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Mineralogy and chemistry of clay-rich sediments in the contact zone of the Bullion Creek and Sentinel Butte Formations (Paleocene), Billings County, North Dakota

David W. Brekke
University of North Dakota

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MINERALOGY AND CHEMISTRY OF CLAY-RICH SEDIMENTS IN THE CONTACT
ZONE OF THE BULLION CREEK AND SENTINEL BUTTE FORMATIONS
(PALEOCENE), BILLINGS COUNTY, NORTH DAKOTA

by
David W. Brekke

Bachelor of Science, North Dakota State University, 1973

A Thesis
Submitted to the Graduate Faculty
of the
University of North Dakota
in partial fulfillment of the requirements
for the degree of
Master of Arts

Grand Forks, North Dakota

May
1979



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This thesis submitted by David W. Brekke in partial fulfillment of the requirements for the Degree of Master of Arts from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

Frank Kerner
(Chairman)

Walter Mow
Edwin D. Christensen

This thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

A. William Johnson
Dean of the Graduate School

Permission

MINERALOGY AND CHEMISTRY OF CLAY-RICH SEDIMENTS IN THE CONTACT
ZONE OF THE BULLION CREEK AND SENTINEL BUTTE FORMATION
Title (PALEOCENE), BILLINGS COUNTY, NORTH DAKOTA

Department Geology

Degree Master of Arts

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Date

April 18, 1979

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ABSTRACT

The Bullion Creek and Sentinel Butte Formations (Paleocene) form over 50 percent of the surface and near surface sediments in the North Dakota part of the Williston Basin. These rocks are composed of sandstones, siltstones, claystones, and numerous lignite beds. A distinct surface color change from light colors in the Bullion Creek Formation to dark colors in the Sentinel Butte Formation serves as a boundary marker and is widely exposed in the Little Missouri River badlands. The color boundary is a product of weathering and is not readily apparent in the subsurface. The use of clay mineralogy was investigated as a possible criterion to distinguish between the two formations and provide an explanation of the coloring.

Argillaceous units of both formations were sampled at three widely spaced sites along the Little Missouri River in Billings County, North Dakota. Samples were collected 32 km north of Medora, near Medora, and 25 km south of Medora. X-ray diffraction analysis of thirty-five samples established sodium montmorillonite with lesser amounts of mica-illite and iron chlorite as the major clay minerals. Minor amounts of kaolinite and the non-clay minerals quartz, calcite, dolomite, and feldspar are present in the clay-size fraction. The relative amounts and types of clay minerals are the same in both formations. Mica-illite and chlorite occur in about equal amounts and vary inversely with the amount of montmorillonite. The variation in clay mineral relationships within either formation is

greater than the variation between the formations. Any difference in clay mineralogy across the formational contact is localized. Chemical analyses of the clay-rich sediments showed a greater amount of iron and sodium in the Sentinel Butte Formation. The increase in iron, probably in disseminated form, is suggested as the cause of the darker colors observed in outcrop.

There appear to be two mechanisms of origin of the clay minerals in the Bullion Creek and Sentinel Butte Formations. Most of the clays are detrital material from highly montmorillonitic Cretaceous shales to the west and northwest. Some of the montmorillonite may be diagenetic and derived from the breakdown of eolian volcanic ash from the west.

INTRODUCTION

General Statement

Strata of the Paleocene Bullion Creek and overlying Sentinel Butte Formations compose over 50 percent of the surface and near surface sediments of the Williston Basin in the northern Great Plains. Extensive outcrops are found in the unglaciated portion of North Dakota south and west of the Missouri River. There are excellent exposures in the Little Missouri River badlands, where the contact of the two formations is readily seen. A striking color change, from light to dark colors, at the contact provides a distinguishing feature for field mapping. However, this appears to be largely a weathering phenomenon and cannot easily be extended to the subsurface. A result is poor stratigraphic control outside of the badlands area.

The objective of this study was to identify the specific clay minerals and to determine whether changes in clay mineralogy can be used to distinguish the contact between the Bullion Creek and Sentinel Butte Formations. This would provide a method for identifying the contact in samples from the subsurface.

Semi-quantitative analysis of the clay mineralogy of argillaceous units near the contact of the two formations in Billings County indicates that the amounts and type of clay minerals in both formations are similar. Chemical analysis of the sediments indicate a greater amount of iron and sodium in the overlying formation, which

may be the cause of the darker color. The clay mineralogy, together with other mineralogical, chemical, and sedimentological data, suggests the occurrence of a single depositional episode with two mechanisms of origin of the clay minerals. Most of the clay is detrital, but a limited amount may be diagenetic.

Study Area

Location

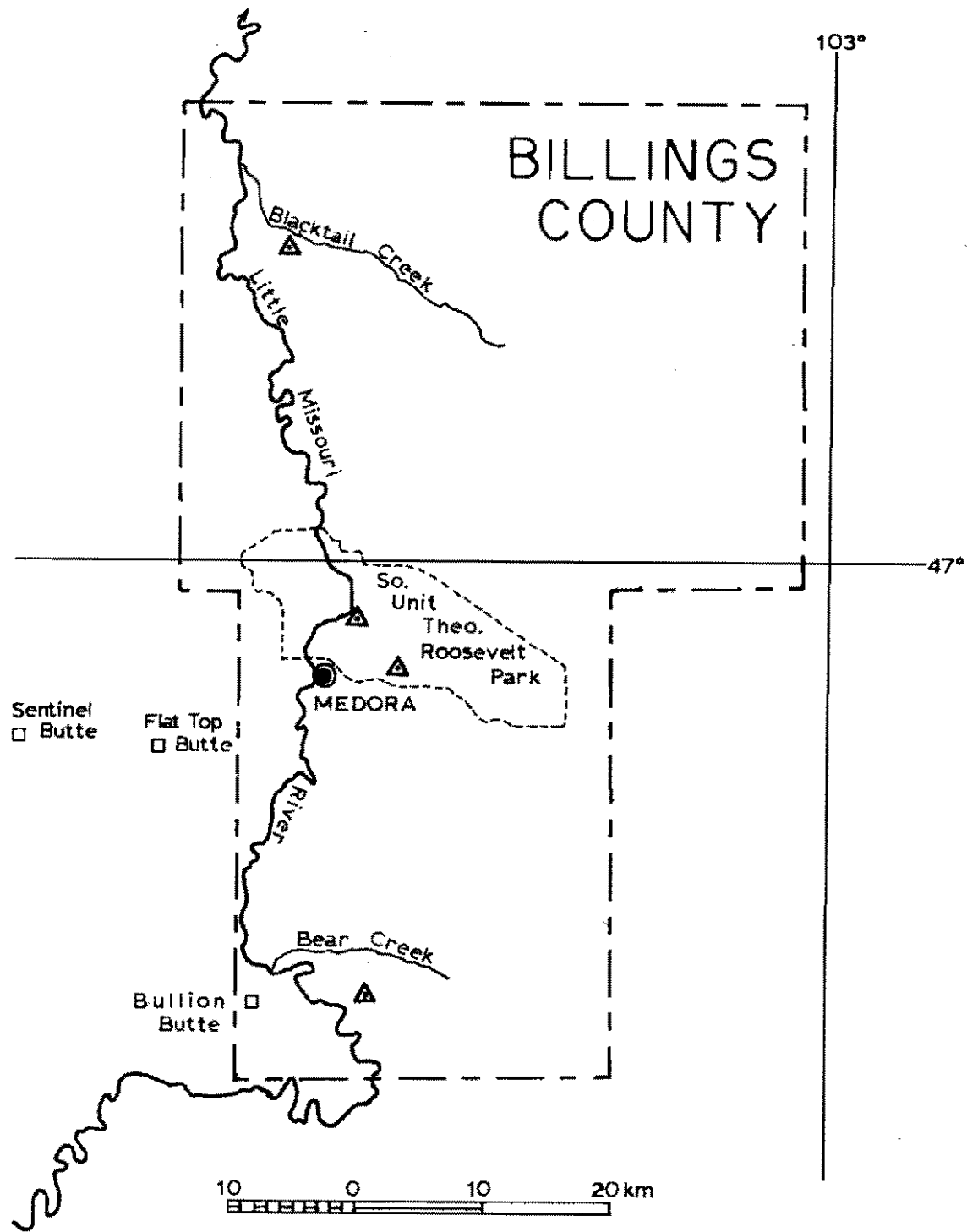
The Little Missouri River badlands in Billings County, western North Dakota, contain good exposures of the Bullion Creek and Sentinel Butte Formations and the contact zone between them. After extensive reconnaissance, three widely spaced sampling sites were chosen on the eastern bluffs near the Little Missouri River (Figure 1). The sites were located near Blacktail Creek, 32 km north of Medora; near Scoria Point in the South Unit of the Theodore Roosevelt National Memorial Park; and near Bear Creek, 25 km south of Medora.

Geologic Setting

The Williston Basin is a major intracratonic structure that actively subsided from Middle Ordovician to Cenozoic time. Summaries of the tectonic history of the Williston Basin are given by Ballard (1942) and by Carlson and Anderson (1966). The Laramide Orogeny at the end of the Cretaceous Period produced highlands to the west which provided a source of sediments for the Cenozoic rocks in the basin.

The upper Paleocene Fort Union Group is a series of non-marine lignite-bearing sediments that dip gently toward the center of the basin. The Bullion Creek and Sentinel Butte Formations compose the

Fig. 1. Location map of Billings County, North Dakota showing sample sites and major topographic and drainage features.



upper sequence of the group. They are conformably underlain by the lower Paleocene Slope Formation or Cannonball Formation and are generally conformably overlain by the lower Golden Valley Formation (Paleocene-Eocene).

Bullion Creek Formation

Taff (1909) named a "Tongue River coal group" along the Tongue River in the Powder River basin, Wyoming. Royse (1967) formally suggested the term Tongue River Formation, calling it a part of the Fort Union Group. This terminology has been used by the North Dakota Geological Survey. The name Bullion Creek Formation is suggested as a replacement for Tongue River Formation by Clayton and others (1977). Throughout this report, the term Bullion Creek Formation will be used as a direct replacement for Tongue River Formation.

The Bullion Creek Formation is a sequence of light colored sandstones, siltstones, claystones, and lignites. The unit thickens slightly toward the center of the basin, ranges from 95 to 160 metres in thickness, and is generally poorly consolidated. Royse (1970a) suggested that the environment of deposition was fluvial with a low paleoslope gradient and a sediment source from the west. Uniform subsidence of the Williston Basin is indicated by the continuity of the stratigraphic record.

Sentinel Butte Formation

Leonard and Smith (1909) named a Sentinel Butte coal group in Golden Valley County, North Dakota. The rank of the unit was in dispute until Royse (1967) formally suggested that the unit be raised to formational status, based on his study of its contact with the Bullion Creek Formation.

The Sentinel Butte Formation consists of dark colored sandstones, siltstones, claystones, and lignites, with the clastics generally darker in color than those of the Bullion Creek Formation. The unit thickens slightly toward the center of the basin, ranges from 115 to 190 metres in thickness, and the sediments are slightly more consolidated than those of the Bullion Creek. The base of the Sentinel Butte is conformable with the Bullion Creek Formation, and the conformable upper contact with the Golden Valley Formation can be seen in a few isolated buttes. The Sentinel Butte is unconformably overlain by the White River Group near the edges of the Williston Basin. The depositional environment of the unit is fluvial with a variable paleoslope and a sediment source from the west and northwest (Royse, 1970a).




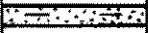

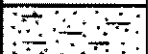
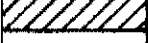






Description of Contact

A detailed discussion of the contact between the Bullion Creek and Sentinel Butte Formations by Royse (1967) described three main features: a distinct surface color change, a carbonaceous marker bed, and a basal sand unit of the Sentinel Butte Formation (Figure 2).

An abrupt surface color change from the light grays and yellows of the Bullion Creek to the dark grays and browns of the Sentinel Butte is easily seen at a distance. This distinguishing feature may fail locally due to rapid erosion exposing fresher rock, and becomes less distinct in the eastern outcrop areas. Since the color boundary is largely the result of weathering, it is very difficult to detect in subsurface samples.

The HT Butte bed, a carbonaceous zone, is the uppermost Bullion Creek unit and can be either a lignite, a lignitic shale, or both.

Fig. 2. Generalized stratigraphic section of the Bullion Creek and Sentinel Butte Formations. Modified from Royse (1970).

AGE	GROUP	FORMATION	POSITION	MARKER BED	SURFACE COLOR
PALEOCENE	FORT UNION GROUP	SENTINEL BUTTE FM. 115 to 190 metres thick		UPPER SAND	DARK GRAYS AND BROWNS
				BULLION BUTTE LIGNITE	
				UPPER YELLOW BED	
				LOWER YELLOW BED	
				BLUE BED	
				BASAL SAND	
		BULLION CREEK FM. 95 to 160 ⁺ metres thick		HT LIGNITE	LIGHT GRAYS AND YELLOWS
				MEYER LIGNITE	
				GARNER CREEK LIGNITE	
				HARMON LIGNITE	
				HANSON LIGNITE	
				H LIGNITE	
				BASAL SANDSTONE BED	

Thickness of the unit ranges from a few centimetres to several metres. The lignite can be locally burned and the overlying beds altered to a red clinker. The unit is fairly recognizable in the field, but slumping commonly covers it. The variable thickness of the bed makes subsurface recognition difficult.

A persistent, cross-bedded, silty sand unit marks the base of the Sentinel Butte Formation. The unit is fairly well sorted, can have ferruginous concretions or lignite clasts along bedding planes, and ranges from several metres to over 30 m thick. Locally, the sand grades into a fine-grained equivalent and may have a clay wedge between it and the underlying HT Butte bed. The characteristic large-scale features of the sand cannot be recognized in the subsurface.

Characteristics for distinguishing the two formations based on sand grain analysis have been described by Jacob (1975). In his analysis, the Bullion Creek Formation contained a larger percentage of sedimentary rock fragments. The major heavy minerals were tourmaline, zircon, and hornblende. The Sentinel Butte Formation has a larger percentage of volcanic and metamorphic rock fragments plus the metamorphic minerals kyanite and epidote. However, there is an overlap of the rock categories between the two formations. This would make recognition of the contact difficult.

MINERALOGY AND CHEMISTRY

Previous Investigations

Since the early 1900's, most studies of the Fort Union Group clays have been engineering studies to determine the suitability for brick and ceramic manufacture. Numerous chemical and firing characteristic analysis of clays in North Dakota are given by Clapp and Babcock (1906), Clarke (1948), and Manz (1953). Other investigations have centered around alumina content as a possible mineral resource (Hansen, 1959).

Studies of the clay mineralogy of the Bullion Creek and Sentinel Butte Formations have been infrequent. The term "bentonite" has been widely used in describing the clays. Clarke (1948), when discussing Tertiary clays in North Dakota, suggested a composition within the montmorillonite-beidellite series. He suggested that a sodium montmorillonite was present because of physical properties such as suspension pH and the $Al_2O_3:SiO_2$ ratio.

Differential thermal analysis (DTA) of selected samples shows the presence of montmorillonite, illite, and kaolinite (Benson, 1952, Meldahl, 1956, Hansen, 1959). Hansen states that the Bullion Creek-Sentinel Butte clays associated with lignite seams were illite, montmorillonite, or mixtures of the two. Difficulties are encountered in the interpretation of DTA curves when working with multi-component clays. Hansen (1959) found that carbonates and dolomites masked some

of the curves so that a reliable clay mineral identifications could not be made.

X-ray diffraction analysis of selected samples by later workers established montmorillonite as the dominant clay mineral, with lesser amounts of illite and kaolinite (Clark, 1966; Sigsby, 1966; Metzger, 1969; Emanuel, Jacob, and Karner, 1976). Clark (1966) mentioned a possible mixed-layer clay; Sigsby (1966) reported nontronite, chlorite, muscovite, and biotite; and Metzger (1969) stated that the "blue bed" was a sodium montmorillonite. Emanuel, Jacob, and Karner (1976) characterized the Bullion Creek as generally having higher mica-illite group, quartz, and carbonate contents, and the Sentinel Butte as having a higher montmorillonite content.

Field Work and Methods

Sampling was carried out during the summer of 1975. Three widely spaced sites were chosen near the Little Missouri River (Figure 1).

Blacktail Creek	SW $\frac{1}{4}$, Sec. 7, T137N, R101W
South Unit, Theodore Roosevelt National Memorial Park	
SB	SE $\frac{1}{4}$, Sec. 19, T140N, R101W
BC	SE $\frac{1}{4}$, Sec. 1, T140N, R102W
Bear Creek	NE $\frac{1}{4}$, Sec. 7, T143N, R101W

Measured sections of the sampling sites are given in Appendix B. Sites were chosen on the basis of maximum exposure of both formations and freedom from slumping and slope wash. An attempt was made to sample

both formations on the same slope in order to minimize weathering variations. Samples were taken from clay-rich units up and down section from the contact. Pits were dug deep enough to obtain fresh appearing material and samples of about 600 grams were sealed in plastic bags.

The laboratory preparation of the samples for x-ray analysis was modified after a procedure outlined in Carroll (1970). Semi-porous unglazed porcelain tiles and deposition of a clay slurry with a vacuum were used in preparing the mounts. This provided a durable mount and eliminated clay peeling under the various treatments. Distilled water was used throughout the preparation to prevent any alteration of the clays. Sand-silt-clay ratios were obtained by a settling and pipette method modified from Karner (1975, oral communication). The techniques used in the separation of the clay fraction and the preparation of x-ray diffraction mounts are given in Appendix F and Appendix G, respectively. Bulk sample analysis of one of the sites was accomplished using glycolated pellets (Karner and Wosick, 1975).

X-ray diffraction analysis of the clay fraction (less than 2 microns) was conducted using a Philips-Norelco high angle diffractometer and Cu K-alpha radiation. The oriented mount was x-rayed in the untreated state, after exposure to ethylene glycol, and after heating to 600° C providing information of characteristic changes in the d_{001} spacings. The (0k0) d-spacings of the clay minerals were determined by using a side-loaded mount similar to that described in Carroll (1970). The clay minerals were initially identified by using mineral descriptions and identification charts in Carroll (1970), Warshaw and Roy (1961), and the Joint Committee on Powder Diffraction Standards (1976a,b) Powder Diffraction File and Search Manual.

Several methods of quantitatively estimating the amounts of each clay mineral in a simple mixture are available. Pierce and Seigel (1969) give a summary and comparison of five basic methods. Diffraction intensity is dependent upon orientation effects, crystallite size and perfection, compositional variations, interstratification of the clays, and the diffraction angle at which the particular peak appears. These factors make quantitative estimates of mineral abundances in these clays extremely difficult.

In this study, montmorillonite, the mica group, and chlorite abundances are expressed by integrated intensities (Appendix C). The small amount of kaolinite and non-clay minerals of the clay-size fraction are expressed using peak heights. Comparing the relative chart intensities of each component between samples is a good method with acceptable precision ~~if~~ instrument conditions are monitored and sample preparation techniques are identical. Diffraction intensity is proportional to the number of diffracting planes oriented to the x-ray beam at a particular angle. Therefore peak intensity is a function of the amount of a mineral present in the sample. Mineral abundances are better represented by peak areas (integrated intensities) rather than peak heights. This procedure allows for the shifting of the primary peak due to the varying crystallinity of the clay mineral.

Determining the accuracy of the clay mineral amounts would require extensive analysis with internal standards and prepared mixtures together with an independent method of analysis. This was not done. The precision of the sample preparation and analysis techniques was evaluated by making several independent investigations on the same bulk sample (table 1). The largest spread of intensities from the

TABLE 1
PRECISION OF THE ANALYSIS TECHNIQUE

sample	XRD Peak Intensities			
	mont 001	mica 002	chl 002	qtz 101
Bc-TR-2	647	53	59	17
Bc-TR-2 A	556	43	31	19
Bc-TR-2 B	663	38	36	21
Bc-TR-2 C	650	49	36	23
Bc-TR-2 D	680	45	36	20
mean	639.2	45.6	39.6	20.0
std dev	48.3	5.7	11.1	2.2
var	1866.2	26.2	97.8	4.0

NOTE: Montmorillonite, mica group, and chlorite are given in integrated intensities. Quartz is given in peak height.

mean of the main minerals montmorillonite, mica, chlorite, and quartz was 1.7 standard deviations. This is within the 2.0 standard deviation spread of a normal distribution curve that corresponds to a 95% confidence level.

Scanning electron microscopy and electron microprobe analysis of selected samples was used as an aid to the identification of the clay minerals. In addition, a limited microprobe chemical analysis was conducted on sample Bc-SB-3. The analysis included scans of the bulk sample and of selected minerals in the sample. The sample chosen has a 95.6% clay content and is very high in montmorillonite. The

analysis was done on a fresh fracture surface in order to observe the surface morphology of the clays. However, the uneven surface introduces inaccuracy into the chemical analysis results. The oxide percentages were recalculated on an oxygen free basis. The cation proportions were computed using a method outlined by Shaw (1969).

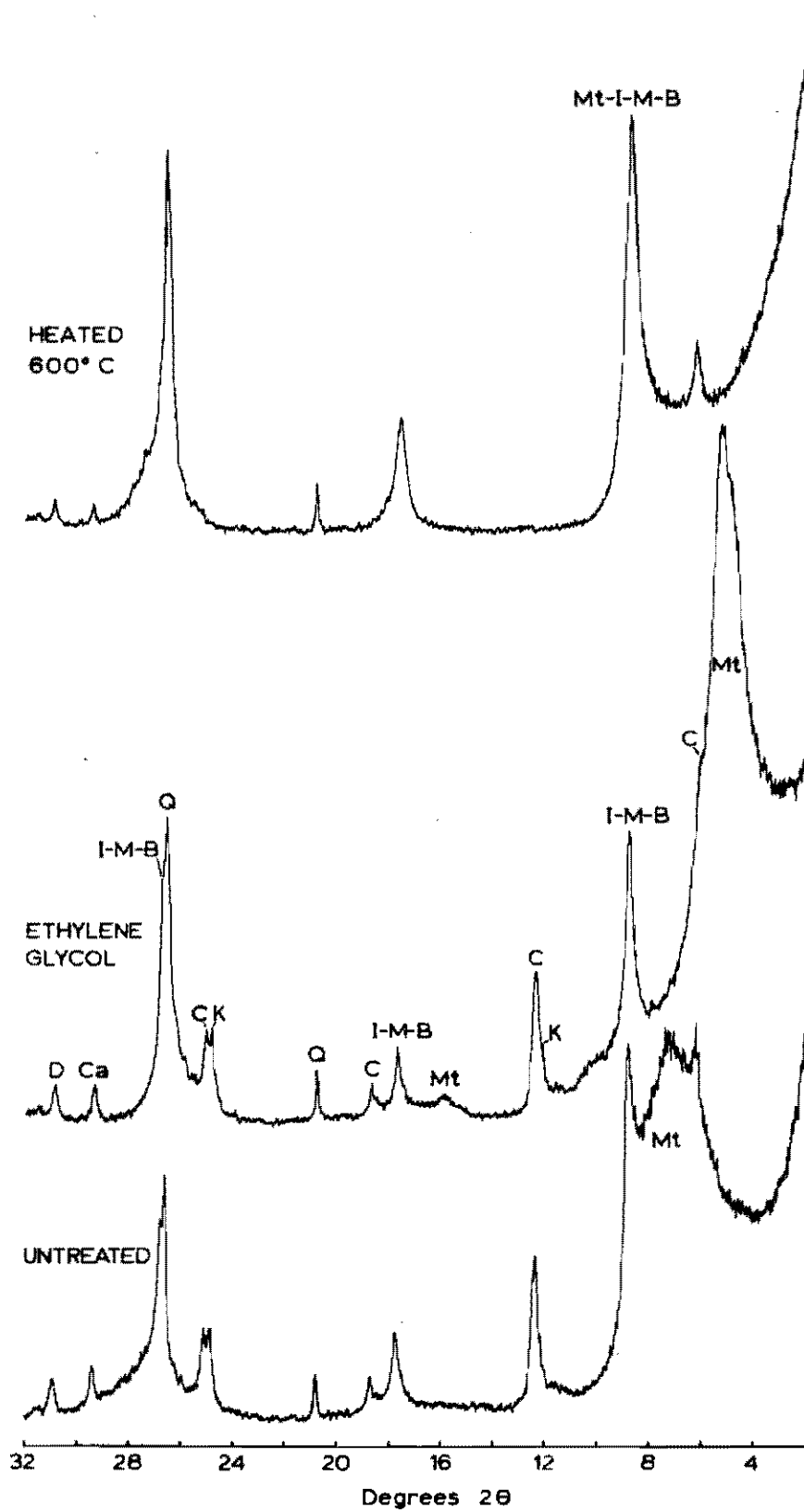
Rapid whole-rock chemical data was obtained by electron microprobe analysis of powders (Karner, 1978, oral communication) using a JEOL 35 scanning electron microscope with an energy dispersive x-ray fluorescent detector. The samples were ground to a fine powder, dried at 105°C, and loaded into bakelite holders. The x-ray fluorescence spectra were processed using a Tracor Northern XML fitting program and the matrix correction program of Bence and Albee (1968). Carbon dioxide was determined by the total reactive carbonate titration technique (Royse, 1970b). Closure using these techniques ranged 96.4-109.8% with a mean of 104.1% and a standard deviation of 3.46.

Clay Mineralogy

The major clay minerals in both the Bullion Creek and Sentinel Butte Formations are Na-montmorillonite, mica-illite, and Fe-chlorite. Minor amounts of kaolinite are present along with other clay-size minerals including quartz, feldspar, and carbonates. Typical diffractometer traces are given in Figure 3.

Sand-silt-clay ratios of the samples were determined during the sample preparation. The percent sand of the bulk sample ranged 0-1.2% silt 4.4-83.1%, and clay 16.8-95.6%. Since the sand percentage is very low, only the weight percent clay is given in the figures. Sand-silt-clay ratios are given in Appendix E.

Fig. 3. X-ray diffractogram traces of the clay-size fraction of sample Bc-TR-3. Cu K-alpha radiation at 37 Kv and 18 ma, Ni filter, ratemeter 2×10^3 , scanning speed $1^\circ 2\theta/\text{min}$, chart speed $30''/\text{hr}$. B, biotite; C, chlorite; Ca, calcite; D, dolomite; I, illite; K, kaolinite; M, muscovite; Mt, montmorillonite; Q, quartz.



Montmorillonite

Both formations contain dioctahedral Na-montmorillonite as the major clay mineral component. This identification is based on an observed basal d_{001} spacing near 12.5 \AA and an 060 peak of $1.49 - 1.52 \text{ \AA}$ in the diffractograms.

Montmorillonite is a 2:1 expandable layer clay mineral. The basal d_{001} spacing of the mineral varies with the type of interlayer cation and amount of interlayer water. Under ordinary humidity conditions the basal spacing for a pure montmorillonite with sodium as the interlayer cation is 12.5 \AA , and with calcium it is from about 14.5 to 15.0 \AA (Deer, Howie, and Zussman, 1962). This corresponds to one layer of interlayer water and two layers of interlayer water, respectively.

The humidity in the laboratory was not controlled, but the samples were thoroughly dried at room conditions. The 001 peak for untreated montmorillonite was broad probably due to varying hydration states of the crystallites. All samples but two had basal spacings of less than 14 \AA , with an overall average of 12.5 \AA . The two samples with larger spacings, 14.0 and 14.2 \AA , could have resulted from excess humidity in the room, incomplete drying, or a slight amount of calcium montmorillonite present. The integral series of basal peaks, d_{002} , d_{003} , etc., are masked by the mica-illite group peaks.

After treatment with ethylene glycol, the mineral expanded to a characteristic 17 \AA d_{001} spacing in all samples. A marked sharpening of the peak suggests that the broadness of the untreated peak is due to varying hydration states. Since the basal spacings are shifted, the

integral series of basal peaks appear at about 8.6 Å (d_{002}) and 5.6 Å (d_{003}). Heat treating to 600° C resulted in a peak shift to about 10 Å, which is caused by driving off the interlayer water and collapse of the crystal structure. A dioctahedral structure is indicated by an 060 peak of 1.49-1.52 Å.

A bulk chemical analysis of sample Bc-SB-3 should closely approximate the composition of montmorillonite. The sample is high in clay and highly montmorillonitic in relation to the other clay minerals. The computed formula for the sample, assuming that it is entirely montmorillonite, is close to the general formula for an idealized montmorillonite (table 2). The excess cations, Al, and Si probably result from a small amount of quartz and feldspar in the field of view of the microprobe. The field of view of the chemical analysis is given in Figure 4.

Some of the montmorillonite in the samples occurs as a mixed-layer structure with illite and is discussed later.

Surface morphology of montmorillonite is observed as curled plates in scanning electron microscope photographs (Figures 4 and 5).

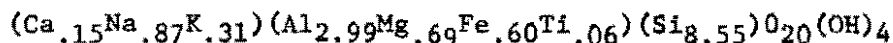
Mica Group

Mica group minerals in the two formations are a complex mixture of the 10 Å minerals: dioctahedral muscovite, trioctahedral biotite, and dioctahedral illite. The mica group minerals were identified by the presence of a strong peak at 10 Å followed by an integral series of basal peaks near 5.0, 3.3, and 2.0 Å. Because of the complexity of the mixture, only the relative abundance of the mica group minerals was estimated.

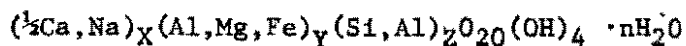
TABLE 2
CHEMICAL ANALYSIS OF BULK SAMPLE Bc-SB-3

oxide	weight %	number of ions based on 24 oxygens
SiO ₂	64.00	8.554
TiO ₂	0.58	0.059
Al ₂ O ₃	18.97	2.990
FeO	5.33	0.596
MgO	3.45	0.687
CaO	2.04	0.292
Na ₂ O	3.37	0.873
K ₂ O	1.30	0.307
SO ₃	<u>0.43</u>	0.043
	99.47%	

NOTE: The oxides are recalculated to an oxygen and water free basis. The number of ions is calculated for montmorillonite. The computed formula for this sample is:



where, X=1.33, Y=4.33, and Z=8.55. The general formula for montmorillonite is:

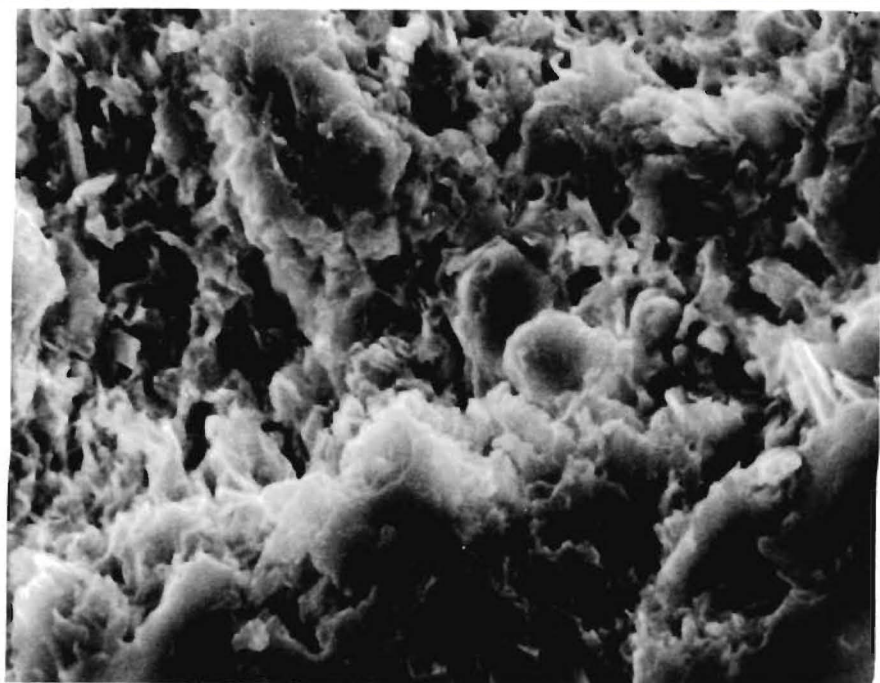
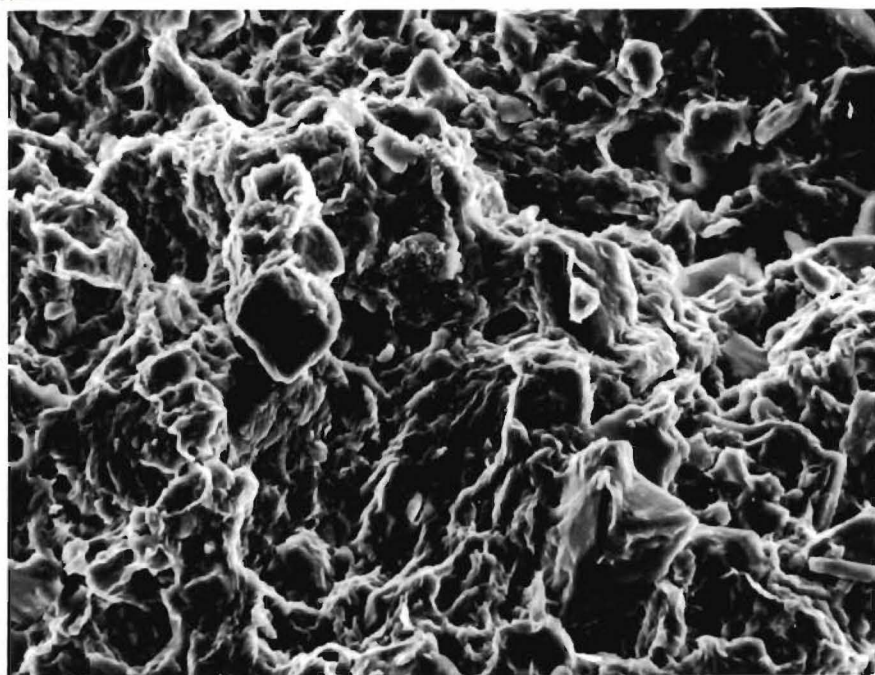


where, X=0.7, Y=4.4, and Z=8 (Deer, Howie, and Zussman, 1962).

Muscovite constitutes the smallest proportion of the mica mixture. In diffractograms, it is seen as a relatively small, sharp peak superimposed on the broad illite peak or lost within the biotite peak. The muscovite is dioctahedral as indicated by a d_{060} spacing of 1.50 Å and an intense 002 peak (Grim, Bradley, and Brown, 1951). Although it

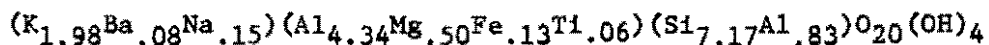
Fig. 4. Scanning electron microscope photograph of bulk sample Bc-SB-3. The photograph is of a fresh fracture surface that is oblique to the bedding planes. Montmorillonite is shown as curled plates and the mica minerals as large flat plates. (650 X).

Fig. 5. Scanning electron microscope photograph of a replica of bulk sample SR-SB-2. Montmorillonite is shown as slightly curled plates and the mica minerals as large flat plates. The replica shows montmorillonite in the hydrated state. Sample preparation removes the absorbed water and shows montmorillonite as curled plates. (2000 X).



is difficult to distinguish polytype in small quantities, the writer believes the muscovite is a 2M variety. This type is very stable, derived from high temperature crystalline rocks, and is detrital in sediments (Yoder and Eugster, 1955). A small amount of muscovite is observed petrographically in the greater than 2 micron fraction.

A chemical analysis of a muscovite flake in sample Bc-SB-3 gives a computed formula of:



where, $X=2.21$ and $Y=5.04$. The excess Y site Al can be taken care of by attributing one Si atom to quartz. This allows the transferring of one Al atom to the Z site. The resulting cation proportions become closer to the theoretical Si_6Al_2 structure. The muscovite crystal is shown in Figure 6.

Biotite makes up the next largest amount of 10 Å clay. It accounts for most of the sharpness of the 10 Å peak. Biotite normally has a trioctahedral structure and this shows in the diffractograms as a broad d_{060} spacing of 1.54 Å beneath the quartz 211 peak. Clear flakes are observed petrographically in the sand-size fraction of most samples and are fairly abundant in some.

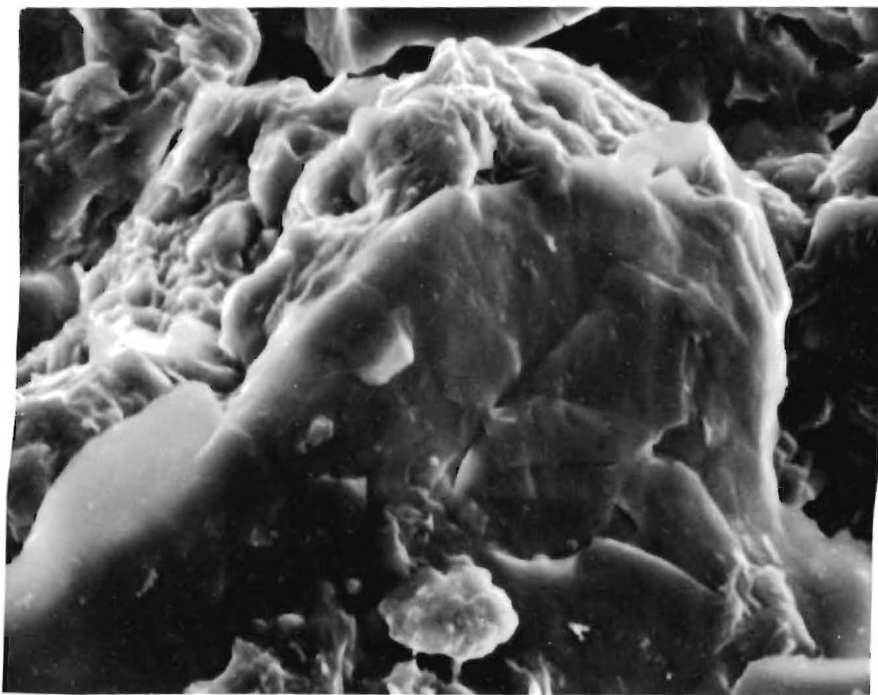
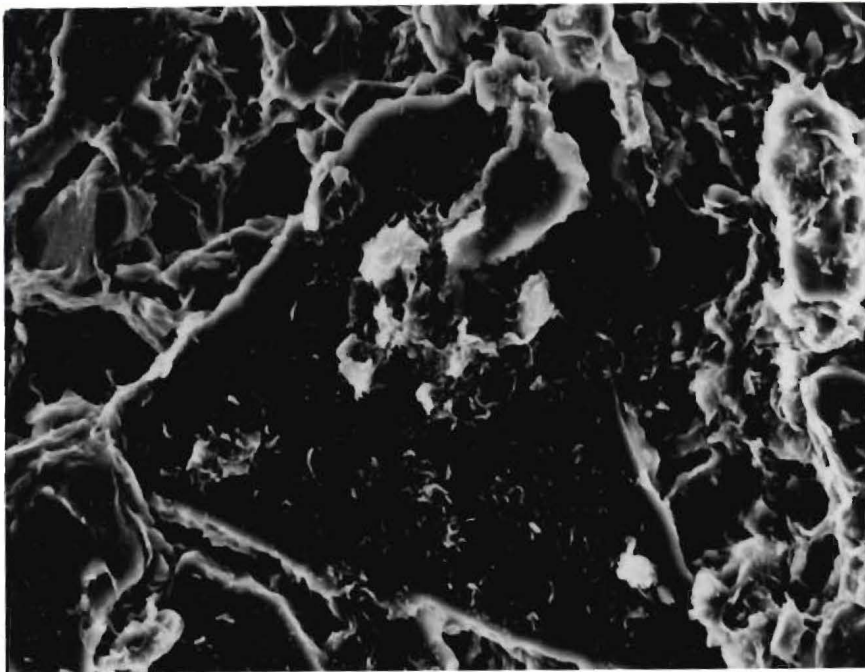
A chemical analysis of a biotite flake in sample Bc-SB-3 gives a computed formula of:



where $X=1.85$ and $Y=4.97 + 1.05=6.02$. Normally the amount of Na does not exceed 0.5 atoms per unit formula (Deer, Howie, and Zussman, 1962). The excess here plus the excess Si at the Z site may be the result of feldspar dust on the crystal surface. A deficiency of K may be due to

Fig. 6. Scanning electron microscope photograph of a muscovite flake in sample Bc-SB-3. The background is mostly montmorillonite. (1100 X).

Fig. 7. Scanning electron microscope photograph of a biotite flake in sample Bc-SB-3. (1800 X).



weathering of the biotite flake. A photograph of the biotite flake is shown in Figure 7.

Illite is the most abundant of the mica minerals in the Bullion Creek and Sentinel Butte Formations. Illites in general have the same 2:1 layered structure as muscovite except for a depletion of inter-layer potassium ions and an increase in water and silica (Gaudette, Eades, and Grim, 1966). The illite is dioctahedral as shown by a d_{060} spacing of 1.50 \AA . The clay is a 1Md polytype as indicated by the presence of only the basal d-spacings (Yoder and Eugster, 1955). In diffractograms it resembles Fithian illite (API 35), which is a 1Md polytype mixed with a small amount of muscovite (Gaudette and others, 1966). The illite probably has varying degrees of crystallinity as shown by peak broadening into a prism shape. This is especially evident in the higher order basal spacings.

Some mixed-layer illite-montmorillonite occurs in most samples. This is indicated by an illite d_{001} spacing slightly greater than 10 \AA and an asymmetry of the peak toward the low angle side of the diffractogram. True illite has an d_{001} spacing of slightly less than 10 \AA . The peak sharpens on glycolation and becomes asymmetrical again with heating. The larger basal spacing and other effects result from the interaction of the 001 illite peak and the mixed-layer illite-montmorillonite 001/002 peak (Heller-Kallai and Kallman, 1972). The mixed-layering is random because there is a lack of a definite peak intermediate to the basal spacings of the two components (Reynolds and Hower, 1970), and there is no peak at lower 2θ values as is typical of allevardites.

Chlorite

Chlorite occurs in these sediments as an iron-rich variety appearing at 14 Å with an integral series of basal peaks at 7.1, 4.7, and 3.5 Å. The chlorite structure is unaffected by ethylene glycol and retains its structure at 600° C. The basal series of d-spacings show large 002 and 004 peaks and relatively small 001 and 003 peaks, indicating an Fe-chlorite (Brindley, 1961). Further identification of the chlorite polytype was not made because of the complexity of the total clay system. Chlorite can be confused with kaolinite in diffractograms at the 7 Å spacing (001 kaolinite/002 chlorite), but in these sediments the two can be easily resolved at the 3.58 Å spacing (002 kaolinite/004 chlorite). In addition, heat treatment sharpens and intensifies the 14 Å chlorite 001 peak and destroys the kaolinite structure.

Kaolinite and Others

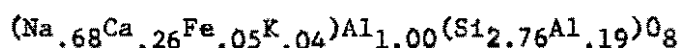
Kaolinite is a minor constituent of the Bullion Creek-Sentinel Butte clays. This 7 Å mineral appears on the diffractograms as a small shoulder or peak superimposed on the chlorite peak. The relative sharpness of the 002 peak indicates that it is fairly well-crystallized. The mineral becomes amorphous on heating to 600° C.

Halloysite in the dehydrated state can be confused with kaolinite, but examination with a scanning electron microscope failed to show the characteristic tubular structure of halloysite.

Other clay-size minerals were observed in varying amounts. Quartz was always present in the less than 2 micron fraction. Dolomite

and lesser amounts of calcite were present in three-fourths of the samples. Feldspar, either alkali feldspar or plagioclase, occurred in half of the samples. A scanning electron microscope photograph shows a possible corroded feldspar crystal in the clay fraction of one of the samples (Figure 8). This may indicate that the sediments have not been strongly modified by chemical weathering.

A chemical analysis of a feldspar crystal in sample Bc-SB-3 gives a computed formula of:



where, $X=1.02$ and $Z=3.95$. This is very close to the theoretical formula of plagioclase and is in the oligoclase to andesine compositional range. A photograph of the feldspar crystal is shown in Figure 9.

Distribution of Clay Minerals

Previous work has suggested that the clay mineralogy of the Bullion Creek and Sentinel Butte Formations was sufficiently dissimilar to provide a possible criterion for distinguishing the contact. Data presented here indicates that the variation in clay mineralogy within either formation is greater than the variation between the two units. Clay mineral relationships of all the clay-size minerals of each section are given in Figures 11, 12, and 13.

Montmorillonite has the highest integrated intensities of all clay minerals in both formations and is interpreted to be the most abundant mineral on the basis of both x-ray diffraction study and chemistry. There is slightly more of the mineral in the Sentinel Butte Formation when considering all three sites (BC=665, SB=856, integrated intensities). Trends can be observed locally, such as

Fig. 8. Scanning electron microscope photograph of a possible corroded feldspar crystal in sample SR-SB-4. The background is mostly montmorillonite. (10,000 X).

Fig. 9. Scanning electron microscope photograph of a feldspar crystal in sample Bc-SB-3. The elongate feldspar crystal is probably resting on a mica flake. The background is mostly montmorillonite. (3300 X).

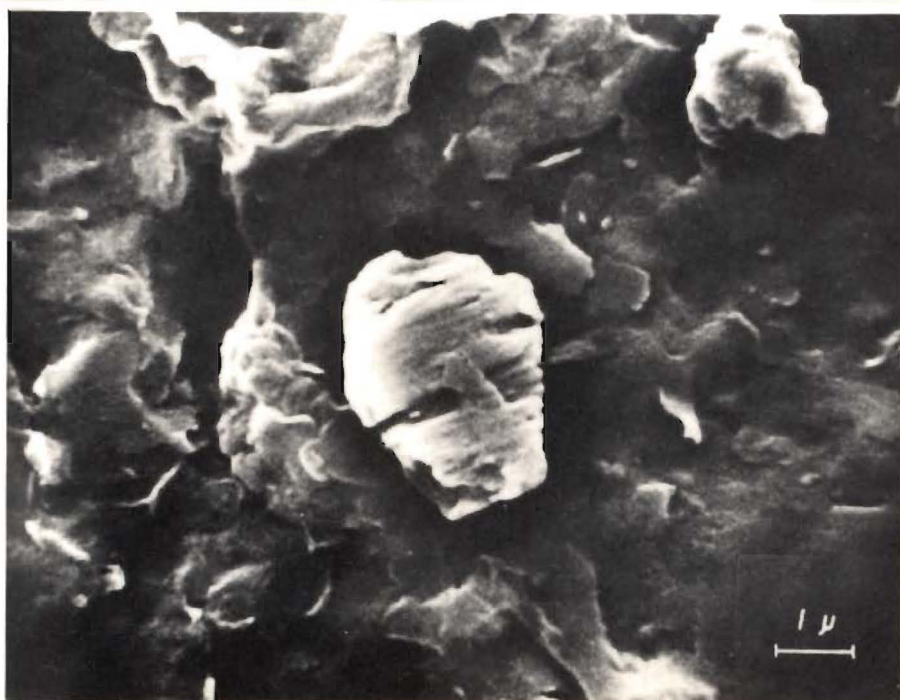


Fig. 10. Clay mineralogy at Bear Creek, South Unit Theodore Roosevelt Park, and Blacktail Creek. The intensities given on the diagram are integrated intensities. The samples are taken from clay-rich units and the lines between the points are for reference only.

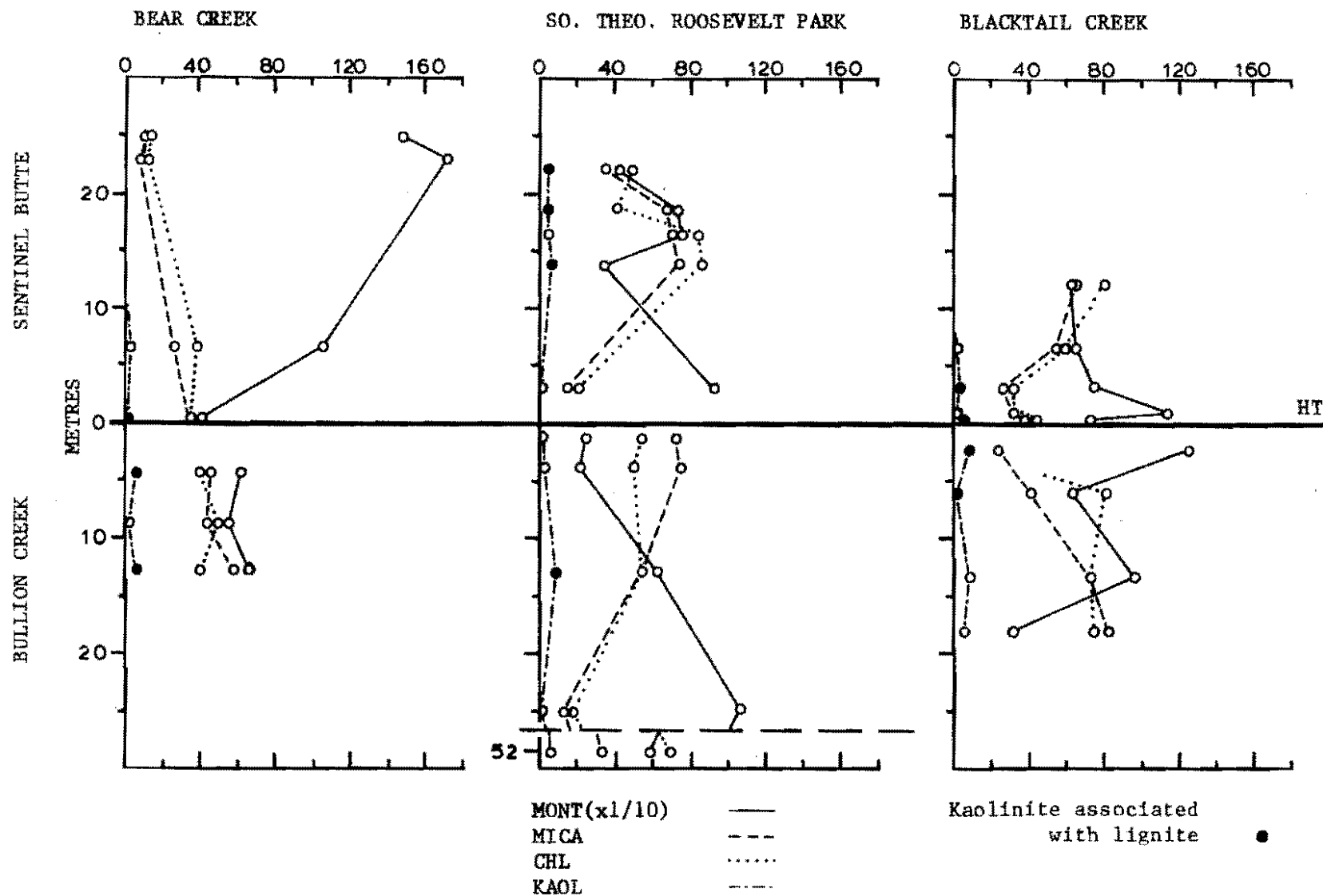


Fig. 11. Mineralogy of the clay-size fraction at Bear Creek. Clay mineral amounts are given in integrated intensities, non-clay minerals in peak intensities.

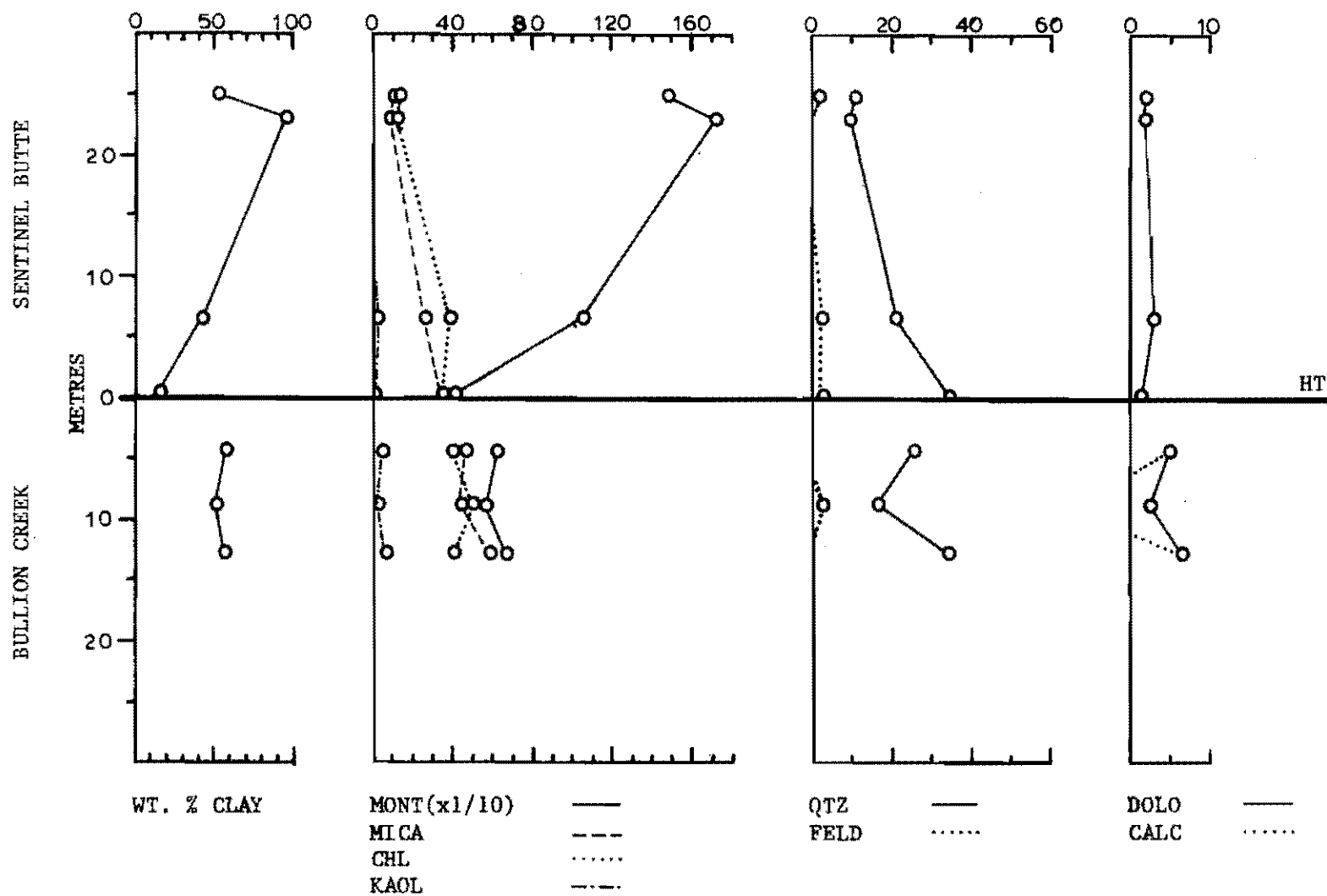


Fig. 12. Mineralogy of the clay-size fraction at the South Unit Theodore Roosevelt Park. Clay mineral amounts are given in integrated intensities, non-clay minerals in peak intensities.

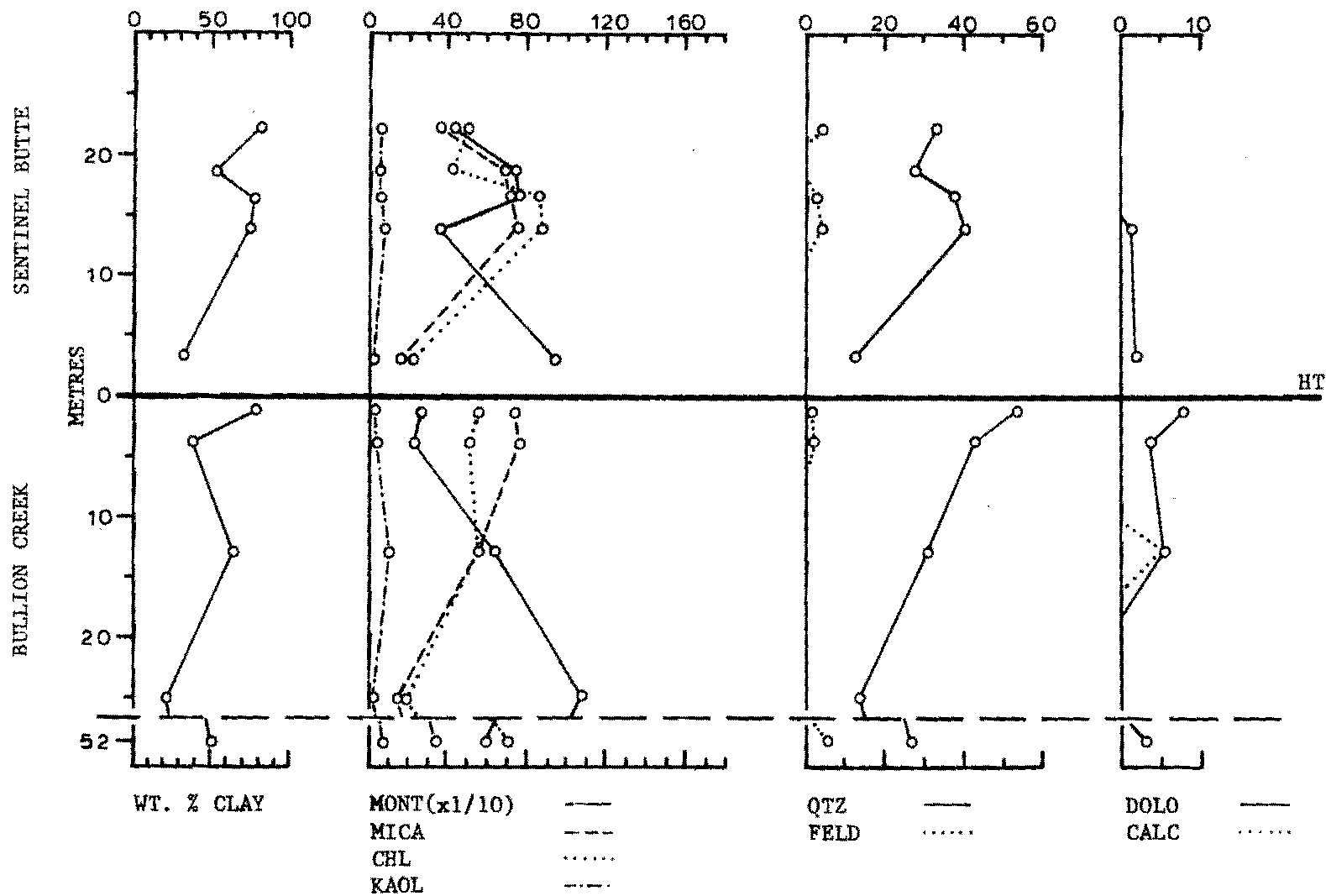
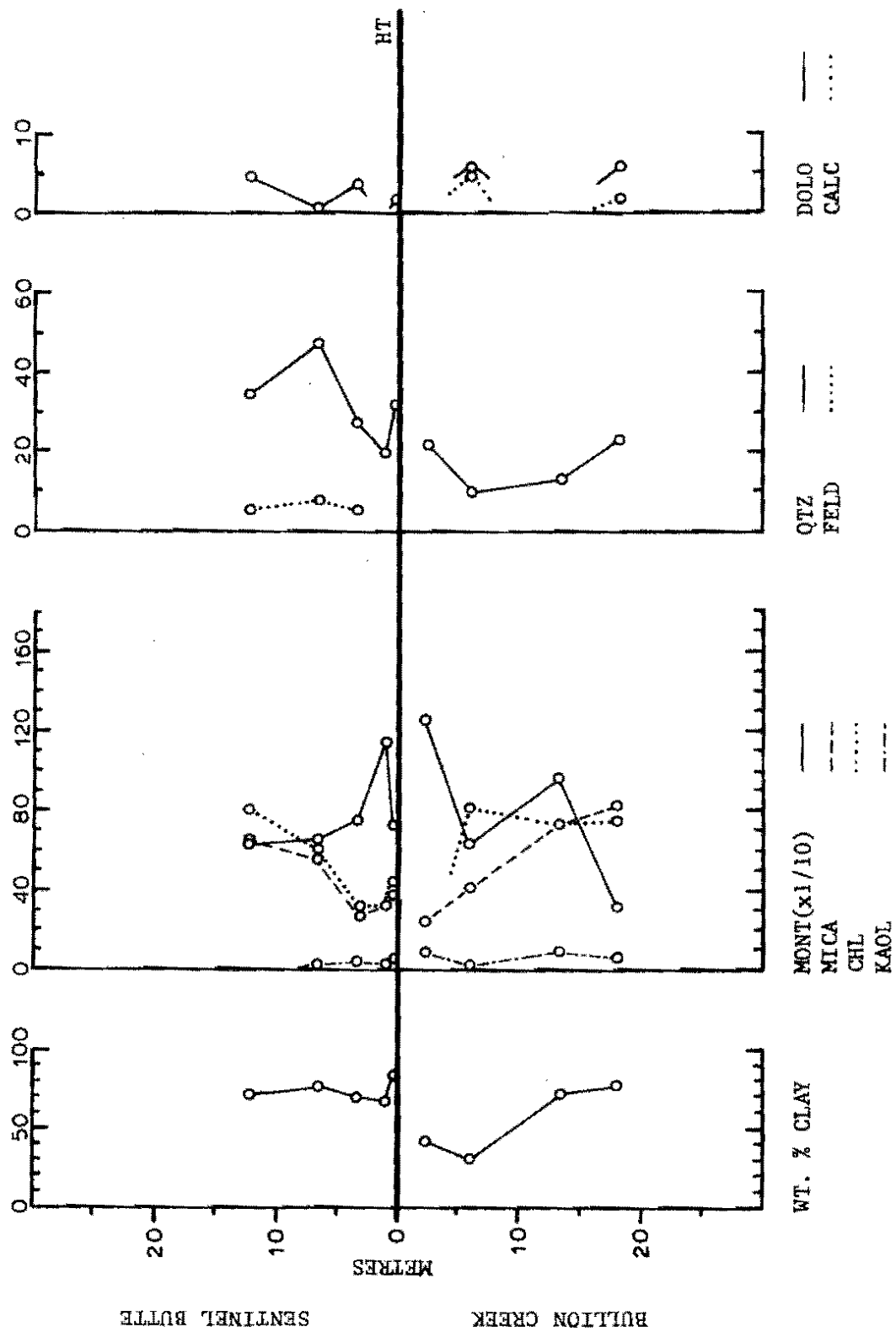


Fig. 13. Mineralogy of the clay-size fraction at Blacktail Creek. Clay mineral amounts are given in integrated intensities, non-clay minerals in peak intensities.



the increase in montmorillonite up section from the contact at Bear Creek or down section at the Park (Figure 10). Abrupt changes across the contact appear at all three sites, but the change is irregular. There is no consistent change in the abundance of montmorillonite.

The mica group and chlorite have similar intensities and vary directly. Particularly good correlations exist in the Sentinel Butte section at all sites. Exceptions to this can be found locally, especially the Bullion Creek Formation section in the Park (Figure 10). These minerals exhibit the same irregular variation at the contact as montmorillonite.

Mica and chlorite intensities vary inversely with montmorillonite. A particularly good example of this can be found in the Sentinel Butte Formation at Blacktail Creek (Figure 13). This inverse association generally holds true throughout both formations, notably in the Sentinel Butte. There is slightly more mica and chlorite in the Bullion Creek.

Kaolinite tends to increase when associated with a lignite (Figure 10). The Bullion Creek Formation has a larger amount of kaolinite overall, but the amounts are very low.

The non-clay minerals in the less than 2 micron fraction show some slight differences across the contact. Quartz, potassium feldspar, and plagioclase are slightly more abundant in the Sentinel Butte, and tend to vary sympathetically with mica and chlorite. Clay-size calcite is present in a few Bullion Creek samples. Dolomite occurs in both formations, but tends to increase in the Bullion Creek. These observations of the non-clay components are in general agreement with

those of Clark (1966), Crawford (1967), Royse (1970a), Jacob (1975), and Steiner (1978).

A standard computer correlation analysis using the Pearson product moment method (UND Computer Center, 1977) was performed on the diffraction data. The calculated coefficients confirm the strong positive correlation between the abundances of the mica group, chlorite, quartz, and to a lesser extent, feldspar. The figures support the strong negative correlation of the above minerals to montmorillonite. They also corroborate the lack of correlation between mineralogy and stratigraphic position. The correlation coefficients of the various relationships are given in Appendix D, Table 5.

A computer discriminant analysis (Nie and others, 1975) of all the clay-size fraction minerals of both formations was conducted to determine if there was any mineralogical distinction between the two units. It was found that the x-ray intensities of quartz, dolomite, and kaolinite defined a discriminant function and could be used to classify a sample into either the Bullion Creek or Sentinel Butte Formations. The three minerals, acting as a group, were sufficiently different in each formation to serve as a discriminating feature. This discriminant function correctly classified into the proper formation 22 out of 26 samples, or 84.6%. Although there appears to be a statistical method for distinguishing the two formations based on mineralogy, two of the components of the discriminant function, dolomite and kaolinite, are minor constituents of the clay-size fraction. Quartz and dolomite amounts increase in the bulk sample and may change the discriminant function. If this statistical distinction is to be of

any value, an analysis will have to be conducted on bulk samples from a large number of sample sites.

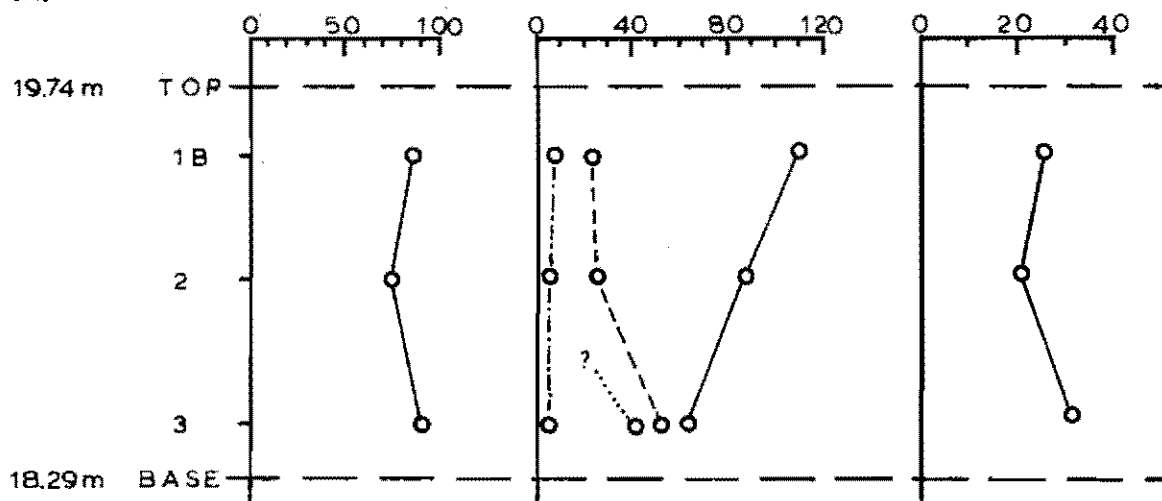
Clay Mineralogy of the "Blue Bed"

A separate clay analysis of the "blue bed" was performed to determine the effect of surface weathering and vertical variation within a single unit. The "blue bed" is a distinctive marker bed in the lower half of the Sentinel Butte Formation. As in the rest of the formation, mica varies inversely with montmorillonite and quartz varies directly with mica (Figure 14).

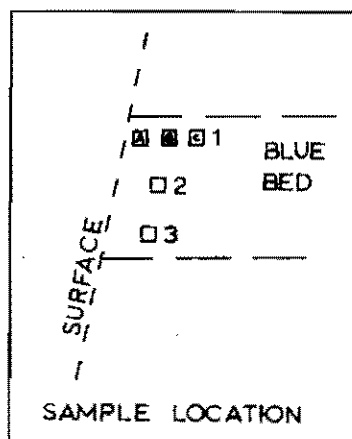
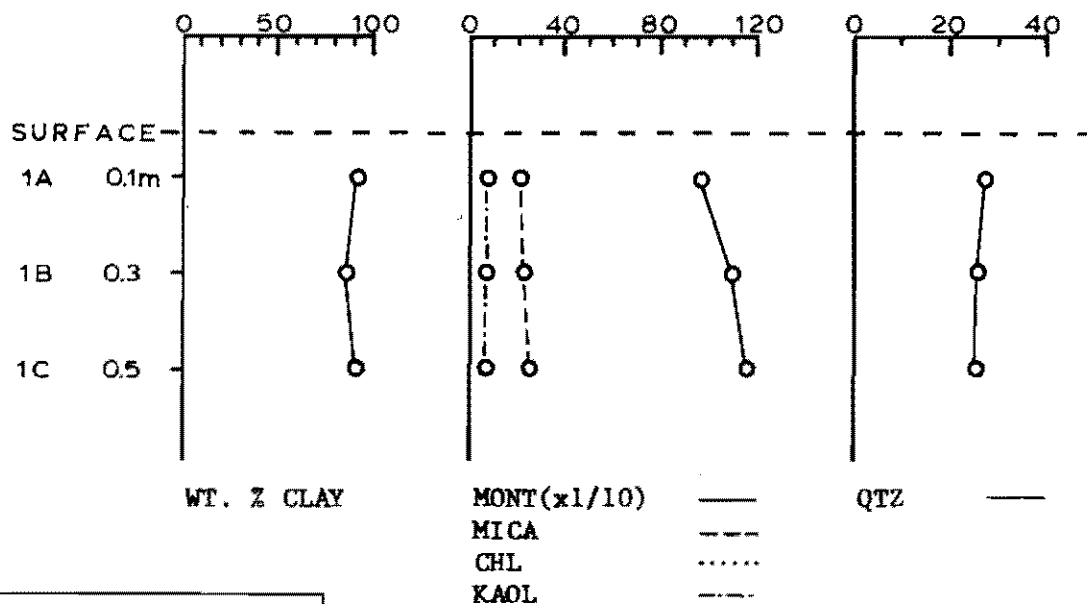
The increase in montmorillonite from the base to the top of the unit could be caused by a fining upwards of the sediment at the time of deposition. However, the sand-silt-clay ratios remain relatively constant. The grain size analysis for samples taken from the surface inwards exhibit an unusual distribution. It would be expected that the sediment should coarsen at the surface due to differential erosion, but the sand-silt-clay ratios remain relatively constant. Probably the ratios indicate vertical and lateral variation in an otherwise homogeneous appearing unit. Although the small number of samples analyzed makes interpretation uncertain, one observation can be considered. Montmorillonite decreases and mica and quartz persist approaching the surface on the same stratigraphic level. The decrease in montmorillonite is only 15 percent, but may be the result of a decrease in crystallinity due to surface expansion and contraction during weathering. This would account for the observed lower x-ray intensity.

Fig. 14. Mineralogy of the clay-size fraction of the Sentinel Butte Formation "blue bed" marker unit. (A) Mineralogy of a vertical section through the bed. Distances at the extreme left are measured from the Bullion Creek-Sentinel Butte contact. (B) Mineralogy of a section taken perpendicular to the plane of the outcrop surface. Samples were taken at the South Unit Theodore Roosevelt Park. Clay mineral amounts are given in integrated intensities, non-clay minerals in peak intensities.

(A)



(B)



X-ray Analysis of Selected Bulk Samples

A bulk mineral analysis was performed on one of the sites, Bear Creek, to compare the clay-size fraction to the total fraction. As expected, the clays exhibited the same general relationships (Figure 15). The intensities of the non-clay minerals increased.

Assuming that all of the montmorillonite is clay-size, the bulk sample analysis showed a relative increase in the x-ray intensities of mica and chlorite. This implies that chlorite and probably muscovite and biotite are abundant in the greater than 2 micron fraction.

Chemistry of Clay-Rich Sediments

Bulk samples from all locations were analyzed for eleven major elements using a scanning electron microprobe. The results are given in oxide percent on a water free basis in table 3. Carbon dioxide was determined by the amount of total reactive carbonate and the results given as percent CO_2 . The data obtained agrees closely with published average analysis of 277 shales primarily of eugeosynclinal origin (Wedepohl, 1969). The average SiO_2 in shale is 58.9% and the normalized average for data in this report is 58.3%. Average Al_2O_3 in shale is 16.7% and total Fe is 6.5%. This report shows normalized averages of 16.5% and 6.4%, respectively. The only large deviations from the published averages are found in MgO and CaO . The average shale has 2.6% MgO and 2.2% CaO . Data given here shows 4.0% and 3.8%, respectively, probably resulting from the high calcite and montmorillonite contents of these sediments.

The chemistry of the Bullion Creek and Sentinel Butte Formations is generally similar as suggested by their similar clay mineralogy.

Fig. 15. Bulk sample mineralogy at Bear Creek. Clay mineral amounts are given in integrated intensities, non-clay minerals in peak intensities.

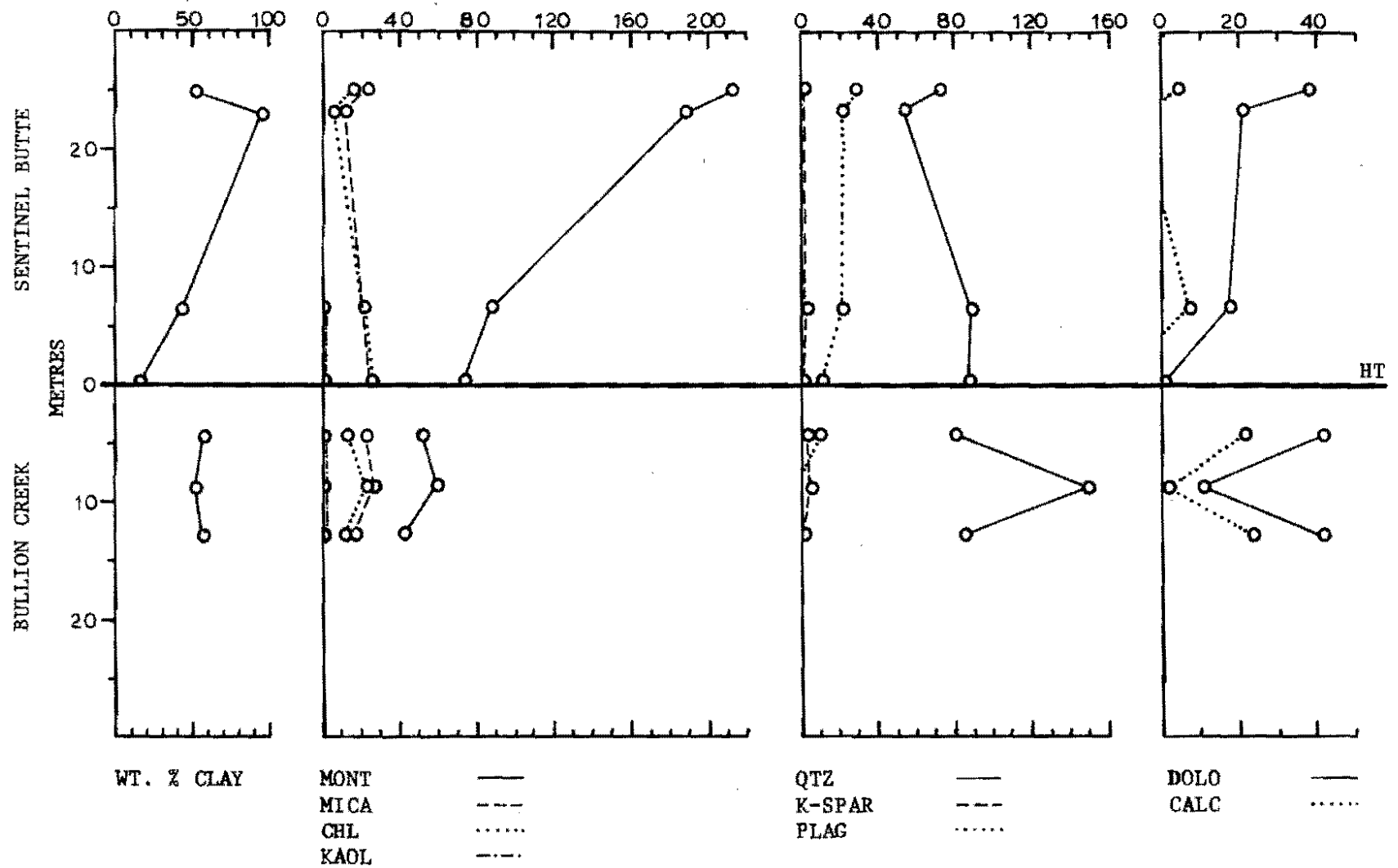


TABLE 3

CHEMICAL ANALYSES

	Bc-SB 2	Bc-SB 3	Bc-SB 4	Bc-TR 1	Bc-TR 2	Bc-TR 3	SR-SB 1	SR-SB 2	SR-SB 3	SR-SB 4	SR-SB 5	SR-TR 1
SiO ₂	59.7%	59.5%	58.1%	52.5%	67.9%	53.5%	56.5%	63.3%	62.3%	64.9%	61.6%	67.4%
Al ₂ O ₃	17.2	16.6	15.9	14.1	17.8	14.7	16.7	21.4	19.4	18.8	18.8	16.6
Fe ₂ O ₃	8.0	5.8	6.2	5.1	6.6	5.0	9.3	7.9	8.0	9.1	8.7	5.0
MgO	4.3	4.3	5.2	5.3	3.0	5.2	4.1	3.9	4.0	3.2	3.3	5.3
CaO	4.4	2.7	4.7	11.3	0.6	11.5	5.6	1.0	1.0	0.4	0.4	2.8
Na ₂ O	2.3	2.5	1.9	1.3	1.1	0.7	2.0	1.6	1.7	1.7	1.9	1.1
K ₂ O	3.0	1.4	2.2	2.9	3.5	3.1	2.6	3.8	3.7	3.3	3.4	4.1
TiO ₂	0.8	0.5	0.7	0.6	0.9	0.5	0.9	1.0	1.0	1.0	0.9	0.6
P ₂ O ₅	0.1	0.1	0.2	0.3	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.1
MnO	0.1	0.1	0.1	0.2	0.0	0.1	0.2	0.3	0.1	0.0	0.1	0.0
SO ₃	0.4	1.0	0.8	0.9	0.6	0.4	0.5	0.4	0.6	0.2	0.4	1.1
CO ₂	<u>4.9</u>	<u>3.1</u>	<u>5.2</u>	<u>10.7</u>	<u>1.9</u>	<u>11.8</u>	<u>6.2</u>	<u>2.5</u>	<u>2.4</u>	<u>1.5</u>	<u>1.5</u>	<u>4.6</u>
Total	105.2	97.6	101.2	105.2	104.1	106.6	104.8	107.2	104.4	104.2	101.1	108.7
H ₂ O ⁻	1.7	3.6	2.7	1.3	1.5	1.4	1.8	1.8	2.1	2.6	2.7	1.4
L.O.I.	10.9	11.7	12.0	16.1	7.7	17.0	11.8	8.9	9.1	8.7	8.4	9.8

TABLE 3--continued

	SR-TR 2	SR-TR 3	SR-TR 4	SR-TR 5	BT-SB 1	BT-SB 2	BT-SB 3	BT-SB 4	BT-SB 5	BT-TR 1	BT-TR 2	BT-TR 2	BT-TR 4
SiO ₂	62.0%	56.8%	56.7%	57.2%	56.2%	57.5%	62.5%	61.9%	62.4%	74.6%	53.2%	66.9%	64.0%
Al ₂ O ₃	16.9	15.7	14.7	17.6	17.3	17.1	17.8	17.7	17.1	15.1	15.7	21.0	17.3
Fe ₂ O ₃	5.0	5.5	5.7	6.5	7.2	8.8	6.5	8.3	7.3	3.8	4.5	7.7	6.0
MgO	5.6	5.0	4.0	3.9	3.2	4.0	4.5	3.8	5.0	1.9	5.3	3.2	5.1
CaO	5.3	8.7	6.9	3.7	2.4	4.1	4.0	1.1	2.0	0.4	10.4	0.5	4.1
Na ₂ O	1.4	0.9	1.8	1.3	1.4	1.3	1.5	1.7	1.5	1.1	1.0	1.0	0.8
K ₂ O	4.0	3.1	2.3	2.8	2.8	2.7	3.0	3.4	3.7	2.6	2.7	3.7	3.9
TiO ₂	0.7	0.6	0.8	0.8	0.7	0.9	1.0	0.8	0.8	0.8	0.6	1.1	0.8
P ₂ O ₅	0.2	0.1	0.3	0.2	0.2	0.1	0.2	0.2	0.1	0.2	0.1	0.2	0.2
MnO	0.2	0.0	0.2	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0
SO ₃	1.7	0.5	0.9	0.8	2.1	0.4	0.5	0.6	0.6	0.8	0.5	0.6	0.5
CO ₂	<u>6.8</u>	<u>9.5</u>	<u>7.2</u>	<u>4.3</u>	<u>2.9</u>	<u>5.5</u>	<u>4.9</u>	<u>2.8</u>	<u>4.0</u>	<u>0.1</u>	<u>11.8</u>	<u>1.4</u>	<u>6.3</u>
Total	109.8	106.4	101.5	99.1	96.4	102.5	106.4	102.4	104.6	101.4	105.8	107.3	109.0
H ₂ O ⁺	1.4	1.7	0.6	1.8	3.8	2.6	2.8	2.8	2.4	1.5	1.1	1.9	1.2
L.O.I.	11.6	15.4	11.8	10.1	11.6	12.6	12.2	10.4	9.7	5.1	16.4	8.0	10.9

There are a few interesting consistent differences. The Sentinel Butte has a higher total iron content than the Bullion Creek ranging from 6.2-9.3% and averaging 7.8% total iron expressed as Fe_2O_3 . The Bullion Creek ranges 3.8-7.7% and averages 5.5%. Sodium has a similar distribution. The Sentinel Butte sodium content ranges 1.3-2.5% and averages 1.8% Na_2O . The Bullion Creek ranges 0.7-1.8% and averages 1.1%. A plot of iron versus sodium shows a two field distribution (Figure 16). Almost all of the Sentinel Butte samples contain greater than 6.5% iron and greater than 1.4% sodium. Almost all the Bullion Creek samples plot less than these amounts.

Calcium in the two formations is largely present in calcite and dolomite. A plot of calcium versus carbon dioxide is shown in Figure 17. Some of the calcium is present in gypsum which was observed in minor amounts in outcrops. Potassium occurs in the mica group clay minerals and is shown plotted against the relative amount of mica in Figure 18. Iron is plotted against the relative amount of chlorite in Figure 19, but shows no distinct relationship similar to potassium and mica group clays. The points on the graph are widely scattered and do not fall on a general trend line. This indicates there is excess iron tied up in other minerals, probably disseminated sulfides and concretions. The greater iron contents in the Sentinel Butte Formation suggests a larger amount of iron associated with minerals other than chlorite.

In summary, the chemistry of the claystones of the Bullion Creek and Sentinel Butte Formations is comparable to other shales. There is a greater amount of sodium and total iron in the Sentinel Butte Formation. Calcium is tied up as carbonate and potassium is

Fig. 16. Percent total iron, expressed as Fe_2O_3 , plotted against percent Na_2O for all analyzed samples.

Fig. 17. Percent CO_2 plotted against percent CaO for all analyzed samples. Reference lines are shown for stoichiometric calcite and dolomite.

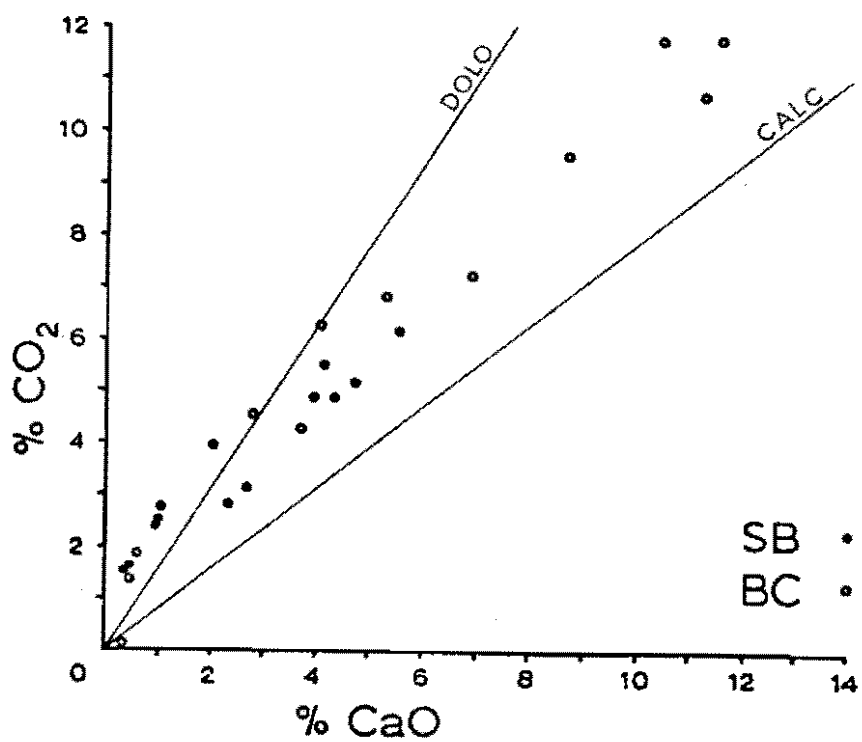
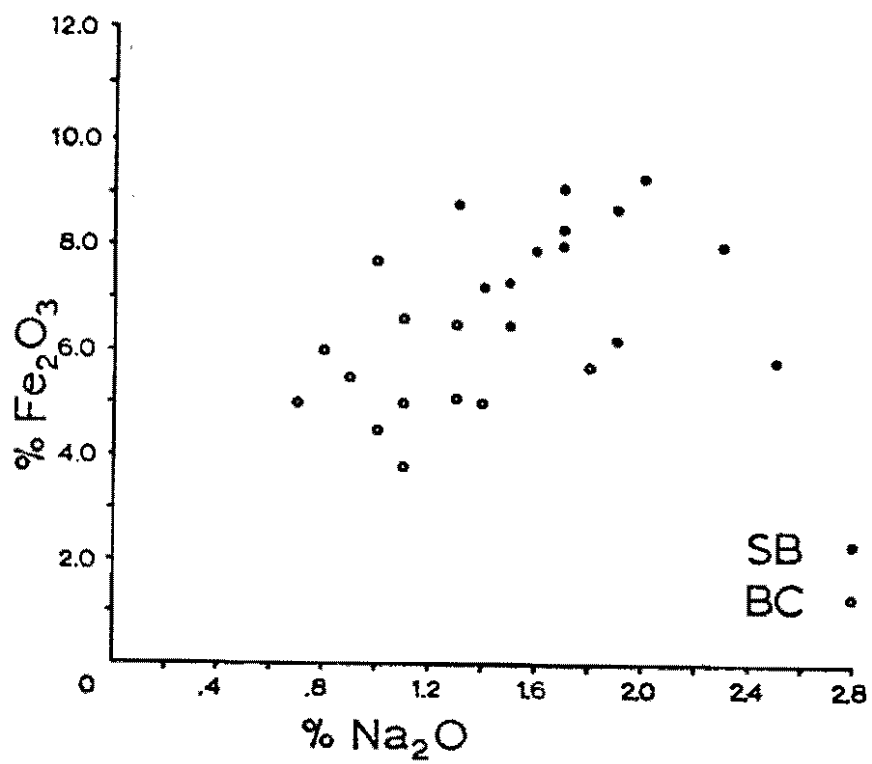
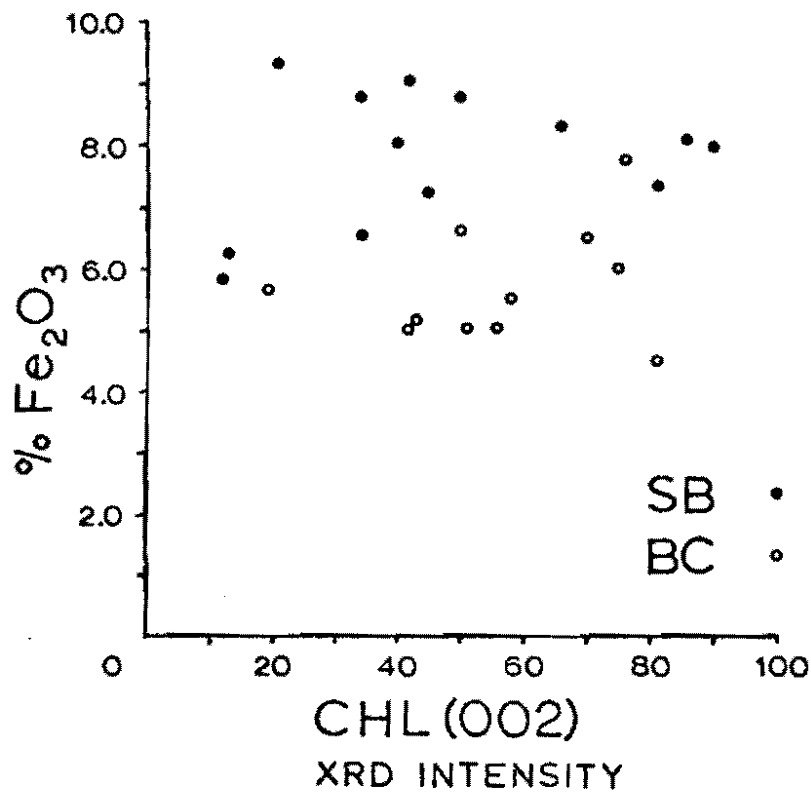
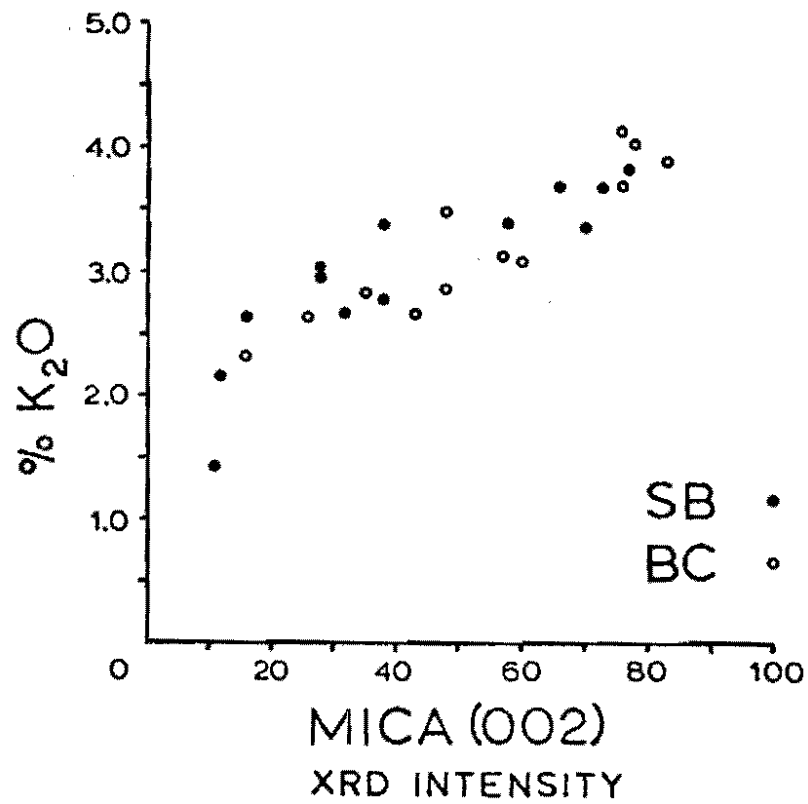


Fig. 18. Percent K_2O plotted against integrated x-ray diffraction intensity of mica group clay minerals for all analyzed samples.

Fig. 19. Percent total iron, expressed as Fe_2O_3 , plotted against integrated x-ray diffraction intensity of clay-size chlorite.



associated with the mica group clays. While some iron is associated with chlorite, there is an excess which is probably derived from sulfides and concretions.

ORIGIN OF THE CLAY MINERALS

The source and mode of deposition of the Bullion Creek Formation and Sentinel Butte Formation sediments have been interpreted by Royse (1970a). The origins of the clay minerals in these sediments has not been studied comprehensively. The highly montmorillonitic or "bentonitic" units have been speculated to be derived from volcanic ash. The results of this investigation suggest that there may be two origins of the clay minerals contained in the Bullion Creek and Sentinel Butte Formations. Most of the clay is detrital, but some is believed to be diagenetic.

Detrital Origin

The interpretation of a detrital origin of the Bullion Creek and Sentinel Butte clay minerals is based on evidence of the stability of clay minerals and the composition of the postulated source rocks to the west and northwest.

Weaver (1958) states that most clay minerals in sediments are detrital and are not generally strongly modified by their depositional environment. Furthermore, no particular clay mineral is restricted to a particular environment. Many processes that alter existing clay minerals or those that result in the formation of authigenic clay minerals have probably not occurred to any extent in the Bullion Creek and Sentinel Butte Formations. Metamorphic processes which can induce structural changes or extreme leaching conditions to strip away cations have

not taken place. Seawater can provide excess Na, Mg, and K to convert some clays to other varieties, but all of the rocks immediately older and all sediments younger than the Bullion Creek and Sentinel Butte are considered to be non-marine (Carlson and Anderson, 1966). Certain post-depositional chemical conditions preserve clay minerals. The sediments under investigation here are calcareous to a varying degree. Carbonates, especially those containing a Ca cation, tend to inhibit the breakdown or alteration of clay minerals (Grim, 1968, p. 518).

Another important consideration in establishing a detrital origin of the Bullion Creek and Sentinel Butte clays is the mineralogy of the source rocks. The source area for the Bullion Creek sediment is to the west. The source is to the west and northwest for the Sentinel Butte (Royse, 1970a). Extensive outcrops of Cretaceous shales exist to the west of the Williston Basin and these rocks contain large amounts of montmorillonite (Grim, 1968, p. 553). Several analyses of Upper Cretaceous shales in southern Alberta, Canada, have been published. Lerbekmo (1963) found the non-marine Belly River Formation to have a considerable proportion of mixed-layer montmorillonite and mica. Byrne and Farvolden (1959) in their study of the Bearpaw Formation shales report in order of abundance, montmorillonite, illite, and chlorite. The clay mineralogy of the postulated source areas is similar to the clay mineralogy of the Bullion Creek and Sentinel Butte Formations of this study.

The clay minerals of the Bullion Creek and Sentinel Butte Formations are largely detrital. This is indicated by the relatively stability of clay minerals, the post-depositional environment of the sediments, and the type of clays in the source area sediments.

Some of the clays may be degraded in place, however. Weaver (1958) points out that strong evidence indicates clays are degraded in fluvial and subaerial continental environments. This could explain the varying degrees of crystallinity in the clays described earlier in this report. The corroded feldspar crystal in Figure 8 may also indicate in situ alteration of aluminum silicates to clay minerals.

Diagenetic Origin

A diagenetic origin for some of the montmorillonite and kaolinite in the Bullion Creek and Sentinel Butte Formations is likely. Montmorillonite can be an alteration product of volcanic ash. A small number of glass shards were observed in the greater than 2 micron fraction. Clark (1966) and Forsman and Karner (1975) reported volcanic glass shards in the "blue bed" of the Sentinel Butte Formation. It is assumed that the ash originated from extrusive igneous activity to the west during the Laramide orogeny.

Grim (1968) suggests that the presence of a suite of non-clay minerals such as feldspars, biotite, hornblende, etc., are characteristic of igneous material, and may provide evidence for origin of montmorillonite from volcanic ash. He states further that montmorillonite possibly develops contemporaneously with fluvial transportation and sedimentation of the ash into water. These conditions typify the postulated paleoenvironment of the Bullion Creek and Sentinel Butte Formations.

The amount of diagenetic montmorillonite is unknown and would be difficult to determine. However, alteration of volcanic ash could account for the occurrence of occasional samples with very high montmorillonite contents. These samples contain relatively low abundances

of the mica group and chlorite. The low abundances may result from dilution of the total clay mineral system by montmorillonite. The alteration of volcanic ash produces excess amorphous silica which may form cristobalite or allophane. These minerals were not detected in the clay fraction samples or in the bulk samples. If this diagenetic process occurred in these sediments, the excess silica generated may have played a part in the formation of the silicified wood that is commonly found in these rocks.

Some of the kaolinite may be diagenetic. Acidic conditions produced by a lignite coupled with locally high leaching, promotes the removal of K, Na, Mg, and Ca cations from clay structures. This favors the development of kaolinite. Kaolinite tends to increase in amount when associated with a lignite in the Bullion Creek and Sentinel Butte Formations. However, the amount of the clay is small in these sediments and the mineral could have a detrital origin. Well-crystallized flakes of kaolinite were not positively identified in scanning electron microscopy.

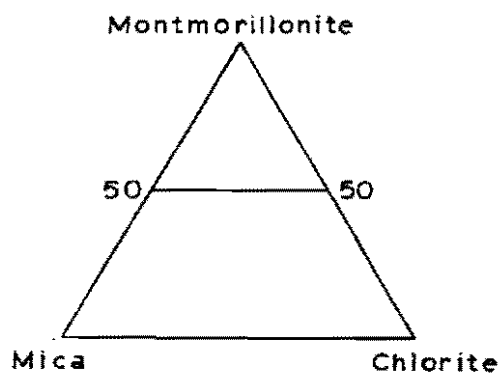
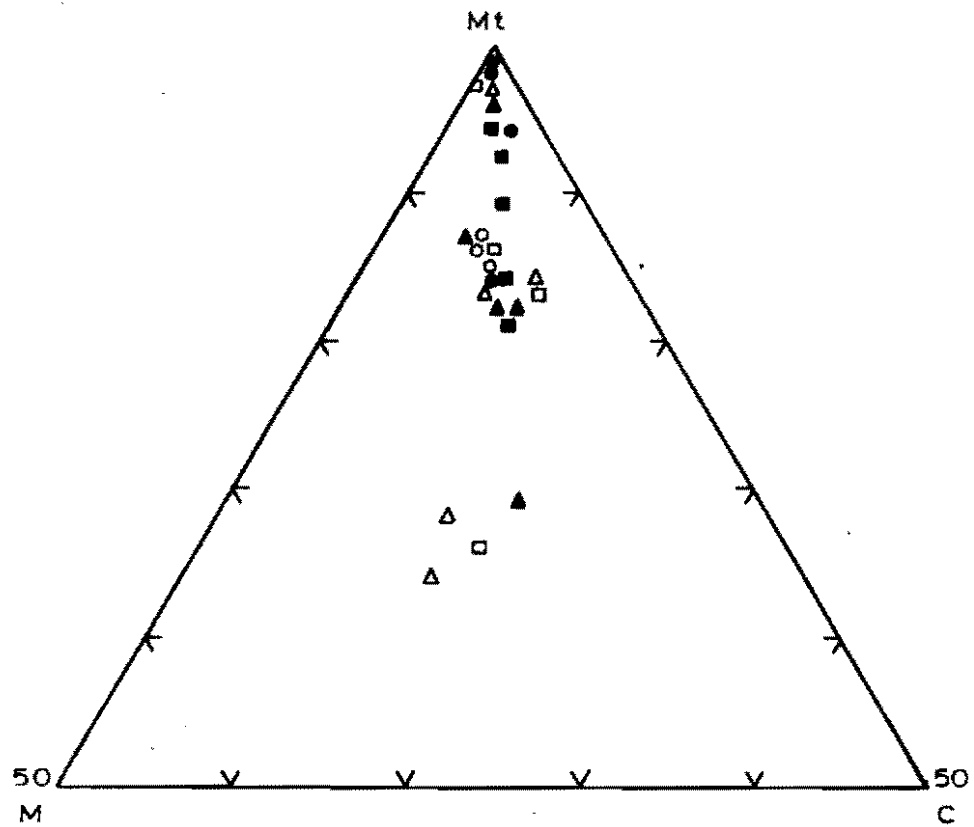
Summary of Clay Mineral Relationships and Origins

It appears there are two origins for the clay minerals in the upper Paleocene rocks of North Dakota. Detrital material from crystalline rocks and pre-existing highly montmorillonite shales to the west and northwest contributed the bulk of the clay minerals in the Bullion Creek and Sentinel Butte Formations. This conclusion is based on the stability of clay minerals, the composition of the source rocks to the west, and the post-depositional history of the sediments. Volcanic ash from tectonic activity to the west may have provided material for

the diagenetic formation of some of the montmorillonite. Diagenetic kaolinite may occur in association with lignite.

A semi-quantitative analysis of the Bullion Creek and Sentinel Butte clay minerals shows that the same types of clay minerals and same relative amounts of each occur in both formations. A triangular plot of the three major clay minerals that illustrates this is shown in Figure 20. There is no observable consistent variation of the clay minerals within each formation or between the two formations. The Bullion Creek and Sentinel Butte contact in Billings County cannot be distinguished on the basis of clay mineralogy.

Fig. 20. Triangular plot of the major clay minerals of the Bullion Creek and Sentinel Butte Formations at Bear Creek, South Unit Theodore Roosevelt Park, and Blacktail Creek.



	BC	SB
Bear Creek	○	●
So. Theo. Roosevelt Pk.	□	■
Blacktail Creek	△	▲

DISCUSSION

The origin of the abrupt surface color change at the Bullion Creek and Sentinel Butte Formations contact has been a subject of speculation for some time. Change in clay mineralogy from one formation to the other has been suggested by Jacob (1975). The results of this study show that variation in clay mineralogy is not responsible for the color effects since both formations have very similar clay mineral compositions. The chemical data of this study suggest that higher iron content in the Sentinel Butte Formation is a major cause of the color difference. The key to the coloring of the formations may be a pre-conditioning of the sediments by post-depositional factors affecting the chemistry and distribution of iron. Since the clay mineralogy of both formations is similar, it is assumed that the chemistry of incoming sediment was similar at the time of deposition. The depositional environment in both formations is fluvial with periodic swamps. However, slightly different post-depositional environments may account for the larger amount of iron in the Sentinel Butte.

The color and iron content suggest that the Bullion Creek swamps may have been seasonal and well drained, while the Sentinel Butte swamps may have been non-seasonal and poorly drained. The Bullion Creek could have had intermittent streams and oxidizing conditions at least part of the time. Iron would have been oxidized into particulate form and partly eroded away. Sodium would tend to have been dissolved and removed in such an environment. The Sentinel Butte could have had

steady streams and probably reducing conditions. Iron would have remained in a disseminated form, possibly as sulfides. Some of the iron could have been tied up in a chelated form with organic matter. Sodium would have tended to remain in place under the poor drainage conditions. The consequence of this speculated pre-conditioning for color may be expressed in the weathering phenomenon observed today. The darker surface color of the Sentinel Butte Formation would be due to a greater amount of iron, probably in disseminated form, than that found in the lighter colored Bullion Creek Formation.

There may be some indications that the Bullion Creek and Sentinel Butte Formations should be considered as one major unit with two subdivisions. The depositional environments of the two formations are nearly the same. They both contain fluvial overbank and floodplain sediments with numerous lignite beds. They both contain essentially the same clay minerals and clay mineral relationships. The bulk chemistry of the clay-rich sediments are nearly the same. There is a slight difference in sedimentary petrography. According to Jacob (1975), the Bullion Creek contains more sedimentary rock fragments and the Sentinel Butte has more volcanic and metamorphic rock fragments. The increase in crystalline and volcanic rock fragments in the Sentinel Butte sediments may indicate increasing exposure of basement rock and increased volcanic activity to the west during Sentinel Butte time. This agrees with Royse's (1970a) contention that the paleoslope to the west increased during Sentinel Butte time as a result of tectonism. However, the clay minerals do not indicate increased volcanic activity expressed as increased volcanic ash and subsequent increased montmorillonite. The

clay mineral relationships imply that volcanic activity was relatively constant throughout the Paleocene. It may be that, as a unit, the Bullion Creek and Sentinel Butte Formations represent a single depositional episode during the Paleocene. The unit reflects an increasing exposure of crystalline rocks to weathering to the west and a relatively constant influx of eolian volcanic material. The color difference between the two formations may be the result of iron distribution that may have been produced by differing post-depositional environments. Further geological and geochemical work in the non-clay units of both formations is needed to properly understand these two formations.

APPENDICES

APPENDIX A
KEY TO ABBREVIATIONS

LIST OF ABBREVIATIONS

Å	angstrom
Bc	Bear Creek section
BC	Bullion Creek Formation
BT	Blacktail Creek section
calc	calcite
chl	chlorite
d	spacing between successive identical planes in a crystal structure
dolo	dolomite
feld	feldspar, plagioclase and potassium
glycol	ethylene glycol
HT	HT Butte bed
K	potassium feldspar
kaol	kaolinite
mica	muscovite, biotite, illite
mont	montmorillonite
P	plagioclase feldspar
qtz	quartz
SB	Sentinel Butte Formation
S.Pos	sample position
SR	South Unit, Theodore Roosevelt Park section
std dev	standard deviation
TR	Tongue River (Bullion Creek Formation)
untr	untreated
var	variance
XRD	x-ray diffraction

APPENDIX B

MEASURED STRATIGRAPHIC SECTIONS OF THE SAMPLE SITES

Section at Bear Creek
SW $\frac{1}{4}$, Sec. 7, T137N, R101W
Billings Co., N.D.

<u>Lithology</u>	<u>Thickness</u>	<u>Sample</u>	<u>Distance to contact</u>
Sentinel Butte Formation:			
Claystone; sandy	0.28 m	Bc-SB-4	24.9 m
Sandstone	1.60		
Claystone; sandy	0.38	Bc-SB-3	22.9
Lignite	0.13		
Claystone; sandy, gypsum layer near bottom	0.48		
Sandstone; scattered concretion layers, few lignite stringers	13.11		
Claystone	0.05		
Lignite; sandy	0.23		
Sandstone	1.83		
Claystone; concretion layer at top	0.71	Bc-SB-2	6.5
Sandstone; interbedded with clay-rich layers, FeO banding	3.66		
Sandstone; fine, massive, thin lignite stringers near top	1.27		
Sandstone; fine, clayey	0.89		
Claystone; massive, thin con- cretion layer at top	0.38	Bc-SB-1	0.3
Bullion Creek Formation:			
HT lignite	1.14		
Sandstone; fine, interbedded with silts	3.96		
Lignite	0.08		

<u>Lithology</u>	<u>Thickness</u>	<u>Sample</u>	<u>Distance to contact</u>
Bullion Creek Formation--continued			
Claystone; sandy	0.23 m	Bc-TR-1	4.2 m
Sandstone and siltstone; interbedded	4.27		
Claystone; sandy	0.28	Bc-TR-2	8.7
Sandstone and siltstone; interbedded, lignite stringer 1.8 m from bottom	3.96		
Claystone; sandy	0.25	Bc-TR-3	12.9
Sandstone; fine	0.76		
Lignite	0.30		

Section at South Unit Theodore Roosevelt Park
 Sentinel Butte Formation--SE $\frac{1}{4}$, Sec. 19, T140N, R101W
 Bullion Creek Formation---SE $\frac{1}{4}$, Sec. 1, T140N, R102W

<u>Lithology</u>	<u>Thickness</u>	<u>Sample</u>	<u>Distance to contact</u>
Sentinel Butte Formation:			
Lignite	0.23 m		
Claystone; concretion layer at bottom	1.53	SR-SB-5	22.2 m
Sandstone; fine	1.35		
Lignite	0.36		
Claystone; "blue bed," concretion layer at bottom	1.63	SR-SB-4	18.7
Lignite	0.05		
Claystone; massive, concretion layer at bottom	0.25		
Sandstone; fine, massive, concretion layers at top and bottom	1.35		
Claystone; laminated, concretion layer at bottom, snail fossils	0.36	SR-SB-3	16.3
Sandstone, siltstone, and claystone; interbedded, FeO banding	1.40		
Claystone	0.30		
Claystone; laminated, concretion layer at top, thin lignite stringer 0.30 m from bottom	1.22	SR-SB-2	13.8
Lignite	0.38		
Sandstone and siltstone; interbedded, FeO banding, scattered concretions	9.45		
Claystone; FeO staining at top and bottom	0.30	SR-SB-1	3.2
Sandstone; fine, reddish color	3.05		

<u>Lithology</u>	<u>Thickness</u>	<u>Sample</u>	<u>Distance to contact</u>
Bullion Creek Formation:			
HT "scoria"	2.74 m		
Siltstone; sandy, heavy slope wash	0.91		
Claystone	0.46	SR-TR-1	1.2 m
Sandstone; silty	1.17		
Claystone; sandy	1.52	SR-TR-2	3.7
Sandstone; interbedded with siltstone and thin claystone	8.53		
Lignite	0.08		
Claystone	0.36	SR-TR-3	12.8
Sandstone	1.75		
Sandstone; massive, resistant	1.12		
Claystone	0.56	SR-TR-4	25.3
Sandstone; fine	2.97		
Sandstone; resistant	0.28		
Sandstone and siltstone; interbedded	3.35		
Sandstone; massive	1.83		
Sandstone and siltstone; interbedded	3.05		
Claystone	0.91	SR-TR-5	52.0
Siltstone	2.13		

Section at Blacktail Creek
NE $\frac{1}{4}$, Sec. 7, T143N, R101W
Billings Co., N.D.

<u>Lithology</u>	<u>Thickness</u>	<u>Sample</u>	<u>Distance to contact</u>
Sentinel Butte Formation:			
Lignite	0.30 m		
Claystone; massive, organic-rich	0.61	BT-SB-5	12.3 m
Sandstone; very fine	1.22		
Claystone; FeO banding	0.30		
Sandstone; massive, FeO banding	1.52		
Claystone; FeO banding	0.25		
Sandstone; massive, FeO banding	1.50		
Claystone; laminated, concretion layer at top, FeO banding at top and bottom	1.22	BT-SB-4	7.0
Sandstone; fine, massive, FeO banding	2.13		
Lignite	0.05		
Claystone; organic-rich, sandy at top, Ca zone near bottom	0.69	BT-SB-3	3.5
Sandstone; fine, clayey, massive concretion layer at top, molluscs near top	3.05	BT-SB-2	0.5
Claystone; laminated, abundant gypsum	0.18	BT-SB-1	0.1
Bullion Creek Formation:			
HT lignite	0.15		
Sandstone; fine, moderately resistant	1.52		
Lignite	0.03		
Sandstone; fine	0.51		

<u>Lithology</u>	<u>Thickness</u>	<u>Sample</u>	<u>Distance to contact</u>
Bullion Creek Formation--continued			
Claystone; massive, thin lignite at top	0.41 m	BT-TR-1	2.3 m
Siltstone	0.91		
Concretion layer	0.08		
Sandstone; silty	1.52		
Claystone; sandy, laminated, 0.13 m thick lignite stringers near top and center	1.50	BT-TR-2	6.2
Sandstone and siltstone; interbedded	6.40		
Claystone; massive, concretion	0.76	BT-TR-3	13.5
Sandstone and siltstone; interbedded	4.27		
Claystone; sandy	0.90	BT-TR-4	18.2

APPENDIX C

X-RAY INTENSITIES OF CLAY-FRACTION MINERALS

TABLE 4

X-RAY INTENSITIES OF CLAY-FRACTION MINERALS

SAMPLE	MONTMORILLONITE 001 *				MICA GROUP 001 *			CHLORITE 002 *		KAOL	QTZ	FELD		CALC	DOLO
	untr	d	glycol	d	untr	glycol	heat**	untr	glycol	002	101	K	P	104	104
Bc-SB-4	1300	13.0	1490	17.2	11	12	284	13	13	-	12	-	2	-	2
Bc-SB-3	1316	11.9	1732	17.0	5	11	334	11	12	-	10	-	-	-	2
Bc-SB-2	1050	12.2	1070	17.2	35	28	211	49	40	4	21	-	3	-	3
Bc-SB-1	435	11.9	403	17.2	40	38	122	41	38	3	35	-	3	-	2
Bc-TR-1	786	13.1	627	17.0	43	48	188	38	43	7	26	-	-	6	5
Bc-TR-2	647	11.7	592	16.8	53	48	204	59	50	4	17	-	3	-	3
Bc-TR-3	889	12.2	689	17.1	76	60	225	46	42	8	55	-	-	7	7
SR-SB-5	554	12.0	441	16.8	56	38	179	53	50	8	33	2	3	-	-
SR-SB-4	675	12.2	776	16.9	70	70	212	37	42	5	28	-	-	-	-
SR-SB-3	616	12.2	778	16.7	96	73	201	75	86	7	38	2	2	-	-
SR-SB-2	464	12.0	386	17.2	78	77	142	90	90	8	41	3	2	-	2
SR-SB-1	749	11.5	954	17.1	9	16	218	18	21	2	13	-	-	-	2
SR-TR-1	350	14.0	288	17.2	90	76	153	60	56	5	54	-	2	-	8
SR-TR-2	342	12.9	236	17.1	81	78	133	53	51	5	43	2	-	-	4
SR-TR-3	840	12.5	650	17.1	53	57	216	61	58	11	31	-	-	6	6
SR-TR-4	918	13.1	1099	17.1	12	16	252	20	19	2	14	-	-	-	-
SR-TR-5	662	13.3	605	17.0	50	35	154	73	70	9	27	3	3	-	4
BT-SB-5	800	13.6	644	17.0	62	66	182	74	81	-	35	2	4	-	5
BT-SB-4	730	12.1	676	17.0	70	58	175	66	66	2	48	3	5	-	1
BT-SB-3	819	12.1	774	17.0	36	28	189	38	34	4	28	2	4	-	4
BT-SB-2	840	12.1	1150	17.0	32	32	205	36	34	4	20	-	-	-	-
BT-SB-1	759	11.9	715	17.0	48	38	174	45	45	5	32	-	-	-	2
BT-TR-1	1165	12.8	1256	17.0	?	26	218	-	-	9	22	-	-	-	-
BT-TR-2	647	14.2	637	17.1	53	43	135	59	81	3	10	-	-	5	6
BT-TR-3	905	12.2	979	17.0	74	76	264	74	76	10	13	-	-	-	-
BT-TR-4	550	13.0	322	17.0	98	83	148	83	75	6	23	-	-	2	6

TABLE 4--Continued

SAMPLE	MONTMORILLONITE 001 *				MICA GROUP 001 *			CHLORITE 002 *		KAOL	QTZ	FELD		CALC	DOLO
	untr	d	glycol	d	untr	glycol	heat**	untr	glycol	002	101	K	P	104	104
B-1 A	831	11.2	978	17.0	16	21	254	-	-	9	28	-	-	-	-
B-1 B	955	11.6	1100	17.0	20	24	241	-	-	9	26	-	-	-	-
B-1 C	912	11.7	1157	16.9	33	26	245	-	-	9	26	-	-	-	-
B-2	766	11.5	890	16.8	23	26	233	-	-	6	21	-	-	-	-
B-3	806	12.1	639	16.8	47	53	223	38	42	6	32	-	-	-	-
BULK SAMPLE***															
Bc-SB-4			213			24			16	-	75	3	30	5	39
Bc-SB-3			189			12			8	-	54	2	23	-	22
Bc-SB-2			98			23			22	1	90	4	23	8	18
Bc-SB-1			74			25			25	3	89	4	12	-	1
Bc-TR-1			52			19			13	2	81	5	11	22	42
Bc-TR-2			60			28			26	2	150	7	-	2	11
Bc-TR-3			44			17			12	2	87	3	1	24	42

*Integrated intensity

**Mica group + montmorillonite

***Glycolated pellet

APPENDIX D
SAMPLE CORRELATION COEFFICIENTS

TABLE 5

SAMPLE CORRELATION COEFFICIENTS

SENTINEL BUTTE FM			BULLION CREEK FM		ALL SAMPLES	
Variable	mean	std dev	mean	std dev	mean	std dev
1 S.POS.	10.857	8.984	-13.392	14.099	-0.335	16.775
2 MONT	856.357	394.767	665.000	315.077	768.038	366.308
3 MICA	41.721	23.021	54.008	21.643	47.392	22.819
4 CHL	46.428	25.548	51.783	24.032	48.900	24.514
5 QTZ	28.107	11.576	26.250	12.983	27.250	12.031
6 FELD	2.814	2.635	1.042	1.864	1.996	2.440
7 CALC	0.0	0.0	2.083	2.083	0.962	2.140
8 DOLO	1.714	1.528	3.917	2.762	2.731	2.413
9 KAOL	3.607	2.712	6.500	2.900	4.942	3.112

Variable	correlation	correlation	correlation
1 2	0.324	-0.084	0.265
1 3	0.065	0.328	-0.067
1 4	-0.001	-0.228	-0.164
1 5	-0.189	0.213	0.092
1 6	0.019	-0.617	0.102
1 7	0.0	0.192	-0.270
1 8	-0.197	0.185	-0.297
1 9	-0.005	-0.188	-0.413
2 3	-0.664	-0.704	-0.701
2 4	-0.679	-0.582	-0.642
2 5	-0.830	-0.606	-0.674
2 6	-0.516	-0.305	-0.302
2 7	0.0	-0.097	-0.179
2 8	0.078	-0.780	-0.433
2 9	-0.595	0.228	-0.335
3 4	0.906	0.610	0.775
3 5	0.811	0.461	0.595
3 6	0.432	-0.124	0.104
3 7	0.0	0.075	0.176
3 8	-0.205	0.524	0.309
3 9	0.517	0.138	0.419
4 5	0.842	-0.051	0.406
4 6	0.609	0.232	0.392
4 7	0.0	0.145	0.137
4 8	-0.031	0.455	0.265
4 9	0.513	0.054	0.316
5 6	0.716	0.215	0.494
5 7	0.0	-0.004	-0.041
5 8	-0.128	0.591	0.244
5 9	0.484	0.085	0.211

TABLE 5--continued

<u>Variable</u>	<u>correlation</u>	<u>correlation</u>	<u>correlation</u>
6 7	0.0	-0.453	-0.382
6 8	0.282	0.027	-0.060
6 9	0.077	0.021	-0.129
7 8	0.0	0.555	0.596
7 9	0.0	0.187	0.334
8 9	-0.497	-0.102	0.028

APPENDIX E
SAND-SILT-CLAY RATIOS

TABLE 6

SAND-SILT-CLAY RATIOS

Sample	Sand	Silt	Clay
Bc-SB-4	0.08%	46.7%	53.2%
Bc-SB-3	0.04	4.4	95.6
Bc-SB-2	0.08	55.9	44.0
Bc-SB-1	0.12	83.1	16.8
Bc-TR-1	0.08	41.9	58.0
Bc-TR-2	0.36	46.4	53.2
Bc-TR-3	0.24	40.6	59.2
SR-SB-5	0	18.0	82.0
SR-SB-4	0.40	45.0	54.0
SR-SB-3	0	21.2	78.8
SR-SB-2	0	22.4	77.6
SR-SB-1	0.04	65.6	34.4
SR-TR-1	0	20.4	79.6
SR-TR-2	0.04	60.0	40.0
SR-TR-3	0.04	35.6	64.4
SR-TR-4	0.20	77.0	22.8
SR-TR-5	0.12	48.3	51.6
BT-SB-5	0.04	28.8	71.2
BT-SB-4	0.04	22.4	77.6
BT-SB-3	0.04	29.6	70.4
BT-SB-2	0.04	31.6	68.4
BT-SB-1	0.08	14.7	85.2
BT-TR-1	0.08	56.7	43.2
BT-TR-2	0.04	68.0	32.0
BT-TR-3	0.12	28.7	71.2
BT-TR-4	0.16	21.8	78.0
B-1 A	0	8.4	91.6
B-1 B	1.16	10.8	88.0
B-1 C	0.32	8.1	91.6
B-2	0	25.2	74.8
B-3	0	9.6	90.4
BC-TR-2 A	0.64	37.8	61.6
BC-TR-2 B	0.60	37.0	62.4
BC-TR-2 C	0.72	38.9	60.4
BC-TR-2 D	0.68	37.7	61.6

APPENDIX F

SEPARATION OF THE CLAY-SIZED FRACTION FROM A BULK SAMPLE
FOR PREPARATION OF X-RAY DIFFRACTION MOUNTS

SEPARATION OF THE CLAY-SIZED FRACTION FROM A BULK SAMPLE
FOR PREPARATION OF X-RAY DIFFRACTION MOUNTS

- This procedure produces:
- a) clay slurry ($<2\mu$) for oriented mounts
 - b) dry clay ($<2\mu$) for unoriented mounts or side-loaded mounts
 - c) sand fraction ($>62\mu$)
 - d) silt fraction (>2 to $<62\mu$)
 - e) sand-silt-clay ratio of bulk sample
1. Crush and air-dry representative chips of the bulk sample (about 60 gm).
 2. Split sample by using a small splitter or other methods.
 3. Weigh out 25 gm of dry sample to the nearest 0.1 gm.
 4. Disaggregate the bulk sample completely using 500 ml distilled water in a 600 ml beaker. Place beaker in a water-filled ultrasonic vibrator, stirring occasionally, until sample is disaggregated. (optional) A 4% Calgon solution could be used if a slight ion substitution in the clays is not objectionable. The time for disaggregation varies.
 5. Stir 5 minutes with a magnetic mixer.
 6. Let the mixture stand undisturbed for 50 minutes. Withdraw 50 ml with a pipette at a depth of 4 cm. Dry this portion in a pre-weighed dish at $60-80^{\circ}\text{C}$. Weigh to 0.1 gm and multiply by 10 to get the weight of clay in the bulk sample. Scrape up and save the dry clay for unoriented or side-loaded mounts.

If the water-clay mixture flocculates, centrifuge down and re-mix with 500 ml water. Repeat if necessary. The mixture must be able to stand 50 minutes without flocculating.

7. Re-stir the original mixture with a magnetic mixer for 5 minutes and let stand for 60 seconds to settle out the sand fraction (>62 μ).
8. Pour off the silt and clay fraction, and save.
9. Save the sand for further analysis and for calculating the sand-silt-clay ratio of the bulk sample. Mix the sand with water and let it settle long enough to make sure that all the sand-size particles are down. The time required depends on the depth of the water. Pour off the suspended silt and clay that remained with the sand in step 8. Repeat until water is clear.
10. Wash the sand into an evaporating dish, remove excess water, and dry the sand. Seive through a no. 230 mesh screen to remove remaining silt. Weigh and store sand.
11. The sand-silt-clay ratio can be computed from the bulk sample weight in step 3, clay weight in step 6, and sand weight in step 10.
12. Using the slurry obtained in step 8, centrifuge the silt out of the mixture:

<u>temp.</u>	<u>time @ 750 rpm*</u>
18° C	4m 37s
20	4m 23s
22	4m 11s
24	3m 59s
26	3m 49s
28	3m 39s

*These times are for large baby food jars spun in an International Centrifuge model UV, using a no. 242 head and no. 373 cups. The baby food jars and accompanying lids must weigh approximately the

same for all four holders. Make sure that either two or four jars are in the centrifuge so that balance is maintained.

13. Pour off the clay fraction after centrifugation and store. This slurry is for oriented mounts. Save the silt, if desired for further analysis. The silt can be purified by using step 9, substituting the centrifuge for natural settling time.

If the clay fraction slurry obtained in step 12 is too "thin," it may be necessary to concentrate the slurry by centrifugation. If the bulk sample contains about 50% clay or more, only one centrifuge jar of the slurry is needed for oriented mounts. If the bulk sample has a low clay content, it is necessary to centrifuge the silt out of all the mixture obtained in step 8 and concentrate.

APPENDIX G

PREPARATION OF ORIENTED CLAY-FRACTION SAMPLES ON
PORCELAIN TILES

PREPARATION OF ORIENTED CLAY-FRACTION SAMPLES ON
PORCELAIN TILES

1. The sample tiles are made from 50 X 50 X 6 mm semi-porous porcelain (Coors no. 75001) that are sawed in half. The faces are trued on both sides using a thin section grinder. In order to fit into the bottom-loaded sample holder of the Philips diffractometer and still use the radiation shield, about 2 mm must be ground off the end of each tile. This can be done on a bench grinder.
2. A dry tile is placed on a suction plate that is connected to a vacuum pump. The suction plate can be constructed from a large rubber stopper (larger than the tile). Cut a rectangular opening smaller than the tile on one side and taper the hole down to a round opening on the other side that will accept a stopper with a short glass tube. This is placed on a vacuum erlenmeyer flask by using another stopper. The apparatus can be supported by a ring stand.
3. With a strong vacuum on the tile, the clay slurry is placed on the tile with an eye dropper. Slurries with a high concentration of clay need 2 to 3 dropperfuls on the tile. Lower concentrations or "thin" slurries may need 5 to 6. It is very important to try and cover the entire tile with the first eye dropperful. The water will soak in fairly fast and the objective is to obtain an even coating over the entire surface of the tile. The thickness of the deposited clay should be enough to mask the diffraction pattern of the porcelain tile.

4. The tile is left under vacuum until the surface no longer appears "wet." The time will vary, but 15 minutes is about maximum. The tile is then placed on a paper towel and dried at least overnight.
5. The sample can be x-rayed untreated, then glycolated, then heated to 600° C with little danger of peeling. If the sample does peel, leave it under vacuum a while longer the next time.
6. The tiles can be cleaned by soaking in water. If they are really dirty, they can be reground on the thin section grinder.
7. Glycolation of the samples can be done in an ethylene glycol filled dessicator. It will take at least 24 hours, but once glycolated the sample will remain that way for several days at room conditions.
8. Heating the sample to 600° C can be done in a muffle furnace. The furnace must be cold when starting the procedure. Place the tiles on the rack, turn on the furnace, and let it heat to a pre-set temperature of 600° C. Let the samples remain at that temperature for one hour. Turn off the furnace, open the door, and let the samples cool off in the furnace. This will prevent cracking and peeling of the sample.

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