soil types occurring in Illinois, either as concretions, or in the form of diffuse reddish splotches. In general, concretions were found to be most abundant in the surface horizons of poorly drained, light-colored soils, though a few small ones were present in virtually all horizons of nearly every soil type.

Wheeting (13) found "shot" in upland soils which developed from both glacial and residual material. The pellets formed under forests, but were absent under prairie conditions. "Shot" were found in soils belonging to both the brown and gray forest soil groups, but were absent in forested lowland soils where poor drainage occurs and were not generally found in soils that were excessively drained. The most abundant formation of "shot" occurred in soil with restricted internal drainage, but where the movement of water in the soil was essentially downward. Where "shot" occurred, the soils were invariably acid in reaction. "Shot" appeared to be a natural development in the normal soil profile of the region.

Drosdoff and Nikiforoff (2) reported that the formation of iron-manganese concretions apparently are a typical feature of certain poorly drained soils which are subject to permanent or seasonal water-logging.

Composition of Soils and Their Concretions

Winters (14) reported that the concretions were much higher in Mn and Fe, slightly higher in Al, and lower in SiO_2 and organic matter than were the soils in which they occurred. Large concretions were found to be higher in Mn than small ones.

Drosdoff and Nikiforoff (2) reported the concretions in Dayton soils contained a much higher percentage of iron and manganese, which were present as free oxides, than does the whole soil. There was two to four times as much Fe_2O_3 and up to seventy times as much MnO in the concretions as was in the whole soil.

In the "shot soils" of western Washington, Wheeting (13) found that the "shot" were richer in the sesquioxides and phosphorus than was the soil surrounding them. On the other hand, the soil was richer in silica than were the "shot." Phosphorus in particular was concentrated in the "shot."

III. MATERIAL AND METHODS

History of Latimer County

Latimer County was organized in 1902 and was named for J. S. Latimer, Representative in the First Constitutional Convention.

It is located in southeastern Oklahoma. It borders on Pushmataha County which lies almost in the extreme southeastern corner of Oklahoma.

Its greatest length east and west is approximately 36 miles. Its greatest width is approximately 26 miles. The total area of Latimer County is approximately 738 square miles or 471,680 acres. It has less wealth than any other county in the state of Oklahoma, and is surrounded by four counties with very little wealth.

Geology of Latimer County

The county lies in that part of the state which is primarily underlain by Pennsylvanian sandstones and shales. The rocks have been folded into a series of anticlines and synclines, causing the beds to stand at angles with the surface ranging from practically level to almost perpendicular. An impervious shale is found 12 to 22 feet under the top soil in Latimer County according to seismograph logs. "Shot Clays" are formed where there is restricted internal drainage in the profile.

A typical soil profile containing concretions is described as follows:

Horizon A_1--Whitish gray, fine-grained texture found as surface layer 2" to 3" thick with very few concretions present.

Horizon A_2—Compact, yellowish grey to white material, which becomes much lighter in color when dried and also becomes very hard. The layer was 5" to 9" thick. Concretions were very plentiful in lower portions of this layer.

Horizon B—A compact, clayey layer with some dark and brown irregular shaped concretions. The color was mostly grayish blue, with yellowish black mottling. The mottles range in size from microscopic to very large.

When the soil in Latimer County is becoming dry in the A_1 horizon, water from the lower horizons rise to the surface by capillary action. The capillary water is concentrated with complex salt compounds. When it evaporates it leaves a white residue of salts on the top of the soil. The surface becomes an horizon of accumulation in areas where concretions are found in the horizons below. Through evaporation the capillary water becomes super-saturated and results in the formation on concretions in the lower horizons. Concretions are a very distinctive feature of Latimer County soil.

A map of Oklahoma showing approximately the area concerned is found in Figure 1.

Climate of Latimer County

The climate of Latimer County, although temperate, is extremely variable from year to year. The seasonal changes in temperature may range from several degrees below zero in winter to above 100° F. in summer. There is an annual precipitation of more than 40 inches. In 1950, Latimer County had more than 50 inches of rainfall.

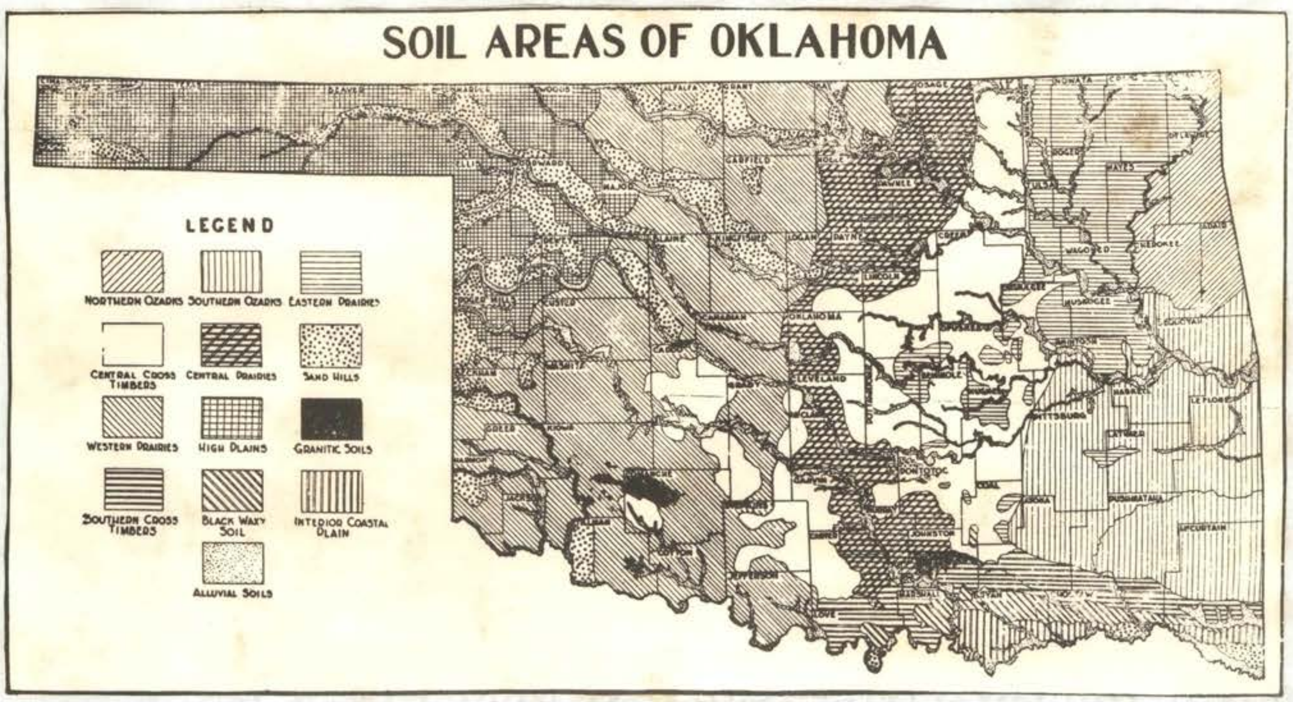

Fig. 1--A map showing the soil areas of Oklahoma. (Courtesy of Agronomy Department, Oklahoma A. and M. College); "X" locates approximately the soil area concerned in this report.

Physical Determinations

Soil samples from the horizons of many soil profiles in Latimer County were collected during the spring and dry summer season of 1952. Thirty samples were taken from grass lands and fallow fields in various areas. Samples were also taken under deciduous trees. These samples were brought into the laboratory for chemical and physical analysis.

The material was screened through a 2 mm. sieve. Gentle pressure with a rubber pestle was employed to break up the soil granules and to crush everything except the coarse gravel and concretions. After the concretions were separated from the coarse gravel by visual selection, they were washed to free them of their yellow clayey coat. Then the percentage of concretions in the whole soil was calculated.

The microscope was employed to determine the nuclei of the different shaped concretions. Concretions were filed down a fraction of 1 mm. each time before viewing them under a microscope. Many concretions were crushed and examined for nuclei. Others were dissolved in HCl and the insoluble residue examined for a possible nucleus.

A millimeter measure and microscope were used to determine size and shape of the concretions.

Chemical Methods

Determination of exchangeable bases of the soils and concretions was performed according to Official Methods of Analysis of the A. or O.A.C. (7)

Ten grams of 0.5 mm. air-dried material was weighed and placed into a 250 ml. pyrex Erlenmeyer flask. One hundred ml. of neutral normal ammonium acetate solution was added to the ten grams of soil. The flask was stoppered and shaken vigorously for 2 to 3 seconds. The solution and soil was then allowed to stand one hour, however it was agitated every fifteen minutes by shaking it for 2 to 3 seconds. The soil was transferred to a 70 mm. Buchner funnel which had a light suction on the filter paper. Soil that adhered to Erlenmeyer flask was washed out with more ammonium acetate solution. After all the soil was out of the Erlenmeyer flask, ammonium acetate solution was leached through the soil in the funnel until the volume of filtrate equaled 250 ml.

After the ammonium acetate had leached through the soil, the leachate was transferred to 400 ml. pyrex beaker and evaporated to dryness on a hot plate. The residue from the evaporation treatment was placed in an oven and ignited for fifteen minutes at 550° C. The residue was dissolved in a known excess of 0.1N HCl in the presence of methyl red. Fine particles of carbon were filtered out of solution. The beaker and filter paper were washed five or six times with distilled H_2O. The filtrate was back titrated with 0.1 N NaOH until the orange red color was a distinct yellow. Each ml. of net acid equals 1 milliequivalent of replaceable bases per 100 grams of soil.

Qualitative analysis of the concretions and soils were determined according to Sorum (9). Samples of soil and "shot" from several horizons were dried and ground to pass 100 mesh screen. These soils and concretions were put into solution with HCl.

Five different samples of soil and their concretions were analyzed quantitatively for silicon dioxide, sesquioxides, calcium and manganese. The analyses were made according to the procedures described by Lincoln and Walton (4).

IV. RESULTS AND DISCUSSION

Physical Properties of Concretions

In the whole soil the concretions possess a rusty or ocher-yellow shell. The shell is very clayey and is the same color as the soil around the concretion. Small concretions appear like true soil aggregates. When concretions are subjected to extreme weathering, they lose their rusty shell and expose their real color which is black. Concretions found around "Harvest Ant Hillocks" are black.

When the interior of the concretions are subjected to microscopic analysis, they display some beautiful colors, such as ruby red, saphire blue, oriental topaz yellow or oriental amethyst violet. The matrix of the concretions are grayish black. A drawing of six of these concretions is shown in figure 2. These drawings illustrate the way the concretions appear under a microscope.

Some of these crystals were qualitatively analyzed and were found to contain aluminum oxide. Aluminum oxide is found in nature in crystals that are nearly as hard as diamonds. When these crystals are colored with minute quantities of iron or other metals they display colors similar to the ones depicted in figure 2. In the literature cited by the author, investigators who have made studies of concretions have not reported colors in the material they have analyzed.

Concretions in Latimer County soil are irregular shaped to perfectly rounded balls. Figure 3 shows the shape of the concretions which were

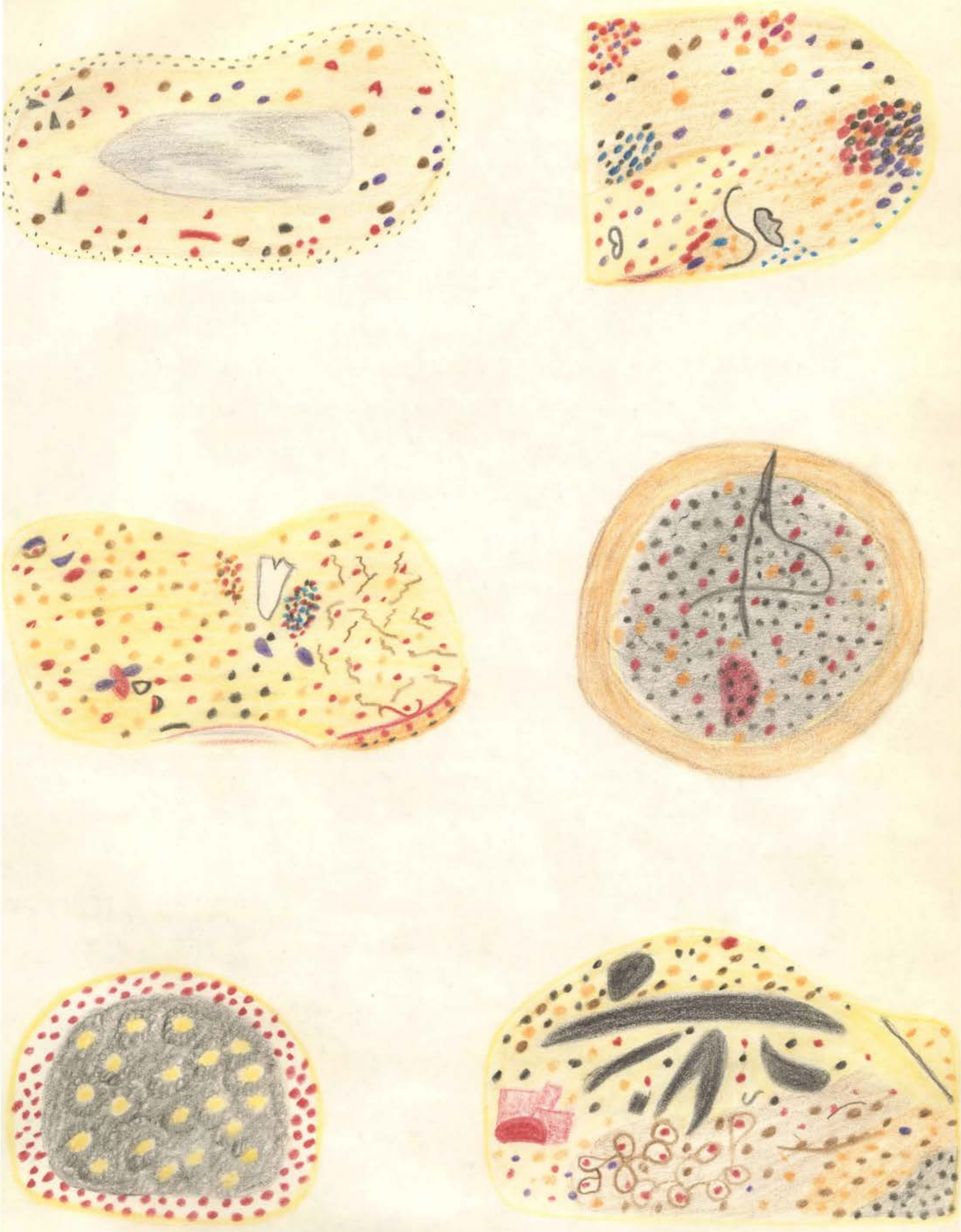

Fig. 2—A Microscopic Study of the Interior of Several Concretions.

Legend to Figure 2.

Concretion Upper Left - Core was a concentration of iron carbonates; surrounding the core was less concentrated iron with manganese dioxide, sand grains, and alumina. The outside coat was limonite and clay.

Concretion Upper Right - The colored areas are most probably alumina.

Concretion Center Left - White area is a cavity. This concretion is approximately 5 mm. in length and 3 mm. in width.

Concretion Center Right - The line design depicts a root as a possible nucleus in the formation of the concretion.

Concretion Lower Left - A small concretion with a dark center of material similar in composition to core in the concretion shown in the upper left-hand corner.

Concretion Lower Right - The dark areas show cavities in the concretion.

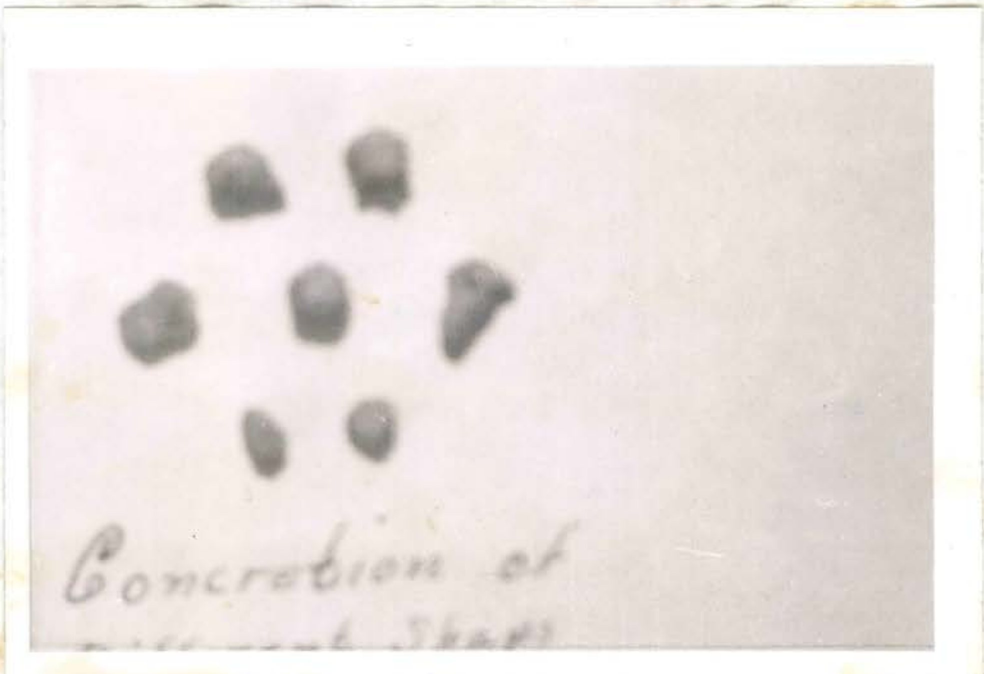

Fig. 3—Shape of Concretions.

taken from the soil.

Spherical concretions are less numerous than irregular shaped concretions. In general spherical concretions are scattered uniformly throughout the A_2 and B_1 horizons. Small grains of sand or aggregates of sand could be the material spherical concretions developed around. The conditions under which these concretions have been formed prevents the inclusion of the surrounding soil.

Spherical concretions and irregular shaped concretions vary in size from invisible specks to perfectly rounded balls 11 mm. or more in diameter.

Figure 4 illustrates the average size concretions found in Latimer County soils; however, there are many concretions of irregular shapes that will measure more than 11 mm. in either width or length.

The data in Table I give the percentage distribution of concretions in Latimer County soils. Soils in Latimer County show an uneven distribution of concretions throughout the horizons. The greater concentration of concretions are found in B_1 and A_2 horizons. Firm, hard concretions are rather rare in B_2 and C horizons; however, the C horizon is marked by minute dark brown and black specks. An examination of these specks under a magnifying glass indicates that they are formed by segregations of presumably the same material by which the firm concretions are cemented. It is possible that such soft segregations differ from concretions mainly in the lack of cementation.

Table II shows a more even distribution of concretions in the soils sampled under deciduous trees. The A_2 horizon has the most concretions in it. A_2 horizon has an average of 24.4 per cent concretions, whereas the B_1 has an average of 23.75 per cent.

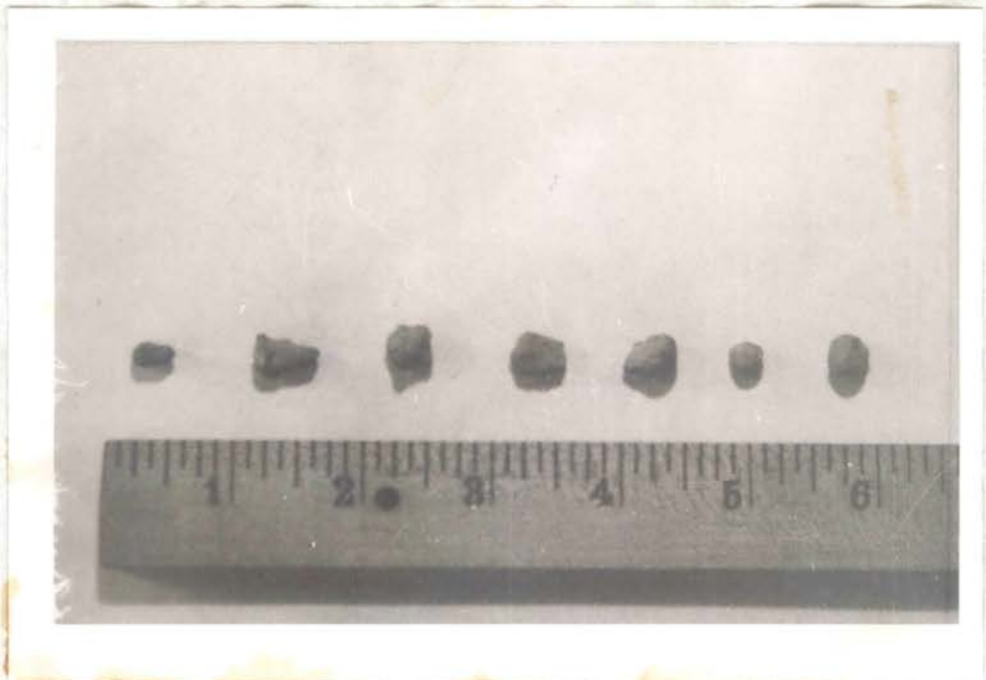

Fig. 4—Size of Concretions.

TABLE I

PERCENTAGE DISTRIBUTION OF CONCRETIONS IN LATIMER COUNTY SOILS

Soil No.	Location	Horizon	Depth	Per Cent Concretions
A—1	Eastern A. and M.	A_1	3" – 6"	0.8
A—2	Dairy farm	A_2	6"–12"	12.2
A—3		B_1	12"–16"	14.3
A—4		B_2	16"–24"	10.9
A—5		C	24" –	2.3
B—1	Eastern A. and M.	A_1	3" – 8"	1.8
B—2	Beef Stock farm	A_2	8"–14"	13.3
B—3		B_1	14"–20"	16.01
B—4		B_2	20"–30"	11.3
B—5		C	30" –	4.1
C—1	Extreme W. wide	A_1	3" – 7"	2.1
C—2	of Latimer Co.	A_2	7"–14"	8.2
C—3		B_1	14"–21"	14.8
C—4		B_2	21"–32"	7.3
C—5		C	32" –	2.8
D—1	Moore farm S.E.	A_1	4"–10"	1.4
D—2	of Wilburton 4	A_2	10"–16"	7.3
D—3	miles	B_1	16"–28"	10.9
D—4		B_2	28"–36"	6.3
D—5		C	36" –	1.4
E—1	Potts farm 13	A_1	3"–12"	0.9
E—2	miles S. of	A_2	12"–24"	8.4
E—3	Wilburton. (Indian	B_1	24"–30"	9.1
E—4	allotment)	B_2	30"–40"	6.3
E—5		C	40" –	1.0
F—1	Williams Dairy	A_1	3" – 6"	1.4
F—2	East side of	A_2	6"–14"	4.6
F—3	Latimer County	B_1	14"–20"	3.3
F—4		B_2	20"–28"	6.1
F—5		C	28" –	1.4

TABLE II

PERCENTAGE DISTRIBUTION OF CONCRETIONS UNDER DECIDUOUS TREES

Soil No.	Location	Horizon	Depth	Per Cent Concretions
H—1	Under Elm Tree	A_1	3"-18"	2.8
H—2	W. of E. A. and	A_2	18"-24"	31.4
H—3	M. Dairy Barn	B_1	24"-30"	30.2
H—4		B_2	30"-36"	24.1
H—5		C	36"-	8.1
I—1	Under White Oak	A_1	3"-11"	4.8
I—2	Tree Pots Farm	A_2	11"-21"	26.3
I—3	(Indian allotment)	B_1	21"-30"	24.8
I—4		B_2	30"-38"	16.3
I—5		C	38"-	4.1
J—1	Under Elm Tree	A_1	1"- 6"	2.0
J—2	Williams Dairy	A_2	6"-14"	16.4
J—3	Farm	B_1	14"-24"	16.3
J—4		B_2	24"-30"	11.9
J—5		C	30"-	3.6

Chemical Composition of Concretions and Surrounding Soil

Table III shows that the soil in Latimer County is very much on the acid side of the pH scale. The soil also has a very low level of exchangeable bases. The concretions have practically no replaceable bases.

Table IV shows that the concretions are higher in sesquioxides, calcium and manganese than the soil around them. The concretions contain less SiO_2 than the whole soil. These results agree with the findings of Wheeting (13) and Drosdoff (2).

The concretions from Latimer County will liberate CO_2, when HCl is placed with them. They will also act as a catalytic agent, to liberate oxygen from $KClO_3$ in the preparation of oxygen in the laboratory.

Origin of Concretions

The origin or source of Latimer County concretions has been a subject of much speculation. There is usually a humid season and an arid season in the area. During the dry season the soil moisture becomes concentrated in the horizons. The concretions appear to form from the materials that seed out of the super-saturated ground water.

Small grains of sand or aggregates of sand could be the material spherical concretions developed around. Irregular shaped concretions show no indication of having any nuclei present.

The concentrated ground water that evaporates on the surface horizon leaves a white residue which cracks an curls when it becomes dry. The white residue has all the appearance of alkali areas. On the contrary, they are very acid and are principally compounds of iron, aluminum, manganese with traces of bisimuth and phosphorus. Practically the same

TABLE III

EXCHANGEABLE BASES AND pH VALUES OF SOME CONCRETIONARY SOILS

Soil Number	Depth	pH	Exchangeable Bases △1
D—1	4"–10"	4.6	4.88
D—1 Concretions	4"–10"	——	.00
E—1	3"–12"	4.7	5.43
E—1 Concretions	3"–12"	——	.00
E—2	12"–24"	4.9	7.68
E—2 Concretions	12"–24"	——	.65
F—2	6"–14"	4.5	4.95
F—2 Concretions	6"–14"	——	.00
C—1	3"– 7"	5.5	4.50
C—1 Concretions	3"– 7"	——	.50

△1 Milliequivalents per 100 grams of soil.

TABLE IV

PERCENTAGE CHEMICAL COMPOSITION OF CONCRETIONS AND SOIL

Soil Number	Depth	SiO_2	R_2O_3	Ca	Mn
D—1	4"-10"	72.253	18.632	.02	0.124
D—1 Concretions	4"-10"	62.300	22.627	.03	0.42
E—1	3"-12"	62.530	28.421	.02	0.104
E—1 Concretions	3"-12"	54.115	34.812	.03	0.58
E—2	12"-24"	31.320	32.147	.04	0.108
E—2 Concretions	12"-24"	19.850	39.315	.23	0.40
F—2	6"-14"	42.480	29.733	.08	0.110
F—2 Concretions	6"-14"	27.330	32.176	.10	0.57
C—1	3"- 7"	35.118	38.113	.06	0.122
C—1 Concretions	3"- 7"	29.340	41.300	.06	0.42

elements are found in the concretions as one finds in the residue the ground water leaves on the surface.

V. SUMMARY

The physical properties, chemical composition, and origin of concretions found in the soils of Latimer County were investigated.

These concretions ranged in size from minute specks to approximately 11 mm. in diameter. Those with spherical forms seemed to have developed where solutions became supersaturated and precipitated around tiny nuclei. The irregular shaped concretions appeared to have formed by the same process, but they have very indefinite nuclei.

A microscopic analysis revealed that the interior of the concretions contained several brilliant colors. The aluminum oxide present within these concretions is probably responsible for these colors.

Of the soils examined, the A_2 and B_1 horizons contained the greatest percentage of concretions. The largest quantity of concretions was found under deciduous trees.

The concretions contained more R_2O_3, calcium, and manganese than the surrounding soil; whereas the silica content of the soil exceeded that of the concretions.

The origin of concretions has been a subject of much speculation. A possible mechanism of their formation is advanced.

VI. LITERATURE CITED

1. Bester, B. E. 1940. Concretions and Refractory Deposits in Some Natal Coastal Soils. Soils Sci. 50:313-324.

2. Drosdoff, D. and Nikiforoff, C. C. 1939. Iron-Manganese Concretions in Dayton Soils. Soil Sci. 49:333-345.

3. Frijimoto, Charles K. and Sherman, Donald G. 1950. Behavior of Manganese in the soil and the Manganese Cycle. Soil Sci. 66: 131-145.

4. Lincoln and Walton. 1916. Elementary Quantitative Analysis. The MacMillan Company.

5. Marbut, C. F. 1928. A Scheme for Soil Classification Proc. First International Congress of Soil Sci. 4:1-32.

6. Mehlich, A. 1948. Determination of Cation, and Anion Exchange Properties of Soil. Soil Sci. 66:429-445.

7. Official Methods of Analysis of the Association of Official Agricultural Chemists. (Seventh Edition) Association of Official Agricultural Chemistry. 1950.

8. Oklahoma Geological Survey: General information of. Bulletin 40. 1930.

9. Sorum, C. H. Semimicro Qualitative Analysis 1949. Prentice-Hall, Inc.

10. Sherrenan, Donald G., Annie, K. S., Tom, and Charles K. Frijimoto. 1949. The Origin of Pyrolusite Concretions in Hawaiian Soils: Pacific Science 3:120-123.

11. Statistics for Counties. Agriculture Volume 1. 5:227, 1950-1952.

12. Thompson, L. M. 1949. Soils: Their Formation and Classification. William C. Brown Pub.

13. Wheeting, L. C. 1936. Shot Soils of Western Washington. Soil Sci. 41:35-45.

14. Winters E. 1938. Ferromanganiferous Concretions from Some Podzolic Soils. Soil Sci. 46:33-40.

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