A STUDY OF THE DISTRIBUTION AND RELATIONSHIPS OF FREE IRON TO THE SOIL MORPHOLOGY OF SELECTED CENTRAL OKLAHOMA SOILS

Βу

BENCHAWAN MEKSOPON Bachelor of Science Chulalongkorn University Bangkok, Thailand

1967

Submitted to the Faculty of the Graduate College of the Oklahoma State University in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE May, 1973

OKLAHOMA STATE UNIVERSITY LIBRARY

JUN 1 1973

A STUDY OF THE DISTRIBUTION AND RELATIONSHIPS OF FREE IRON TO THE SOIL MORPHOLOGY OF SELECTED CENTRAL OKLAHOMA SOILS

Thesis Approved:

on Thesis Advi ser Ner be 9. 00

Dean of the Graduate College

ii

ACKNOWLEDGMENTS

The author wishes to express gratitude and sincere appreciation to:

Her major adviser, Professor Fenton Gray, for his encouragement, guidance, and inspiration throughtout this study and during the past sixteen months;

Dr. Lester W. Reed, for his encouragement, inspiration and interest in the author's graduate study;

Dr. Dale E. Weibel, for his kind assistance and guidance as a member of the advisory committee;

Professors Julian Q. Lynd, Ralph S. Matlock, and Lawrence G. Morrill, for their encouragement and guidance;

Her parents, Pen and Bugha Meksopon, for inspiration, love and guidance during all these years;

All members of the departmental staff and fellow students for their thoughtful suggestions, assistance, and fellowship.

iii

TABLE OF CONTENTS

Chapte	er	Page
Ι.	INTRODUCTION	1
II.	REVIEW OF LITERATURE	3
	Morphology of Soils Investigated	3 4 8 9 11 12 12
III.	MATERIALS AND ANALYSIS PROCEDURES	14
	Soil Profiles	14 14 18 21 23 23
IV.	RESULTS	25
	Physical Analysis Data	25 26
V.	DISCUSSION OF RESULTS	33
	Aline Loamy Fine Sand	33 35
VI.	SUMMARY AND CONCLUSIONS	38
LITER/	ATURE CITED	39

LIST OF TABLES

Table		Page
I.	Profile Description: Aline Loamy Fine Sand	15
II.	Profile Description: Zaneis Loam	18
III.	Profile Description: Port Clay Loam	21
IV.	Physical Data: Zaneis Loam and Port Clay Loam	25
۷.	Physical Data: Aline Loamy Fine Sand	26
VI.	Chemical Data: Aline Loamy Fine Sand	27
VII.	Chemical Data: Zaneis Loam and Port Clay Loam	28
VIII.	Clay-Iron Distribution in Aline Loamy Fine Sand	29
IX.	Clay-Iron Distribution in Zaneis Loam and Port Clay Loam Profiles	32

LIST OF FIGURES

Figu	re	Page
1.	Location of Payne County in Oklahoma	16
2.	Soil Sample Site Locations	16
3.	Block Diagram: Aline Soils of Central Oklahoma	17
4.	Block Diagram: Soils of Reddish Prairie Zone (Port and Zaneis Series)	19
5.	Two Views of Aline Loamy Fine Sand Profile Showing Band (Lamellae) Formation	20
6.	Scaled Diagrams of Soil Profiles: Zaneis Loam and Port Clay Loam	22
7.	Three-Dimensional Representation of Clay and Iron Distri- bution in Aline Loamy Fine Sand Profile	30
8.	Three-Dimensional Representation of Clay and Iron Distri- bution in Soil Profiles	31

LIST OF ABBREVIATIONS AND NOTATIONS

Sand	S
Loamy sand	1s
Sandy loam	s]
Clay loam	c1
Silt loam	sil
Silty clay loam	sicl
Very friable	mvfr
Friable	mfr
Firm	mfi
Granular	gr
Single grain	sg
Blocky	bk
Subangular blocky	sbk
Total clay content	C _t
Free iron content	Fe _d
Total iron content	Fe_t

.

vii

•~

CHAPTER I

INTRODUCTION

The occurrence and distribution of free iron in soil profiles, its relationship to important physical, chemical, and mineralogical characteristics of certain North American soils, and their related morphological and genetic features have been the subject of considerable study and research by several soil scientists in the United States, Canada, and elsewhere over the past two decades or so.

Likewise, the characteristics and mode of origin of subsoil bands (lamellae), the physical and chemical mechanisms, and the geomorphic and medogenetic processes that may involve textural band formation in some soils, have also received wide attention, especially over the last twenty-two years.

Historically, as early as 1896, Liesegang demonstrated colored band formation in gels. Holmes, in 1918, attributed the (Liesegang) ring formation in gels to a differential diffusion rate of ions in a gel, causing a periodic precipitation of ions present as insoluble salts where they are in contact with each other in suitable concentrations (24).¹

Contents of soil colloidal fraction (clay) and iron, and such other elements as Al and Mn have thrown some light on the type, direction and extent of soil-forming processes, how these parameters may be used to

¹Figures in parentheses refer to "Literature Cited."

define soil orders and other soil groups, and how they may serve as differentiators in soil classification on soils with similar morphology and in distinguishing between different types of B horizons.

For purposes of this study, three local soils were sampled: (a) Aline loamy fine sand, characterized by banded texture in the A22 and B2t horizons, and (b) two soils of similar morphology, i.e., Zaneis loam and Port clay loam. Sampling for (a) was from 12'-13', and for (b) from 6'-7' depths below surface of the soil from three distinct locations in Payne County, Oklahoma. The soil profiles were identified and soil from each significant horizon was analyzed for particle size distribution and chemical properties, such as pH, cation exchange capacity (C.E.C.), base saturation (B.S.), and organic matter content. Each soil was also analyzed for free iron (Fe_d) and total iron (Fe_t) in designated horizons and concretions.

The purpose of this investigation was to evaluate the distribution of free iron and total iron in relation to the important chemical properties analyzed, the morphology of the soils, and the nature of the soilforming processes.

CHAPTER II

REVIEW OF LITERATURE

Morphology of Soils Investigated

The three soils of this study from designated locations of Payme County in the north-central part of Oklahoma represent geological formations of the Permian Red Beds of the Western Prairie Plains. The Aline loamy fine sand is typical of wind-sorted old Pleistocene Terraces. The Zaneis loam marks the upland in the Stillwater Creek region, and the Port loam is characteristic of alluvial sediments of the bottomland (floodplain) of the Stillwater Creek region (4, 8).

In general, the soil-forming forces of the region are known to produce, at maturity, a soil: (a) having a dark- or reddish-brown, friable surface horizon, (b) with heavier and thicker claypan subsoils, and (c) underlain by the upper portion of the partially oxidized and leached, though not entirely weathered, parent material. Also, along the Cimarron river and other streams, sandy aeolian deposits are known to occur as broad belts (4, 8). Morphological development in these soils is estimated to be mature.

The climate of the region where the soils under study have developed is generally moist subhumid with less than 36 inches average, annual precipitation, and the vegetation varies from small grains, iron weeds, wheat, and tall and mixed grasses (8).

Profile Distribution of Iron

Blume and Schwertmann (2) stated that the distribution of the pedogenic oxides and hydroxides of Fe (and elements Al and Mn) is greatly affected by the processes of soil profile morphology and genesis.

Rich and Obenshain (17) associated most of the free iron with the clay fraction. In a study of Virginia soils (17), they reported the variation of free iron within the soil profile as large and associated with soil factors which cause or affect the reduction of iron, its mobility in solution and accumulation elsewhere by oxidation and precipitation. Iron movement in particles is associated with factors affecting the eluviation of clay. In general, leaving some exceptions, the horizon of clay illuviation also is the horizon of base and Fe₂0₃ concentration; and the horizon of iron accumulation is also one of the high pH, base saturation and clay content. Physical movement of solid phase iron oxides was found to be greater for well-drained soils, concurrent with the eluviation of clay and for poorly drained soils, the movement of iron was greater in solution (ferrous state).

Also, in several well-drained moderately fine-textured North Carolina soils investigated by Soileau and McCracken (22), except for horizons containing intense iron mottling, nearly all of the free iron oxide occurred in the clay fraction, predominantly in the < 0.2 μ clay.

Wurman et al. (24) regarded clay concentrations in soils as taking place by bulk movement of clay-size particles or as sesquioxides in solution or suspension which then recombine to form silicate clay. Iron movement in the soil is regarded as taking place in the organic chelated form. The movement and deposition of free iron oxides in the soil may be due to: (a) independent movement of amorphous oxides in suspension

or solution; (b) movement as an organic-iron oxide complex; and/or (c) movement in an iron-silicate clay complex (24). It is also believed that a simultaneous movement of two or three constituents such as silicate clay-organic matter-iron oxides, silicate clay, and organic colloids is possible without mutual interference. The accumulation of these components of the soil suspension can be brought about in the following ways:

 Deposition by sedimentation or due to the lack of water to flush them through, or else by the withdrawal of water by evapotranspiration.

2. Free CaO presence causing the flocculation of clay minerals or clay complexes and/or the organic-iron complex.

3. Mutual flocculation of free iron oxide and clay, as suggested by Folks and Riecken (7).

4. The beginning of deposition in fine pores of the original materials due to textural or structural conditions originally present in the soil.

Blume and Schwertmann (2) also reported that leaching of carbonates and accumulation of organic matter or other strong changes of soil mass could change the amount of iron oxide in one horizon relative to another.

Clay concentration along with high pH and oxidizing conditions were thought to be important factors in the immobilization of iron in a soil horizon (17).

Free iron includes the iron oxides and other forms of iron found in soils, but not as a part of the crystal lattice of other minerals present. Although several workers have reported a close association between clay and free iron in soils, Coffin (3), however, found for some Canadian Podzol soils a closer relationship between total iron and clay content. Total iron values for the coarse $(2 - 0.2 \mu)$ and fine $(< 0.2 \mu)$ clay fractions from the major horizons indicated a higher and a more uniform iron content for the fine fraction than for the coarse clays. This suggests that the fine clay fraction is dominated by iron-bearing clays which have been little affected by weathering.

Mechanism of Textural Band Formation

Bands or lamellae are known to occur in the lower horizons of many sandy soils of central and eastern United States.

Several theories have been proposed to date to explain the origin and mechanism of textural banding relative to soil formation processes. If the bands are pedogenetic, they may indicate a periodic or cyclic type of soil formation in which clay and iron oxides are concentrated in relatively narrow bands separated by coarse textured interbands. However, for soils having sandy loam and finer textured solums, the eluviated clay is relatively uniformly dispersed throughout the horizon of illuviation. Robinson and Rich (18) go on to hold that for bands of depositional origin they would represent stratified parent materials and soil development processes in these sandy deposits would be similar to those in finer textured materials.

The works of Folks et al. (7), Wurman et al. (24), and others for sandy soils lend support to an extension of the above processes: a kind of periodic precipitation for the formation of bands, involving the mobilization of clay in the upper horizons and its translocation and deposition in bands in the lower horizons of the soil. The bands are thus considered to be pedogenetically related to the upper solum. A similar view was held by Folks et al. (7) in their study of clay-iron

bands in sandy Iowa soils, i.e., a rhythmic precipitation of iron oxide from a soluble organic chelated form as increased amounts of the organic chelating agent were withdrawn by absorption on the soil matrix through which the solution was percolating. Clay moving through the soil was believed to be flocculated upon coming in contact with the iron band and thus produced an iron-clay band. Smith et al. (24) in their study of soils developed from sandy parent materials in Iowa also related band formation to clay movement accompanied by a flocculation action of free Fe_2O_3 .

The above mechanism may be physical or chemical or both. According to Jenny et al., the physical mechanism may begin by the lodging of the coarse clay first in a zone or band with subsequent movement of fine clay into the band. The chemical process, held Neuman, may involve the translocation of Fe in a reduced condition (18).

A second line of thought involves the deposition of the banded material as a geologic phenomenon, i.e., the sandy soil is deposited by water and reworked by wind with the bands representing strata of fine textured sediments. Kuenen et al., in studying the formation of lamellae in sandy deposits, showed that they can be formed by what is known as turbidity flow. It is also held that much of the banding may be the result of a combination of the forces involved in the above-described general theories (18).

Robinson and Rich (18) further believe that the origin of the sediments deposited may have been very similar, and thus the free iron content in the clay fraction is essentially the same. This indicates that the iron was retained in proportion to the amount of clay present and that the soils were developed under oxidizing conditions.

Nature of Textural Bands

Textural bands consist of relatively thin, often wavy, deposits of materials that are finer in texture and redder or browner in color than the material above or below. Bands occur most generally in acid, unconsolidated, and well-drained sands (18). These may vary in thickness from 1/16 to 2+ inches, may make up 10 to 40+% of the volume of the banded section of a soil profile, and contain up to a measured 12% clay. The soils showing banding usually have slopes of 0 to 15%; however, for sand pits and cut sections of roads the bands are known to be nearly level.

In studying the relief of bands, it was noted that waviness and irregularities are usual characteristics, except in cuts deeper than 15 feet in which the bands are straight and level except when cross-bedding occurs.

Folks et al. (7) in studying the nature of clay-iron bands of some sandy soils of Iowa noted that banding occurs often enough in loamy fine sand to indicate that this phenomenon is usual rather than an exception in their genesis, and that the bands of iron and clay enrichment are the product of profile genesis.

Teas (18) held that textural bands were probably of both fluviatile and aeolian origin. Kuenen (18) stated that distortion due to turbidity flow may occur in the lamellae by slumping or subaqueous sliding, and that even with this distortion, the original bedding is retained.

Wurman et al. (24) found that the textural bands may or may not be from the same initial material as the horizons immediately above or below them. Three kinds of textural bands or lamellae were distinguished: (a) pedo-petrogenetic, (b) pedogenetic, and (c) petrogenetic.

These layers were found to contain two to seven times as much clay as the intervening bands or interbands, and were identified as horizons with greater specific surface, higher exchangeable capacity, slightly lower pH, and higher organic matter content. However, no significant difference between the bands and interbands relative to the free iron content in the clay fraction was reported (18).

Occurrence of segments of bands and "clay balls" in the upper portions of the profile, and clay coatings on sand grain surfaces for both bands and interbands, and some clay bridges were also reported (18). Field studies have further shown that the bands may extend to great depths, lie nearly horizontal, and may not necessarily conform to the relief of the present surface.

Analysis of Free Iron

Since 1877, when Bemmelen and others used mineral acids and alkalies to dissolve iron oxides (and clays as well), various methods have been developed which are more selective. Most of them lack, as claimed Mehra and Jackson (13), some of the essential requirements of a desirable iron oxide removal method, i.e., the method should be: (a) effective, (b) rapid, (c) free of analytical difficulties, and (d) should not attack iron silicate minerals in clays. With few exceptions, these methods are all based on the relative ease with which naturally occurring oxides may be reduced to the ferrous state and then brought into solution (9).

Comparing the buffered dithionite method proposed by them (13) with three other types of methods using (a) H_2S , (b) unbuffered dithionite, and (c) nascent hydrogen, they found the buffered dithionite method most effective and least time-consuming.

Two methods have found wide application for the quantitative separation of crystalline and amorphous iron:

Dithionite-citrate-bicarbonate procedure by Mehra and Jackson (13), and

Acid ammonium oxalate procedure, originally proposed by Tamm
(16) and later modified by McKeague and Day (12).

Pawluk (16) found the dithionite-citrate-bicarbonate procedure highly effective in removing iron from soils, both amorphous and crystalline oxides of iron and iron closely associated with clay. The acid ammonium oxalate method, refined by McKeague et al., was considered a more effective means for the measurement of amorphous iron content. From experimental data for Canadian soils, he also concluded that double extractions with acid oxalate and single extractions with dithionitecitrate-bicarbonate solutions served as fairly reliable indicators of the relative amounts of amorphous iron oxide and free Fe₂0₃ content, respectively.

Among other variations in procedure for free iron determination in soils and clays, that of Coffin (3) employing a single extraction at 50°C with sodium hydrosulphite (dithionite) in a citrate buffer at pH 4.75 deserves mention. The author claimed that crystal structures of clay minerals other than nontronite were not attacked by this procedure. The single extraction also removed as much or more iron than was removed by successive extractions in three other procedures employing dithionite as the reducing agent under varying conditions regarding buffers, pH, temperature, and reagent concentrations. Generally, those methods using sodium hydrosulphite (dithionite) have been found to give efficient removal of free iron with a minimum of lattice destruction of silicates. Deb (5) also advocated the use of hydrosulphite as an extracting agent for free iron oxide removal from soils, assuming it to have the least destructive action on clays with iron-bearing lattices.

Haldane (9) developed a method of determining iron oxides in soils using zinc powder and an acid ammonium oxalate buffer solution, whereby complete solution of iron oxide particles was achieved in one hour at room temperature and no loss of iron by precipitation during extraction resulted.

Holmgren (10) proposed a method he termed as both convenient and reliable and involves shaking the samples overnight in a citratedithionite buffer, followed by a colorimetric iron determination using orthophenanthroline. The use of an automatic pipette, a flocculating agent, and non-critical quantities of dry reagents facilitates the determination, and the results show increased effectiveness and reliability over Kilmer's (11) method used for high-iron Oxisols and Ultisols from Puerto Rico.

Significance of Free Iron (Fe_d)/Clay (C_t) Ratio

The Fe_d depth function in soil profiles has been studied extensively by Stonehouse et al. (23), and Blume et al. (2), and were found to be of diagnostic value for profiles developed in homogeneous material. The comigration of clay and iron was confirmed by the high correlation seen between Fe_d (both amorphous and crystalline oxides) and total clay, C_t. The increase in Fe_d/C_t ratios can be related to clay movement. Even though dithionite-extractable iron (Fe_d) increases as the clay increases, it was found that the extractable iron does not increase in proportion

to the clay translocated. Clay maxima and minima in the Bt and the A horizons, respectively, generally are known to coincide with Fe_d maxima and minima. However, the variation in Fe_d /clay ratios throughout the profile is thought to reflect the influence of fluctuating water tables on the distribution of iron.

Iron Extractability (Fe_d/Fe_t)

Blume et al., Michalyne (14), and Stonehouse et al. (23) also stressed the importance of iron extractability, measured by the ratio, Fe_d/Fe_t , in studying the distribution of pedogenic iron oxides in a soil profile. A change in the extractability of iron in the B horizons, indicated by $Fe_d/clay$ ratios, suggests slight accumulations of iron occurring above that resulting from clay movement.

Iron Concretions

Based on their experimental data and studies for Dayton soils, Drosdoff and Nikiforoff (6) had this explanation for the formation of concretions of Fe: The soil solution under submerged conditions contains a high concentration of ferrous bicarbonate as a result of waterlogging and microbiological action on organic matter. As the soil dries, the iron is precipitated and oxidized to the oxide on the surface of the mineral grains at points with the smallest pore space. The nuclei may be formed also through precipitation by microorganisms. Once the nuclei of ferric oxides are formed, the concretions grow from year to year by absorbing and oxidizing the ferrous salts at their surface.

It is believed that the composition of concretions may vary in different soils, but the general process of formation is essentially the same. This process may be regarded as a horizontal mobilization and segregation of certain compounds within the horizons, unlike the process of vertical translocation from one profile horizon into another. If, then, the factors affecting horizontal mobilization are prepondering, it is possible that eluviation and illuviation may not be the main processes leading to the development of the general profile.

The concretions contained a much higher proportion of iron as Fe_2O_3 than did the whole soil, and ranged from 0.05 to about 15 mm. in diameter. Except in the very small concretions, $%Fe_2O_3$ in the smaller concretions was found to be greater than that in the larger ones (6).

CHAPTER III

MATERIALS AND ANALYSIS PROCEDURES

After field observations, three profiles of soils from designated locations were sampled in detail for identification and laboratory studies. Location maps appear in Figures 1 and 2. Figure 3 is a block diagram showing aline soils derived from recent alluvium in central Oklahoma.

Soil Profiles

Aline Loamy Fine Sand

Location: Site, 3168 feet S. of Highway 33; 464 feet E. of SW_4^{1} ,

sec. 1, T17N, R2E, Payne County, Oklahoma.

Relief: 1-3%.

Order: Alfisol.

Subgroup: Psammentic Paleustalfs.

Family: Sandy, mixed, thermic.

Parent Material: Old alluvium, wind reworked.

Profile Description: The soil profile was collected from the existing excavated sand pit. From 50 to 180+ inches of sample depth, the profile was marked by textural banded formation, the bands ranging in thickness from 1/8" to 2+". The soil profile showing band formation appears in Figure 5. A graphic description of the profile is given in Table I.

loriz	zon	Depth (inches)	Color (m)	Texture	Structure	Consistence
A1		0-8	10.YR 4/3	s]	sg	mvfr
A21		8-49	10 YR 5/4	1s	sg	mvfr
Г	0B*	49-61	10 YR 5/8	s1	sg	mvfr
	BB **		10 YR 5/4	S	sg	mvfr
	OB	61-72	10 YR 5/8	1s	sg	mvfr
A22	BB		10 YR 5/4	S	sg	mvfr
B2t	OB	72-100	10 YR 5/8	1s	sg	mvfr
	BB		10 YR 5/4	S	sg	mvfr
	OB	100-148	10 YR 5/8	ls	sg	mvfr
L	BB		10 YR 5/4	S	sg	mvfr
C1	OB	148-180	10 YR 5/8	1s	sg	mvfr
	BB		10 YR 5/4	S	sg	mvfr
Ç2		180-180+	10 YR 5/8	1\$	sg	mvfr

PROFILE DESCRIPTION: ALINE LOAMY FINE SAND

TABLE I

. 1 ·

*OB: material representing textural band.

**BB: material representing interband layer.



Figure 1. Location of Payne County in Oklahoma



.





Figure 3. Block Diagram: Aline Soils of Central Oklahoma

Zaneis Loam

Location: Site, 700 feet E. and 85 feet S. of NE corner of SW₄, sec. 4, T19N, R1W, Payne County, Oklahoma.

Relief: 3-5%. Landform: Uplands.

Order: Mollisol. Subgroup: Udic Paleustolls.

Family: Loamy, mixed, thermic.

Parent Material: Permian sandstone.

Profile Description: The soil profile taken represents 5'-1" depth below surface. Fe-Mn concretions were found in the B horizon, and mostly in the B22t horizon. Figure 4 is a block diagram showing Port and Zaneis soils in the Reddish Prairie area of central Oklahoma. A scaled diagram of the horizons is shown in Figure 6. Table II is a graphic description of the profile.

TABLE II

PROFILE DESCRIPTION: ZANEIS LOAM

Horizon	Depth (inches)	Color (m)	Texture	Structure	Consistence
Al	0-14	7.5 YR 3/2	1	gr/sbk	mvfr; mfr
B21t	14-22	2.5 YR 3/6	cl	sbk	mfr
B22t	22-52	2.5 YR 3/6	cl	sbk/bk	mfr; mfi
B3	52-61	2.5 YR 4/6	cl	sbk	mfi





Figure 5. Two Views of Aline Sand Profile Showing Band (Lamellae) Formation

Location: Site, 867 feet E. and 990 feet S. of NW¼, sec. 4, T19N, R1W, Payne County, Oklahoma. Relief: 0-1%. Under: Mollisol. Family: Fine-silty, mixed, thermic.

Parent Material: Loamy alluvial sediments from surrounding Permian materials.

Profile Description: The profile represents a sampled depth of 5'-7". A scaled diagram of the horizons is shown in Figure 6, and a graphic description of the profile is given in Table III.

TABLE III

Depth Color Horizon (inches) Consistence (m) Texture Structure Аp 0-11 7.5 YR 2.5/2 sil gr mfr A1 10 YR 2.5/1 11-17 sicl sbk mfi B2t 17-46 10 YR 3/2 sicl bk/sbk mfi, mfr С 5 YR 4/4 46-67 sil mfr sbk

PROFILE DESCRIPTION: PORT CLAY LOAM



•

Figure 6. Scaled Diagrams of Soil Profiles: Zaneis Loam and Port Clay Loam

Mechanical Analysis

Particle size distribution of soil samples from each significant horizon was determined on air-dried unsieved soil, first by removal of carbonates and soluble salts using 1 N NaOAc solution, heating to 80°C in centrifuge tubes immersed in water bath, and then centrifuging at about 5000 RPM for five minutes. Organic matter was then removed using H_2O_2 . The sample was washed through a 10-mesh sieve separating the gravel size, if any. Hydrometer analysis was then run on the soil solution to obtain the clay fraction. The suspension was washed through a nest of sieves: 20-mesh, 40-mesh, 60-mesh, 140-mesh, and 300-mesh, wherever applicable. The fractions of sand size material were oven-dried and weighed. Percent silt was thus calculated on the basis of the difference of the original weight and cumulative sand plus clay weight.

Chemical Analysis

The soil pH was determined using a Beckman glass electrode pH meter on both 1:1 soil-water mixture and 1:1 soil-1N KCL paste. For soil organic matter, the potassium dichromate wet oxidation method of Schollenberger (20) was used. Cation exchange capacity (C.E.C.) was determined by the sodium acetate (NaOAc) saturation method outlined in USDA Handbook 60 (19). The exchangeable cations were determined by a method also given in USDA Handbook 60 (19). These cations were displaced with ammonium acetate (NH_AOAc) and extracted by leaching.

For effective removal of free iron (Fe_2O_3), the laboratory-modified dithionite-citrate-bicarbonate procedure proposed by Mehra and Jackson (13) was employed. Total iron content was determined by HClO₄ - HF

digestion method outlined by Olson (15) and which permits dissolution of every form of iron: iron oxides, hydroxide of iron and iron in silicate layer, in the solution.

Following is a brief stepwise sequence of laboratory procedure used for free iron determination:

1. Weighed one (1) gram air-dried soil into 50 ml or 100 ml centrifuge tube.

2. Added (a) 4 ml 0.3 M sodium citrate, (b) 1 ml 1 M sodium bicarbonate, and (c) 0.1 gram sodium dithionite $(Na_2S_2O_4)$ to sample in step 1.

3. Placed sample in water bath maintained at 80°C, stirred occasionally for 15 minutes.

4. Cooled the sample, and centrifuged at 5000 RPM for five minutes; repeated process and washed the sample twice with 1 N NaCl.

5. All clear supernatant solution was saved for free iron analysis.

6. Treated solution in step 5 with 1 ml 30% H_2O_2 to remove organic matter; washed treated solution into 100 ml volumetric flask.

7. Iron content was determined by colorimetric method, using Bausch and Lomb colorimeter and 4% Tiron reagent and acetate buffer (pH 4.7) to form iron-Tiron color complex giving percent light transmittance at 565 millimicrons.

8. Previously established curve for standard Fe was used for comparison and iron content estimate.

CHAPTER IV

RESULTS

Physical Analysis Data

Results of physical analysis of the three soils studied are summarized in the following tables.

.

TABLE IV

PHYSICAL DATA: ZANEIS LOAM AND PORT CLAY LOAM

Denth		Partic	Particle Size Distribution, %			
(Inches)	Horizon	Sand	Silt	Clay	V.F.S.	Class
Zaneis Loa	<u>m</u>					
0-14	A1	26.6	45.2	28,2	15.6	loam
14-22	B21t	22.7	45.5	31.8	13.8	clay loam
22-52	B22t	21.7	45.9	32.4	13.6	clay loam
52-61+	B3	26.9	46.8	26.3	17.1	clay loam
Port Clay	Loam				- -	
0-11	Ар	10.7	66.6	22.7	7.9	silt loam
11-17	A1	6.5	64.1	29.4	5.1	silty clay loam
17-46	B2t	7.5	57.4	35.1	5.6	silty clay loam
46-67+	С	17.3	48.3	34.4	4.7	silt loam

TABLE V

Denth		Partic	le Size [Textural		
(Inches)	Horizon	Sand	Silt	Clay	V.F.S.	Class
0-8	Al	66.5	31.0	2.5	11.7	sandy loam
8-49	A21	84.8	12.7	2.5	10.6	loamy sand
49-148	C 0B*	78.7	10.6	10.7	10.9	sandy loam
	BB **	91.7	5.6	2.5	10,6	sand
	A22 OB	81.8	8.8	9.4	25.5	loamy sand
	+ BB	88.5	8.8	2.5	12.6	sand
	BZT OB	81.8	8.9	9,5	25.3	loamy sand
	BB	88.6	8.6	2.6	12.9	sand
	OB	80.4	9.6	10.0	19.9	loamy sand
	- BB	90.7	6.7	2.4	8.1	sand
148-180	C1 OB	75.7	15.3	[*] 9.0	11.1	loamy sand
	BB	87.2	11.3	0 ,9	9.0	sand
180-188+	C2	85.2	6.8	8.0	16.9	loamy sand

PHYSICAL DATA: ALINE LOAMY FINE SAND

 * OB: material representing textural band.

BB: material representing interband layer.

Chemical Analysis Data

Test data on the chemical properties of the soils investigated are summarized in Tables VI and VII.

á .

TABLE VI

	······································	p Soil	H Soil	······	C.E.C.			
Depth (Inches)	Horizon	+ Water 1:1	+ KC1 1:1	Organic Matter %	meq per 100 g	B.S. %	Free Iron Fe ₂ 0 ₃ (% Fe _d)	Total Iron (% Fet)
0-8	A1	5.0	4.1	0.96	4.6	42	0.08	0.52
8-49	A21	6.8	5.4	0.19	1.8	88	0.08	0.45
49-148	OB	7.2	5.6	0.13	6.3	79	0.10	0.46
	BB	7.0	5.8	0.10	1.7	83	0.05	0.30
	OB*	7.0	5.5	0.15	5.9	93	0.10	0.46
	A22 BB	7.1	5.9	0.00	1.7	93	0.05	0.30
	+ OB	7.0	5.5	0.14	5.9	93	0.12	0.75
	BB**	7.1	5.9	0.01	1.8	93	0.06	0.47
	B2t OB	7.2	5.8	0.14	6.9	95	0.12	0.75
	L BB	7.4	6.0	0.07	2.0	100	0.06	0.47
148-180	C1 OB	7.2	5.9	0.13	7.4	89	0.14	0.99
	BB	7.3	6.2	0.01	1.1	149	0.07	0.49
180-188+	C2	7.2	6.0	0.02	4.5	101	0.12	0.88
· ·				,				

CHEMICAL DATA: ALINE LOAMY FINE SAND

*OB: represents material within band.

**BB: represents material within interband layer.

TABLE VII

CHEMICAL DATA: ZANEIS LOAM AND PORT CLAY LOAM

÷

		pH						
Depth (Inches)	Horizon	Soil + Water 1:1	Soil + KCl 1:1	Organic Matter %	C.E.C. meq per 100 g	B.S. %	Free Iron Fe ₂ 0 ₃ (% Fe _d)	Total Iron (% Fe _t)
Zaneis Loa	<u>m</u>		- · · · ·				· · · · · · · · · · · · · · · · · · ·	
0-14	A1	6.1	5.1	2.01	17.7	78	0.31	1.55
14-22	B21t	6.3	4.9	0.97	22.2	66	0.39	2.16
22-52	B22t	7.6	6.3	0.54	17.8	111	0.37	2.08
	Concretions						0.82	2.85
52-6]+	В3	8.1	6.9	0.21	17.2	113	0.32	1.75
Port Clay	Loam							
0-11	Ар	6.4	5.3	2.37	19.8	92	0.31	1.53
]]-]7	A1	7.5	6.2	2.86	24.5	107	0.35	1.90
17-46	B2t	8.4	7.3	1.10	27.7	179	0.30	2.27
46-67+	С	8.5	7.3	0.71	27.8	142	0.24	2.24

A three-dimensional representation of clay and iron distribution in the banded section of the sand profile and in the Port and Zaneis soil profiles is shown in Figures 7 and 8. Clay (C_t) and iron (Fe_d and Fe_t) relationships appear in Tables VIII and IX.

TABLE VIII

	·····			
Depth (Inches)	Horizon	Total Clay <2µ % C _t	$\left(\frac{Fe_{d}}{Ct}\right)$	Extract- ability Fe _d /Fe _t
0-8	A1	2.5	3.2	0.15
8-49	A21	2.5	3.2	0.18
49-148	OB	10.7	0.9	0.22
	BB	2.5	2.0	0.17
	QB	9.4	1.1	0.22
	A22 BB	2.5	2.0	0.17
	+ ОВ	9.5	1.3	0.16
	B2t BB	2.6	2.4	0.13
	0B*	10.0	1.2	0.16
	BB	2.4	2.4	0.13
148-180	C1 QB	9.0	1.4	0.14
	BB **	0,9	2.8	0.14
180-188+	Ç2	8.0	1.2	0.14

CLAY-IRON DISTRIBUTION IN ALINE LOAMY FINE SAND

*OB: material within textural band.

BB: material within interband layer.



Figure 7. Three-Dimensional Representation of Clay and Iron Distribution in Aline Loamy Fine Sand Profile

30



Figure 8. Three-Dimensional Representation of Clay and Iron Distribution in Soil Profiles

ω

TABLE IX

Depth (Inches)	Horizon	Total Clay <2µ % C _t	$\left(\frac{Fe_{d}}{C_{t}}\right)$	Iron Extract- ability Fe _d /Fe _t
Zaneis Loam			<u> </u>	
0-14	AT	28.2	1.5	0.20
14-22	B21t	31.8	1.2	0.18
22-52	B22t	32.4	1.2	0.18
52-61+	B3	26.3	1.3	0.18
Port Clay Lo	am			
0-11	Ар	22.7	1.4	0.20
11-17	Al	29.4	1.2	0.19
17-46	B2t	35.1	0.8	0.13
46-67+	C	34.4	0.7	0.10

CLAY-IRON DISTRIBUTION IN ZANEIS LOAM AND PORT CLAY LOAM PROFILES

CHAPTER V

DISCUSSION OF RESULTS

Aline Loamy Fine Sand

Field observations indicated thin finer textured layers or lamellae, 1/8 to 2+ inches in thickness, in the Aline sand profile between subsoil depths of 49"+ and 170"+ within the A22 and B2t horizons. These multiple bands are browner in color than the adjoining interband layers. Though nearly level or horizontal, these are characterized by waviness, irregularity, bending, and some segmentation at depths. Below 125"+ subsoil depth, the band thickness becomes larger.

Evidence of scour is also seen in the 130"-170" depth region by the downward curving of the thicker bands for some distance, and then leveling out.

While sand and silt size composition of the soils, both in the banded and interband layers, showed no significant difference, the total clay content and the very fine sand fraction in the bands were appreciably higher than in the interband sands.

The banded material is slightly alkaline to neutral and only marginally so as compared to the interband sands. The bands have several times higher organic matter content, and three to four times greater cation exchange capacity than the interband layers. The percent base saturation in both banded and interband layers was relatively high and of the same order. The free iron content of the soil lamellae was

generally twice as much as in the interbands, and the total iron in bands ranged 55 to 100% higher than in the adjoining soils.

The presence of significantly higher very fine sand fraction in all textural bands in contrast to the interband layers indicates that the old alluvial sandy parent material has been perhaps more thoroughly wind-sorted and has undergone redistribution within the banded section of the profile as a result of periodic or seasonal flooding.

The test data lend support to the geologic deposition of the finer textured material in the bands by both wind and water action, and the translocation of the clay with iron oxide from the (top 49"+) surface horizon into the subsoil, and the distribution of these colloidal sizes and their deposition in the soil lamellae.

The percentage of free iron and the clay content of individual bands are essentially of the same order. The ($Fe_d/clay$) ratios indicate that no differential movement of iron relative to clay has occurred, or the iron was retained nearly in proportion to the clay content, and that the banded soils were developed under oxidizing conditions.

Another concept that appears convincing insofar as band formation in the profile is concerned follows: The iron may be reduced or complexed by organic decomposition products and, following reduction, it is precipitated by oxidation or mineralization of the organic compounds, and free iron oxide-clay-organic matter complexes thus formed are deposited to form the lamellae. However, some alteration of the bands by pedogenic processes is not ruled out.

From the small quantity of free iron present in the profile, one may infer that a relatively small amount of iron is probably required

to produce the banding effect in a media with very little interfering color, such as sand.

Zaneis Loam and Port Clay Loam

While the clay content of both soils throughout their profiles is nearly of the same order, the Zaneis loam is sandier, and the Port clay loam has a higher silt fraction. However, silt is the dominant size fraction in both soils.

Organic matter in both soils was relatively high: 2.0+ and 2.8+% in the Zaneis and the Port, respectively, and decreased with depth. Over the top 14 to 17 inches, organic matter content exceeded 0.9% giving the soils a thick dark A horizon.

Base saturation in both soils, in general, increased with depth and was considerably higher in B2t horizon of the Port soil. Cation exchange capacity (C.E.C.) of the Zaneis soil was high and nearly of the same order in most of the horizons, while in the Port soil, C.E.C. values were significantly higher and progressively greater in the lower horizons. For the Zaneis soil, there was a sharp increase in base saturation with pH from B21t to B22t horizon, while a marked decrease in C.E.C. value was noted. For the Port soil, on the other hand, both C.E.C. and alkalinity increased with depth.

Free iron content (Fe₂0₃) in the Zaneis soil was marginally higher than in the Port soil, % Fe in none of the horizons reached even fourtenths of one percent. Fe_d/clay ratios in the surface horizons were higher for both soils, and for the Zaneis soil, were also higher in the lower horizons. Total iron in both soils increased with depth, except in the B3 horizon of the Zaneis loam; percentages of Fe_d and total iron were generally of the same low order in the two soils.

Both Zaneis and Port series are within the Reddish Prairie Zone, and the soil-forming processes for both soils seem to be associated with those forming Mollisols. Loss of organic matter, silt, and clay from the mollic epipedon and gains in thick clayey argillic horizons in the two soils are quite marked, of course, to varying degree.

The general increase in pH, and hence, alkalinity, with depth in the lower horizons of both soils suggests calcareous parent materials, and is believed to be associated with the degree of weathering of basic minerals of the soils. The alkaline to calcareous environment probably accounts for the low percent Fe found in all horizons.

Comigration of clay and iron has a higher correlation in the Zaneis soil. However, nearly constant $Fe_d/clay$ ratio throughout the lower horizons of the Zaneis soil suggests impeded drainage, which is expected in the erosive uplands. It seems the Port soil is subjected to long wetting, and $Fe_d/clay$ minimum in the B2t and C horizons has been caused by lateral removal of Fe in solution, independent of clay movement, resulting in wet bleaching of these horizons.

The decrease in the extractability of iron in the B horizons, as indicated by $Fe_d/clay$ and Fe_d/Fe_t ratios, suggests that slight accumulations of iron have occurred above that resulting from the downward movement of clay. These accumulations may have resulted from in-place weathering within the B horizons or downward movement of weathering products from the A horizons. These ratios also suggest a high carbonate content of the parent materials.

The Fe content of ferruginous concretions, found at several locations throughout the argillic B horizon, and particularly in the B22t horizon of the Zaneis soil, was more than double the iron content of any horizon. These concretions are believed to be formed during dessication periods.

CHAPTER VI

SUMMARY AND CONCLUSIONS

This study of the three soils of Payne County, Oklahoma, leads to the following broad conclusions:

 Bands or lamellae may occur often enough in coarse-textured loams, loamy sands and sands to indicate that the banding phenomenon is quite usual in their genesis.

2. Iron accumulation and clay enrichment in bands show significant correlation.

3. Band formation is perhaps best explained by the rhythmic precipitation theory and the geologic deposition of eluviated clay with iron oxide, by wind and/or water action, in the lower horizons.

4. The two Mollisol soils have several similar morphological features, and their physical and chemical properties have much in common.

5. They are both developed from alkaline to calcareous parent materials, and represent about the same degree of maturity.

6. However, the drainage and physiographic features of their landform are different, as is their relative behavior in relation to clay and iron movement through the argillic horizons.

7. To understand the fine differences in their morphological behavior, more detailed physical (fine and coarse clay fractionation), chemical (Al, Mn, N, P, and exchangeable base and CaCO₃ content) properties and data, and mineralogical analysis are needed.

LITERATURE CITED

- Aurin, F. 1917. Geology of the Redbeds of Oklahoma. Okla. Geol. Bull. 30.
- (2) Blume, H. P. and U. Schwertmann. 1969. Genetic Evaluation of Profile Distribution of Al, Fe and Mn Oxides. Soil Sci. Soc. Proc. 33: 438-444.
- (3) Coffin, D. E. 1963. A Method for the Determination of Free Iron in Soils and Clays. Can. J. Soil Sci. 43: 7-17.
 - (4) Cobb, W. B. and H. W. Hawker. 1918. Soil Survey of Payne County, Oklahoma. USDA-Bur. of Soils.
 - (5) Deb, B. C. 1950. The Estimations of Free Iron Oxide in Soils and Clays and Their Removal. J. Soil Sci. 1: 212-220.
 - (6) Drosdoff, M. and C. C. Nikiforoff. 1940. Iron-Manganese Concretions in Dayton Soil. Soil Sci. 49: 333-345.
 - (7) Folks, H. C. and F. F. Riecken. 1965. Physical and Chemical Properties of some Iowa Soil Profiles with Clay-Iron Bands. Soil Sci. Soc. Am. Proc. 20: 575-580.
 - (8) Gray, F. and H. M. Galloway. 1959 Rev. 1969. Soils of Oklahoma. Okla. State Univ. Misc. Pub. MP - 56.
 - (9) Haldane, A. D. 1956. Determination of Free Iron Oxides in Soils. Soil Sci. 82: 483-489.
- (10) Holmgren, G. S. 1967. A Rapid Citrate-Dithionite Extractable Iron Procedure. Soil Sci. Soc. Am. Proc. 31: 210-211.
- (11) Kilmer, V. J. 1960. The Estimation of Free Iron Oxides in Soils. Soil Sci. Soc. Am. Proc. 24: 420-421.
- (12) McKeague, J. A. and J. H. Day. 1966. Dithionite- and Oxalate-Extractable Fe and Al as Aids in Differentiating Various Classes of Soils. Can. J. Soil Sci. 46: 13-22.
- (13) Mehra, O. P. and M. L. Jackson. 1960. Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate. 7th Nat. Conf. Clays and Clay Minerals: 317-327.

- (14) Michalyna, W. 1971. Distribution of Various Forms of Al, Fe and Mn in the Orthic Gray Wooded, Greyed Orthic Gray Wooded and Related Gleysolic Soils in Manitoba. Can. J. Soil Sci. 51: 23-36.
- (15) Olson, R. V. 1965. Iron-Method of Soil Analysis. Am. Soc. Agron.: 963-973.
- (16) Pawluk, S. 1972. Measurement of Crystalline and Amorphous Iron Removal in Soils. Can. J. Soil Sci. 52: 119-123.
- (17) Rich, C. I. and S. S. Obenshain. 1956. Distribution of Free Iron Oxides in Four Coastal Plain Soils of Virginia. Sixth Int. Cong. of Soil Sci. B-II: 447-451.
- (18) Robinson, G. H. and C. I. Rich. 1960. Characteristics of the Multiple Yellowish-Red Bands Common to Certain Soils in the Southeastern United States. Soil Sci. Soc. Am. Proc. 24: 226-230.
- (19) Salinity Lab. Staff. 1954. Diagnosis and Improvement of Saline and Alkali Soils. USDA Handbook No. 60.
- (20) Schollenberger, C. J. 1931. Determination of Organic Matter. Soil Sci. 31: 483-496.
- (21) Soil Survey Staff. 1960 Amend. 1964. Soil Classification, A Comprehensive System, 7th Approximation, SCS and USDA.
- (22) Soileau, J. M. and R. J. McCracken. 1967. Free Iron and Coloration in Certain Well-Drained Coastal Plain Soils in Relation to Their Other Properties and Classification. Soil Sci. Soc. Am. Proc. 31: 248-255.
- (23) Stonehouse, H. B. and R. J. St. Arnaud. 1971. Distribution of Fe, Clay and Extractable Fe and Al in Some Saskatchewan Soils. Can. J. Soil Sci. 51: 283-292.
- (24) Wurman, E., E. P. Whiteside and M. M. Mortland. 1959. Properties and Genesis of Finer Textured Subsoil Bands in Some Sandy Michigan Soils. Soil Sci. Proc. 23: 135-143.

VITA

Benchawan Meksopon

Candidate for the Degree of

Master of Science

Thesis: A STUDY OF THE DISTRIBUTION AND RELATIONSHIPS OF FREE IRON TO THE SOIL MORPHOLOGY OF SELECTED CENTRAL OKLAHOMA SOILS

Major Field: Agronomy

Biographical:

- Personal Data: Born in Rayong, Thailand, January 15, 1943, the daughter of Bugha and Pen Meksopon.
- Education: Attended Wattana Wittaya Academy, Bangkok, Thailand, and graduated from high school in 1961; received a Bachelor of Science degree in Chemistry from Chulalongkorn University, Bangkok, Thailand, in 1967; completed the requirements for the Master of Science degree in Agronomy in May, 1973.
- Experience: Employed with the Royal Thai Government in the Ministry of Agriculture as Soil Chemist, 1967-71; on sabbatical leave of absence since August, 1971.