GEOCHEMISTRY OF IRON AND CLAY MINERALOGY
OF PLAYA SEDIMENTS FROM
TEELS MARSH, NEVADA

by

PATRICIA DREW

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF ARTS
(Geology)
at the

UNIVERSITY OF WISCONSIN

1970

TABLE OF CONTENTS

PAGE

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Teels Marsh, Mineral County, Nevada is a salt-crusted discharge playa which has remained a closed basin since probably Pleistocene time. Relatively few rock types have contributed detritus to the basin and mineral reactions going on within the saline water-saturated lake clays are possibly important here.

A relatively sharp color boundary appears in the sediments approximately twelve feet below the playa surface. Chemical analyses for acid-soluble iron, total iron, iron as free iron oxides, total sulfur, and total carbon and x-ray analyses of zeolite nodules and the silt and clay fractions of the sediments were made to determine the nature of this boundary and its interpretation with respect to sedimentation conditions in the area. The environment at Teels Marsh is typical of that of many playa basins in the western Basin and Range province; hence, conclusions derived from this study may be significant in the interpretation of other areas as well.

No sudden change in total iron or acid-soluble iron occurs across the color boundary, although acid-soluble iron is generally lower in the deeper samples. Free iron oxides contain a constant proportion of total iron regardless of the depth of the sample. Both total sulfur and total carbon increase

sharply below the color boundary. The boundary is believed to be an oxidation-reduction boundary coinciding with a change from pluvial to subaerial conditions about 8500 years ago. The deeper black samples contain unoxidized organic matter and, possibly, authigenic FeS.

The clay mineralogy was studied as a function of depth and of grain size for the samples. Montmorillonite and mixed-layer clays are concentrated at depth and in the finer clay, relative to illite and chlorite. No kaolinite is present. Some of the clays may be authigenic and they may provide an important source of acid-insoluble iron. Zeolites formed diagenetically from the alteration of volcanic ash are phillipsite, clinoptilolite, and searlesite.

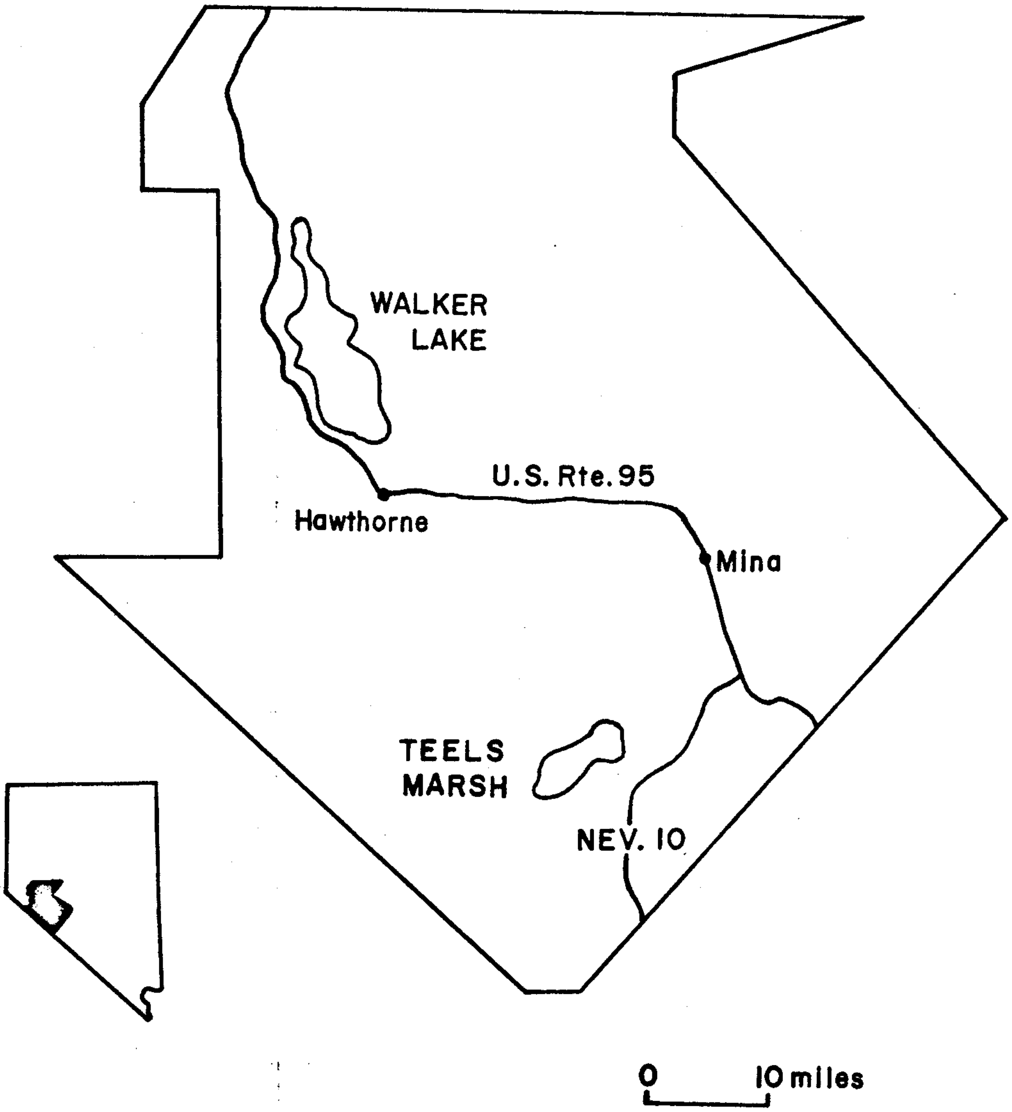
INTRODUCTION

The subsurface mineralogy and geochemistry of a vertical sediment core from Teels Marsh, Nevada have been studied in terms of the mineralogy of silt and clay fractions, organic carbon content, and the chemistry and mineralogy of possible iron minerals. The depositional history of this isolated basin during Pleistocene and Recent time is reflected in the sediment core. Post-depositional mineralogical and chemical changes defined for this area may be similar to those occurring in other alkaline playas and, therefore, studies of these lake sediments should lead to a better understanding of diagenesis in saline lake environments.

Teels Marsh, Nevada is located in Mineral County in southwestern Nevada, about thirty miles southesat of the town of Hawthorne (figure 1). The playa surface is eight square miles in total area. It is bounded to the west and north by the Excelsior Mountains and by a more irregular range of low hills to the south and east. The elevation of the basin is 4900 feet above sea level, and the present drainage basin is 340 square miles in area (Everts, 1969).

The major bedrock types surrounding the eastern portion of Teels Marsh are Quaternary-Tertiary mafic

Figure 1. Outline maps of Nevada and Mineral County showing the location of Teels Marsh.



MINERAL COUNTY, NEVADA

volcanic rocks, Tertiary intermediate volcanic rocks, and Jurassic Dunlap Formation sediments. Other contributors to the alluvium filling the basin are Cretaceous age granitic rocks; the Triassic Excelsior Formation, composed of intermediate to felsic volcanic rocks; and Tertiary felsic volcanic rocks. The playa surface is at least in part covered by a salt crust, and clay makes up a large part of the Quaternary deposits of the playa. Uranium, tungsten, and sulfide mineralization has been found to the west and north of Teels Marsh (Ross, 1961). In several locations in the playa a tuff layer is located only a few feet below the surface, proving that ash was deposited in the basin not long ago. Some zeolites have been produced within the mud by alteration of this volcanic ash (Hay, 1966).

Hydrologically, Teels Marsh is classified as a discharge playa, with interior drainage of both groundwater and surface runoff (Neal, 1965). Teels Marsh is a particularly good area in which to study mineral chemistry because it probably remained closed since at least the late Tertiary. Ross (1961) quotes Axelrod: "'The late Tertiary continental basins in this area (western Basin and Range province) were relatively local in extent... Each basin appears to record a different history, not only in terms of the rock represented, but also in a structural sense.'" During the Pleistocene, while glacial Lake Lahontan covered part of northern Mineral County, an isolated lake also occupied the Teels Marsh basin. Shorelines and beach deposits surrounding the present playa surface attest that the lake was filled with water to a level approximately 150 feet higher than the present playa surface (D.A. Stephenson, oral communication). Teels Marsh most likely remained isolated during post-Pleistocene times as well; the Excelsior Mountains to the north were a protective barrier to drainage from Lake Lahontan, and the topographic level of Lake Lahontan was always considerably below that of Teels Marsh. Thus Teels Marsh has been subject to influences of only a relatively small area and few rock types.

Because Teels Marsh is a discharge playa, an evaporite mineral crust is present over much of the playa area much of the year. Some evaporite minerals were present in sufficient quantity to be economically mined. Halite was produced from Teels Marsh several times since the 1860's. Borax was mined there from 1872 to 1892 (Ross, 1961).

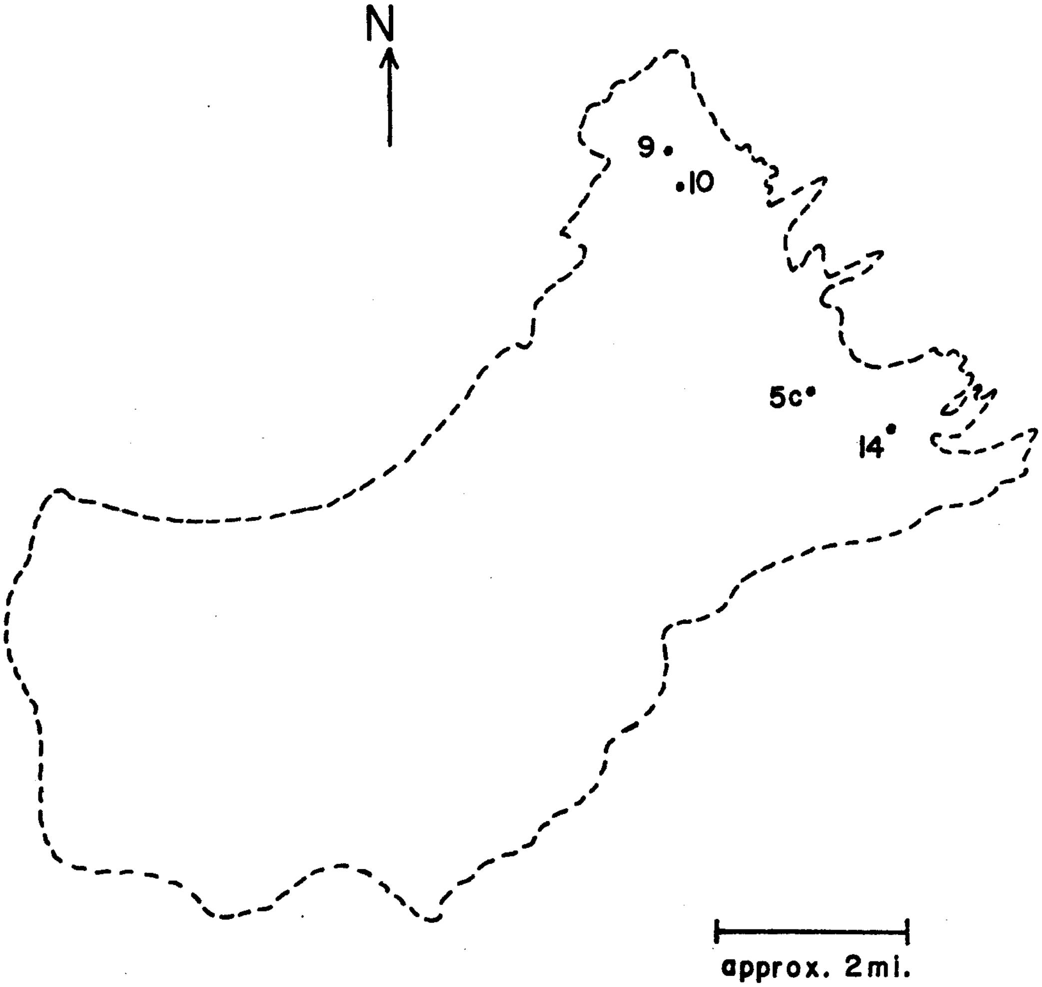
The collection of the core samples for this study was done by Mr. Craig Everts during the summer of 1967. The results of the project are found in Everts (1969). The cores were drilled by either truck-mounted drilling auger or by hand auger. Samples from the core were collected and sealed in polyethylene bags and cardboard pint-sized cartons. Soon after shipment the samples were frozen and stored frozen until used for analysis. These precautions were taken to minimize moisture loss from the samples and to prevent oxidation or alteration of primary phases present in the mud. Once analysis was begun, the samples were kept refrigerated and the polyethylene bags were opened only under a nitrogen atmosphere.

Core TM-5c (Everts, 1969) was selected for this study because it is sampled in detail throughout its thirty-eight foor depth. It is located out on the playa surface (figure 2) and probably represents a point which was always in the playa proper as the basin changed shape and extent with variations in precipitation and evaporation. A log for core TM-5c is given in figure 3 (Everts, 1969).

A significant color boundary of variable sharpness occurs in this and the other cores from the playa. The surface samples are red-brown, grading into green clay and silt below that vary in color from green to bluish-green to gray-green. Several feet below the surface of the playa, the green sediments grade downward to black. There are two possibilities

Figure 2. Outline map of Teels Marsh showing the location of samples used in the present study.

5c= Core TM-5c, studied in detail.
9 = TM-9-5, nodule only studied.
10= TM-10-3, nodule only studied.
14= TM-14-3, nodule only studied.



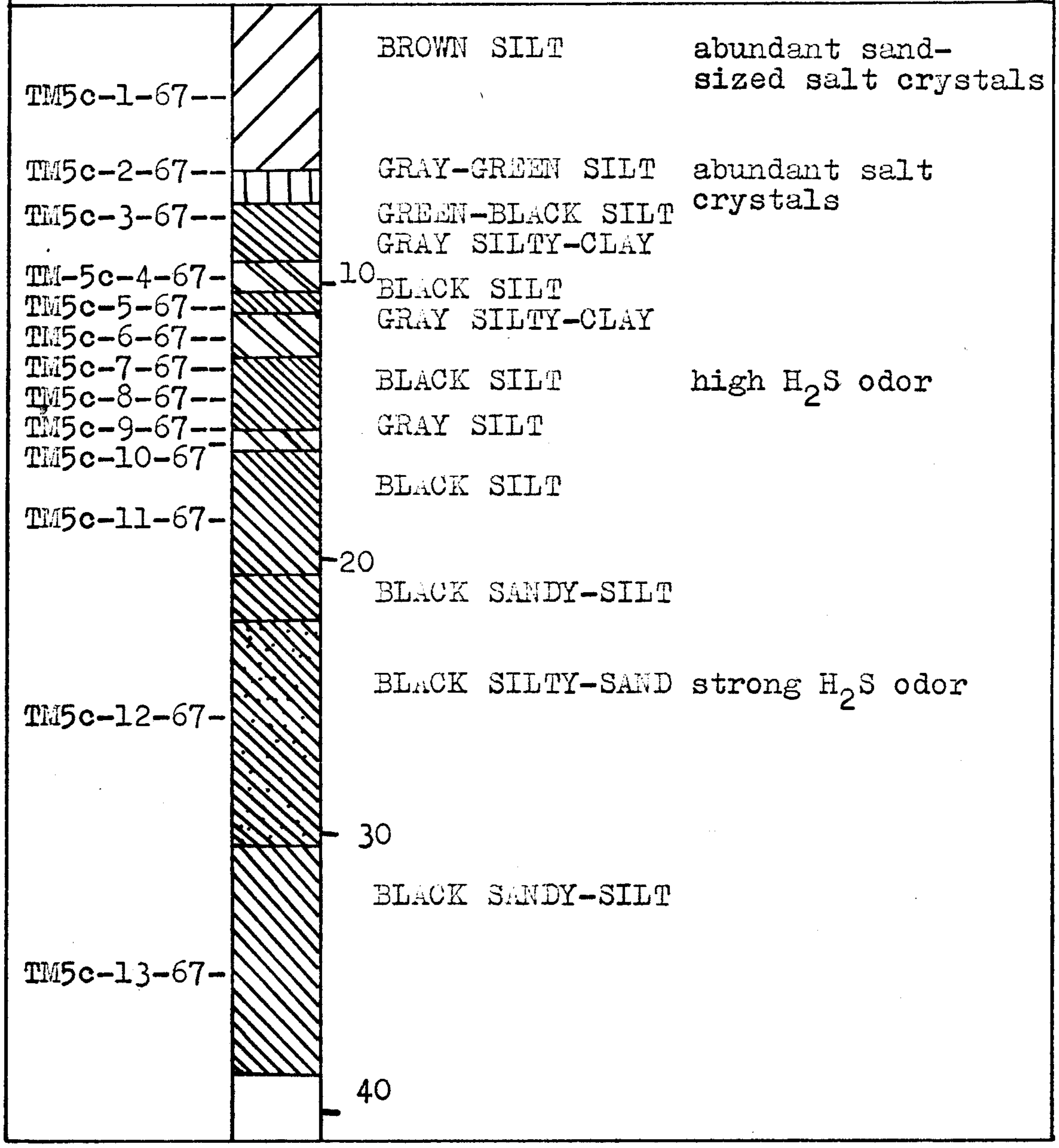
TEELS MARSH, NEVADA

Figure 3. Log and description of core TM-5c.
(from Everts, 1969).

SEDIMENT SAMPLES AND SECTION
TEELS MARSH, MINERAL COUNTY, NEVADA

Hole number: TM5c
Collection date: 6/27/67
Depth to water table: at surface on 8/26/67
Surface: brown silt and tan salt crust, efflorescent crust and salt puddles

SAMPLE NO. DEPTH



as to the source of the color boundary. One possibility is that the color change is a "fossil" boundary representing a change in lake sedimentation conditions; the other is that it is a chemical boundary, possibly due to changing oxidation-reduction potential, related to the present day hydrologic regime. Chemical analyses for iron, sulfur, and carbon were made to help determine which of these hypotheses is more reasonable for Teels Marsh. A sharp change in free iron oxides, or of acid-soluble iron with a concomitant change in sulfur content would indicate a shift from oxidizing to reducing conditions, with the possible appearance of acid-soluble iron sulfides. A sudden increase of carbon in the mud across the color boundary would suggest that more organic matter is being retained in the black mud, either as a result of a reducing environment or due to conditions inherited from the time of deposition.

ACKNOWLEDGEMENTS

The advice and guidance of Dr. Carl J. Bowser, Department of Geology and Geophysics, University of Wisconsin, are gratefully acknowledged. Financial support for laboratory investigations was supplied in part by the Union Carbide Corporation and by the Wisconsin Alumni Research Foundation. The sulfur analyses were done in the laboratory of the Soils Department, University of Wisconsin, under the direction of Dr. Dennis Keeney. The carbon analyses were done in the Water Chemistry Laboratory, University of Wisconsin. Dr. T.D. Tiemann of the Department of Minerals and Metals Engineering, University of Wisconsin, provided advice on the flotation experiment. Dr. E. Jenne of the United Stated Geological Survey suggested analytical techniques for treating the mud samples.

PREVIOUS WORK

Little previous work has been done specifically on Teels Marsh, although other closed basins and playas of the western United States have been studied in a similar manner. The geologic mapping of the area of Teels Marsh was done by Ferguson, Muller, and Cathart (1954) and Ross (1961). Everts (1969) has written a master's thesis at the University of Wisconsin concerning the dissolved constituents in near-surface water samples and the surface salts from Teels Marsh. R.L. Hay (1964, 1966), Hay and Moiola (1963a,b), and Cook and Hay (1964) have studied the authigenic zeolites forming from buried tuff beds in Teels Marsh and similar environments. Their results agree with those of the present study except that they found analcime in addition to phillipsite, searlesite, and clinoptilolite.

Similar lake basins in California have been the subjects of much study by several investigators. Jones (1965b) investigated Deep Springs Lake, Inyo County, California by studying water samples, the mineralogy and zoning of evaporite minerals, the clay mineralogy, and the influences of surrounding bedrock. This lake is notable also for the high content of carbonate minerals in the sediments, including what apparently is primary dolomite.

Searles Lake has been very important because of the deposits of saline minerals found there. One of the first major attempts to study evaporites and their source solutions was made by Gale (1915). Smith and Pratt (1957) present detailed logs of cores and descriptions of evaporite mineral assemblages similar to those found at Teels Marsh. Eugster and Smith (1965) used an experimental approach to find that certain evaporite assemblages reflect conditions during deposition and others during diagenesis. The clay mineralogy at Searles Lake and similar playa lake basins was studied by Droste (1961), who concluded that the clay minerals are not affected by diagenesis.

The authigenic minerals described by Smith and Haines (1964) include mention of the zeolites found at Teels Marsh. Sheppard and Gude (1968) found zeolites, potassium feldspar, searlesite, and clays formed diagenetically from tuffs deposited in a saline lake basin similar to the Teels Marsh environment. Hardie (1968) described a zonal pattern of evaporite minerals and identified some of the same evaporites and zeolites as those at Teels Marsh at Saline Valley, Inyo County, California.

The presence of the color boundary at Teels Marsh suggests the interesting possibility for the formation of iron sulfides <u>in situ</u> in the black mud below the possible oxidation-reduction boundary. The principal worker in the area of sedimentary iron sulfides in recent years has been R.A. Berner (1964a,b,c, 1967, 1969). He has studied them from theoretical and experimental points of view, as well as citing field instances of their formation.

ANALYTICAL TECHNIQUES

The analytical procedures used are wet chemical analyses for acid-soluble iron, iron as free iron oxides, total iron, total sulfur, and total carbon. "Organic" iron and acid-insoluble iron are determined by differences of the above values. X-ray diffraction was used to determine the mineralogy of the silt and clay portions of the samples and of the nodules found in a number of samples. Flotation was used in an attempt to collect iron sulfides from the mud samples.

Acid-soluble Iron

Acid-soluble iron includes any iron which can be brought into solution by digestion in hot acid. This would include iron present as FeS (crystalline or amorphous); $Fe_{1-x}S$ (pyrrhotite); free iron oxides (limonite, goethite, lepidocrocite, or hematite); iron carbonates (iron-bearing calcite, siderite, or iron-bearing dolomite); iron dissolved in the interstitial water of the mud; clay-adsorbed iron; and possibly iron involved structurally in extremely fine particles of authigenic minerals, here called "protosilicates." "Organic" iron, iron organically complexed, may also be included in the acid-soluble iron values.

The analytical procedure (Nriagu, 1967) consists of putting a half a gram of dried, ground mud into an erlenmeyer flask with 25 ml. of 1N hydrochloric acid. The mixture is digested on a hot plate under reflux for one hour and filtered under suction through a five micron "Millipore" filter. The filtrate is made up to volume and the iron content determined by atomic absorption spectrophotometry, using a Perkin-Elmer model 303. The analytical absorbing line used for iron is 2492 angstroms.

Iron as Free Iron Oxides

Iron as free iron oxides includes iron existing in the sample as ferric oxides such as limonite, goethite, lepidocrocite, or hematite.

The experimental technique is that of Jackson (1956) and Mehra and Jackson (1960). The organic matter is removed from one gram of dried mud sample with 30% hydrogen peroxide. The iron is then reduced and complexed by a sodium dithionite-sodium citrate system buffered with sodium bicarbonate. The iron concentration is then determined by atomic absorption spectrophotometry in the same way as for acid-soluble iron.

Adjusted Acid-soluble Iron

Adjusted acid-soluble iron is here defined as acid-soluble iron minus iron as free iron oxides and "organic" iron. This value would include all forms of acid-soluble iron except those which represent free iron oxides in the sediment or organically complexed iron.

Total Iron

Total iron includes acid-soluble iron; pyrite or marcasite, if present; magnetite, and any iron structurally involved in silicate minerals.

Two analytical procedures for determination of total iron are utilized. The method of Black (1965) prescribes digestion of one gram of dried sample in a mixture of perchloric, nitric, and hydrofluoric acids. The sample is then evaporated to dryness on a sand bath, dissolved in sulfuric acid, and the iron content determined. The method of Angino and Billings (1967) is analytically easier than that of Black. Therefore, because the results of the two methods are in close agreement with one another, the second technique is used for most of the samples. Hydrofluoric acid is added to the sample and it is evaporated to dryness on a hot plate three times, breaking down the silicates and releasing silicon as SiF_4. The residue is dissolved in 9:1 hydrochloric acid and filtered.

The black residue which does not pass through the filter is supposedly organic in nature. The residue is dissolved in 30% hydrogen peroxide and added to the previous filtrate. This solution is made up to volume and the iron then determined by atomic absorption spectrophotometry.

Acid-insoluble Iron

Acid-insoluble iron includes iron in pyrite or marcasite, magnetite, and silicate minerals. The values for acid-insoluble iron are determined by subtracting the experimental values for acid-soluble iron from those for total iron.

"Organic" Iron

Values for "organic" iron (iron organically complexed) are determined by difference. After the removal of the organic matter and the iron as free iron oxides from the bulk sample, the residual sample is run for total iron. The difference between this residual value plus the iron as free iron oxides value, and the original total iron determination is taken to be due to "organic" iron. This iron may be in the constituents of the mud or dissolved in the interstitial water.

Total Sulfur

Total sulfur values include all sulfide and sulfate minerals, as well as sulfide, polysulfide, or sulfur radical ions in the interstitial water. There may also be hydrogen sulfide dissolved in the water. Any sulfur which may be involved in organic compounds or any free sulfur present is included in the total sulfur values. Because no sulfate minerals appear in the x-ray data and the sulfate content of the water sample from TM-5c is relatively low (300 ppm, Everts, 1969), most of the sulfur probably represents sulfide sulfur. However, the water sample taken by Everts is from near the surface, where oxidizing conditions would make sulfate the predominant form of sulfur in the water. At depth, the conditions probably change to reducing, and an odor of H_2S was detected. Here, reduced forms of sulfur are expected to predominate.

Experimental determination of total sulfur involves ignition of the sample to oxidize all the forms of sulfur to sulfate. The sulfate is precipitated as barium sulfate, $BaSO_4$, and determined turbimetrically (Blaedel and Meloche, 1957).

Total Carbon

Total carbon includes all carbonates and all organic matter present in the samples. The carbonate content in the samples used in this study is low in proportion to all the other material present, so total carbon values are used as a non-quantitative index to the amount of organic matter in the samples.

Total carbon is analyzed by a Leco carbon analyzer. This instrument combusts all of the carbonaceous material in the presence of metallic catalysts and excess oxygen to form carbon dioxide. The amount of carbon in the carbon dioxide is determined by comparison with the readings for standard samples containing known amounts of carbon (Blaedel and Meloche, 1957).

<u>X-ray Analyses</u>

X-ray diffraction is used to determine the mineralogical composition of silts, zeolite nodules, and clays. The clay and silt fractions are separated by centrifugation.* The suspension containing the clay is poured off of the collected silt. The silt is wet-ground by hand under methanol and mounted on a glass slide in methanol or ethyl acetate, or dried and packed into an aluminum sample holder. The silt-sized material is scanned at one degree 2θ per

---

*The silt fraction as used here includes all material larger than two microns in diameter, and the clay fraction all material less than two microns in diameter (Jackson, 1956).

minute, from 10 degrees to 60 degrees 2θ. Quartz is present in all of the silt samples and is used as a standard for the peak positions of other minerals.

Several nodules from different locations (figure 2) were also treated by x-ray analysis. The nodules range in size from half a centimeter to one and one-half centimeters in diameter and are very close to spherical in shape. They are very dry and hard and are coated with a whitish, somewhat powdery coating. The same procedure for grinding, mounting, and x-raying is followed for the nodules as for the silt. The samples from which the nodules are taken are TM-9-5, TM-10-3, and TM-14-3. Sample TM-9-5 comes from a depth of 13 feet, TM-10-3 from 13½ feet, and TM-14-3 from 12 feet.

The bulk clay fraction includes all particles less than two microns in diameter. This bulk fraction was also fractionated into coarse clay (2-0.2 microns in diameter), medium clay (0.2-0.08 microns), and fine clay (less than .08 microns). According to the procedure described in Jackson (1956), each clay sample is x-rayed untreated, saturated with ethylene glycol, after heating for one hour at 300°C., and after heating for one hour at 550°C. The clay is saturated with ethylene glycol by placing the slide in contact with ethylene glycol vapor for twenty-four hours.

The slides are heated in a muffle furnace for one hour and then kept in a dessicator until x-rayed. All the clay slides are run from two degrees 2θ to thirty-two degrees 2θ.

Some experimentation with mounting techniques helped to determine the most suitable one for these samples. Porous porcelain plates were found especially unsatisfactory (Gibbs, 1965). The technique consists of pouring a slurry of clay and water onto a porcelain plate; the water rapidly seeps through the plate and leaves an oriented clay sample on the top surface of the plate. This method has the advantage of very fast and relatively uniform preparation but the plates give x-ray peaks of their own which interfere with some of the clay mineral peaks. The most successful method, and the one used in this study, is the "smear" mount. A thin layer of clay is smeared on a glass slide with a spatula and allowed to dry (Gibbs, 1965). This technique eliminates error due to settling out of a water suspension, but does give preferred orientation to the clay mineral grains. The peak intensity obtained with the smear mount is superior to that for any other type of preparation tried during the course of this study.

Mineral Flotation

To investigate the possibility of separating sulfide minerals from the sediment samples, an experimental flotation cell was constructed similar to that described by Sirois and Takamori (1964). Nitrogen gas is bubbled through the fritted glass bottom of a Buchner funnel. The sample is placed into the funnel with a drop of commercial "Pine-Sol" (used as a substitute for pine oil); a drop or two of ethylxanthic acid potassium salt solution; and water. The desired material should collect in the froth at the top where it can be skimmed and collected. This material is then washed and collected by centrifugation. However, because of the very fine particle size, the method proved unsatisfactory for differential separation of the sulfides and clay minerals.

Uncertainties and Problems of Treatment

Uncertainty in the iron values arises from instrumental and analytical errors and inhomogeneity of the sample. The samples are taken from depth intervals and there is no guarantee that a portion of the sample taken for analysis is representative of the entire depth interval. This is probably the cause for any major differences between duplicate analyses. The data for the iron analyses are given in the Appendix, Table A, with the percent error of the difference of the average values. The average values are given in table 1; in the iron vs. depth plots, the center of the depth interval assigned to the sample is used. To check that some of the iron as free iron oxides did not escape the acid treatment, reagent Fe_2O_3 was run through the procedure and essentially all of the iron was drawn into solution from it.

The sulfur values are more reliable, although errors caused by analytical techniques and inhomogeneous samples still apply. An error of ±25 ppm. can be assigned to the total sulfur values.

The carbon analyses also require dilution, and the same errors hold as for iron and sulfur. The values plotted against depth are the average values. The range of values is given in the Appendix, table A.

The x-ray data for the clays can be considered only very semi-quantitatively. One problem is that in almost all of the samples only a very small proportion of the clay was less than .08 microns in diameter and collection of sufficient material of this size for analysis was difficult.

A modification of the method of Biscaye (1965) for normalizing treatment of clay half-height peak areas was used to determine the relative abundance of each clay mineral of the Teels Marsh samples. The results as presented in this study have only qualitative significance and the relative abundances are not to be interpreted quantitatively. Clay mineral "percentages" cannot be determined accurately by Biscaye's method because of the presence of non-clay minerals in the samples.

As described above, precautions were taken to assure that the samples remained as closely as possible in the condition in which they existed in the playa at the time of collection. Oxidation and drying of the samples would represent alterations from their original state. For core TM-5c, the centers of the samples are still moist and the deeper ones are black. However, all samples have a rim of grayish- or brownish-colored material about one to two millimeters thick. Analyzed fractions were chosen so as to avoid these altered portions.

EXPERIMENTAL RESULTS

Chemical Analyses

The experimental values for the chemical analyses are tabulated in parts per million (table 1) and in molar percentages (table 2). The values include the direct analytical results and calculated values. The data are plotted against depth in figures 4 through 7. These plots show the variation in content of sulfur, carbon, and each form of iron across the color boundary, which occurs between 11 feet 6 inched and 12 feet.

Acid-soluble iron follows the same general downward trend as that of total iron. The two samples nearest the surface are relatively high, and the values fluctuate irregularly below these. There does not appear to be any sharp change in the trend of values across the color boundary. The plot of iron as free iron oxides also has the same general distribution with depth, although the variations and absolute values are not nearly so great as for total iron or acid-soluble iron. Samples 10, 11, and 13 are considerably lower in acid-soluble iron than the other samples in the core, but are not appreciably lower in total iron content.

Total sulfur, except for the two shallowest samples, is distributed very much like total iron with depth, except that total sulfur increases markedly at the color boundary.

Total carbon also shows a sudden increase in samples taken below 11 feet 6 inches.

X-ray Analyses

The results of the x-ray study of the silt fractions are presented in table 4. The clay mineralogy of the samples is given for the bulk clay and for each size range within the clay-sized portion of the samples (figures 8 and 9). The relative abundance of each clay mineral and the presence of other minerals have been noted.

Consistent with the working definition of Grim (1953), 10 angstrom inexpansible clay is called "illite," 14 angstrom inexpansible clay is called "chlorite," and clay which is expansible to 17 angstroms when saturated with ethylene glycol and collapses to 10 angstroms on heating is called "montmorillonite." More than one type of mixed-layer clay is present in these samples. One variety is a regular alternation of montmorillonitic and illitic layers. Another kind appears to be a random interstratification in various ratios of montmorillonitic and vermiculitic clay. The mixed-layer clays generally are expansible to some degree and do not collapse fully until heated to 550°C. These types are here collectively called "mixed-layer clay." A sketch of an example of "mixed-layer clay" from Teels Marsh is given in the Appendix, figure A. This terminology is to be considered as giving only general class names and implies no single chemical composition for each species. The relative abundances of the clay minerals presented in figures 8 and 9 are determined from the half-height peak areas. In all cases the intensities are sufficiently different to make qualitative statements concerning the abundance of each clay mineral unambiguous.

The nodules described previously were found by x-ray diffraction to contain zeolitic material. All the samples consist of mixtures of calcite, quartz, phillipsite, and searlesite.

Table 1. Depth variations of iron, sulfur, and carbon (ppm.) in core TM-5c.

A = Total iron

B = Acid-soluble iron

C = Iron as free iron oxides

D = "Organic" iron

E = "Adjusted acid-soluble iron"

= Acid-soluble iron less iron as free iron oxides and "organic" iron

F = Acid-insoluble iron

= Total iron less acid-soluble iron

G = Total sulfur

H = Total carbon

— — = Sediment color boundary

SAMPLE NUMBER	DEPTH INTERVAL	A	B	C	D	E	F	G	H
TM-5c-2	6'6"-6'9"	29,600	19,200	4500	0	14,700	10,400	1010	2700
TM-5c-3	7'6"-7'9"	31,800	22,600	3700	0	18,900	9200	1110	3900
TM-5c-4	9'9"	14,600	11,900	1500	0	10,400	2700	1290	5900
TM-5c-5	10'6"	18,100	12,100	2200	0	8900	6000	1160	4000
TM-5c-6	11'6"	13,800	11,700	1600	0	9100	2100	1140	6400
TM-5c-7	12'0"	20,400	15,000	2000	200	12,800	5400	2430	32,300
TM-5c-8	12'4"-12'7"	18,700	13,000	2400	400	10,200	5700	2830	21,900
TM-5c-9	14'6"-15'0"	21,400	15,600	2500	0	13,100	5800	3320	20,800
TM-5c-10	15'6"	13,500	6600	1200	0	5400	6900	1660	10,800
TM-5c-11	18'3"-18'6"	17,100	5800	1500	0	4300	11,300	3270	21,000
TM-5c-12	27'	20,000	14,500	3500	0	11,000	5500	4130	17,500
TM-5c-13	38'	14,700	6600	2400	200	4000	8100	1700	5600

Table 2. Depth variation of molar percentages of iron, sulfur, and carbon in core TM-5c, multiplied by 10^4.

A = Total iron

B = Acid-soluble iron

C = Iron as free iron oxides

D = "Organic" iron

E = "Adjusted acid-soluble iron"

= Acid-soluble iron less iron as free iron oxides and "organic" iron

F = Acid-insoluble iron

= Total iron less acid-soluble iron

G = Total sulfur

H = Total carbon

— — — = Sediment color boundary

SAMPLE NUMBER	DEPTH INTERVAL	A	B	C	D	E	F	G	H
TM-5c-2	6'6"-6'9"	531	344	80	0	264	187	31.4	225
TM-5c-3	7'6"-7'9"	569	404	66	0	338	165	34.6	325
TM-5c-4	9'9"	262	213	27	0	186	49	40.2	492
TM-5c-5	10'6"	324	216	39	0	177	108	36.2	333
TM-5c-6	11'6"	248	209	29	0	180	38	35.5	533
TM-5c-7	12'0"	366	269	36	4	229	97	75.7	2690
TM-5c-8	12'4"-12'7"	336	233	43	7	183	103	87.6	1820
TM-5c-9	14'6"-15'0"	383	279	45	0	234	104	103	1730
TM-5c-10	15'6"	242	118	22	0	96	124	51.7	900
TM-5c-11	18'3"-18'6"	306	104	27	0	77	202	102	1750
TM-5c-12	27'	358	260	63	0	197	98	129	1460
TM-5c-13	38'	263	118	43	4	71	145	53.0	467

Figure 4. Plots of various forms of iron vs. depth.

A= Total iron.

B= Acid-soluble iron.

C= Iron as free iron oxides.

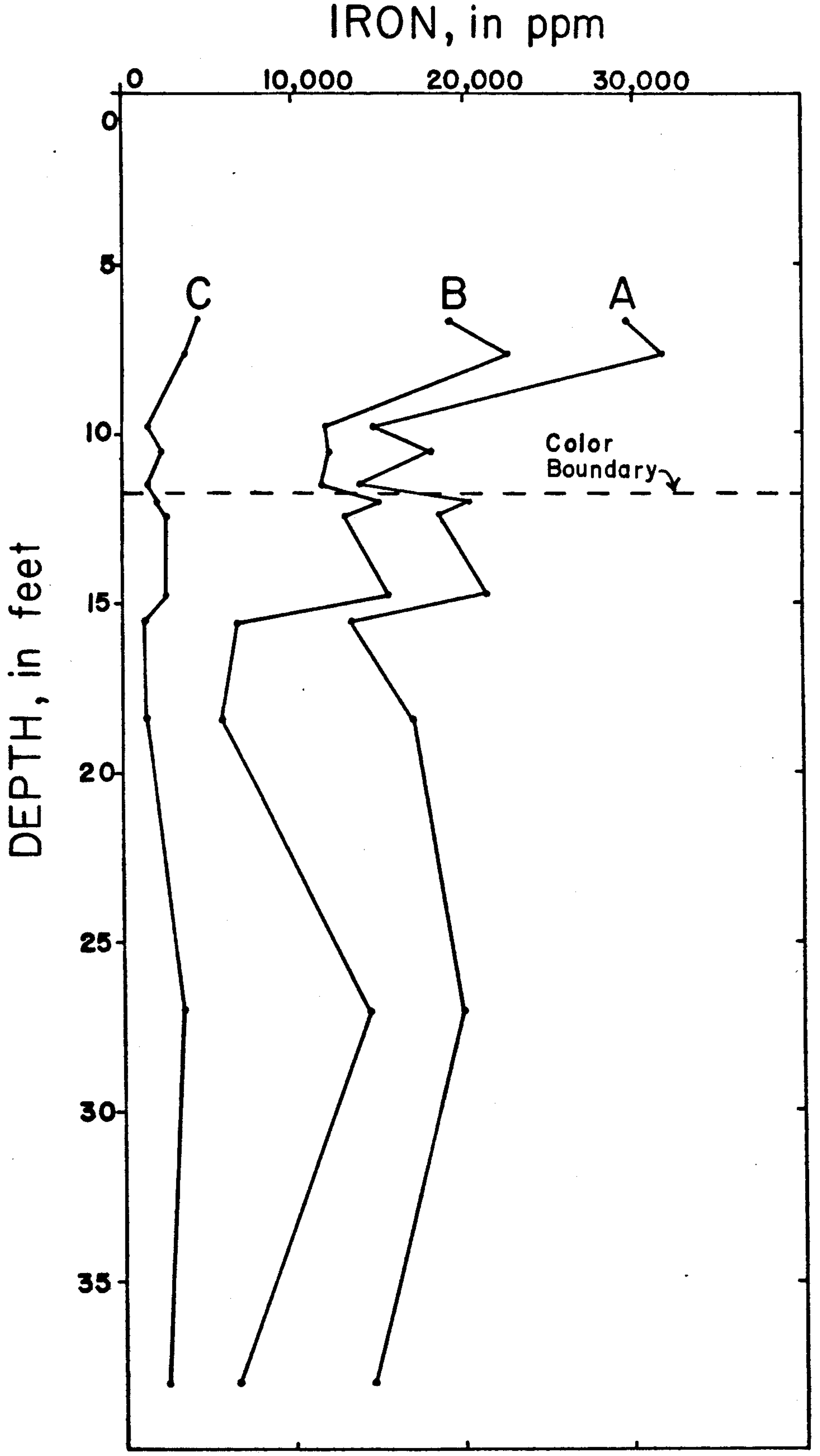

IRON, in ppm
0
10,000
20,000
30,000
DEPTH, in feet
0
5
10
15
20
25
30
35
C
B
A
Color Boundary

Table 3. Various forms of iron expressed as percentages of total iron.

A = Total iron

B = Acid-soluble iron

C = Iron as free iron oxides

D = "Organic" iron

E = "Adjusted acid-soluble iron"

= Acid-soluble iron less iron as free iron oxides and "organic" iron

F = Acid-insoluble iron

= Total iron less acid-soluble iron

— — — = Sediment color boundary

SAMPLE NUMBER	DEPTH INTERVAL	A	B	C	D	E	F
TM-5c-2	6'6"-6'9"	100.0	64.9	15.2	0	49.7	35.1
TM-5c-3	7'6"-7'9"	100.0	71.0	11.6	0	59.4	29.0
TM-5c-4	9'9"	100.0	81.4	10.3	0	71.1	18.6
TM-5c-5	10'6"	100.0	66.9	12.2	0	54.7	33.1
TM-5c-6	11'6"	100.0	84.7	11.6	0	73.1	15.3
TM-5c-7	12'0"	100.0	73.5	9.7	0.1	63.7	26.5
TM-5c-8	12'4"-12'7"	100.0	69.5	12.8	0.5	56.2	30.5
TM-5c-9	14'6"-15'0"	100.0	72.9	11.7	0	61.2	27.1
TM-5c-10	15'6"	100.0	48.9	8.9	0	40.0	51.1
TM-5c-11	18'3"-18'6"	100.0	33.9	8.8	0	25.1	66.1
TM-5c-12	27'	100.0	72.5	17.5	0	55.0	27.5
TM-5c-13	38'	100.0	44.9	16.3	0.7	27.9	55.1

Figure 5. Various forms of iron expressed as percentages of total iron vs. depth.

Area C= Iron as free iron oxides + "organic" iron.

Area E= "Adjusted" acid-soluble iron.
= Iron sulfides except FeS_2, iron carbonates, adsorbed iron, iron in interstitial water, and protosilicate iron.

Area F= Acid-insoluble iron.
= Magnetite, FeS_2, and silicate iron.

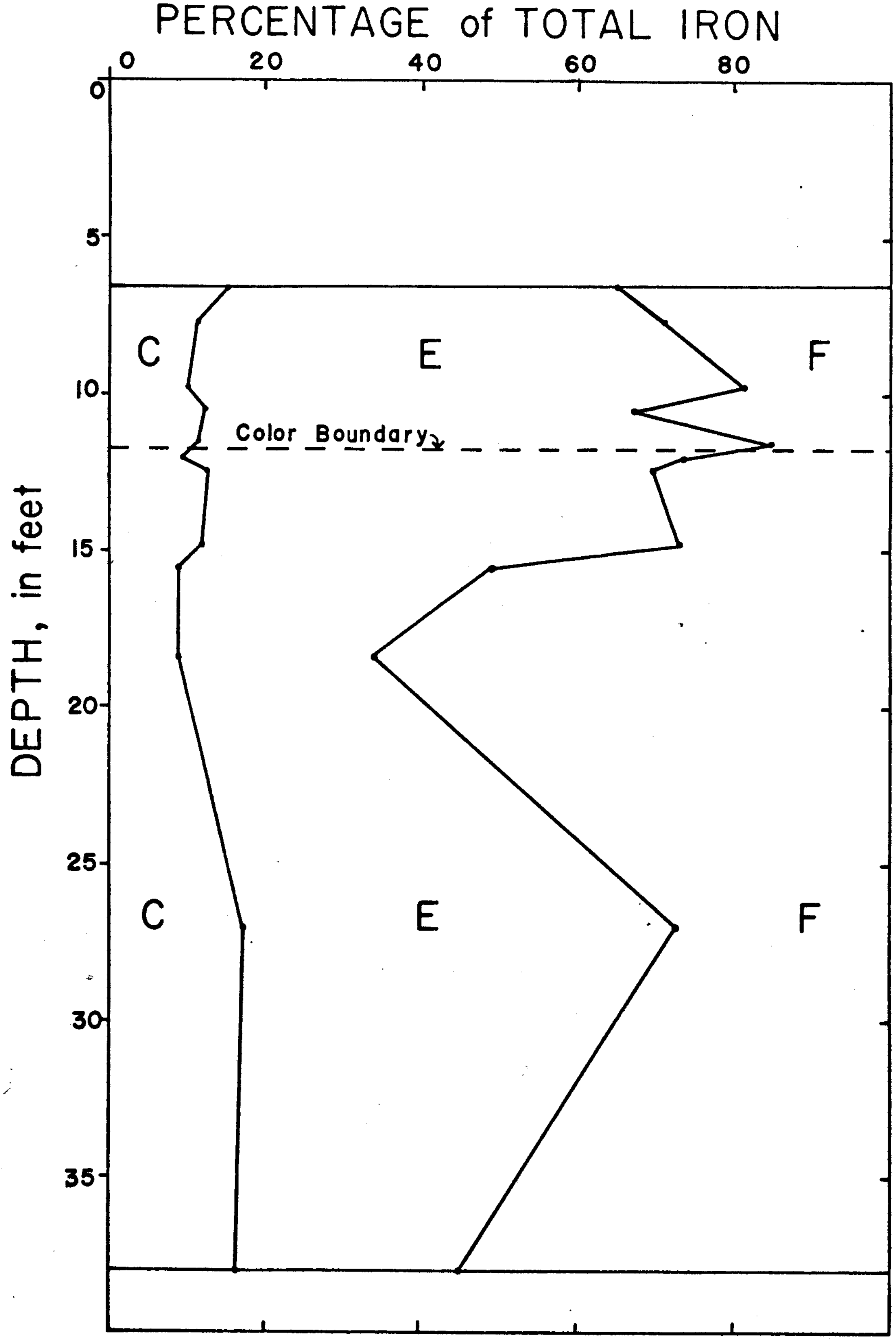

PERCENTAGE of TOTAL IRON
0
20
40
60
80
DEPTH, in feet
0
5
10
15
20
25
30
35
C
E
F
Color Boundary
C
E
F

Figure 6. Total sulfur concentration vs. depth.
Left-hand curve on same scale as iron plots.
Right-hand curve on scale expanded 10x.

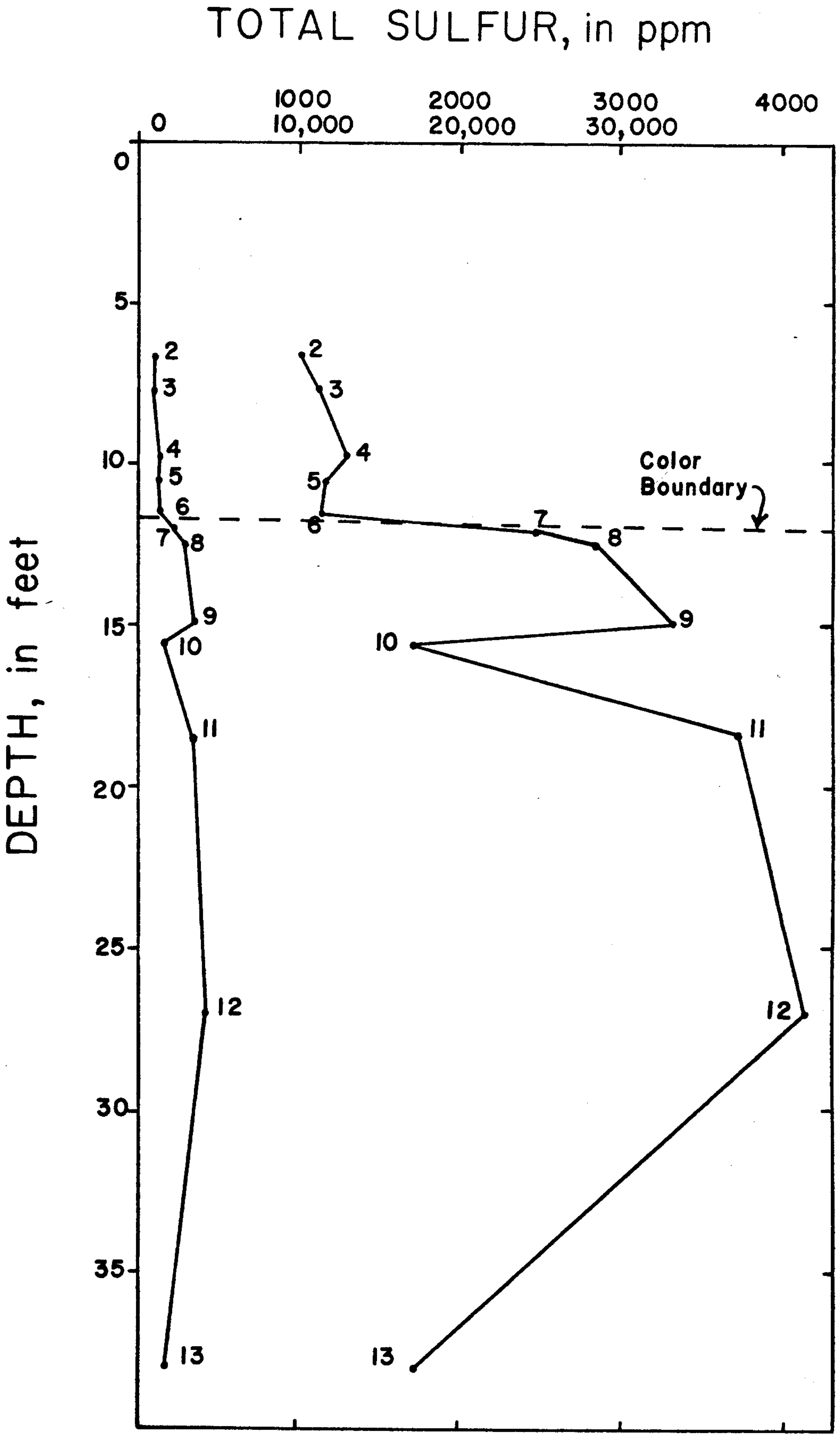

TOTAL SULFUR, in ppm
0
1000
10,000
2000
20,000
3000
30,000
4000
DEPTH, in feet
0
5
10
15
20
25
30
35
2
3
4
5
6
7
8
9
10
11
12
13
Color Boundary

Figure 7. Total carbon concentration vs. depth.

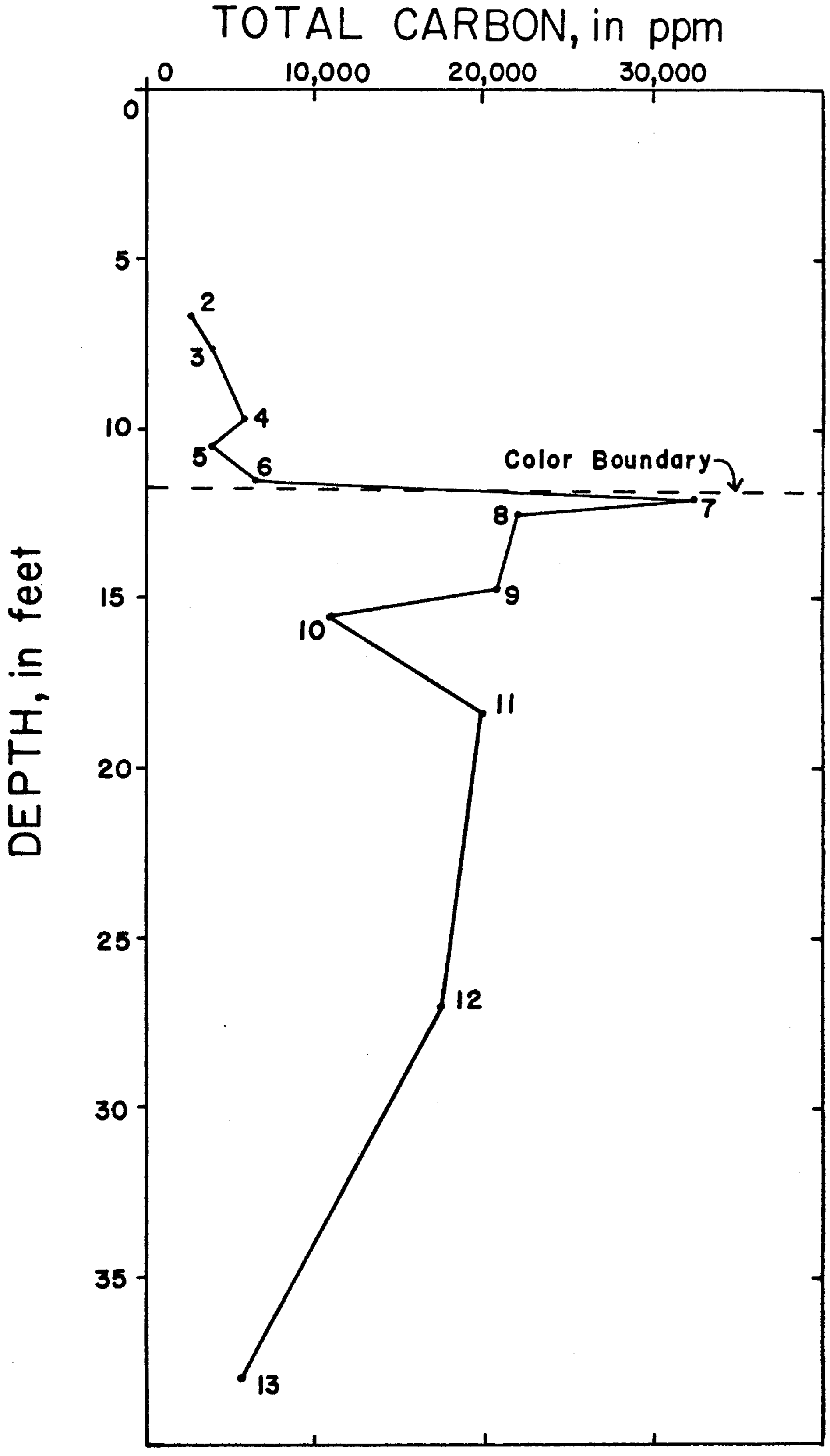

TOTAL CARBON, in ppm
0
10,000
20,000
30,000
DEPTH, in feet
0
5
10
15
20
25
30
35
2
3
4
5
6
Color Boundary
7
8
9
10
11
12
13

Table 4. X-ray diffraction data for silt-sized fraction of samples for core TM-5c.

M= major constituent.
p= present, but minor.
?= questionably present.

SAMPLE NUMBER	- QUARTZ	LOW ALBITE	CALCITE	SEARLE-SITE	PHILLIP-SITE	GAYLUS-SITE
TM-5c-2	M	M	p	-	p	-
TM-5c-3	M	M	p	-	p	-
TM-5c-4	M	M	p	-	M	-
TM-5c-5	M	p	p	-	p	?
TM-5c-6	M	p	M	-	M	-
TM-5c-7	p	-	M	-	p	-
TM-5c-8	M	-	M	-	p	-
TM-5c-9	M	p	p	-	-	-
TM-5c-10	M	p	M	?	p	-
TM-5c-11	p	M	p	-	-	-
TM-5c-12	M	p	M	-	-	-
TM-5c-13	M	?	p	-	?	-

Figure 8. Clay x-ray diffraction data vs. depth.

Length of horizontal line at any depth represents the relative, but not quantitative, abundance of each species of clay mineral. When three clay minerals are present, the most abundant is assigned a line ½ of the total width; second most abundant 1/3 of total width; least abundant 1/6 of total width. When only two clay minerals are present, the most abundant is assigned a line 2/3 of the total width; second most abundant 1/3 of total width. When only one clay mineral is present, it is assigned the entire width.

☐ = Illite

☐ = Chlorite

░ = Montmorillonite

▓ = Mixed-layer clay

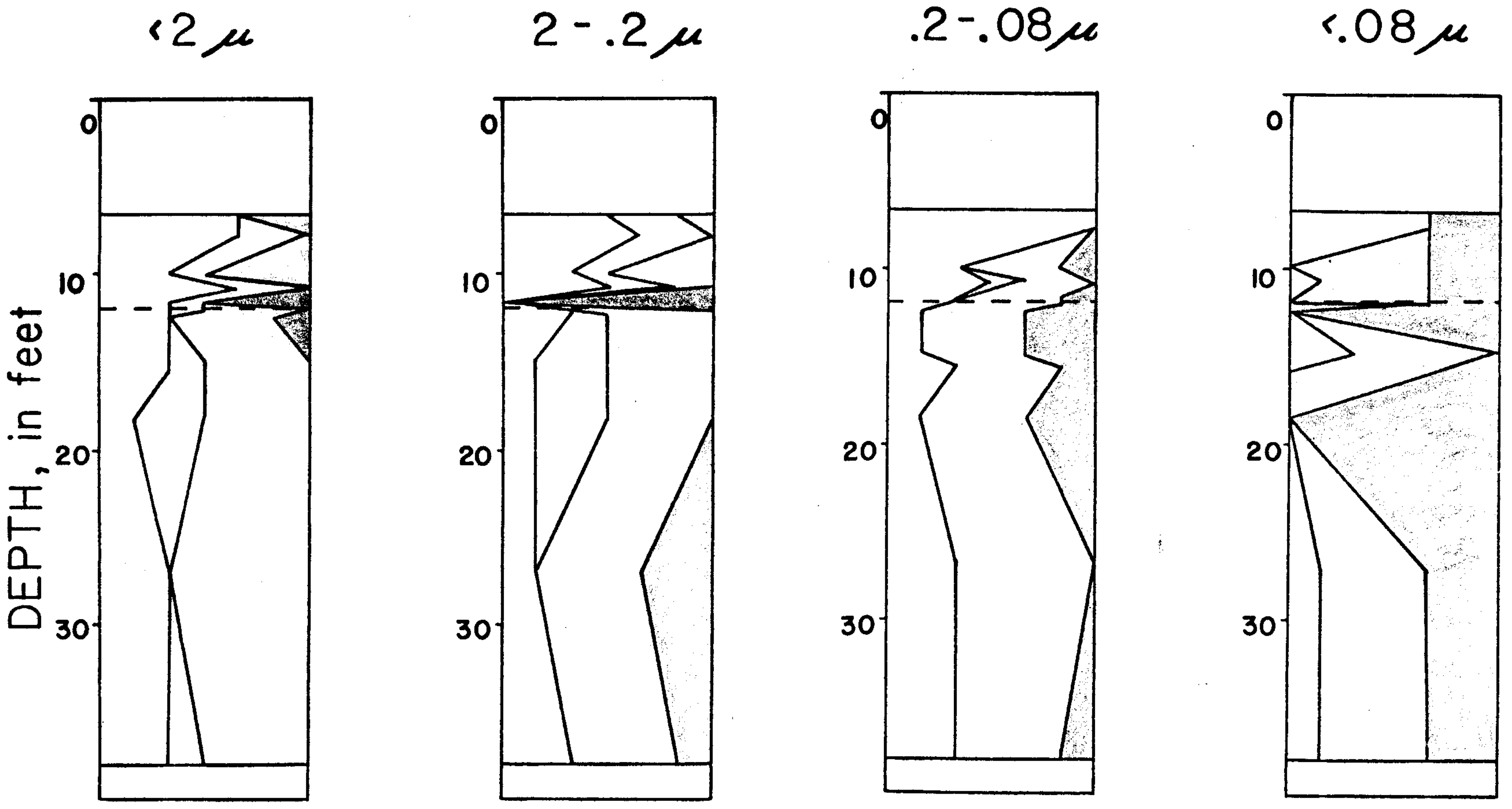

‹2 μ
2 -.2 μ
.2-.08μ
‹.08 μ
DEPTH, in feet
0
10
20
30

Figure 9. Clay x-ray diffraction data as a function of particle size for each sample.

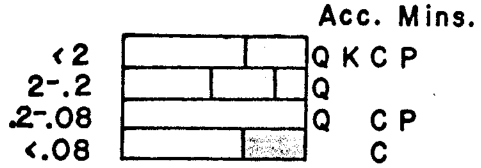
Length of bar represents relative, but not quantitative, amount of each species of clay mineral.

Lengths of bars determined as for the previous figure.

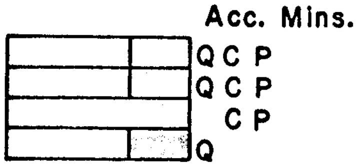
☐= Illite.
☐= Chlorite.
☐= Montmorillonite.
▨= Mixed-layer clay.

Accessory Minerals:
Q= Quartz.
K= Potassium feldspar.
C= Clinoptilolite.
S= Searlesite.
P= Phillipsite.

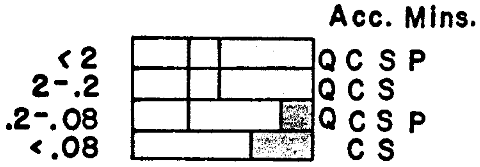
TM-5c-2



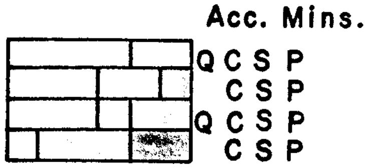
TM-5c-3



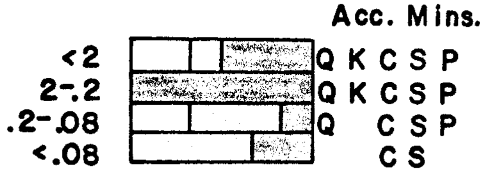
TM-5c-4



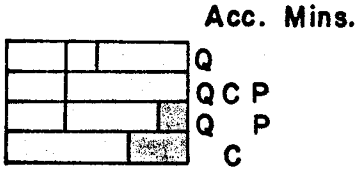
TM-5c-5



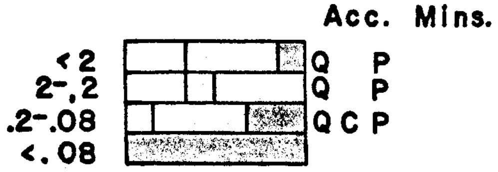
TM-5c-6



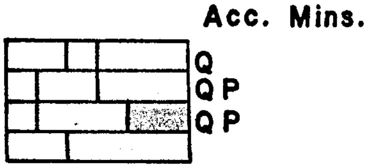
TM-5c-7



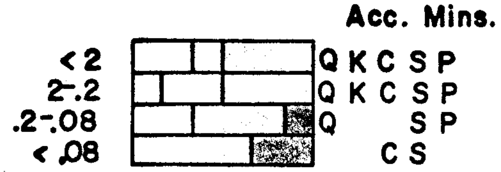
TM-5c-8



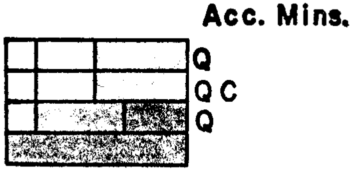
TM-5c-9



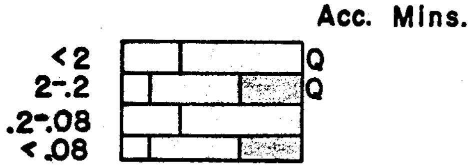
TM-5c-10



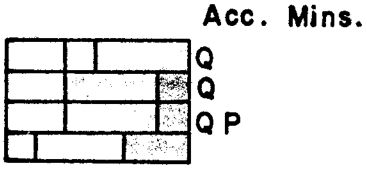
TM-5c-11



TM-5c-12



TM-5c-13



DISCUSSION

Iron

The distribution of the various forms of iron with depth shows a marked increase in acid-insoluble iron in the lower part of the core (with the exception of sample 12), at the expense of adjusted acid-soluble iron. The variations probably reflect original differences in iron content at different depth levels. Assuming that at least an approach toward equilibrium has been maintained throughout the time the basin has been closed, there appears to have been very little or no movement of iron vertically within the section. If iron, or any form of it, were able to move freely via water transport or solid diffusion, there should have been at least a partial equilibration of iron between all the samples.

Ratios of one form of iron to another help to describe the situation more accurately. The ratios of various forms of iron to total iron are presented in table 5 and graphically in figures 10 through 13.

When acid-soluble iron is plotted against total iron (figure 10), the values fall on or near a straight line except for samples 10, 11, and 13,

Figure 10. Concentration of acid-soluble iron vs. concentration of total iron.

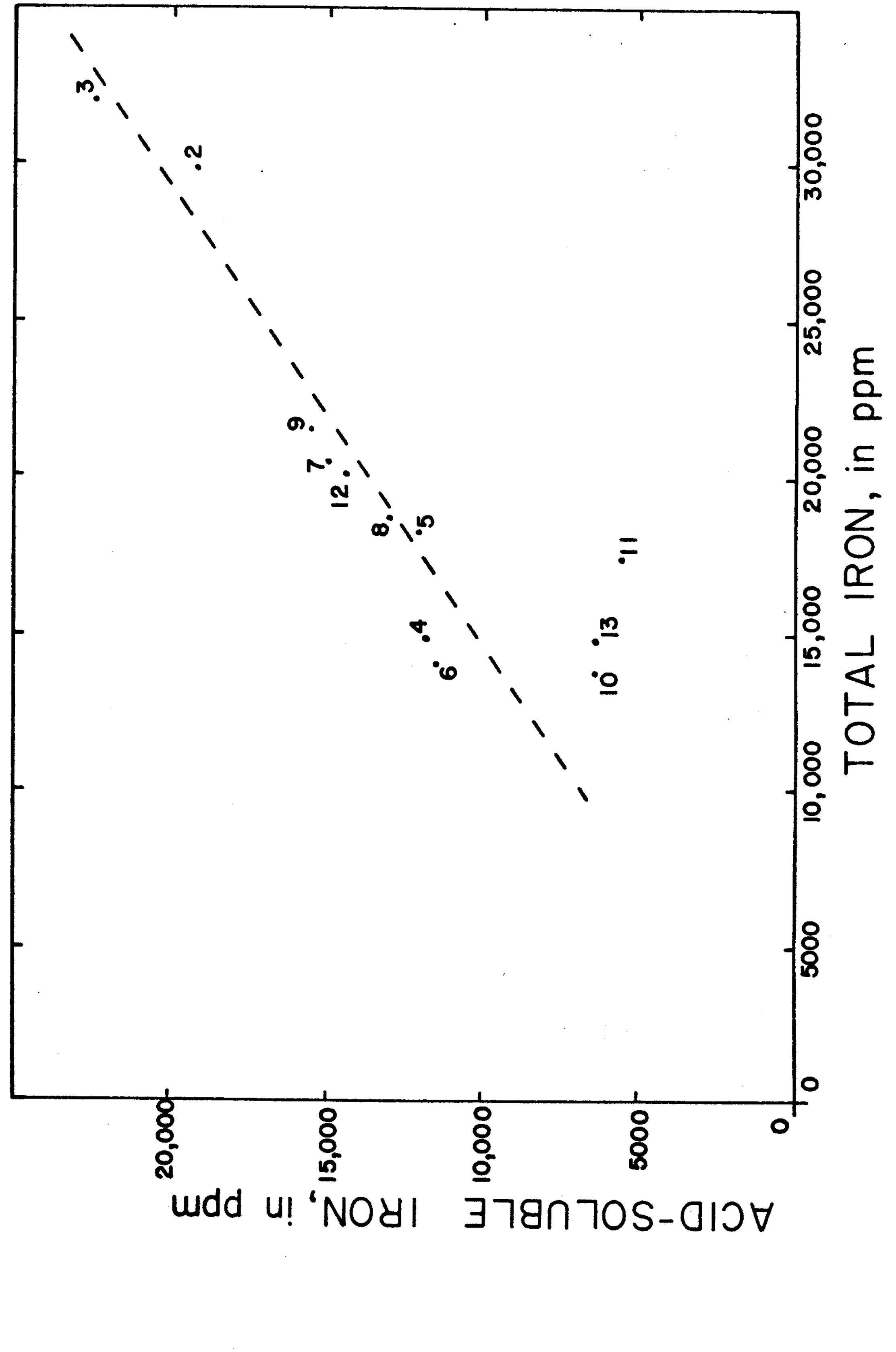

TOTAL IRON, in ppm
0
5000
10,000
15,000
20,000
25,000
30,000
ACID-SOLUBLE IRON, in ppm
0
5000
10,000
15,000
20,000
3
2
9
7
12
8
5
4
6
11
13
10

TABLE 5

RATIOS OF VARIOUS FORMS OF IRON TO TOTAL IRON

SAMPLE NUMBER	ACID-SOLUBLE IRON/ TOTAL IRON	ADJUSTED ACID-SOLUBLE IRON/ TOTAL IRON	IRON AS FREE IRON OXIDES/ TOTAL IRON	ACID-INSOLUBLE IRON/ TOTAL IRON
TM-5c-2	.648	.498	.152	.350
TM-5c-3	.711	.596	.116	.290
TM-5c-4	.814	.712	.103	.185
TM-5c-5	.669	.493	.122	.330
TM-5c-6	.847	.657	.116	.152
TM-5c-7	.736	.627	.098	.267
TM-5c-8	.695	.546	.128	.304
TM-5c-9	.730	.613	.117	.272
TM-5c-10	.489	.326	.089	.512
TM-5c-11	.339	.251	.088	.661
TM-5c-12	.725	.551	.175	.276
TM-5c-13	.449	.272	.163	.551

which cluster together considerably below the line. These three samples are therefore very much lower in acid-soluble iron than the other samples in the core. This is also evident from figure 4.

The low acid-soluble iron contents of the three samples may be caused by a number of factors. The effect could be due to: a decrease in FeS for these three samples, possibly as a result of conversion of FeS to FeS_2; a lower content of free iron oxides; absence or decrease in the amount of iron carbonates; fewew easily removable adsorbed iron ions; a decrease in the amount of iron in the interstitial waters of the mud, all with a concomitant relative increase in the amount of iron involved in pyrite, magnetite, and/or silicates. All or only some of these factors may be important in each of the three samples, and the same factors may not be significant for all of them.

Everts (1969) gives the iron content of the groundwater at the level of the water table (at the surface of the playa) as less than one part per million. Hence the possibility that variation of iron in interstitial waters may cause the acid-soluble iron to total iron ratios to vary seems unlikely. Support for this conclusion is also provided by data of Krauskopf (1967) and Hem (1960), who point out the low solubility of iron in alkaline aqueous solutions.

Free iron oxides and "organic" iron cannot by themselves account for the low acid-soluble iron contents of samples 10, 11, and 13. A plot of acid-soluble iron less iron as free iron oxides and "organic" iron vs. total iron (figure 11) is again nearly linear for all samples except samples 10, 11, and 13. Hence the difference of free iron oxides plus "organic" iron alone does not linearize the ratio of acid-soluble iron to total iron for all the samples.

A plot of iron as free iron oxides plus "organic" iron (figure 12) is nearly linear, indicating that the

Figure 11. Concentration of adjusted acid-soluble iron vs. concentration of total iron.

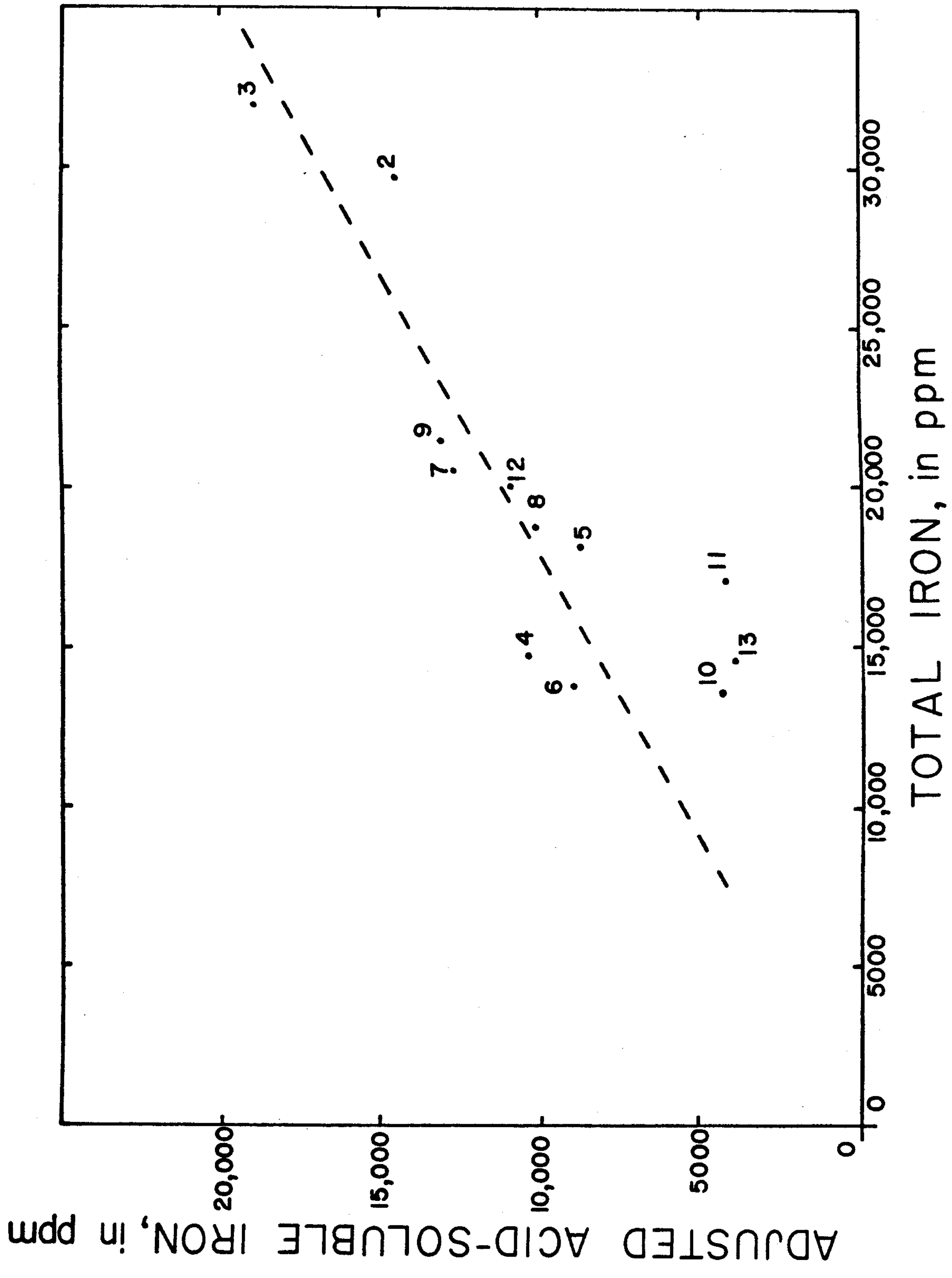
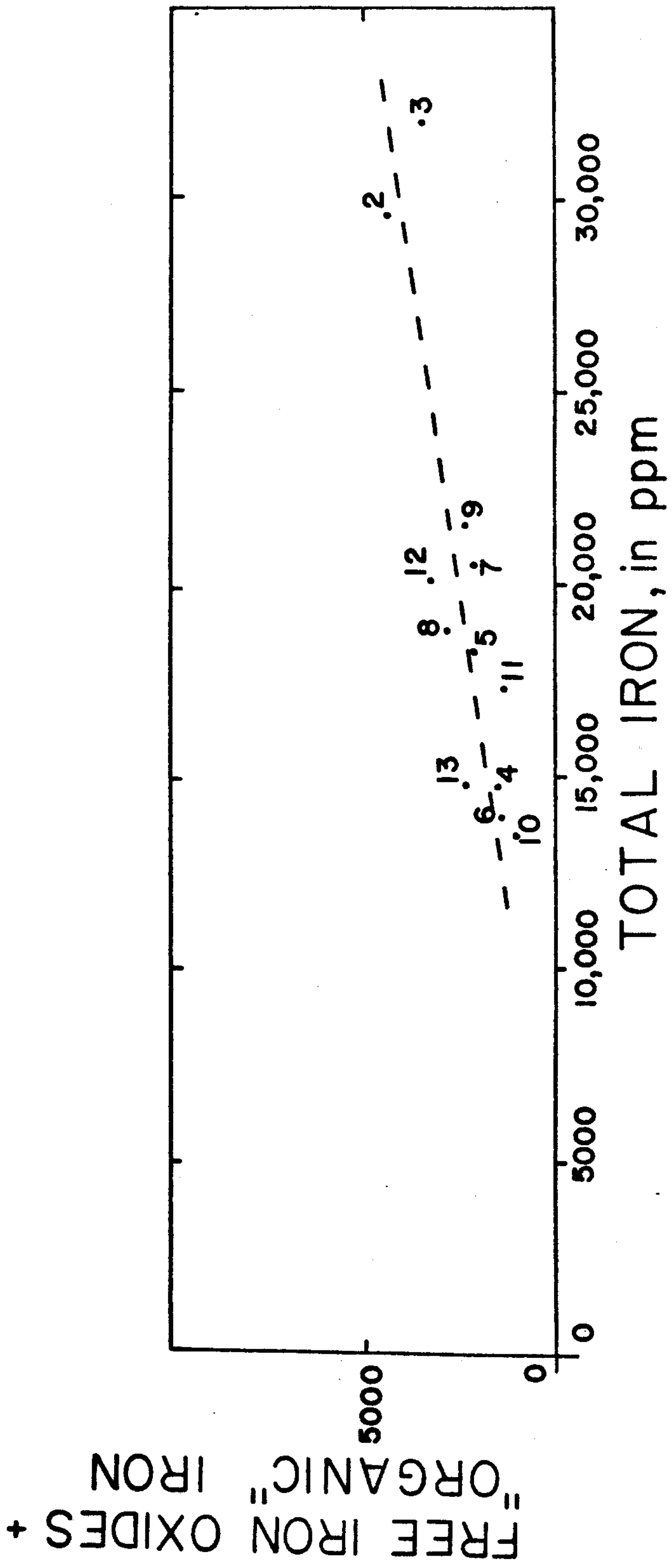

TOTAL IRON, in ppm
ADJUSTED ACID-SOLUBLE IRON, in ppm
0
5000
10,000
15,000
20,000
25,000
30,000
0
5000
10,000
15,000
20,000
2
3
4
5
6
7
8
9
10
11
12
13

Figure 12. Concentration of iron as free iron oxides plus "organic" iron vs. concentration of total iron.

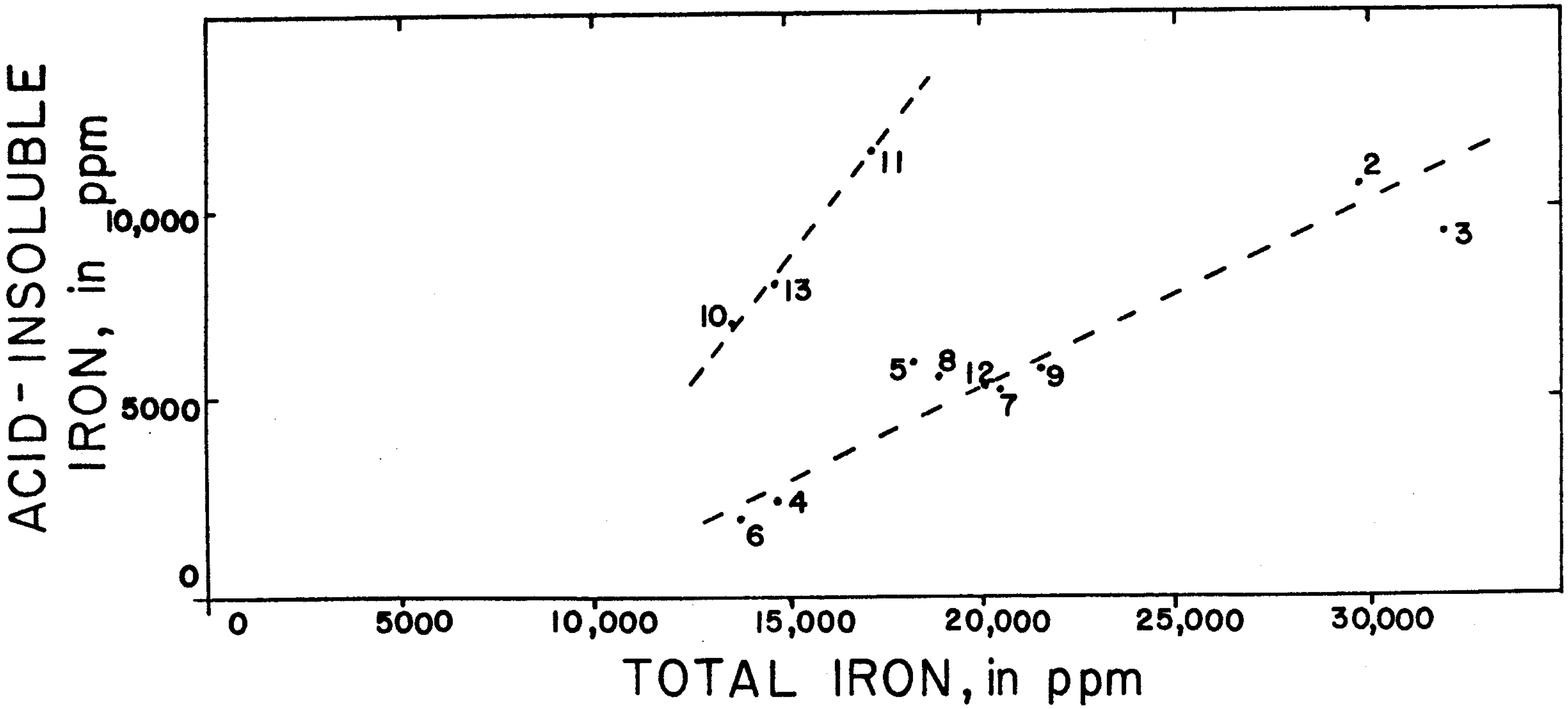

FREE IRON OXIDES +
"ORGANIC" IRON
0
5000
TOTAL IRON, in ppm
0
5000
10,000
15,000
20,000
25,000
30,000
2
3
4
5
6
7
8
9
10
11
12
13

sum of iron as free iron oxides plus "organic" iron represents a constant proportion of total iron for all samples, regardless of depth or total iron concentration. Thus deviations from linearlty in figures 10 and 11 must be due to acid-soluble iron not organically complexed or as free iron oxides. The small variability in the ratios is evident from table 5.

Interpreting the color transition from green or gray-green down to 11'6" to black below this in terms of the iron data, the color boundary apparently does not reflect an oxidation boundary. One interpretation is that the iron components are exclusively detrital and not related at all to lake processes. Another is that they are related to post-depositional effects. The percentage of iron as free iron oxides of total iron does not change across the color boundary. Assuming that equilibrium has been maintained during deposition, superficially the constancy in the ratio suggests that the whole depth of the core has been equally oxygenated, at least at some time in its history. However, this is contradictory to evidence from the total carbon data.

A plot of acid-insoluble iron vs. total iron (figure 13) shows that nine of the samples fall close to a straight line. Samples 10, 11, and 13 fall on a different straight line. The slope of the second line is greater than that of the first one, so a greater

Figure 13. Concentration of acid-insoluble iron vs. concentration of total iron.


ACID-INSOLUBLE IRON, in ppm
0
5000
10,000
TOTAL IRON, in ppm
0
5000
10,000
15,000
20,000
25,000
30,000
2
3
4
5
6
7
8
9
10
11
12
13

proportion of the iron in samples 10, 11, and 13, is acid-insoluble than for the other samples of the core. The two trends both converge on the total iron axis at about 8500 ppm. total iron, which represents acid-soluble iron. Samples 10, 11, and 13 fall on a line with a slope about equal to one, indicating a constant addition of acid-insoluble iron with no increase in acid-soluble forms. Sample 12 does not belong to the trend of samples 10, 11, and 13. Its anomalous values may be related to its coarser grain size. The other points fall on a line with a slope less than one. This indicates an increase in both acid-soluble and acid-insoluble forms as total iron is increased. This relationship may be fortuitous; or it may possibly be the effect of acid-soluble forms of iron being derived from the breakdown of acid-insoluble iron compounds. A reciprocal relationship may also exist: some acid-soluble iron may be converted into insoluble forms.

Iron-Sulfur

To relate the iron data to the values for total sulfur, molar values for sulfur and iron must be used. Pyrite or marcasite does not appear in x-ray diffractograms from either the silt-sized or the clay-sized fraction of the mud, but one or the other may be present in small amounts.

Free iron oxides and "organic" iron are forms of acid-soluble iron which cannot be involved in iron sulfides. The molar ratios of adjusted acid-soluble iron to total sulfur are given in table 6. This assumes that all of the sulfur present in the mud is involved in acid-soluble iron sulfides and that the excess of acid-soluble iron is due to some or all of the factors mentioned earlier. The ratios show a general decrease with depth, with one sample (sample 11) having an excess of sulfur relative to the iron.

TABLE 6

MOLAR RATIOS OF ADJUSTED ACID-SOLUBLE IRON TO TOTAL SULFUR

SAMPLE NUMBER	ADJUSTED ACID-SOLUBLE IRON/ TOTAL SULFUR
TM-5c-2	8.41
TM-5c-3	9.79
TM-5c-4	4.62
TM-5c-5	4.42
TM-5c-6	4.59
TM-5c-7	3.03
TM-5c-8	2.09
TM-5c-9	2.26
TM-5c-10	1.53
TM-5c-11	0.77
TM-5c-12	1.53
TM-5c-13	1.34

A Fe/S molar ratio of one would correspond to stoichiometric FeS with all of the acid-soluble iron not used in free iron oxides or "organic" combination combined with sulfur. A value slightly less than one could be due to the presence of pyrrhotite, $Fe_{1-x}S$. A value of 0.75 would indicate that all of the sulfur is combined with iron in the form of greigite (cubic Fe_3S_4). Values greater than one suggest that all of the iron used in determining the Fe/S ratio is not really involved in acid-soluble sulfides.

All of the samples except sample 11 have Fe/S ratios greater than one. For sample 11, the ratio is 0.77, which is close to what it should be for greigite. This correspondence may be real or fortuitous. In general, the downward decrease in ratio suggests, but does not prove, that more iron is involved in sulfides as depth increases.

It is unlikely, however, that <u>all</u> of the sulfur is combined as acid-soluble sulfides. Everts (1969) determined the sulfate content of the surface water for core TM-5c as 300 ppm, and it is likely that HS^- is present in solution at greater depths.

The particular species of iron sulfide present cannot be determined by x-ray diffraction of these samples. Berner (1967) gives x-ray diffraction patterns for the sedimentary iron sulfides greigite (cubic Fe_3S_4), mackinawite (tetragonal FeS), freshly precipitated FeS, and pyrrhotite ($Fe_{1-x}S$). All except freshly precipitated FeS show sharp peaks on Berner's diffractograms. Absence of x-ray evidence for the existence of greigite, mackinawite, or pyrrhotite in the Teels Marsh mud suggests that freshly precipitated FeS is the form of acid-soluble iron sulfide present.

Experimental evidence suggests that it is indeed possible for iron sulfides in acid-soluble form to exist at Teels Marsh. When dilute hydrochloric acid is added to a sample of wet mud, there is a distinct color change from grayish or blackish to brownish-yellow with a concomitant evolution of hydrogen sulfide gas. In one or two of the samples, after centrifugation for a long time at high speed, a suspension of fine black particles remains. This supernate becomes a true solution when dilute hydrochloric acid is added, and an odor of hydrogen sulfide gas is generated.

Berner's experimental studies of sedimentary iron sulfides (Berner, 1964b, 1967) were done over a range of geologic conditions. He was primarily interested in marine environments but application of his results to the present study are meaningful. Considering his data, certain iron sulfides may be eliminated from existence at any depth in the Teels Marsh sediments. Pyrite and marcasite form experimentally only if the pH is less than four and the conditions include oxidation in contact with the air. At Teels Marsh, the pH of the surface water is about pH nine (Everts, 1969). The pH may decrease somewhat with depth, but it is not likely that it goes below seven. So compounds which form in acid solution are not expected in the Teels Marsh sediments. Greigite, cubic Fe_3S_4, is formed only with oxidation in contact with the atmosphere and when ferrous ions in solution are present as the iron source. Pyrrhotite forms only under acid conditions with a metallic iron source (Berner, 1967).

On the other hand, Berner (1967) finds that tetragonal FeS, mackinawite, forms at all pH's in the range three through nine and at all temperatures between 20° and 90°C. Any type of iron-bearing reactant (dissolved ferrous ions, goethite, metallic iron, poorly crystalline goethite used as an approximation of limonite) gives rise to the same final product in all cases. Berner gives the following reaction as the controlling one for the experimental formation of mackinawite:

$$2\ HFeO_2(\text{goethite}) + 3\ H_2S_{(aq)} = FeS_{(tet)} + S^0_{(rhom)} + 4\ H_2O,$$

the free sulfur dissolving as a polysulfide ion. Goethite is probably present in abundance at Teels Marsh, being an alteration product of the original mafic minerals in the country rocks. But here it is more likely that HS^- is the sulfur species in solution.

The conditions at depth combine a basic pH with, conjecturally, a low oxygen content (low Eh). These conditions would cause the transition from interstitial waters with dissolved sulfate ion nearer the surface to more poorly oxygenated interstitial brines with HS^- in solution at depth (Garrles and Christ, 1965). So a more likely possibility for Teels Marsh is:

$$HFeO_2(\text{goethite}) + HS^-_{(aq)} = FeS_{(tet)} + 2\ OH^-_{(aq)}.$$

From Berner's work (1967), it is mackinawite, crystalline tetragonal FeS, or a partly crystalline form of it, that is most likely the form of acid-soluble iron sulfide present in the Teels Marsh alkaline playa environment.

This, then, indicates that an excess of adjusted acid-soluble iron exists in all samples except possibly sample 11. The assumption that all of the sulfur is involved in mackinawite provides an absolute minimum limit on the excess acid-soluble iron which must be accounted for by other means.

The number of moles of excess acid-soluble and acid-insoluble iron after combining all of the sulfur into mackinawite is given in table 7. Sample 11 is a special case because after using all of the acid-soluble iron to form FeS, there is some sulfur left uncombined. In this case it has been combined with acid-insoluble iron to form pyrite or marcasite, FeS_2. The leftover acid-insoluble iron is assumed to be combined into silicate mineral structures or magnetite.

TABLE 7

EXCESS MOLES OF IRON / 10^6 GRAMS DRIED MUD, AFTER FORMING FeS WITH ALL OF THE SULFUR

SAMPLE NUMBER	ADJUSTED ACID-SOLUBLE IRON	ACID-INSOLUBLE IRON
TM-5c-2	233	186
TM-5c-3	304	165
TM-5c-4	146	48.3
TM-5c-5	124	107
TM-5c-6	128	37.6
TM-5c-7	154	96.7
TM-5c-8	95.2	102
TM-5c-9	231	104
TM-5c-10	27.3	124
TM-5c-11	0*	190*
TM-5c-12	68.2	98.6
TM-5c-13	18.4	145

*See text for discussion of sample 11.

The acid-soluble iron excess after accounting for sulfides suggests that iron carbonates are present in the mud as contributors of iron. These may have been present in insufficient amount to be recorded on any of the x-ray diffractograms; however, no effervescence was observed when the samples were acidified. In other lake sediments iron carbonates are quantitatively abundant (Nriagu, 1967). There is probably in fact a greater excess of acid-soluble iron than shown for this limiting case, because less sulfur is really involved in mackinawite than has been assumed in the above model.

Carbon

The carbon content of the samples is plotted as a function of depth in figure 7. A sharp increase is evident in the amount of carbon between sample 6 and sample 7. This change occurs within the six inches between 11 feet 6 inches and 12 feet 0 inches. All of the samples below sample 7 are high in carbon except samples 10 and 13. Sample 10 is still considerably higher in carbon than the samples above sample 7, but sample 13 is in the same range as the shallower samples.

The sediment color boundary noted earlier coincides with this marked carbon change. Because the color boundary is not related to variations in the amount and/or oxidation state of iron, the boundary may be an original sedimentary facies line unconnected to present hydrologic conditions in the playa. The transition upward from black to green or gray-green would in this case represent a change in the amount of organic matter being deposited in the playa. The lighter colored samples would have been originally deficient in carbon relative to the black ones and preservation of this effect gives the situation that now exists.

Although it has not been noted in the log for core TM-5c, elsewhere in the playa a compact gray layer has been described beginning at a depth of thirty to thirty-five feet (Everts, 1969). Sample 13 may be very low in carbon content because it occurs close to this gray zone at depth. However, this sample is arenaceous, which may have had some effect on the distribution of carbon in the sample. The gray layer at depth may be another depositional boundary where the trend of low-carbon sedimentation is reversed at the interface. Sample 10 is gray silt (figure 3) and has a lower carbon content than the black samples immediately above and below it. This sample may therefore represent a temporary change in the sedimentation regime of organic matter in the playa.

If the color boundary does represent an original depositional feature, it has considerable significance as a time horizon which can be correlated over the entire playa surface. In this case it would be the marker for a change in sedimentation conditions at Teels Marsh at some point in its history.

Another interpretation of the color boundary is that it is an oxidation-reduction transition related to the hydrology of the area. The gray, shallower samples contain oxidized organic matter and the black samples at depth retain the pigmentation of organic matter under reducing conditions. This model assumes a fairly constant contribution of organic matter to the basin with time.

Oxidation-reduction is a more likely interpretation of the nature of the boundary in the light of the sulfur and carbon data and the work of other investigators. The apparently contradictory iron oxide data may be due to the fact that hematite may be metastably retained in a moderately reducing environment for long periods of time. A sudden increase in sulfur occurs coincidentally with the color boundary between samples 6 and 7. This becomes more evident when the sulfur values are plotted on an expanded scale (figure 6). This is the expected effect when passing downward from an oxidizing to a reducing environment.

Manheim (1961) made direct measurements of pH and Eh in stagnant bodies of water and underlying sediments and found that the Eh decreased with depth in the sediments, passing from positive values through zero and becoming reducing. He found that the concentration of H_2S increased considerably slightly below the level at which the Eh became negative. This is very likely what occurs at Teels Marsh due to the present hydrologic system in the playa. Water with a positive Eh containing dissolved sulfate ion occurs high in the section. The interstitial water in the deeper samples contains HS^- resulting from the reduction of sulfate ion. These conditions have caused the alteration of the original sediments and the formation of the color boundary.

Clay Mineralogy

The clay mineral data are presented in figures 8 and 9. Biscaye (1965) has provided a method for determination of "percentages" of clay minerals in a sample, but the technique is not strictly applicable to the Teels Marsh clays. Biscaye requires the assumption that the sum of illite plus chlorite plus kaolinite plus montmorillonite equals one hundred percent of the total mineralogy of the sample under study. This means that all of the non-clay minerals must be removed or absent from the clay-sized portion of the sample. Biscaye than uses the half-height peak areas of the clays with correction factors for each type of clay to calculate the clay mineral "percentages." However, for the Teels Marsh samples non-clay minerals are a considerable percentage of the clay-sized fraction (figure 9), and only relative abundances within each sample may be determined.

For figures 8 and 9, when there are three clay minerals present in one sample in a given size fraction, the most abundant is assigned a horizontal line or a bar ½ of the total width of the plot. The second most abundant clay mineral is assigned 1/3 of the total width, and the least abundant is assigned 1/6 of the total width. When only two clay minerals are present, the most abundant is assigned 2/3 of the total width of the plot and the least abundant 1/3 of the total width. When only one clay mineral is present, it is assigned the entire width of the plot.

Splitting the whole, less than two micron fraction into coarse, medium, and fine clay does in some cases point out occurrences of clay minerals which are not evident in the diffractograms for the bulk clay fraction. Illite is present in all of the samples of the bulk clay fraction. Montmorillonite (figure 8) is relatively minor or absent in all of the samples down to a depth of 11 feet 6 inches in the core. In all samples deeper than twelve feet, montmorillonite suddenly becomes by far the most abundant clay mineral relative to the others. This suggests the possibility that some montmorillonite has been diagenetically converted to illite. If this were true, it would support the conclusion that the present hydrologic cycle has has a major effect on the sediments. The occurrence of chlorite is scattered, but fairly common.

The mineralogy of the 2 - 0.2 micron fraction is not significantly different from that of the bulk clay material. Again, montmorillonite becomes more abundant in all samples below 12 feet in depth. Illite is measurably present in all samples except sample 6. Chlorite has a widespread, but irregular, occurrence and kaolinite is absent. Mixed-layer clay is present in only a very small number of samples for both size fractions.

For the 0.2 - 0.08 micron clay, the mineralogy is slightly different. Chlorite is present only in sample 5. Illite is present in all of the samples and is the most abundant clay nearest the surface. Montmorillonite appears in sample 4 and is the major clay mineral from there downward. Mixed-layer clay is more abundant in this size fraction than in the coarser one. Quartz, clinoptilolite, and phillipsite are the most common accessory minerals. Halite occurs for the first time in the diffractograms for this size fraction, but is believed to be due to the evaporation of saline interstitial water which was not completely removed by washing. It would appear also in the coarser size fractions if they had not been thoroughly washed.

In the less than 0.08 micron clay fraction, no chlorite appears. Illite is irregularly present in the samples but is the major clay mineral in only the

SUMMARY AND CONCLUSIONS

Study of the forms and distribution of iron in the playa sediments of Teels Marsh does not shed light on the nature of the color boundary occurring between 11 feet 6 inches and 12 feet 0 inches. There is no change in total iron or acid-soluble iron across the color boundary. Free iron oxides account for a constant proportion of total iron in all samples, regardless of depth or color of the samples. This suggests that the color boundary does not represent an oxidation differential.

This conclusion is contradicted, however, by the carbon and sulfur data. There is a sudden increase in the amount of total carbon across the color boundary, and a concomitant increase in total sulfur at this depth level. This is the expected effect of passing downward from an oxidizing to a reducing environment. Unoxidized organic matter is the chief pigmenting material of the black mud. The reducing environment at depth, with a high concentration of HS^-, provides a favorable site for the formation of authigenic iron sulfides. From experimental stabilities under conditions similar to those in the black mud of Teels Marsh, the acid-soluble iron sulfides, if any, present at Teels Marsh are probably mackinawite, tetragonal FeS, or partly crystalline forms of it.

The change from carbon-rich to carbon-poor sediments at the color boundary is possibly due to a change from pluvial to dry lake conditions. Wright and Frey (1965) describe the glacial history of the Great Basin area, using Lake Lahontan as an example. It is reasonable to assume that Teels Marsh was affected similarly to Lake Lahontan during the Pleistocene. The last major deep-lake period in the area coincided with a glacial maximum. These conditions were replaced about 8500 years ago by a subaerial to shallow-lake environment which continues to the present. During this time, sedimentation conditions provided for air-oxidation of the sediments in the Teels Marsh basin. The sediments deposited during this time would be expected to be bleached gray-colored by oxidation of organic matter. But while pluvial conditions were maintained, the environment on the lake bottom was kept unoxygenated and organic matter was not oxidized.

The color boundary, therefore, has considerable significance as a time line. The transition upward from black to grayish at the color boundary may be correlated over the entire playa surface and possibly be tied to a similar change of conditions in neighboring playa basins. The position of the color boundary gives an indication of the sedimentation rates for the post-pluvial time period. For core TM-5c, twelve feet of sediment have been deposited in approximately the past 8500 years, giving an estimated sedimentation rate of 0.43 mm. per year.

The zeolite nodules and zeolites present in the silts and clays are phillipsite, searlesite, and clinoptilolite. These minerals are presumably formed from alteration of volcanic ash in contact with the alkaline playa waters. This association is common in the western Basin and Range province sediments. Analcime is often present as well, but none was identified in the samples studied.

The clay minerals reflect detrital and possibly diagenetic origins. Chlorite is present only in the coarse and medium clay fractions and is detrital. Kaolinite is absent altogether. Illite and montmorillonite are very abundant and some of the illite may be formed by alteration from montmorillonite. Some montmorillonite, on the other hand,may be forming in conjunction with zeolites from volcanic ash deposits. Montmorillonite and mixed-layer clay become more abundant at the expense of the other clay minerals in the finer size fractions. Although quantitative analysis of the clay mineralogy at Teels Marsh is not siutable, relative abundances of each species can be determined.

SUGGESTIONS FOR FUTURE INVESTIGATIONS

One of the most helpful things to amplify this study would be the collection of continuous core samples, particularly from the central area of the playa. Smaller increments in depth would provide a more detailed picture of the changes in the sediments with depth and should substantiate the conclusion that the color boundary is an oxidation-reduction transition.

Immediate treatment of the samples after collection is also important. This would assure that water loss and oxidation of the sediments are kept at a minimum and would be a better representation of present playa conditions.

Analyses for specific forms of sulfur (free sulfur, sulfate, sulfude, organic) would also be helpful in locating the oxidation-reduction boundary. This could as well prove the assumption made in this study that sulfide sulfur constitutes almost all of the total sulfur.

X-ray photographs of isolated clay species would indicate whether iron was important in their compositions. Iron-rich chlorites and montmorillonites may be important retainers of acid-insoluble iron in the playa environment.

APPENDIX

Table A. Values for iron and carbon for duplicate analyses.

% E is given by Range / Average x 100.

SAMPLE NUMBER	TOTAL IRON	% E	ACID-SOLUBLE IRON	% E	IRON AS FREE IRON OXIDES	% E	TOTAL CARBON	% E
TM-5c-2	31,000	3.4	19,700	4.7	4400	2.2	2600	3.7
	29,100		18,800		4500		2700	
TM-5c-3	30,700	6.9	22,900	3.1	3700	0.0	3700	7.7
	32,900		22,200		3700		4000	
TM-5c-4	14,600	0.7	12,000	2.5	1500	6.7	5800	3.4
	14,700		11,700		1600		6000	
TM-5c-5	18,400	3.3	12,200	1.7	2300	9.1	4100	2.5
	17,900		12,000		2100		4000	
TM-5c-6	14,200	5.1	12,000	4.2	1600	6.2	6300	3.1
	13,500		11,500		1500		6500	
TM-5c-7	20,600	1.5	15,300	3.3	2100	5.0	32,500	1.2
	20,300		14,800		2000		32,100	
TM-5c-8	19,000	3.2	13,500	6.9	2500	8.3	21,600	2.3
	18,400		12,600		2300		22,100	
TM-5c-9	22,000	5.2	15,900	3.8	2600	8.0	20,500	2.4
	20,900		15,300		2400		21,000	
TM-5c-10	13,900	5.2	6700	3.0	1200	8.3	10,600	2.8
	13,200		6500		1100		10,900	
TM-5c-11	17,300	1.8	5700	5.2	1600	6.7	21,400	3.3
	17,000		6000		1500		21,700	
TM-5c-12	21,000	5.5	14,300	2.9	3600	5.7	17,200	2.9
	19,900		14,700		3400		17,700	
TM-5c-13	15,000	3.4	6600	1.5	2400	4.2	5400	5.3
	14,500		6700		2300		5700	

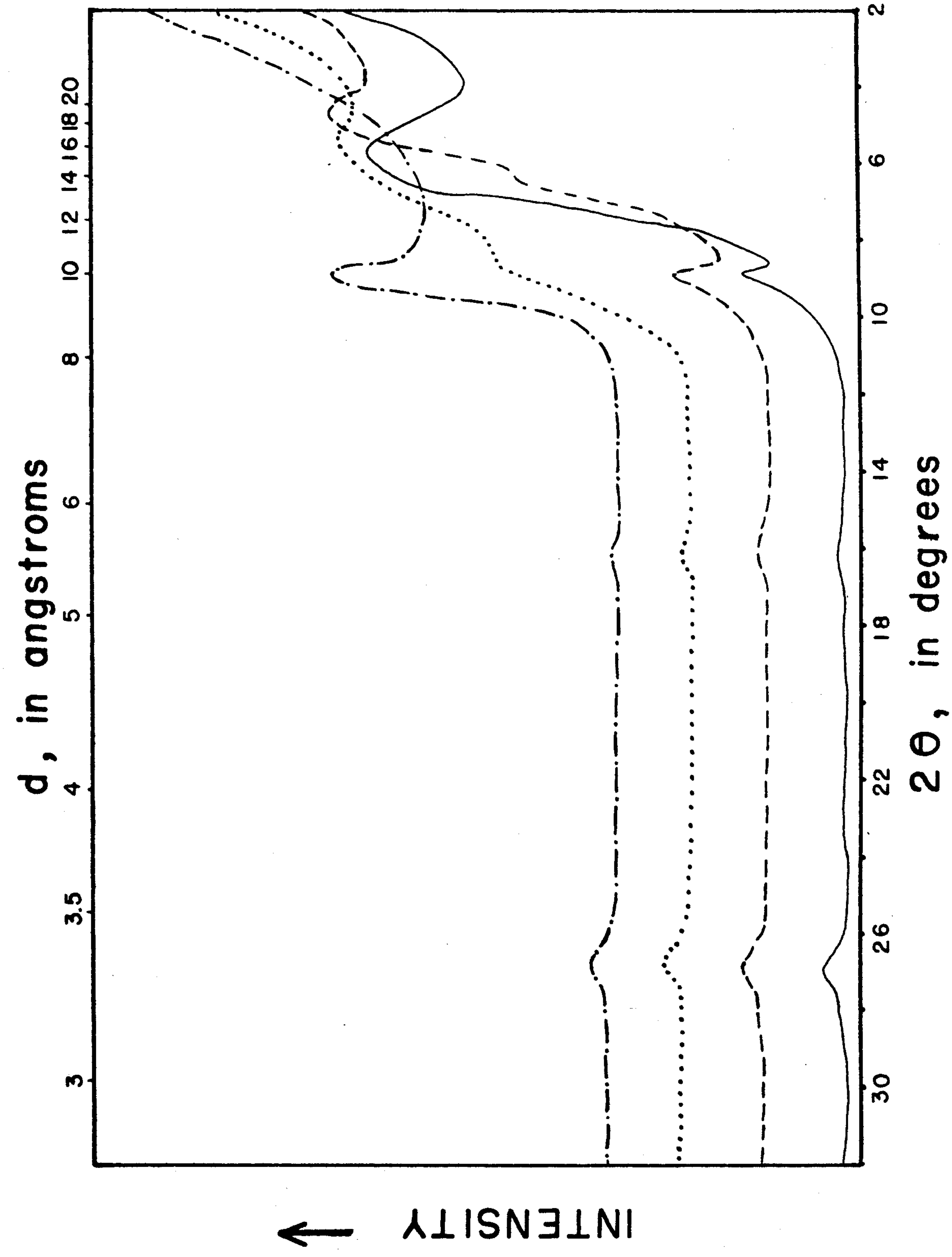
Figure A. Sketch of a diffractogram of a sample of mixed-layer clay from core TM-5c.

—— = Untreated (water saturated air)

— — = Glycolated

•••• = Heated for one half hour at 300° C.

·—·— = Heated for one half hour at 550° C.


d, in angstroms
20
18
16
14
12
10
8
6
5
4
3.5
3
2θ, in degrees
2
6
10
14
18
22
26
30
INTENSITY

BIBLIOGRAPHY

Angino, E.E., and Billings, G.K., 1967, Atomic Absorption Spectrometry in Geology, Amsterdam, Elsevier.

Berner, 1964a, "Distribution and diagenesis of sulfur in some sediments from the Gulf of California," Marine Geology, 1, 117-140.

_____, 1964b, "Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure," Jour.Geol., 72, 293-306.

_____, 1964c, "Stability fields of iron minerals in anaerobic marine sediments," Jour. Geol., 72, 826-834.

_____, 1967, "Thermodynamic stability of sedimentary iron sulfides," Am. Jour. Sci., 265, 773-785.

_____, 1969, "Migration of iron and sulfur within anaerobic sediments during early diagenesis," Am. Jour. Sci., 267, 19-42.

Biscaye, P.E., 1965, "Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans," GSA Bull., 76, 803-832.

Black, C.S., ed., 1965, Methods of Soil Analysis, Part 2, Univ. of Wisc. Press, Am. Soc. of Agronomy, Inc.

Blaedel, W.J., and Meloche, V.W., 1957, Elementary Quantitative Analysis, Evanston, Ill., Row, Peterson & Co.

Cook, H.E., and Hay, R.L., 1964, "Salinity control of zeolite reaction rates in Teels Marsh, Nevada," abstract, GSA Spec. Paper 82.

Droste, J.B., 1961, "Clay minerals in sediments of Owens, China, Searles, Panamint, Bristol, Cadiz, and Danby Lake basins, California," GSA Bull., 72, 1713-1722.

Eugster, H.P., and Smith, G.I., 1965, "Mineral equilibria in the Searles Lake evaporites, California," Jour. Petrol., 6, 473-522.

Everts, C.H., 1969, "The evolution of playa waters, Teels Marsh, Mineral County, Nevada," unpublished thesis, University of Wisconsin, Madison.

Ferguson, H.G., Muller, S.W., and Cathart, S.H., 1954, "Geologic map of the Mina quadrangle, Nevada," USGS Geol. Quad. Map Series, GQ 45.

Gale, H.S., 1915, "Salines in the Owens, Searles, and Panamint basins, California," *USGS Bull.*, *580*, 251-323.

Garrels, R.M., and Christ, C.L., 1965, *Solutions, Minerals, and Equilibria*, New York, Harper and Row.

Gibbs, R.J., 1965, "Error due to segregation in quantitative clay mineral x-ray diffraction mounting techniques," *Am. Mineralogist*, *50*, 741-751.

Grim, R.E., 1953, *Clay Mineralogy*, New York, McGraw-Hill.

Hardie, L.A., 1968, "The origin of the recent non-marine evaporite deposits of Saline Valley, Inyo County, California," *Geochim. et Cosmochim. Acta*, *32*, 1279-1301.

Hay, R.L., 1964, "Phillipsite of saline lakes and soils," *Am. Mineralogist*, *49*, 1366-1387.

_____, 1966, "Zeolites and zeolitic reactions in sedimentary rocks," GSA Special Paper 85.

_____, and Moiola, R.J., 1963a, "Authigenic silicate minerals in three desert lakes in eastern California," abstract, GSA Special Paper 76, p. 76.

_____, and _____, 1963b, "Authigenic silicate minerals in Searles Lake, California," *Sedimentology*, *2*, 312-332.

Hem, J.D., 1960, "Chemistry of iron in natural waters," USGS Water Supply Papers 1459A-1459I.

Jackson, M.L., 1965, "Soil Chemical Analysis- Advanced Course," Univ. of Wisc. Dept. of Soils.

Jones. B.F., 1965a, "Geochemical evolution of closed basin water in the western Great Basin," *Second Symposium on Salt*, vol. 1, Northern Ohio Geol. Soc., 181-200.

_____, 1965b, "The hydrology and mineralogy of Deep Springs Lake, Inyo County, California," USGS Prof. Paper 502-A.

Krauskopf, K.B., 1967, Introduction to Geochemistry, New York, McGraw-Hill.

Manheim, 1961, "In situ measurements of pH and Eh in natural waters and sediments," Stockholm Contrib. in Geology, 8, 27-36.

Mehra, O.P., and Jackson, M.L., 1960,"Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate," p. 317-327 in Swineford, A., ed., Clays and Clay Minerals, Proceedings of the Seventh National Conference, London, Pergamon Press.

Neal, James, ed., 1965, "Geology, mineralogy, and hydrology of the U.S. playas," Office of Aerospace Research, US Air Force.

Nriagu, J., 1967, "The distribution of sulfur and iron in Lake Mendota sediments," unpublished thesis, University of Wisconsin, Madison.

Ross, D.C., 1961, "Geology and mineral deposits of Mineral County, Nevada," Nevada Bureau of Mines, Bull.58.

Sheppard, R.A., and Gude, A.J., 3rd., 1968, "Distribution and genesis of authigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Inyo County, California," USGS Prof. Paper 597.

Sirois, L.L., and Takamori, T., 1964, "Experimental flotation cell," Dept. of Mines and Technical Surveys, Ottawa, Research Report R 135.

Smith, G.I., and Haines, D.V., 1964, "Character and distribution of non-clastic minerals in the Searles Lake evaporite deposit, California," USGS Bull. 1181-P, 1-58.

_____, and Pratt, W.P., 1957, "Core logs from Owens, China, Searles, and Panamint Basins, California," USGS Bull. 1045-A, 1-62.

Wright, H.E. Jr., and Frey, D.G., eds., 1965, The Quaternary of the United States, Princeton, N.J., Princeton Univ. Press, 265-286.

Approved by Carl J Bo............
Carl J. Bowser

Date .....12/8/'69...............