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# Preliminary Investigation of the Geologic Setting and Chemical Composition of the Pierre Shale Great Plains Region

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 390



# Preliminary Investigation of the Geologic Setting and Chemical Composition of the Pierre Shale Great Plains Region

By HARRY A. TOURTELOT

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*A contribution to the geochemistry  
of sedimentary processes*



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# PRELIMINARY INVESTIGATION OF THE GEOLOGIC SETTING AND CHEMICAL COMPOSITION OF THE PIERRE SHALE, GREAT PLAINS REGION

By HARRY A. TOURTELOT

## ABSTRACT

The chemical and mineralogical composition and some physical properties of the Pierre shale and equivalent rocks are being investigated to shed light on the geologic and chemical processes involved in the accumulation of shale, the predominant sedimentary rock. This report presents data on samples from widely separated localities in Montana, Wyoming, and South Dakota to measure the range of variation in chemical and mineralogical composition and related characteristics. The rocks studied are clay sediments, generally free of coarse material and also low in chemical precipitates and biogenic material.

Standard rock analyses for a set of 22 basic samples are given, together with chemical and semiquantitative spectrographic analyses for minor elements, size analyses, X-ray mineralogical determinations, and measurement of slurry pH, liquid limit, and plastic limit. Semiquantitative spectrographic analyses of a set of 45 supplemental samples also are included. The samples were selected to obtain data on composition by stratigraphic zone and geographic region.

The samples contain from 35 to 90 percent material finer than about 4 microns and average 70 percent. Samples from the eastern part of the area are finer grained than those from the western part.

The clay fraction consists primarily of mixed-layered illite-montmorillonite in amounts ranging from about 40 to 75 percent. Montmorillonite ranges in amount from 10 to 45 percent but was absent from one sample. Illite, chlorite, and kaolinite make up the remainder of the clay fraction. Montmorillonite is present in larger amounts in samples from the eastern part of the area. In the nonclay fraction, quartz ranges from 8 to 27 percent; one sample contains 18 percent beta cristobalite. Feldspar is less than 5 percent in most samples; and gypsum, pyrite, dolomite, siderite, and clinoptilolite (a calcium-sodium zeolite) are minor constituents in a few samples. Calcite is a major constituent in two marlstone samples, and a minor constituent in other samples.

The average composition and standard deviation (indicated by parentheses) of 17 of the 22 samples, excluding the two marlstone samples, the two weathering products, and one sample very rich in organic matter is: SiO<sub>2</sub>, 59.68 (3.49); Al<sub>2</sub>O<sub>3</sub>, 15.40 (1.52); Fe<sub>2</sub>O<sub>3</sub>, 4.56 (1.09); FeO, 0.96 (0.64); MgO, 2.11 (0.47); CaO, 1.52 (1.12); Na<sub>2</sub>O, 1.09 (0.42); K<sub>2</sub>O, 2.49 (0.26); H<sub>2</sub>O<sup>-</sup>, 3.73 (1.09); H<sub>2</sub>O<sup>+</sup>, 4.77 (0.83); TiO<sub>2</sub>, 0.60 (0.05); CO<sub>2</sub> (determined in only 16 samples), 0.87 (1.35); P<sub>2</sub>O<sub>5</sub>, 0.15 (0.04); acid-soluble S as SO<sub>3</sub>, 0.85 (0.95); insoluble S as S (determined in only 14 samples), 0.21 (0.17); Cl (determined in only 11 samples), 0.01; F, 0.07; MnO, 0.19 (0.39); BaO, 0.08. The average chemical composition of the analyzed sam-

ples agrees fairly closely with the mineralogical composition.

The suitability of surface samples for this kind of study was investigated by sampling two weathering sequences that showed progressive change from nearly fresh shale to residual soil-like weathering products. The changes are considered on the basis of weight alone and not volume. A part of the organic matter in the rock is lost in weathering. Sulfide sulfur in the fresh shale is oxidized to sulfate sulfur in the weathered material, but the sulfate sulfur is likely to be concentrated in the weathered material by the evaporation of ground moisture carrying soluble compounds to the surface of the outcrop. Ferrous iron in the fresh material becomes ferric iron in the weathered material, but there may be little change in total iron along the weathering sequence. Part of the sodium is lost with weathering and may be partly replaced by calcium or magnesium in ion-exchange reactions. Some calcium is added to the weathered material by accumulation of calcium carbonate near the surface. Total moisture remains about the same along the weathering profile, but the amount of H<sub>2</sub>O<sup>+</sup> increases with weathering and the amount of H<sub>2</sub>O<sup>-</sup> decreases. Except for organic matter, sulfide sulfur, and sodium, these kinds of changes can be allowed for by recalculation of the analyses. Analyses of samples weathered to different degrees thus can be compared.

The average composition of 17 selected samples of the Pierre differs from the average compositions of other shales in relatively minor ways. The Pierre average contains more silica and alumina than some averages and less than others, because of different amounts of detrital quartz in the samples making up the averages and probably because of different original clay minerals. No mineralogical data are available on the rocks included in the other averages, which are based on rocks ranging from clay to schist.

The minor elements determined by semiquantitative spectrographic analysis occur in surprisingly narrow ranges of concentration, the highest reported amount for about half the elements being no more than about twice the lowest reported amount. Compared to generally accepted figures for the crustal abundance of the elements, boron, scandium, lanthanum, and cerium are enriched in the samples of the Pierre, with the enrichment of boron being the most conspicuous. Sodium, calcium, chromium, manganese, iron, strontium, yttrium, and niobium are depleted in the Pierre samples. The other elements occur in about the same amounts as in the earth's crust. Compared to samples of an organic-rich unit at the base of the Pierre, the non-organic-rich samples contain more magnesium and gallium, probably more strontium and barium, and less boron, vanadium, nickel, copper, molybdenum, arsenic, and selenium.

Scandium, vanadium, and gallium, and possibly chromium and copper, are likely to occur in larger amounts in a zone in the lower part of the Pierre than in a middle zone of the Pierre. The middle zone contains larger amounts of calcium and manganese than the lower zone, and nickel, strontium, and possibly yttrium, are likely to be present in larger amounts in the middle zone.

Calcium, manganese, and strontium are present in larger amounts in samples from the eastern part of the area than from the western, and boron and nickel seem to be distributed similarly. Scandium and lanthanum seem to be present in larger amounts in samples from the western part of the area.

The plastic and liquid limits measured for samples of the Pierre are characteristic of clays of mixed mineral composition. The figures for the liquid limit seem to be directly proportional to the amount of montmorillonite in the samples, to the pH produced by the sample, and to the amount of material finer than about 4 microns in the sample. No regularities could be made out between the plastic limit and other characteristics of the samples.

### INTRODUCTION

Shale is the predominant sedimentary rock in the crust of the earth. Knowledge of the expectable chemical composition of shale and its variations is an important part of the data needed to interpret the chemical and physical processes involved in the erosion of source rocks, the mode of transportation of the resulting detritus to depositional sites, and the subsequent modifications of the material during diagenesis and lithification. Kind of source rock and its degree and type of weathering, mode and distance of transportation, and environments of deposition and diagenesis all influence the composition of shale; and characteristics and interactions of these factors must be deduced in large part from the composition of their products. Better understanding of these fundamental earth processes as they affect shale ultimately may lead to better consideration of such different problems as the possibility of ore deposits being formed by segregation of ore elements during metamorphism of shale, and the genesis and migration of petroleum and gas. In addition, data on the composition of shale aid in evaluation of the economic potential of the shale itself and, when related to the physical properties of the shale, in the planning and construction of engineering works located on shale terranes.

The Pierre shale and its equivalent stratigraphic units of Late Cretaceous age seem to offer excellent opportunities for obtaining data that would apply to such questions. The rock mass is thick and extensive, and occupies much of the western interior region of the United States; therefore, interpretations based on its study would be widely representative. The stratigraphy of the units is fairly well known, and abundant fossils permit biostratigraphic zoning throughout

the extent of the units. In addition, the shale is entirely marine in the eastern part of its extent, near the inferred center of the basin of deposition, and passes westward into entirely nonmarine rocks that are not far removed from the source of nearly all the clastic sediments in the units. Since the shale in the Pierre and its equivalent stratigraphic units is made up of several kinds of fine-grained clayey rocks, the interrelations of chemical composition, mineral composition, and physical characteristics of different kinds of shale and the environments in which they were deposited can be investigated.

### PLAN OF STUDY

In 1956, the U.S. Geological Survey began a study of the composition of the Pierre shale as part of the program of the Department of the Interior to implement the President's national minerals policy. A reconnaissance was made in Wyoming, Montana, and South Dakota to obtain preliminary data on the range in composition and nature of the shale in the Pierre and its stratigraphic equivalents. This report presents the chemical and semiquantitative spectrographic analyses and the data on the mineral composition and physical characteristics of the samples obtained during the reconnaissance study. A measure of the range of composition thus is given. In addition, the samples were selected to determine the suitability of outcrop samples for such an investigation, to measure local and wide-area variations geographically and stratigraphically, and to determine whether systematic areal variation exists. The samples are too few for any final interpretations to be reached. The data are intrinsically useful in themselves, and they are considered in some detail as a useful guide to further work.

Further studies, based on more detailed sampling and the use of more precise analytical methods to determine the minor elements, are planned and partly underway. These detailed studies are proceeding on a geographic basis as follows:

1. South Dakota, North Dakota, and Nebraska, and the Black Hills area of Wyoming. The study in this area will provide data on the composition of shale and marlstone, mixed with very minor amounts of sandstone, that accumulated relatively far from shore where reactions between clay and carbonate minerals with sea water within the environment of deposition and diagenesis are responsible for the resulting material.
2. North-central and western Wyoming and western Montana. The study in this area will provide data on the composition of shale and sandstone that accumulated relatively near the shore, along

the shore, and in terrestrial environments extending from behind the shore to near the source areas that furnished the sediments.

- Southern Wyoming, Colorado, and parts of New Mexico and Utah. The study in this area will provide additional data on changes in chemical and mineralogic composition of shale and associated rocks from locations in terrestrial and near-shore environments near source areas on the west and in marine environments near the center of the basin of the Pierre sea.

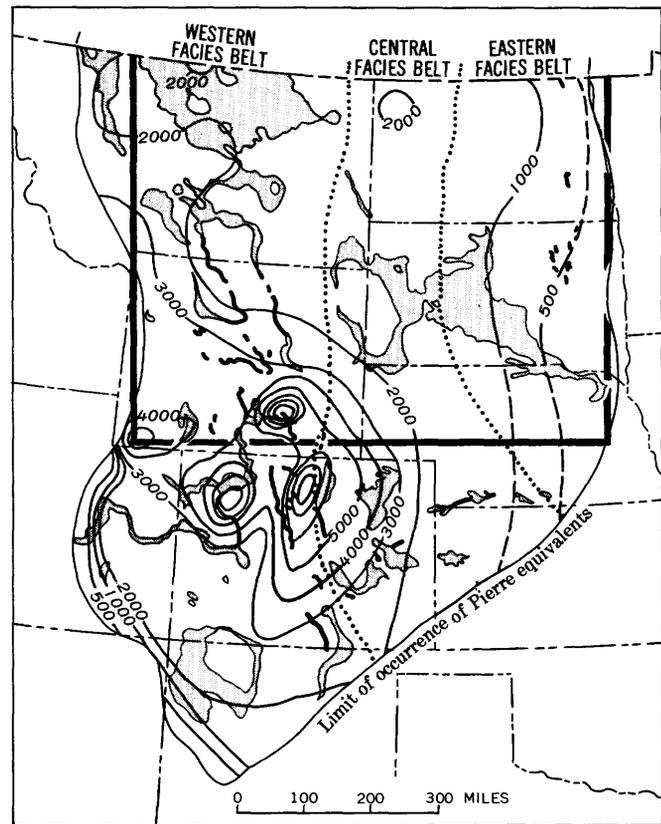
#### ACKNOWLEDGMENTS

Mr. A. H. Burling, project geologist, Oahe Unit, U.S. Army Corps of Engineers, Pierre, S. Dak., provided information on the stratigraphic subdivisions of the Pierre shale in excavations and core holes at the Oahe Dam. Dr. E. P. Rothrock, formerly State geologist of South Dakota, provided much information on the distribution of the Pierre shale in South Dakota and other assistance. Dr. A. F. Agnew, present State geologist of South Dakota, also extended many helpful courtesies.

Important contributions were made by a steering committee consisting of W. W. Rubey, W. S. Burbank, D. J. Varnes, and E. M. Shoemaker of the U.S. Geological Survey and M. N. Bramlette, Scripps Institution of Oceanography, La Jolla, Calif., both in planning the investigations and interpreting the results. All analyses were made in the laboratories of the U.S. Geological Survey, Denver, Colo. L. B. Riley, Lee C. Peck, A. Tennyson Myers, and L. F. Rader, Jr., have assisted in planning the analytical work and aided in the interpretations of analyses. W. A. Cobban has identified the collections of fossils and has generously made available his knowledge of the stratigraphy and paleontology of Upper Cretaceous rocks of the western interior region. J. R. Gill and L. G. Schultz, who are participating in the subsequent investigations of the Pierre shale, have given many helpful suggestions. Mr. Schultz made the X-ray mineralogical determinations.

#### DISTRIBUTION OF PIERRE SHALE AND EQUIVALENT ROCKS

The Pierre shale and equivalent rocks are exposed in many parts of the western interior of the United States (fig. 1). The major areas of exposure are in north-central Montana and in central South Dakota, where the strata are generally flat lying and have broad areas of outcrop. The Black Hills in South Dakota and Wyoming are surrounded for the most part by relatively narrow, linear outcrops such as are characteristic of the outcrops along the flanks of other uplifts in the Rocky Mountain region. In eastern Montana, North



#### EXPLANATION

- Outcrops
- Isopach lines  
Dashed where partly inferred. After Reeside, 1944
- Approximate boundary between facies belts
- Area shown in plate 1

FIGURE 1.—Distribution and thickness of Pierre shale and equivalent rocks in the western interior of the United States. See p. 9 for definition of facies belts.

Dakota, and western South Dakota, the Pierre shale is concealed by younger Cretaceous and Tertiary rocks. Glacial deposits cover the shale in the eastern parts of North Dakota, South Dakota, and Nebraska. In the western parts of Nebraska and Kansas, and in eastern Colorado, the Pierre is overlain by strata of Tertiary age.

The Pierre shale and equivalent rocks cover an area of about 600,000 square miles, based on Reeside's reconstruction of their distribution (1944). (See fig. 1.) The original extent was much larger (Reeside, 1957, figs. 16-20). The indicated volume of the rock mass

in the total area of occurrence is estimated to be about 225,000 cubic miles. The Pierre and its equivalents have been removed by erosion from about 140,000 square miles of uplifted areas within this present area of occurrence. The remaining volume of the Pierre and its equivalents probably amounts to about 175,000 cubic miles. The Pierre and its equivalents are concealed by younger deposits beneath about 370,000 square miles, and the Pierre rocks have an outcrop area of about 90,000 square miles.

The area in Wyoming, Montana, and South Dakota selected for reconnaissance investigation (pl. 1) amounts to about half of the preserved area of the Pierre shale and equivalent rocks and contains probably three-fourths of the total outcrop area of the units.

#### STRATIGRAPHIC RELATIONS OF THE PIERRE SHALE AND EQUIVALENT ROCKS

##### HISTORICAL SUMMARY

The Pierre shale attracted the attention of Lewis and Clark in 1804 (Coues, 1893, p. 113-130) and frequent mention is made in their journals of its prominent dark-colored bluffs along the Missouri River. Lewis and Clark brought back fossils that established the occurrence of Cretaceous rocks in the vicinity of the Great Bend of the Missouri below Fort Pierre (Meek and Hayden, 1858, p. 117). Fort Pierre was located on the west side of the Missouri River about 4 miles above the Bad River, according to Owen, Norwood, and Evans (1852). The Bad River was called the Teton River by Lewis and Clark; it flows into the Missouri River near the present towns of Fort Pierre in Stanley County on the west side of the Missouri and Pierre the State capital of South Dakota, in Hughes County, on the east side of the Missouri. Thomas Nuttall, on his trip up the Missouri in 1810, seems to have been the first to examine Pierre rocks geologically. He mentions specifically (Nuttall, 1821, p. 26) the pyrite-rich unit (the Sharon Springs member) at the base of the Pierre just above the Niobrara formation and speculates that the abundant gypsum throughout the Pierre was formed by the weathering of pyrite. He also collected the specimen that, together with fragments collected by Lewis and Clark, became the type of *Baculites compressus* (Say, 1819, p. 41). In 1839 Nicollet also recognized the Pierre shale as a "thick deposit of clay" above the chalk (Niobrara formation) in the vicinity of the Sioux River in southeastern South Dakota (Nicollet, 1841 and 1843), and collected fossils that were identified by Morton (1841, p. 107-108, and 1842, p. 207-212).

John Evans, an assistant in D. D. Owen's geological

survey of Wisconsin, Iowa, and Minnesota, collected Cretaceous fossils in 1849 at the Great Bend and localities between Fort Pierre and the "Mauvais Terres" of the White River country near the Black Hills (Owen, 1852). In 1853, Meek and Hayden, under the auspices of James Hall, followed Evans' route west of the Missouri River. On this trip, they recognized not only the base of the unit that is now called Pierre shale, as had most of the earlier travelers on the Missouri, but also the top, in exposures along the divide between the Bad and Cheyenne Rivers in central South Dakota. Their section was presented by Hall and Meek (1855, p. 405) and the units were designated by numbers. These designations were used by Meek and Hayden (1857a-e; 1859; and 1861a, b) and Hayden (1858) until 1861; at this time the geographic names Niobrara, Fort Pierre, and Fox Hills were applied (Meek and Hayden, 1862, p. 419).

Hayden remained in the West during 1854 and 1855 and traveled as far up the Missouri River as Fort Benton in western Montana. In November 1856, Meek and Hayden presented a section (1857a, p. 269) in which the first mention was made of beds now known to belong to the Judith River formation, which splits the Pierre shale as a nonmarine tongue from the west. The nonmarine character of the Judith River beds prevented interpretation of the stratigraphy of the rocks on the upper Missouri River for many years. (See Bowen, 1915, p. 105-109.) Meek and Hayden first believed that the beds at the mouth of the Judith River were at the base of the Cretaceous section (1857a, p. 267), but later they (1858, p. 123-125) considered them Tertiary in age because the outcrops, which were slumped and faulted, made it appear that the Judith River beds had been deposited in a basin within older rocks. They erroneously correlated the black shale of the Claggett and the Eagle sandstone, below the Judith River, with the sandstone and associated beds at the base of the Cretaceous sequence near the mouth of the Sioux River in southeastern South Dakota (Hayden, 1858, p. 111, 116; Meek and Hayden, 1858).

Hatcher (1896) showed that the Judith River vertebrate fauna is older than the *Ceratops* beds of eastern Wyoming, and, hence, is definitely Cretaceous in age. He later (Hatcher, 1902) suggested that the black shale above the Judith River beds (the Bearpaw shale) represented the Pierre shale, whereas it is only the upper marine tongue of the Pierre. Hatcher and Stanton (1903) (see also Stanton and Hatcher, 1905, p. 13-14) named the Bearpaw and Claggett shales and suggested that all the rocks from the Eagle sandstone (Weed, 1899) to the top of the Bearpaw shale were equivalent to all the Pierre shale of the Missouri River valley in

South Dakota, which is correct except for the fact that the Eagle sandstone and part of the underlying Colorado shale are also equivalent to beds in the basal part of the Pierre. Their suggestion was substantiated by Stebinger (1915, fig. 9, p. 67) who correctly recognized the stratigraphic position of the shales of the Eagle and Colorado and described the relations between the non-marine formations of western Montana and the marine Pierre shale in much the same way as they are generally accepted today (Cobban and Reeside, 1952, pl. 1) and as shown in figure 2.

#### CORRELATION OF UNITS

The relations of stratigraphic units of the Pierre shale and correlative rocks are shown in figure 2. The position of three widespread faunal zones characterized by species of *Baculites* are also shown; these faunal zones were used as a guide in collecting samples for this study, so that chemical compositions and inferences about depositional conditions could be compared for samples that are approximately contemporaneous.

The baculite zones used in this study, according to W. A. Cobban (oral communication, 1956), are those of the broadest possible application throughout the western interior region, and are susceptible to further subdivision, as is implied by the names of two zones. The *Baculites obtusus* s. l. zone, for example, includes the zones of *Baculites aquilaensis* and several undescribed species, as well as *B. obtusus*. The *Baculites compressus* s. l. zone also includes the zones of several species of the general *B. compressus* kind, such as *B. eliasi* (Cobban, 1958, p. 663) and *B. pseudovatus* Elias, and others that are yet to be described (W. A. Cobban, oral communication, 1956). The *Baculites clinolobatus* zone can be recognized only in the eastern part of the area of Pierre rocks, where the latest part of Pierre time is represented by marine rocks. The zone of *Baculites clinolobatus* is represented by nonmarine deposits in the western part of the area of Pierre rocks.

The Pierre shale of South Dakota is a sequence of marine shale that is equivalent in age to a thick sequence of nonmarine deposits in western Montana. Alternate marine and nonmarine sequences in parts of Montana and Wyoming represent fluctuations of the Pierre sea. During a widespread westward advance of the sea, the Niobrara formation, the Colorado shale, and older units were deposited. Throughout the remainder of Cretaceous time, volcanic material and associated nonmarine deposits represented by the Livingston and Two Medicine formations accumulated in the Livingston area (Richards, 1957, p. 419-422). Farther east, the Pierre sea retreated eastward at two times separated by a period of westward advance. Finally, the sea withdrew

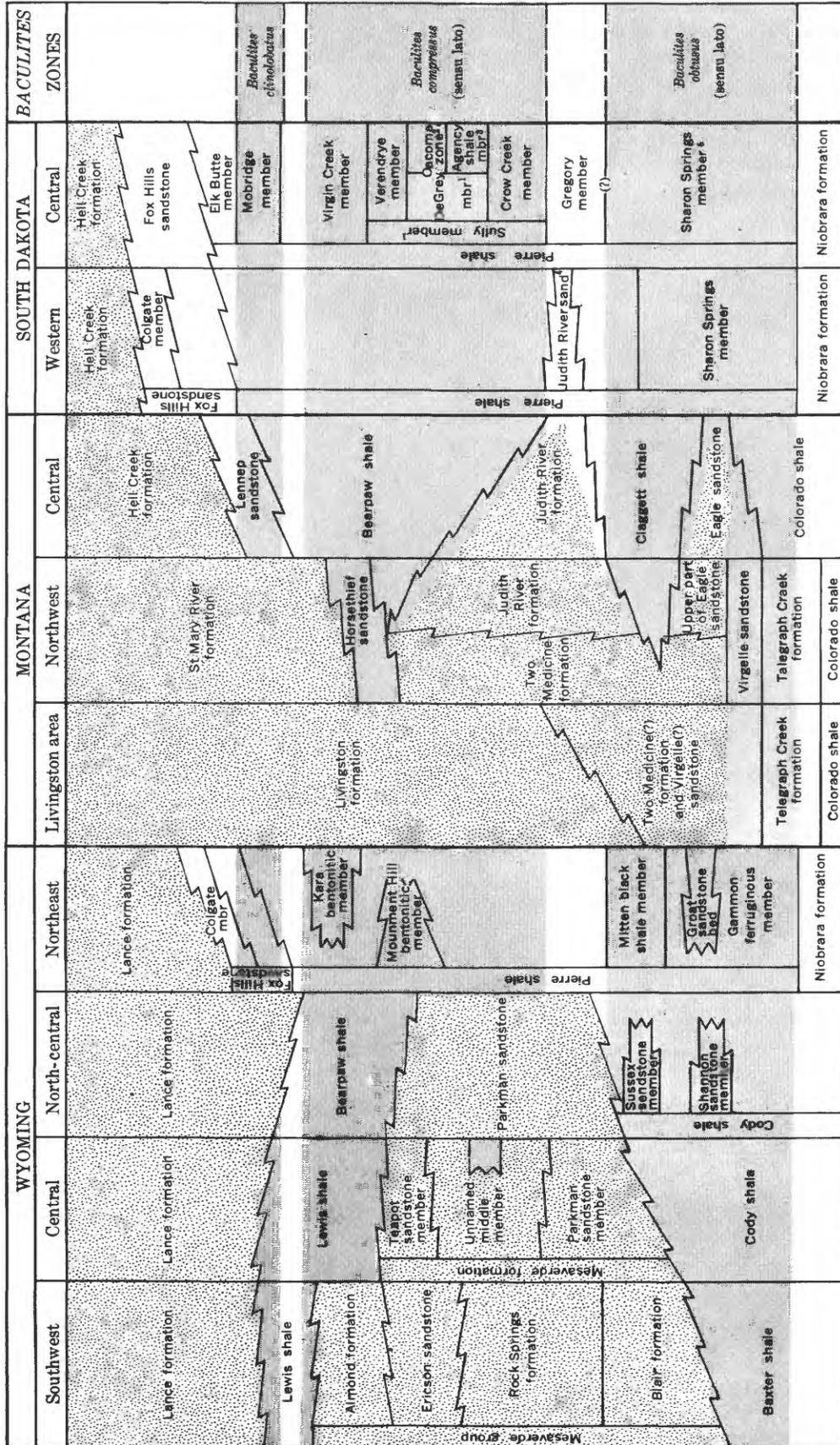
completely at the end of Pierre time. Because these retreats and westward advances were not instantaneous, but were progressive in time, marine tongues of the Pierre shale and equivalent stratigraphic units are of different age from place to place, as shown in figure 2.

The first eastward retreat of the Pierre sea is marked by the Virgelle sandstone, the Eagle sandstone, and the lower part of the Two Medicine formation. The Groat sandstone bed near the top of the Gammon ferruginous member of the Pierre shale and Shannon sandstone member of the Cody shale of northern Wyoming are the easternmost fringes of the Eagle sandstone. These sandstone bodies are equivalent in age to the marine shale in the upper part of the Baxter and Cody shales of Wyoming, the lower part of the Claggett shale in Montana, and parts of the Gammon ferruginous, Sharon Springs, and Mitten black shale members of the Pierre shale in eastern Wyoming and South Dakota.

The Claggett shale, equivalent to the Mitten member and partly to the Sharon Springs member of the Pierre shale, represents the westward advance of the Pierre sea following the deposition of the Eagle sandstone and associated units. The Claggett also is equivalent in age to the Blair formation and the lower part of the Parkman sandstone member of the Mesaverde formation in central Wyoming, and the upper part of the Cody shale in north-central Wyoming and adjacent Montana. It is also equivalent to the lower part of the Two Medicine and Judith River formations in northwestern Montana.

The second eastward retreat of the Pierre sea is represented by the extensive body of nonmarine sandstone of the Mesaverde group and formation and the Parkman sandstone in Wyoming, and the Judith River formation in Montana. These sandstone units have different age spans from place to place, but can be correlated in a general way with the lower middle part of the Pierre shale in South Dakota. The "Judith River" sand of local usage (Dobbin and Larsen, 1934) is identified in the subsurface at the Cedar Creek anticline in southeastern Montana as the easternmost fringe of the Judith River formation and is correlated with the Gregory member of the Pierre in central South Dakota.

The Bearpaw shale in Montana and north-central Wyoming and the Lewis shale in the rest of Wyoming were deposited during the last westward advance of the Pierre sea. The age span of the Bearpaw shale is widely different from place to place; the shale in central Montana is correlated with most of the middle and some of the upper part of the Pierre shale in South Dakota. The Bearpaw represents increasingly smaller parts of the Pierre shale as the Bearpaw is traced westward into Montana. The Lewis shale in Wyoming is correlated with the upper part of the Pierre shale.



EXPLANATION

Predominantly marine strata

Predominantly nonmarine strata

BACULITES ZONES

*Baculites clinolobatus*

*Baculites compressus* (sensu lato)

*Baculites obtusus* (sensu lato)

- 1 Of Searight, 1937; name used by South Dakota Geological Society.
- 2 Of Searight in his Sully member of the Pierre shale.
- 3 Of Russell, 1930.
- 4 Of local usage for subsurface of Cedar Creek anticline, southeastern Montana. (Dobbin and Larsen, 1934)
- 5 The exact time span and the relation of the Sharon Springs member along the Missouri River to overlying and underlying rocks are not known.

FIGURE 2.—Stratigraphic relations of the Pierre shale and equivalent rocks.

Modified from Cobban and Reeside, 1952, and Cobban, written communication, 1957

The final withdrawal of the Pierre sea is marked by a marine regressive sandstone sequence in northeastern Wyoming, central Montana, and South Dakota. The Horsethief, Lennep, and Fox Hills sandstones make up this sequence and have a wide age span. The Horsethief sandstone is correlated with the upper part of the middle Pierre, but the Lennep sandstone is late Pierre in age, and the Fox Hills sandstone is partly Pierre in age. The regressive sandstone sequence is overlain by the St. Mary River, Lance, and Hell Creek formations. The Lance and Hell Creek formations rest directly on the underlying marine beds in much of Wyoming and in parts of Montana (Hose, 1955, p. 65; Richards, 1955, p. 63; and Dobbin and Larsen, 1934).

#### DESCRIPTION OF UNITS

Generalized stratigraphic sections of the Pierre shale and equivalent rocks are shown in plate 2 to illustrate the nature of the rocks and to serve as a basis for brief descriptions of the rock units. The baculite zones shown in figure 2 are also shown in plate 2 so that the changes in age of some of the units can be shown on a true-thickness scale. The stratigraphic units will be described from east to west.

The lithologic features of the Pierre shale along the Missouri River in central South Dakota have been intensively studied by the Geological Survey of South Dakota. The excellent exposures in the river bluffs and along the major tributaries of the Missouri have permitted a detailed subdivision.

The Elk Butte, Mobridge, Virgin Creek, Sully, and Gregory subdivisions of the Pierre shale were established by Searight in 1937. The name Sharon Springs had been applied by Elias (1931, p. 56-76) to the basal beds of the Pierre shale in western Kansas; and in 1938, Searight (Moxon, Olson, Searight, and Sandals, 1938, p. 796) used it for equivalent beds in South Dakota. Russell (1930) previously had distinguished the Agency unit, and Gries and Rothrock (1941, p. 14-18) subsequently named the Crow Creek member. Gries (1942, p. 14-18) combined the Agency and Oacoma units of Searight, treating the combined unit as a zone within the Sully member. The Sully member then consisted of the Verendrye zone at the top, the Agency-Oacoma zone in the middle, and the Crow Creek chalk and sand at the base. In 1950, Crandell (1950, table 1, p. 2340) revised the nomenclature of the Sully unit so that the somewhat informal zone terminology was not necessary. Crandell raised the Verendrye and Crow Creek units to the status of members of the Pierre shale, established the DeGrey member to replace the Agency-Oacoma zone, and abandoned use of the name "Sully member."

The Geological Survey of South Dakota prefers to retain the Sully member subdivided into zones; Crandell's revision is accepted by the U.S. Geological Survey. The column pertaining to central South Dakota in figure 2 shows the relations of these two sets of names.

The detailed subdivisions of the Pierre rocks along the Missouri River reflect actual differences in kinds of material, but some of these differences can be distinguished readily only under the favorable outcrop conditions found along the river, and other characteristics change somewhat away from the river. The Sharon Springs member at the base of the Pierre shale lies on the Niobrara formation and is a black organic-rich shale that is hard and platy. The Gregory member consists of marlstone and claystone in southeastern South Dakota; the upper part becomes increasingly bentonitic as the unit is traced northwards to the central part of the State. The Crow Creek member, only a few feet thick, makes a prominent white band through the dark shale outcrops; it commonly contains a thin sandy bed at its base.

The DeGrey member is highly bentonitic at most places. From about the mouth of the Moreau River south to Pierre (pl. 1), it is distinguished by a facies of siliceous shale, usually called the Agency shale by the Geological Survey of South Dakota, and is similar in character to the Mowry siliceous shale studied by Rubey (1929). The siliceous shale of the Agency partly underlies and partly grades into a facies rich in nodules of manganiferous siderite; this facies usually is called the Oacoma by the South Dakota Geological Survey and makes up most of the unit south of Pierre. The Verendrye member consists of dark-colored shale in which siderite nodules are common. The Verendrye is perhaps the member of the Pierre shale that is most difficult to recognize solely on the basis of its own characteristics. The unit is best distinguished by identifying the DeGrey member below and the Virgin Creek member above. The Virgin Creek member, as defined by Searight (1937, p. 35-43), consists of two parts, a lower unit of dark-colored shale containing nonswelling bentonite and forming characteristic flaky outcrops, and an upper unit containing soft, dark-colored highly bentonitic shale and forming characteristic bald outcrops. Rothrock (1947, p. 9-10) noted that this upper bentonitic unit was calcareous to various degrees in its upper part and included the unit with the overlying Mobridge member. Searight's usage is followed here. The Mobridge member in its type area along the Missouri River in northern South Dakota consists of marlstone and calcareous shale. The Mobridge grades southward into increasingly cal-

careous materials and, in southeastern South Dakota and adjacent parts of Nebraska, parts of it are mostly chalk. The Elk Butte member consists of noncalcareous, dark-colored shale that characteristically weathers to tan colors and becomes increasingly sandy and silty towards its top. The contact with the overlying Fox Hills sandstone is gradational.

The Elk Butte, Mobridge, and Virgin Creek members are recognizable for some distance along the valleys of the streams entering the Missouri River from the west. West of the Missouri River, the Mobridge loses its distinctive carbonate content and the Virgin Creek loses much of its hardness. The lower members of the Pierre do not extend very far up the valleys tributary from the west, and little is known about changes in their character.

In the southern part of the Black Hills, South Dakota and Wyoming, the Pierre shale has a somewhat different age span and sequence of units than it does in the northern part of the Black Hills. Plate 2 shows the relation between two typical sections.

In the southern part of the Black Hills, the Sharon Springs member consists of hard flaky organic-rich shale that lies on the limy beds of the Niobrara formation or is separated from them by a few feet of soft black shale. The Ardmore bentonite bed (Spivey, 1940, p. 3) occurs in the lower part of the organic-rich shale and consists of nonswelling bentonite. The Sharon Springs member seems to lie in the lower part of the *Baculites obtusus* s. l. zone and is overlain by soft bentonitic dark-colored shale that also contains fossils of the *B. obtusus* s. l. zone. The Sharon Springs member has been traced on the surface and in well logs northward along the west side of the Black Hills by J. R. Gill. Gill correlates the Pedro bentonite bed (Rubey, 1930, p. 4) with the Ardmore bentonite bed, although in the type area the Pedro bentonite is of the swelling type. A few miles north of Newcastle, Wyo., a wedge of shale appears between the Sharon Springs member and the underlying Niobrara rocks, and thickens northward. This shale was named the Gammon ferruginous member by Rubey (1930, p. 4); and where it is recognizable, the organic-rich shale is called the Mitten (Rubey, 1930, p. 3). The wedge of shale consists of dark-gray shale and mudstone that contains numerous ferruginous concretions. The Groat sandstone bed (Rubey, 1930, p. 4) lies in the upper part of the Gammon member and consists of light-colored medium- to fine-grained glauconitic sandstone.

The Mitten black shale member continues northward around the north end of the Black Hills. It consists of hard black flaky organic-rich shale and contains a group of beds of nonswelling bentonite called Bed I

by Knechtel and Patterson (1956). In this part of the Black Hills, the Mitten member lies at the top of the *Baculites obtusus* s. l. zone and the Gammon ferruginous member represents the lower part of the zone.

The beds overlying the Mitten black shale member and the *Baculites obtusus* s. l. zone consist of gray to light-gray silty shale with minor amounts of sand and numerous limy concretions. This silty zone is overlain by a thick sequence of generally dark-colored shale and claystone which includes two highly bentonitic members. The older of these is the Monument Hill bentonitic member (Rubey, 1930, p. 3), which is recognized in the northern part of the Black Hills and disappears to the south. The younger bentonitic member is the Kara (Robinson, Mapel, and Cobban, 1959, p. 111-113), which is present in the southwestern and western parts of the Black Hills and disappears to the north. Both bentonitic members consist of gray to light-gray claystone and bentonitic claystone with many beds of bentonite. The units weather to frothy surfaces and form prominent bare outcrops.

In the southwestern part of the Black Hills (pl. 2), the beds above the Kara bentonitic member consist of gray to dark-gray shale and claystone that become increasingly sandy upwards and grade into the overlying Fox Hills sandstone. Limestone concretions are conspicuous, and one or more thin units of bentonitic claystone are present. This unit grades laterally northward into the Fox Hills sandstone (Robinson, Mapel, and Cobban, 1959, p. 103), and in the northwestern part of the Black Hills, the Fox Hills sandstone rests on beds that are nearly as old as the Kara bentonitic member.

The pronounced variations in thickness and lithologic character as well as the discontinuity of units indicate that considerable shifts in the loci of deposition took place in the Black Hills area during the time of deposition of the Pierre shale.

The general character of the rocks equivalent to the Pierre on the northeast side of the Bighorn Mountains near Hardin, Mont., is shown on plate 2. Some of these units in this part of Montana are classified as members of the Cody shale. (See also fig. 2.) The sandstone tongues of the Parkman (Judith River) and Eagle are much thinner here than in areas to the west, and the beds equivalent to the Eagle sandstone are entirely marine.

The rocks in the Hardin, Mont., area have been described by Richards (1955, p. 57-60), based in part on detailed sections measured by W. A. Cobban. The Niobrara shale member of the Cody shale consists chiefly of gray to dark-gray shale with some minor calcareous zones. The Telegraph Creek member is

made up of sandy and silty shale with a few beds of sandstone. The beds identified as equivalent to the Eagle sandstone consist of dark-colored shale with a noticeably sandy zone near the middle and are recognized chiefly by fossils. The Claggett shale member of the Cody shale is dark gray to almost black and contains several beds of bentonite in the lower 35 feet of the member. The bentonite is gray to yellow in color and is of the nonswelling kind, similar to the bentonite in the Sharon Springs and Mitten members of the Pierre shale in the Black Hills region.

The Parkman sandstone consists of yellow-weathering sandstone and some sandy shale. There is no evidence in the Hardin area to indicate whether the Parkman sandstone was deposited under marine or nonmarine conditions. From its gradational relation to the underlying Claggett, the Parkman is at least partly marine in origin. The Bearpaw shale consists of gray to dark-gray shale and claystone with zones of abundant limestone concretions. The unit is very similar in general appearance and character to the upper part of the Pierre shale in the Black Hills region. A bentonitic unit about 250 feet thick lies nearly 400 feet above the base of the Bearpaw. This bentonitic unit perhaps correlates with the Monument Hill bentonitic member of the Pierre shale. The shale grades upwards into the shale and sandstone beds of the overlying nonmarine Hell Creek formation. No marine sandstone that could be interpreted as a regressive sandstone can be recognized.

In central Montana, the alternation of marine and nonmarine strata in Pierre-equivalent rocks is striking. A generalized section for the area south of Bearpaw Mountain (Reeves, 1924, p. 74) is representative (pl. 2). The uppermost part of the Colorado shale is of Niobrara age and grades upward through the increasingly sandy beds of the Telegraph Creek formation into the Eagle sandstone. The Eagle sandstone consists of light-colored sandstone interbedded with minor amounts of shale that is in part carbonaceous and locally contains coal. The Eagle sandstone is overlain by the Claggett shale, which consists of moderately hard flaky black shale that weathers to a characteristic dark-brownish gray. Beds of nonswelling bentonite are conspicuous in the lowermost part of the Claggett shale and a few thin beds occur in the upper part of the formation (Reeves, 1924, p. 82-83).

At some places, the Judith River formation is made up of three units: a basal sandstone that contains marine fossils and with which the underlying Claggett shale is gradational, a middle unit of shale and sandstone including carbonaceous shale and coaly beds, and an upper sandstone that locally contains brackish-water

or marine fossils. The basal sandstone is interpreted as a regressive sandstone and the upper sandstone as a transgressive sandstone, marking the westward advance of the Pierre sea. The overlying Bearpaw shale has not been studied in detail in this region. Reeves (1924, p. 80) describes the unit as consisting principally of steel-gray marine shale that contains many beds of bentonite. The general appearance of the Bearpaw is similar to that in the northeastern Bighorn Mountains (pl. 2) and the bentonite is of the swelling type.

#### FACIES BELTS

The lithologic character and correlation of the units of the Pierre shale and equivalent rocks permit the tentative delineation of three facies belts that are useful in looking for systematic trends of variation in chemical and mineralogical composition and in relating such changes to positions within the basin of deposition. The regional distribution of the facies belts is shown in figure 1, and their position within the area of this reconnaissance is shown in plate 1.

The facies belts are characterized from west to east by decreasing amounts of nonmarine deposits and relatively coarse grained marine rocks derived from the land area to the west of the Pierre sea. Reeside (1957, p. 530-538) showed the geographic distribution of different rock types in epochs of the Pierre shale and equivalent rocks, and the facies belts used here are in large part generalized from these interpretations. The boundaries of the facies belts are indefinite and conceptions of them probably will change somewhat as more information becomes available.

1. The western facies belt consists of alternate units of shale and sandstone; the shale units are entirely marine in origin, but the sandstone units are marine in the eastern part of the belt and nonmarine in the western. This alternate sequence becomes predominantly sandstone and entirely nonmarine along the western part of the belt. For the purposes of this report, the belt is divided from north to south into north-central Montana (region 1 on pls. 1 and 4) and central Wyoming and adjacent southern Montana (region 2 on pls. 1 and 4).
2. The central facies belt consists of marine shale and minor amounts of predominantly marine sandstone in the Black Hills area of Wyoming, Montana, and South Dakota (region 3 on pls. 1 and 4).
3. The eastern facies belt consists of shale and marlstone in central South Dakota (region 4 on pls. 1 and 4).

The division of the Pierre shale and equivalent rocks into facies belts permits consideration of differences in composition from west to east in three groups arranged normal to the western shoreline of the Pierre sea. The

subdivision of the western facies belt facilitates consideration of differences in composition from north to south in two groups arranged parallel to the western shoreline.

#### GEOCHEMICAL HISTORY

The geographic distribution and stratigraphic relations described for the Pierre shale and equivalent rocks permit only an imperfect reconstruction of the source materials and of the geologic and chemical processes and conditions that have acted to produce the rocks under investigation. The relations among source materials, processes, and conditions were very complex; it is thus optimistic to think that any of them can be characterized in a quantitative way by deductions based on data derived from their end product. However, an attempt to recognize the major variables of these complex interactions may reveal feasible points of attack of this problem. The general sequence of interactions stated in a chronological way constitutes the geochemical history. The geochemical history necessarily requires a description of the geochemical system with which we are dealing, prior general knowledge of which is helpful in considering the data.

Such a reconstruction must be highly speculative. It seems unnecessary to give citations for individual facts and concepts, as most are well known. The following papers include many of the basic facts and geochemical and sedimentational concepts that have been integrated here to reconstruct the geochemical history of Pierre rocks:

- Grim, R. E., 1953, *Clay mineralogy*: New York, McGraw-Hill, 384 p.
- 1958, Concept of diagenesis in argillaceous sediments: *Am. Assoc. Petroleum Geologists Bull.*, v. 42, no. 2, p. 246-253.
- Hutchinson, G. E., 1957, *Geography, physics, and chemistry, v. 1 of A treatise on limnology*: New York, John Wiley and Sons, Inc., 1015 p.
- Keller, W. D., 1956, Clay minerals as influenced by environments of their formation: *Am. Assoc. Petroleum Geologists Bull.*, v. 40, no. 11, p. 2689-2710.
- Krumbein, W. C., and Garrels, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: *Jour. Geology*, v. 60, no. 1, p. 1-33.
- Reeside, J. B., Jr., 1957, Paleocology of the Cretaceous seas of the western interior of the United States, in Ladd, H. S., ed., *Treatise on marine ecology and paleocology*, v. 2, *Paleocology*: *Geol. Soc. America Mem.* 67, p. 505-541.
- Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1942, *The oceans, their physics, chemistry, and general biology*: New York, Prentice-Hall, 1087 p.

The Pierre shale and equivalent rocks were deposited in and adjacent to a relatively narrow and shallow sea extending southward across the present western interior region of the United States. The sea probably was

connected at the north with world oceans and at the south from time to time with the seas of the gulf coast. The eastern shore area of this sea has not been preserved and the Pierre rocks contain little evidence of its nature. It must have been made up, however, of rocks of Precambrian and Paleozoic age that probably formed a broad nearly stable lowland in the present northern midcontinent region. The western shore area of the Pierre sea is fairly well known. Its location fluctuated from an eastern position during the deposition of the nonmarine Eagle and Judith River formations to one farther west during the deposition of the Claggett shale and most of the Bearpaw shale. During much of Pierre time, however, the western shore lay between these extremes in what is now western Montana, western Wyoming, central Utah, and perhaps central or eastern Arizona. Most of the land behind the shore was composed of preexisting sedimentary rocks, although crystalline rocks of Precambrian age were exposed in Colorado during Pierre time. Several centers of contemporaneous volcanic activity are known to have existed near the western shore in west-central Montana.

The nonmarine rocks of the Eagle and Judith River formations were deposited on a wide coastal plain bordering the sea, where conditions were suitable for deposition of coal-forming materials.

A weathered mantle may have formed on the rocks of the source areas, particularly where the rate of erosion was slow. The weathered material would be modified from its original state by the solvent action of the ground and surface water. The weathered material, as well as the more rapidly eroded and slightly weathered material, would then move toward the sea in the resulting dilute solutions. These materials would be subjected to many cycles of alternate deposition and erosion in traveling to the sea.

On entering the coastal plain, some of the material would pass through the environments of swamps, lakes, and lagoons containing relatively more concentrated and reactive solutions than the previous environments of erosion and transportation. Assuming a reasonably consistent composition for the material delivered to the coastal plain, some differentiation would take place in the sediments because of their deposition in oxidizing or reducing environments and at the beginning at least of diagenetic reactions, before the material would be picked up again and moved on to the sea. In addition, size sorting would take place resulting in a heterogeneous mass of detritus being delivered to the coastal plain with, for the most part, only the finer grained material being carried on to the sea.

Most of the fine detritus probably was in what might

be called a reactive state when it entered the sea. The alkali and alkaline-earth elements had been leached from the clay mineral structure to some degree and were probably generally deficient. Some of the leached elements may have been resorbed in the more concentrated solutions of the coastal-plain environments, but much of the fine detritus probably was carried into the sea in a still degraded state. Thus a mass of material with a somewhat varied composition was introduced into the sea. The detritus constituted a very dispersed phase in the reacting system; and a series of reactions, mainly the replenishment of alkali and alkaline-earth metals in the clay mineral structure, began to bring the composition of the clay minerals into equilibrium with sea water. Since the gross composition of sea water probably was virtually uniform, the composition of the material settling on the sea floor should have been relatively uniform.

The Pierre sea also received much volcanic material in addition to the weathering products of sedimentary rocks. Some of the volcanic material accumulated on land and underwent the same weathering, erosion, and transportation by water as the preexisting sedimentary rocks, but a large amount of fine-grained volcanic material was delivered to the sea directly from the air. From time to time, this airborne volcanic material arrived on the sea floor so rapidly and in such large amounts that it seems to be unmixed with material derived from the land. This volcanic material was considerably altered in composition, mainly by loss of silica, by reactions that began when the ash hit the water. The change in composition of the volcanic ash to bentonite probably involves the largest chemical change that can be deduced for the clay-sea water system.

During transportation and sedimentation, the clay from the land and the accompanying volcanic material became mixed to a greater or lesser extent with calcium carbonate. Although some calcite may have been inorganically precipitated, the bulk of the calcium carbonate came from planktonic organisms, such as Foraminifera and coccoliths, whose tests were distributed through the upper layers of the sea. There probably were, however, areas where the carbonate-producing planktonic organisms were more abundant than at other places. The abundance or scarcity of carbonate plankton remains in the Pierre shale, thus, is assumed to be a function of this distribution of organisms, and perhaps even more of the distribution of conditions under which calcium carbonate could be preserved in the lower layers of sea water and in the sediment at the sea bottom.

On settling to the sea floor, the clay particles and any

associated planktonic calcium carbonate became mixed with organic material of both plant and animal matter in undetermined amounts. The bulk of the organic material came from planktonic plants and animals, but some could have come from larger forms. Benthonic animals or plants probably contributed little material to sediments that are now conspicuously organic-rich, because conditions that permitted the preservation of the organic matter were not favorable for most living organisms.

The preservation of the organic material in the sediment was dependent on an appropriate combination of several variables, the relations of which can be described best by the statement that the organic material accumulated faster than it was destroyed. Organic-rich rocks of the Pierre shale thus could have been formed in areas where only little organic material was being produced, but all of it was being preserved, in areas where much organic material was being produced but only part of it was being preserved, or in areas where conditions were intermediate between these extremes. In addition to the effect of the relative rates of production and decay of the organic material itself, the relative rates of sedimentation of clay and carbonate also influenced the amount of organic material that is found in the rocks today. In areas of rapid sedimentation of clay, the organic matter was diluted; in areas of very slow sedimentation, the organic matter made up a much larger proportion of the rock. Within certain limits, the conditions suitable for the preservation of organic material may be self-perpetuating, and organic accumulation, once started, could influence the conditions of subsequent accumulations.

After deposition, the variously intermixed clay particles, calcium carbonate, and organic matter entered an environment of greater chemical severity than any other environment through which they had passed since erosion. This is the environment of diagenesis and it may be characterized as the zone of sediment that lies between the sediment-water interface above and an indefinite lower boundary, below which the water content of the sediment has been reduced to 30 to 40 percent by compaction. The primary characteristic of this environment is that it is chemically reducing. Oxygen could no longer be obtained from the overlying water, whether it was oxygenated or not. Bacterial or chemical reduction of sulfate also promoted acidic as well as reducing conditions. Some calcium carbonate and other compounds were increasingly dissolved and were either cycled back to the overlying sea water or were segregated as diagenetic concretions in favorable microenvironments within the zone of diagenesis. Sulfide minerals and carbonate compounds, such as dolomite or

siderite, replaced or cemented parts of the enclosing claystone. The composition of the clay minerals undoubtedly was modified under such conditions, but it is difficult to imagine the reactions and their results. It seems plausible, however, that there would have been exchange and adsorption reactions, whereby alkali and alkaline-earth metals probably were replaced and other elements such as hydrogen, fluorine, phosphorus, and barium became part of the clay minerals.

The environment of diagenesis tended towards an open chemical system, in which reactants and perhaps some reaction products were carried out of the environment by the interstitial water expressed from the clay by compaction. Consequently, reactions may not have approached equilibrium as closely as they did in the clay-sea water system, which can be regarded as a relatively closed system.

After compaction removed most of the interstitial water from the clay-carbonate-organic matter mixture, so that diagenesis was greatly retarded and perhaps virtually completed, the sediments were deeply buried and entered a long period in which further chemical changes, if any, took place very slowly. Although shale and claystone are generally regarded as impermeable, they are only relatively so; and during the length of time represented by the latter part of the Cretaceous and all the Tertiary periods, a considerable amount of water could have moved through the Pierre shale. Most probably, reducing conditions prevailed and were milder than in the zone of early diagenesis. Exchange reactions with clay minerals could have been extensive and many compounds could have been dissolved and deposited again at different places.

Finally, after uplift and erosion of overlying beds, the shale returned to the zone of weathering. Near the present surface, water had greater access to the shale because of fracturing, and exchange reactions of the clay minerals were accelerated and may have been reversed; that is, ions now were added that previously had been removed, or vice versa. Most of the weathering took place under oxidizing and alkaline conditions, but locally the oxidation of sulfide-rich shales could have produced strongly acidic conditions. Ground water moving toward the surfaces of the outcrops would carry some compounds in solution, such as sulfate and iron, and these would be concentrated in the surficial zone by evaporation of the solutions and oxidation. The effects of these weathering processes could be large.

The clay thus moved from an oxidizing and alkaline environment in its source area on the land bordering the Pierre sea to its deposition site on the sea floor through a series of environments that tended to be de-

creasingly oxidizing and increasingly alkaline. On the sea floor, it entered a reducing environment. Following a long period of more or less quiescent conditions that nevertheless may have greatly affected the composition of the shale because of the great length of time involved, the clay returned to the generally alkaline and oxidizing conditions of the zone of weathering near the present surface. Minor alternations between oxidizing and reducing conditions within this major cycle of oxidizing, reducing, and then again oxidizing conditions, probably are characteristic of the geochemical history of the Pierre rocks.

## SAMPLES

### TERMINOLOGY

Rock names and descriptive terms applied to the materials considered in this report are used with the following definitions:

*Bentonite*.—Bentonite is a rock consisting virtually of clay derived from the alteration of volcanic ash (Twenhofel, 1937, p. 99; Knechtel and Patterson, 1955; 1956, p. 1). Bentonite differs from the other rocks composed of clay-sized particles with which it ordinarily is associated by not containing any organic material; and, hence, it weathers to very light colors, commonly shades of yellow and orange. The material commonly occurs in well-defined extensive beds. Most bentonite consists predominantly of montmorillonite, but it has a wide range of physical properties that seem to depend upon complexly related chemical and crystallographic features of the material. Some bentonite is referred to as swelling bentonite because it swells during weathering and produces a frothy, popcornlike crust on the surface of the outcrop. Other bentonite lacks this characteristic and is referred to as nonswelling bentonite.

*Bentonitic*.—Bentonitic applies to light-gray to dark-gray claystone that differs from bentonite chiefly in color. Swelling bentonitic claystone consists of a mixture of swelling bentonite and detrital clay minerals; the amount of swelling seems to depend largely on the proportions of these constituents. Some bentonitic claystone has a characteristic frothy, popcornlike surface similar to that of nearly pure bentonite. Nonswelling bentonitic claystone forms a gumbolike cap as much as half a foot thick upon weathering but lacks the frothy, popcornlike surface.

*Claystone*.—Claystone is a rock consisting of 75 percent material finer than 1/256 mm (about 4 microns). The rock may appear massive, although clay minerals and flaky particles of organic matter may be oriented parallel to the bedding. The terms "silty" or "sandy", are used as modifiers as appropriate, when clay-sized

material amounts to less than 75 percent, but more than 50 percent of the rock.

*Marlstone.*—Marlstone is a soft clayey rock that contains from 35 to 65 percent calcium carbonate (Pettijohn, 1957, p. 411).

*Mudstone.*—Mudstone is a predominantly fine-grained rock containing nearly equal amounts of fine-grained sand-, silt-, and clay-sized particles; also used as a general term for rocks of this character, but for which the size distribution is not known.

*Organic rich.*—The descriptive term "organic rich" is applied to rocks that are very dark gray to black and have a quality of toughness imparted by finely disseminated organic matter of the type generally implied by the terms "sapropel" or "kerogen" rather than the type implied by "carbonaceous" or "bituminous." Much of the organic matter can be distilled and some can be extracted with organic solvents. The organic-rich rocks in the Pierre are mostly shale and are comparable in organic content, and perhaps in type of organic material, to low-grade oil shale in the Green River formation, the Chattanooga shale, and to some other shales, such as parts of the Cherokee shale of Pennsylvanian age of Kansas, and the Swedish Kulm. The noncommittal term "organic rich" is used because more meaningful information is not available on the nature of the organic constituents of the rock.

*Shale.*—In discussions of stratigraphy, gross lithology, and chemical composition, the term "shale" is used to indicate the general group of fine-grained sedimentary rocks, as for example, the Pierre shale.

In descriptions and discussions of individual samples, the term "shale" is applied to a rock that consists predominantly of clay- and silt-sized particles, that characteristically weathers or breaks into fragments whose thickness is much less than the length and width, and that is hard enough not to disintegrate under ordinary weathering conditions (Twenhofel, 1937, p. 93).

*Siliceous shale.*—Siliceous shale is shale that weathers into unusually hard, brittle chips; it is commonly of a lighter gray than other types of shale. The induration is due to cementation with silica.

*Siltstone.*—Siltstone is a rock that consists predominantly of silt-sized particles; the clay content may be considerable, but does not exceed 50 percent.

#### FIELD INVESTIGATIONS

In 1956 brief field studies were made of the Pierre shale and equivalent rocks at many localities selected from the literature. Fossils and samples were collected at nearly all localities. Special efforts were made in each locality to find the best outcrops and to sample the freshest material. Samples were taken in fresh road

cuts and recent excavations of all kinds wherever possible. Fresh core material was collected in the vicinity of the Oahe Dam in central South Dakota. The samples thus differ somewhat in degree of weathering, but all represent the freshest material that could be found at any locality. At localities 1 and 8 (pl. 1), sequences of weathering from the soil zone into reasonably fresh shale were sampled.

In collecting the samples, a hole was dug into the outcrop until firm material was reached, if this was possible; excavation ordinarily was stopped at a depth of about 3 feet. A quantity of the firm shale was broken down into the hole and firm pieces were handpicked until about 10 pounds had been obtained. Nearly all samples had some visible evidence of weathering, such as films of iron oxides or iron sulfates, and gypsum crystals on bedding and joint planes. The surfaces of the pieces were brushed off to remove as much of the iron compounds or gypsum as possible. The iron sulfates tended to impregnate the shale more than the iron oxides or gypsum and could not be eliminated as easily from the samples.

For the most part, the samples consisted wholly of shale, so that the analyses would be of similar material and any differences in composition would be the result of different chemical and physical processes operating on virtually clay-sized material. Sandy and silty shales were avoided, as were shales having an obvious content of calcium carbonate. Two samples of marlstone were collected, however, to obtain some information on the composition of clay-size material in an environment where abundant carbonate could accumulate.

#### LABORATORY INVESTIGATIONS

Samples for laboratory investigation were selected from about 100 samples that were available. A basic set of 22 samples from localities 1 to 10 (table 1 and pl. 1) was first selected. The principal objectives were to investigate the relations between fresh and weathered material and to provide scattered coverage of the entire geographic distribution and stratigraphic range of the Pierre shale and its equivalents. The location and description of these samples are given in table 1. The physical characteristics of the 22 samples in the basic set were investigated by size analyses (table 3), determination of pH, liquid and plastic limits (table 20), and X-ray mineralogical analyses (table 5). The chemical composition is shown by standard rock analyses (table 7); semiquantitative spectrographic analyses (table 14); chemical analyses for fluorine, zinc, arsenic, selenium, and uranium, and the determination of equivalent uranium content (table 17); and carbonate and organic carbon (table 18).



SAMPLES

| Sample No. | Locality | Direction | Depth | State       | Notes                | Description                                  | Other  | Remarks |
|------------|----------|-----------|-------|-------------|----------------------|--|--------|---------|
| 11         | C910     | SE 1/4    | 11    | Montana     | Claggett             | Shale, dark-gray to black, flaky             | XXXXXX |         |
| 12         | C911     |           | 11    | do.         | do.                  | do.  | XXXXXX |         |
| 13         | C912     |           | 11    | do.         | do.                  | do.  | XXXXXX |         |
| 14         | C913     | SE 1/4    | 33    | Bearpaw     | Bearpaw              | Claystone, dark-gray                         | XXXXXX |         |
| 15         | C914     |           | 14    | do.         | do.                  | Shale, light-gray, hard                      | XXXXXX |         |
| 16         | C915     |           | 34    | McCone      | do.                  | Shale, brown, flaky                          | XXXXXX |         |
| 17         | C916     |           | 17    | Fergus      | Claggett             | Shale, gray, silty and sandy                 | XXXXXX |         |
| 18         | C917     |           | 34    | do.         | Judith River         | Shale, gray to dark-gray, sandy              | XXXXXX |         |
| 19         | C918     |           | 5     | do.         | Colorado             | Shale, black, flaky                          | XXXXXX |         |
| 20         | C919     |           | 5     | do.         | do.                  | Shale, yellowish to tannish-gray, bentonitic | XXXXXX |         |
| 21         | C920     |           | 8     | do.         | do.                  | Shale, black, flaky                          | XXXXXX |         |
| 22         | C921     |           | 33    | do.         | Bearpaw              | Claystone, dark-gray to black, flaky         | XXXXXX |         |
| 23         | C922     |           | 16    | Petroleum   | Colorado             | Shale, black, hard                           | XXXXXX |         |
| 24         | C923     | SW 1/4    | 21    | Musselshell | Bearpaw              | Siltstone, dark-gray, clayey                 | XXXXXX |         |
| 25         | C924     | NE 1/4    | 21    | Rosebud     | Claggett             | Shale, brownish-gray                         | XXXXXX |         |
| 26         | C925     |           | 6     | do.         | Bearpaw              | Shale, black, flaky                          | XXXXXX |         |
| 27         | C926     |           | 6     | do.         | do.                  | Shale, dark-gray                             | XXXXXX |         |
| 28         | C927     | NE 1/4    | 9     | Big Horn    | Heil Creek           | Siltstone, sandy                             | XXXXXX |         |
| 29         | C928     | NE 1/4    | 9     | do.         | Bearpaw              | Claystone, gray, silty                       | XXXXXX |         |
| 30         | C929     | NW 1/4    | 9     | do.         | do.                  | Shale, black                                 | XXXXXX |         |
| 31         | C930     | NW 1/4    | 8     | do.         | do.                  | Shale, dark-gray                             | XXXXXX |         |
| 32         | C931     | NE 1/4    | 8     | do.         | do.                  | Claystone, dark-gray, bentonitic             | XXXXXX |         |
| 33         | C932     | NE 1/4    | 17    | do.         | do.                  | Claystone, dark-gray                         | XXXXXX |         |
| 34         | C933     | SW 1/4    | 8     | do.         | do.                  | Shale, black, flaky                          | XXXXXX |         |
| 35         | C934     | SW 1/4    | 7     | do.         | Claggett             | Shale, black, flaky                          | XXXXXX |         |
| 36         | C935     | SW 1/4    | 12    | do.         | do.                  | do.  | XXXXXX |         |
| 37         | C936     | NE 1/4    | 12    | Wyoming     | Bearpaw              | Claystone, gray, sandy and silty             | XXXXXX |         |
| 38         | C937     | SE 1/4    | 4     | Montana     | Pierre               | Shale, dark-gray to black                    | XXXXXX |         |
| 39         | C938     | SE 1/4    | 26    | Fallon      | do.                  | Claystone, light-gray, bentonitic            | XXXXXX |         |
| 40         | C939     |           | 30    | do.         | do.                  | Claystone, dark-gray                         | XXXXXX |         |
| 41         | C940     |           | 12    | Wyoming     | Mitten Monument Hill | Shale, dark-gray, clayey                     | XXXXXX |         |
| 42         | C941     |           | 12    | do.         | do.                  | Shale, gray, bentonitic                      | XXXXXX |         |
| 43         | C942     |           | 12    | do.         | do.                  | Shale, black                                 | XXXXXX |         |
| 44         | C943     | SE 1/4    | 14    | do.         | Belle Fourche        | do.  | XXXXXX |         |
| 45         | C944     | SE 1/4    | 14    | do.         | do.                  | Claystone, dark-gray to black                | XXXXXX |         |
| 46         | C945     | SE 1/4    | 16    | do.         | Pierre               | Claystone, dark-gray                         | XXXXXX |         |
| 47         | C946     |           | 23    | do.         | do.                  | Shale, dark-gray to black, bentonitic        | XXXXXX |         |
| 48         | C947     | NW 1/4    | 4     | S. Dak.     | do.                  | do.  | XXXXXX |         |
| 49         | C948     |           | 20    | do.         | do.                  | Shale, gray, flaky                           | XXXXXX |         |
| 50         | C949     | SW 1/4    | 20    | do.         | Gammon (?)           | Claystone, black, silty                      | XXXXXX |         |
| 51         | C950     |           | 31    | do.         | do.                  | Shale, black, flaky                          | XXXXXX |         |
| 52         | C951     |           | 36    | do.         | do.                  | Shale, dark-gray to black, flaky             | XXXXXX |         |
| 53         | C952     | NE 1/4    | 26    | Wyoming     | Lewis                | Shale, dark-gray, silty                      | XXXXXX |         |
| 54         | C953     | NE 1/4    | 13    | do.         | Carbon               | Siltstone, brownish-gray                     | XXXXXX |         |
| 55         | C954     | SW 1/4    | 3     | do.         | Lance (?)            | Shale, dark-gray, in lens                    | XXXXXX |         |

1 Samples represent a weathering profile from the center of a road cut (C871) into the colluvium and soil zone on the flank of the hill (C874). The samples were taken about a foot above a tuffaceous siltstone bed, 1 to 2 inches thick, that could be traced into the colluvium. (See fig. 7.)

2 From top of the spillway excavation at Oahe Dam. The sample was obtained about 10 feet above sample C881. Sample E310 is similar to sample C883. See figure 8 for relations of this and the following seven samples.

3 Sample represents a horizontal weathering profile along a bed in the spillway excavation at Oahe Dam. Sample C881 was taken vertically from the top of the cut, and sample C883 was taken from the soil zone equivalent to C881; sample C882 was taken from a point between C881 and C883. (See fig. 8.)

4 Sample E314 was taken 10 feet below sample C881, and samples C884, E316, and C885 were taken 20, 30, and 40 feet, respectively, below sample C881. These samples represent a vertical weathering sequence from the bottom of the spillway excavation at Oahe Dam (C885) to the top (E310). (See fig. 8.)

5 U.S. Army Corps of Engineers, Oahe Dam core hole 2040.

6 Samples were taken about 50 feet apart from the same 2-foot zone.

7 Cuttings from seismograph shot hole. Cuttings appear to have been exposed less than a year.

8 Surface outcrop, probably equivalent to sample C820.

A supplementary set of 45 samples from 23 localities numbered from 11 to 34 (table 1 and pl. 1) was then selected to give additional coverage of the geographic distribution and stratigraphic range of the Pierre rocks, and to test for variations in composition within small areas. Semiquantitative spectrographic analyses of these samples are shown in table 14. Size analyses were made of some of these 45 samples (table 3). Chemical analyses for carbonate and organic carbon are shown in table 18.

Table 2 shows the distribution of the samples by area and by faunal zone. Most of the samples come from rocks in the *Baculites compressus* s. l. and *Baculites obtusus* s. l. zones. More samples come from the western facies belt than from either of the other two belts, but this overweighting of the western belt is conspicuous only for the *B. obtusus* s. l. zone. The *Baculites clinolobatus* zone is poorly represented and only a few samples of pre-Pierre rocks are included.

Analytical techniques and their precision will be described in connection with the data derived from them.

TABLE 2.—Distribution by stratigraphic zone and geographic region of samples included in this study

[Explanation of samples: A, Number of samples for which both standard rock and semiquantitative spectrographic analyses were made; B, Number of samples for which semiquantitative spectrographic analyses only were made]

| Zone                                  | Western facies |    |       |            |    |       | Central facies |    |       | Eastern facies |   |       | Total |
|---------------------------------------|----------------|----|-------|------------|----|-------|----------------|----|-------|----------------|---|-------|-------|
|                                       | North part     |    |       | South part |    |       | A              | B  | Total | A              | B | Total |       |
|                                       | A              | B  | Total | A          | B  | Total |                |    |       |                |   |       |       |
| <i>Baculites clinolobatus</i> ...     |                |    |       | 1          | 1  |       | 1              | 1  |       |                |   |       | 2     |
| <i>Baculites compressus</i> s. l. ... | 1              | 6  | 7     | 8          | 8  | 1     | 10             | 11 | 11    |                |   |       | 37    |
| <i>Baculites obtusus</i> s. l. ...    | 4              | 7  | 11    | 1          | 4  | 5     | 1              | 2  | 3     | 3              |   | 4     | 22    |
| Pre-Pierre.....                       |                | 4  | 4     |            |    |       |                | 2  | 2     |                |   |       | 6     |
| Total.....                            | 5              | 17 | 22    | 1          | 13 | 14    | 2              | 15 | 17    | 14             |   | 14    | 67    |

<sup>1</sup> Number of samples reduced to nine on plate 4 by excluding two samples selected at random.

<sup>2</sup> Number of samples reduced to nine on plate 4 by excluding two samples of marlstone.

<sup>3</sup> Total number of *Baculites compressus* zone samples (37) reduced to 25 on plate 3 by excluding 12 samples selected at random.

<sup>4</sup> Includes two samples from strata between the *Baculites obtusus* and *Baculites compressus* zones. These samples are excluded from plate 3 (total of 20 samples) and figure 15, but are included in plate 4 (total of 14 samples).

### PHYSICAL COMPOSITION

The lithologic characteristics of the samples selected for investigation are shown in table 1. The descriptions of the material are based mainly on field observations. The basic set of 22 samples, to which the most attention is given, include 8 of shale, 10 of claystone, 2 of marlstone, and 2 of soil-like residual weathering products. The shale is mostly black and appears to be richer in disseminated organic material than the claystone. The claystone samples range from black to gray; the darker colors of both the shale and claystone apparently are due to evenly distributed finely par-

ticulate organic matter, probably plant fragments. The marlstone samples are yellowish gray and the surface sample of marlstone is darker than the core sample. The samples of the residual weathering products represent initial breakdown of the shale or claystone in the process of soil formation.

### SIZE ANALYSES

Rocks that consist virtually of silt and clay are difficult to disaggregate and disperse for size analysis (Krumbein and Pettijohn, 1938, p. 51). Different kinds of clay respond differently to specific disaggregation and dispersion techniques, and the resulting data are of uncertain value other than to make comparisons between samples analysed by the same techniques. The relation between the particle-size distribution at time of sedimentation and particle size as determined by analyses is uncertain. Even with these limitations, however, the size analyses of fine-grained rocks are useful in classifying the rocks and in making comparisons between samples analysed by the same methods.

The following method of analysis used for 38 samples of the Pierre shale and equivalent rocks was supplied by Joseph Sharps (written communication, July 1958), who performed the analyses (table 3):

The analyses were made in lots of 10. About 50 grams of sample were ground with a rubber pestle until all the material passed through a no. 40 sieve (0.42 mm). The sample was then put in a Buchner funnel and leached with distilled water to remove soluble salts that seemed to be causing flocculation. The sample was leached until it would stay in suspension in the funnel. After oven drying at 95°C and weighing, the sample was soaked in a solution of sodium polyphosphate for about 16 hours and then stirred with about 500 milliliters of distilled water in a small shaft-type mixing machine for 45 minutes. The following day, each sample was again stirred for one minute and poured into a suspension cylinder, enough distilled water being added to the suspension to fill the cylinder to the thousand-milliliter mark. Each cylinder was shaken by hand for one minute and set in a water bath that maintains a temperature of 20°C. A soil hydrometer was then read at intervals of half a minute, 1 minute, 4 minutes, 19 minutes, 1 hour, 2 hours, and 24 hours from the time the cylinder was placed in the water bath and the hydrometer placed in the suspension. The maximum particle size (effective settling diameter or equivalent diameter) in suspension at these times was determined from a chart developed in the laboratories of the U.S. Bureau of Reclamation (1951). The percentage of the total sample in suspension at each of these times was determined from the hydrometer readings after correcting for hydrometer error, meniscus curve, temperature variation, and the presence of sodium polyphosphate. The sample was then washed from the cylinder through a no. 200 sieve (0.074 mm); the material retained on the sieve was dried and weighed, and its percentage amount of the total sample was calculated.

A summary of grain-size distribution of the Pierre shale samples and equivalent rocks compared to other kinds of fine-grained rocks is shown on figure 3.

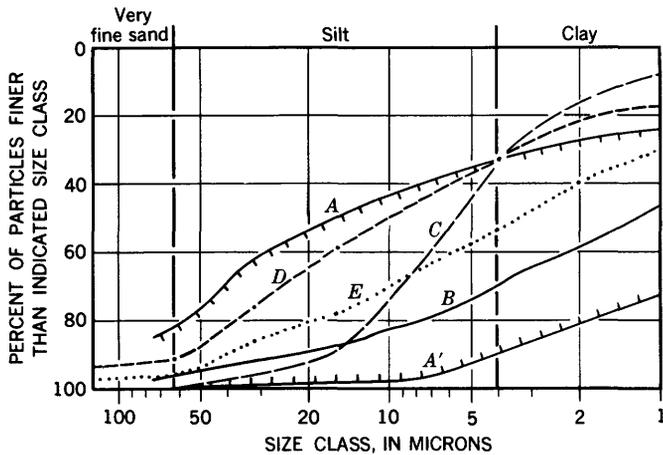


FIGURE 3.—Particle-size classification of samples of the Pierre shale and equivalent rocks and comparison of size distribution with that in some older shales. A, Synthetic curves representing the minimum (A) and maximum (A') percentages for each of the equivalent diameters determined in the 38 samples of the Pierre shale and equivalent rocks given in table 3. B, Average cumulative curve based on the 38 samples of the Pierre shale and equivalent rocks given in table 3. C, A marine shale of Pennsylvanian age from Illinois (Krumbein, 1938, p. 86). D, Average cumulative curve based on 13 samples of shale of Pennsylvanian age from Kansas (McMillan, 1956, appendix 2). E, Average cumulative curve based on 45 samples of underclay of Pennsylvanian age from Kansas (McMillan, 1956, appendix 2).

TABLE 3.—Size analyses of 38 samples of Pierre shale and equivalent rocks

[See table 1 for location and description of samples. Sample: An asterisk (\*) indicates that the sample is part of the basic set of 22 samples (see p. 13); prefix "C" indicates sample numbers that were assigned by the chemical laboratory at Denver, Colo.; prefix "E" indicates samples numbers assigned by the engineering laboratory, Denver, Colo. Median size: Taken from cumulative curves. Analyses by Joseph Sharps]

| Local-ity (see pl. 1) | Sample | Cumulative percent finer than (microns) |      |      |      |      |      |      | Me-dian size (mi-crons) |      |
|-----------------------|--------|---|------|------|------|------|------|------|-------------------------|------|
|                       |        | 74                                      | 50   | 37   | 19   | 9    | 5    | 3.6  |                         | 1    |
| 1                     | *C871  | 94.8                                    | 91.0 | 88.6 | 82.7 | 74.3 | 67.0 | 62.0 | 28.5                    | 1.2  |
|                       | *C872  | 93.4                                    | 86.4 | 83.3 | 76.5 | 67.9 | 60.5 | 54.0 | 35.2                    | 1.9  |
|                       | *C873  | 92.3                                    | 87.1 | 82.7 | 75.7 | 69.2 | 60.3 | 55.5 | 38.6                    | 1.4  |
|                       | *C874  | 95.4                                    | 94.2 | 93.1 | 87.3 | 82.4 | 74.8 | 69.9 | 55.0                    | <1.0 |
| 2                     | *C875  | 92.5                                    | 87.8 | 80.6 | 71.2 | 64.8 | 59.8 | 54.6 | 38.2                    | 2.6  |
| 3                     | *C870  | 99.1                                    | 96.0 | 93.0 | 80.9 | 62.4 | 51.5 | 44.6 | 27.5                    | 4.4  |
|                       | C896   | 84.7                                    | 77.7 | 66.4 | 53.2 | 41.7 | 36.0 | 32.0 | 24.1                    | 16.0 |
| 4                     | *C876  | 99.0                                    | 95.8 | 95.6 | 91.8 | 87.1 | 79.1 | 73.8 | 49.9                    | 1.0  |
| 5                     | *C877  | 96.0                                    | 92.6 | 92.0 | 90.0 | 85.0 | 77.2 | 72.2 | 48.9                    | 1.0  |
| 6                     | *C886  | 99.0                                    | 97.5 | 96.8 | 95.7 | 91.1 | 84.7 | 81.0 | 61.6                    | <1.0 |
| 7                     | *C887  | 95.2                                    | 91.3 | 90.6 | 88.2 | 82.3 | 73.8 | 67.7 | 45.0                    | 1.4  |
| 8                     | E310   | 97.2                                    | 94.5 | 91.3 | 85.0 | 78.4 | 70.4 | 65.4 | 44.2                    | 1.5  |
|                       | *C881  | 99.0                                    | 96.3 | 95.6 | 94.3 | 89.0 | 81.1 | 75.6 | 53.4                    | <1.0 |
|                       | *C882  | 96.1                                    | 92.7 | 92.1 | 90.4 | 85.6 | 75.8 | 70.7 | 49.2                    | 1.0  |
|                       | *C883  | 98.1                                    | 93.1 | 91.5 | 87.6 | 81.0 | 75.0 | 68.6 | 45.0                    | 1.3  |
|                       | E314   | 99.1                                    | 96.1 | 95.9 | 94.7 | 88.6 | 80.5 | 74.8 | 49.6                    | 1.0  |
|                       | *C884  | 98.6                                    | 92.3 | 91.6 | 88.5 | 81.0 | 71.7 | 64.9 | 37.3                    | 1.8  |
|                       | E316   | 99.7                                    | 95.5 | 95.0 | 93.0 | 86.6 | 77.1 | 70.3 | 39.2                    | 1.5  |
|                       | *C885  | 99.2                                    | 96.1 | 95.4 | 92.9 | 84.1 | 73.6 | 67.3 | 38.3                    | 1.6  |
| 9                     | *C878  | 96.0                                    | 94.6 | 94.0 | 93.0 | 86.4 | 74.5 | 66.5 | 43.3                    | 1.6  |
|                       | *C879  | 96.8                                    | 94.5 | 88.2 | 78.5 | 68.9 | 61.0 | 56.7 | 35.8                    | 2.5  |
|                       | *C880  | 98.3                                    | 97.3 | 95.9 | 95.4 | 92.9 | 89.4 | 85.6 | 72.3                    | <1.0 |
|                       | E327   | 97.7                                    | 96.7 | 96.4 | 95.8 | 94.7 | 88.7 | 83.1 | 62.3                    | <1.0 |
|                       | E328   | 99.5                                    | 98.8 | 98.4 | 97.9 | 94.6 | 88.0 | 83.4 | 64.0                    | <1.0 |
|                       | E329   | 99.8                                    | 97.9 | 97.6 | 96.8 | 94.4 | 89.5 | 85.5 | 64.3                    | <1.0 |
| 10                    | *C888  | 98.3                                    | 96.3 | 95.4 | 94.1 | 91.9 | 89.3 | 84.7 | 66.7                    | <1.0 |
|                       | *C889  | 99.3                                    | 98.0 | 97.8 | 96.1 | 92.6 | 86.9 | 79.7 | 51.6                    | <1.0 |
|                       | *C890  | 99.2                                    | 98.8 | 98.6 | 98.4 | 97.6 | 91.7 | 87.8 | 67.1                    | <1.0 |
|                       | *C891  | 76.0                                    | 69.5 | 66.2 | 60.0 | 54.1 | 48.1 | 44.4 | 25.4                    | ?    |
| 12                    | C913   | 95.1                                    | 90.1 | 85.2 | 78.0 | 68.1 | 63.6 | 59.2 | 49.0                    | 1.0  |
| 13                    | C914   | 96.5                                    | 96.0 | 95.6 | 93.6 | 88.2 | 79.8 | 72.4 | 53.1                    | <1.0 |
| 14                    | C899   | 92.4                                    | 86.9 | 84.4 | 78.5 | 70.5 | 63.1 | 56.9 | 39.6                    | 2.4  |
| 16                    | C905   | 95.9                                    | 90.2 | 84.7 | 73.9 | 65.3 | 57.1 | 53.1 | 39.4                    | 3.0  |
| 19                    | C908   | 88.7                                    | 86.4 | 85.6 | 82.8 | 76.6 | 68.6 | 62.6 | 46.9                    | 1.5  |
| 20                    | C907   | 99.1                                    | 97.5 | 96.9 | 90.8 | 83.9 | 75.9 | 69.7 | 50.8                    | 1.0  |
| 21                    | C906   | 98.1                                    | 96.4 | 93.0 | 85.8 | 78.0 | 70.6 | 65.3 | 50.7                    | 1.0  |
| 25                    | C916   | 98.7                                    | 97.0 | 96.2 | 92.8 | 87.2 | 79.2 | 72.8 | 47.8                    | 1.0  |
| 33                    | C894   | 95.0                                    | 91.0 | 90.0 | 81.4 | 67.9 | 57.2 | 50.6 | 33.6                    | 2.5  |

<sup>1</sup> Not used to define minimum curve of figure 3, because apparent coarseness is entirely due to clay aggregates.

The curve for the average percentages of the equivalent diameters determined by hydrometer analysis shows that the samples contain about 70 percent material finer than 1/256 mm (about 4 microns), the upper limit of the clay-size grade. The minimum amount of clay determined in any sample is about 35 percent and the maximum amount is about 90 percent. The samples contain an average of nearly 50 percent material finer than 1 micron. The departure in shape of the minimum curve from the average probably reflects the different extents to which the individual samples were disaggregated, since much of the material coarser than 74 microns in many of the samples consists of aggregates (see table 4), and aggregates probably also are present in the finer size grades. Even allowing for differences in disaggregation techniques, the average for samples of the Pierre seems to be finer than a single shale of Pennsylvanian age reported by Krumbein (1938, p. 86) and the average of the shales and underclays reported by McMillan (1956, app. 2).

Histograms and equivalent diagrammatic cumulative curves of the three kinds of size distributions found in the Pierre shale and equivalent rocks are shown in figure 4. The histograms show that the distribution is highly skewed toward sizes of less than 1 micron, and that the samples have an excess of material in the larger sizes. The cumulative curves apply only to sizes coarser than 1 micron.

The size characteristics of the shale and claystone change from west to east, the rocks being finer in the east, as shown by the following averages:

|                                  | Number of samples | Percent of particles finer than indicated sizes |           |             |           |          |           |
|----------------------------------|-------------------|---|-----------|-------------|-----------|----------|-----------|
|                                  |                   | 74 microns                                      |           | 3.6 microns |           | 1 micron |           |
|                                  |                   | Av-erage  | Range     | Av-erage    | Range     | Av-erage | Range     |
| Western and central facies belts | <sup>1</sup> 15   | 95.2  | 84.7-99.1 | 60.1        | 32.0-73.8 | 41.9     | 24.1-53.1 |
| Eastern facies belt              | <sup>2</sup> 17   | 98.3  | 95.2-99.8 | 75.3        | 56.7-85.6 | 52.7     | 35.8-67.1 |

<sup>1</sup> Excludes samples C872, C873, and C874.  
<sup>2</sup> Excludes sample C891 which could not be disaggregated and samples C882 and C883.

The differences between the amount of material finer than 74 microns in each of the facies belts could be the result of different responses of the shale and claystone to the disaggregating techniques. The differences between the two smaller sizes in the two facies belts are so large that it seems reasonable to infer a real difference in size distribution. This difference is consistent with the general sedimentational setting in which detritus from a western source area is deposited in a broad marine basin to the east, the finer grained material being deposited farthest from the source area.

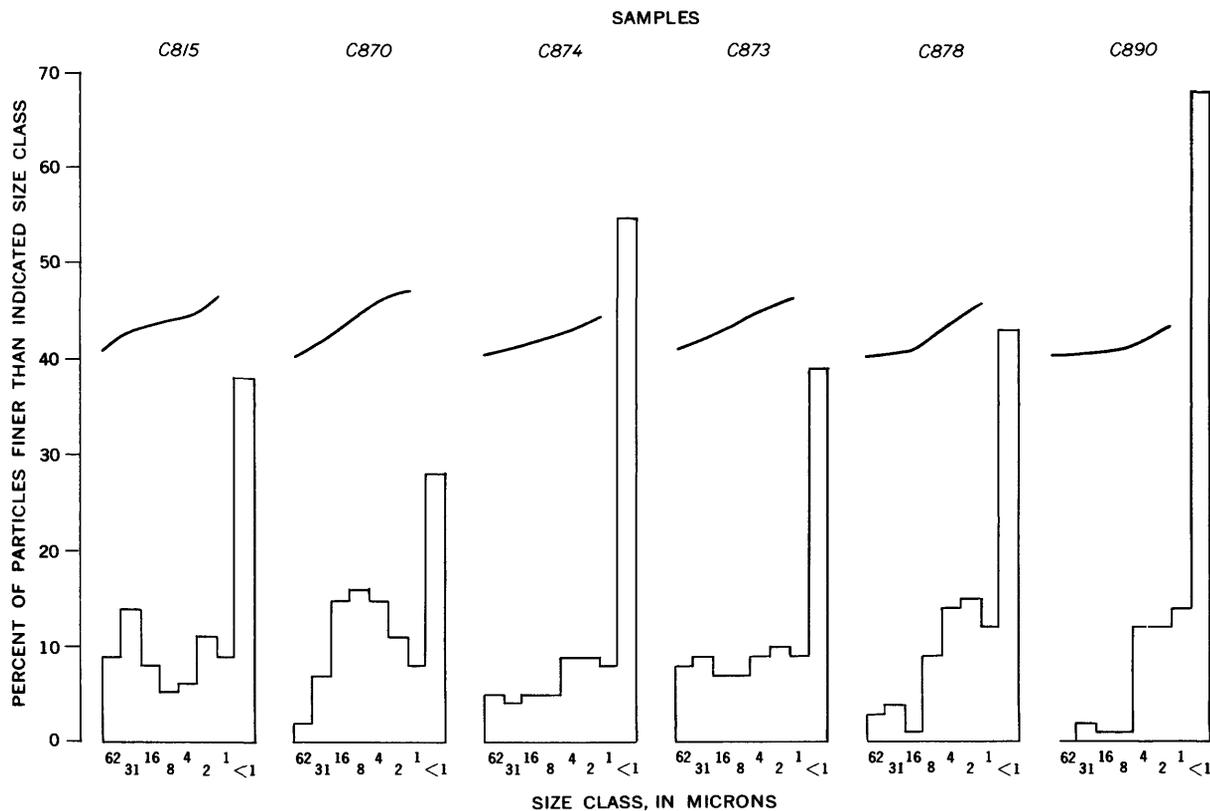


FIGURE 4.—Histograms and diagrammatic cumulative curves representing the different kinds of particle-size distribution found in the samples of the Pierre shale and equivalent rocks. See figure 5 for large-scale cumulative curves and table 3 for size analyses.

The cumulative curves for locality 1 (fig. 5) are based on samples representing different stages of weathering of a single bed. (See table 1 and fig. 7.) Sample C871 is the freshest sample and sample C874 is a soil-like weathering product of the bed; samples C872 and C873 are intermediate in the degree of weathering. The differences in shape between the cumulative curves are slight, although the curve for the freshest sample, C871, is more strongly concave than the other curves and represents a rock that contains smaller amounts of the finer particles than the more weathered samples. The soil-like weathering product, sample C874, is finer grained than the other samples; this could reflect an actual diminution of particle size in weathering, but it seems more likely that the weathered material is more effectively disaggregated and dispersed by the procedures used in the size analyses. The cumulative curves for the intermediate samples, C872 and C873, are anomalous.

Similar relations between size distribution and degree of weathering are shown in figure 5, locality 8. (See table 1 and fig. 8.) The two least-weathered samples (C884 and C885) have a median size of more than 1.5

microns, and the three weathered samples (C881, C882, and C883) have an average median size of about 1 micron or less. However, the most strongly weathered sample (C883) does not have the smallest median size.

Figure 5 also shows the size analyses for samples from the same stratigraphic zones from a drill hole at locality 9 and an outcrop at locality 10. (See fig. 9 for relations between samples.) The core samples have larger median-size diameters than the equivalent outcrop samples for the DeGrey member (samples C878 and C888) and the marl of the Crow Creek member (samples C879 and C889). The two samples from the Gregory member (samples C880 and C890) do not show a significant difference in their size analyses.

Cumulative curves for samples from localities 2 to 7 also are shown on figure 5. These curves are similar in most respects to the curves for the other samples. Samples C870 and C875, however, contain larger amounts of relatively coarse silt-sized material than the other samples. These samples also contain abundant quartz, feldspar, and biotite grains in the fraction coarser than 74 microns (table 4).

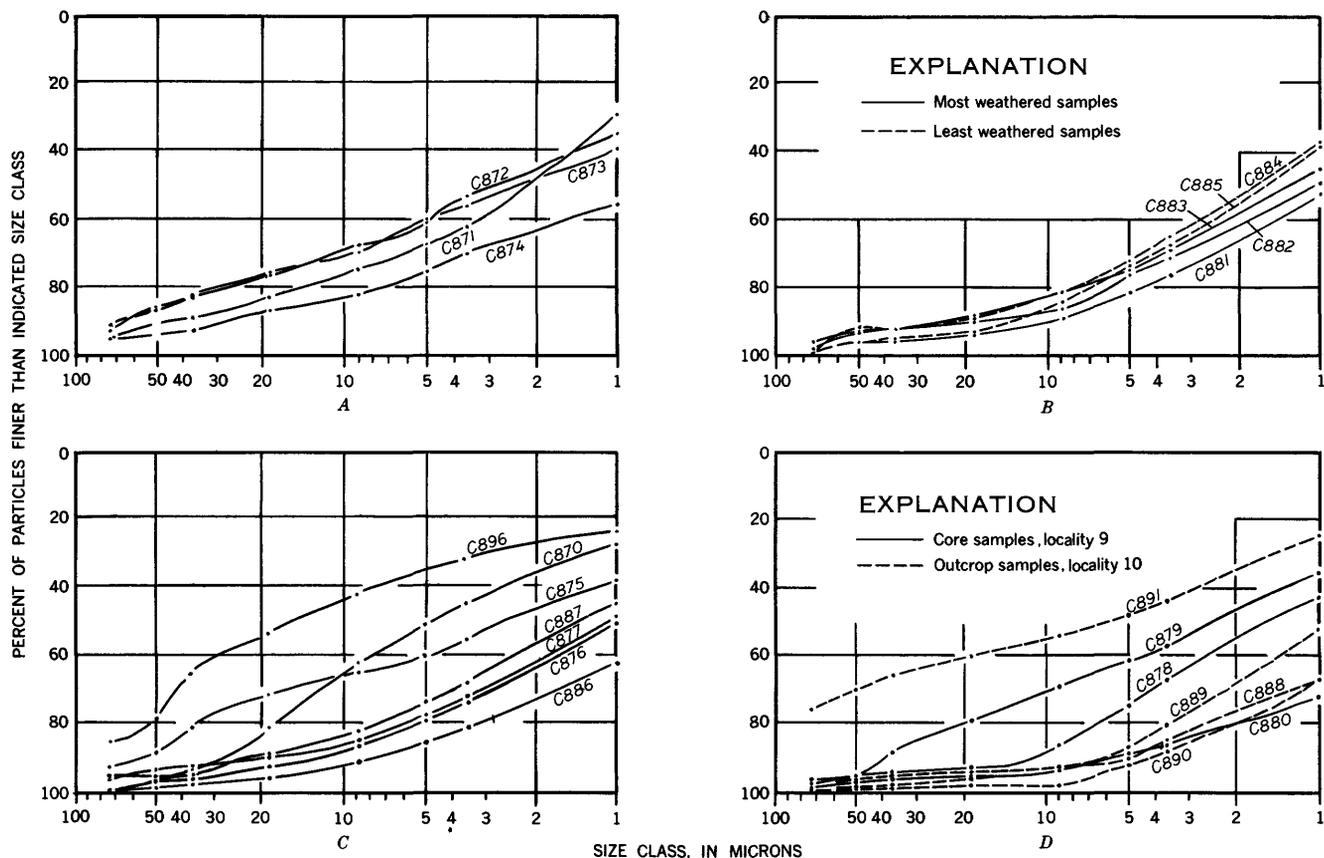


FIGURE 5.—Cumulative curves showing particle-size classification for samples of Pierre shale and equivalent rocks. See table 3 for size analyses. A, Locality 1, samples C871–C874; degree of weathering increases from C871–C874. B, Locality 8, samples C881–C885; samples E310, E314, and E316 (table 3) are nearly within the limits shown here and, therefore, are not plotted. C, Locality 2, sample C875; locality 3, samples C870, C896; locality 4, sample C876; locality 5, sample C877; locality 6, sample C886; locality 7, sample C887, D, Locality 9, core sample C878 from the DeGrey member, C879 from the marl of the Crow Creek member, and C880 from the Gregory member; locality 10, outcrop sample C888 from the DeGrey member, C889 from the marl of the Crow Creek member, C890 from the Gregory member, and C891 from the Sharon Springs member.

**MINERALOGY**

**MATERIAL COARSER THAN 74 MICRONS**

The material coarser than 74 microns, which was separated as the last phase of the size analyses, was examined with a binocular microscope. The minerals and other materials found in this fraction of each of the basic set of 22 samples are shown in table 4. Aggregates cemented with oxides of iron and manganese are the predominant constituent of most of the fractions. The iron-oxide aggregates are most noticeable in the more weathered samples (C871, C881 to C883), and they probably form in the weathered zone from the oxidation products of pyrite and other sources of mobile iron. Pyrite and iron-oxide aggregates do not occur together in the fraction coarser than 74 microns, but many of the samples must contain pyrite in particles finer than 74 microns. Manganese-oxide aggregates accompany pyrite in sample C878, which is a

core sample of unweathered material. This could mean that some of the manganese-oxide aggregates are original constituents of the shale and claystone, but such aggregates are most abundant in weathered samples. Quartz grains coarser than 74 microns are present in many samples, and so are feldspar grains. Both of these minerals must also occur in considerable amounts in sizes smaller than 74 microns. Biotite is an abundant constituent of most of the samples from the western and central facies belts, and also is present in a few of the samples from the eastern facies belt. Foraminifera, however, were found only in the samples from the eastern facies belt.

Petrographic studies were not made on these samples.

**X-RAY ANALYSES**

The X-ray analyses shown in table 5 were made by L. G. Schultz (written communication, February 1959),

TABLE 4.—Mineralogy of material coarser than 74 microns in 22 basic samples of shale and marlstone of Pierre shale and equivalent rocks

[Relative amounts of constituents: A, abundant; C, common; R, rare. See table 3 for complete size analyses of samples]

| Local-ity (see pl. 1) | Sample | Percent of sam-ple coarser than 74 microns | Relative amounts of constituents |                 |        |   |       |        |        |          |         |            |              |  |
|-----------------------|--------|--|----------------------------------|-----------------|--------|---|-------|--------|--------|----------|---------|------------|--------------|--|
|                       |        |  | Aggregates                       |                 |        |   | Shale | Pyrite | Quartz | Feldspar | Biotite | Glauconite | Foraminifera |  |
|                       |        |  | Iron oxide                       | Manganese oxide | Gypsum |   |       |        |        |          |         |            |              |  |
| 1                     | C871   | 5.2  | A                                |                 | C      |   |       | C      | C      | C        |         |            |              |  |
|                       | C872   | 6.6  | A                                |                 | C      |   |       | C      | C      | C        |         |            |              |  |
|                       | C873   | 7.7  | A                                |                 | R      |   |       | C      | C      | C        |         |            |              |  |
|                       | C874   | 4.6  | A                                |                 |        |   |       | C      | C      | C        |         |            |              |  |
|                       | C875   | 7.5  | A                                | R               | R      |   |       | C      | C      | C        |         |            | R            |  |
| 2                     | C870   | .9   |                                  |                 |        |   |       | A      | A      | A        |         |            |              |  |
| 3                     | C876   | 1.0  | A                                |                 |        |   |       | R      | R      | R        |         |            |              |  |
| 4                     | C877   | 4.0  | A                                |                 |        |   |       | R      | R      | R        |         |            |              |  |
| 5                     | C886   | 1.0  | A                                |                 |        |   |       | R      | R      | R        |         |            |              |  |
| 6                     | C887   | 4.8  | A                                |                 |        |   |       | R      | R      | R        |         |            |              |  |
| 7                     | C881   | 1.0  | A                                |                 |        |   |       | R      | R      | R        |         |            |              |  |
| 8                     | C882   | 3.9  | A                                |                 |        |   |       | R      | R      | R        |         |            |              |  |
|                       | C883   | 1.9  | A                                | A               |        |   |       | R      | R      | R        |         |            |              |  |
|                       | C884   | 1.4  |                                  |                 |        | 1 | R     | A      | R      | R        |         |            |              |  |
|                       | C885   | .8   |                                  |                 |        | 1 | C     |        | R      | R        |         |            |              |  |
| 9                     | C878   | 4.0  |                                  | C               |        |   |       | R      | R      | R        |         |            |              |  |
|                       | C879   | 3.2  |                                  |                 |        |   |       | A      | C      |          |         |            |              |  |
|                       | C880   | 1.7  |                                  |                 |        |   |       | C      |        | A        |         |            |              |  |
| 10                    | C888   | 1.7  |                                  | R               |        |   |       |        |        |          |         |            |              |  |
|                       | C889   | .7   |                                  | A               |        |   |       |        |        |          |         |            |              |  |
|                       | C890   | .8   | A                                | A               |        |   |       | C      |        |          |         |            |              |  |
|                       | C891   | 24.0                                       |                                  |                 |        | 2 | A     |        |        |          |         |            |              |  |

<sup>1</sup> Cement not discernible.

<sup>2</sup> Cemented with organic matter.

who describes the analytical methods and the characteristics of the clay minerals:

Clay mineral data shown in table 5 were obtained from X-ray diffractometer traces of one oriented aggregate and one un-oriented powder of the whole rock of each sample. Each oriented aggregate was X-rayed in the natural state, after glycol treatment, after half an hour of heat treatment at 300°C, and after half an hour of heat treatment at 550°C. Clay, whose basal spacing completely expanded to 17A when glycol treated, is listed as montmorillonite. Illite refers to a clay mineral with a 10A basal spacing that shows no expanding lattice characteristics (Grim and others, 1951, p. 155). Mixed-layer illite-montmorillonite is identified by its intermediate expanding characteristics; in the mixed-layer clay of table 5, the expandable layers are generally most abundant. All of the illite-montmorillonite group minerals seem to be predominantly dioctahedral, aluminous varieties. Chlorite gave a series of basal X-ray reflections from 14A and is soluble in warm 6N HCl; kaolinite gave a series from about 7A and is insoluble in warm 6N HCl. Because of the complex nature of the mineral mixtures and the minor amounts of some clay minerals in many samples, reflections other than basal and 060 could not be consistently used for identification and classification.

Data on the relative abundance of different clay minerals are obtained using methods previously described (Schultz, 1960). The values given on table 5 for the total amount of clay in the samples and the amounts of nonclay minerals are based on sizes of X-ray diffraction peaks obtained from the un-oriented powders. The values for total clay have been rounded off to the nearest 5 percent because these values are probably the least accurate on the table. Except where present in amounts of only a few percent, the determinations of abundance of both

clay and nonclay minerals are believed correct within 10 percent of the amount present.

Values for total amounts of minerals identified fall between 84 and 104 percent. Deviations from 100 percent totals probably are largely indicative of the accuracy of the determinations. However, inasmuch as most of the total values are below 100 percent, some of the discrepancies probably represent organic material and perhaps also some nondiffracting, amorphous material. Also, some minerals present in amounts of only a percent or so may have been missed.

TABLE 5.—X-ray analyses, in percent, of 22 basic samples of Pierre shale and equivalent rocks

[See table 1 for location and description of samples. A query (?) indicates not certainly identified. Analyses by L. G. Schultz]

| Local-ity (see pl. 1) | Sample | Total rock    |        |          |         |          |        |        |                | Clay-mineral fraction |                 |                                    |        |          |
|-----------------------|--------|---------------|--------|----------|---------|----------|--------|--------|----------------|-----------------------|-----------------|------------------------------------|--------|----------|
|                       |        | Clay minerals | Quartz | Feldspar | Calcite | Dolomite | Gypsum | Pyrite | Clinoptilolite | Total                 | Montmorillonite | Mixed-layer illite-montmorillonite | Illite | Chlorite |
| 1                     | C871   | 60            | 15     | 4        |         |          | 15     |        | 84             | 20                    | 48              | 20                                 | 4      | 8        |
|                       | C872   | 60            | 18     | 3        |         |          | 15     |        | 86             | 20                    | 53              | 17                                 | 4      | 6        |
|                       | C873   | 70            | 17     | 3        |         |          | 2      |        | 90             | 24                    | 55              | 16                                 | 0      | 5        |
|                       | C874   | 70            | 17     | 2        |         |          |        |        | 89             | 22                    | 53              | 19                                 | 0      | 6        |
|                       | C875   | 75            | 22     | 3        |         |          |        | 2      | 102            | 18                    | 56              | 17                                 | 3      | 6        |
|                       | C870   | 50            | 27     | 3        |         | 10       |        |        | 102            | 15                    | 57              | 30                                 | 2      | 6        |
|                       | C876   | 80            | 21     | 1        |         |          |        |        | 100            | 12                    | 46              | 15                                 | 7      | 4        |
|                       | C877   | 80            | 18     | 1        |         |          | 2      |        | 99             | 36                    | 32              | 19                                 | 2      | 3        |
|                       | C886   | 75            | 15     | 3        | 5       |          | 2      |        | 100            | 45                    | 32              | 19                                 | 2      | 2        |
|                       | C887   | 70            | 15     | 4        |         |          |        |        | 92             | 40                    | 42              | 16                                 | 1?     | 1        |
|                       | C881   | 70            | 17     | 1        |         |          |        |        | 100            | 30                    | 54              | 15                                 | 1      | ?        |
|                       | C882   | 75            | 18     | 1        |         |          | 4      |        | 92             | 39                    | 41              | 20                                 | 1      | ?        |
|                       | C883   | 75            | 15     | 2        |         |          |        |        | 90             | 45                    | 38              | 17                                 |        | 1        |
|                       | C884   | 65            | 17     | 2        |         |          |        | 2      | 90             | 28                    | 51              | 15                                 | 2      | 4        |
|                       | C885   | 75            | 19     | 1        |         |          |        |        | 104            | 33                    | 44              | 18                                 | 3      | 2        |
|                       | C878   | 65            | 433    | 1        |         | 3        |        | 2      | 102            | 30                    | 50              | 16                                 | 2      | ?        |
|                       | C879   | 35            | 12     |          | 38      | 5        |        | 2      | 94             | 45                    | 36              | 17                                 | 2      | ?        |
|                       | C880   | 80            | 18     | 2        |         |          |        |        | 100            | 43                    | 45              | 9                                  | 1      | 2        |
|                       | C888   | 85            | 14     | 2        |         |          |        |        | 104            | 47                    | 41              | 10                                 | 1?     | 1        |
|                       | C889   | 45            | 8      |          | 37      | 3        | 4      |        | 94             | 38                    | 40              | 16                                 | 2      | 4        |
|                       | C890   | 80            | 15     | 1        | 4       |          |        | (?)    | 100            | 36                    | 52              | 9                                  | ?      | 3        |
|                       | C891   | 60            | 20     | 1        |         |          |        | 2      | 86             | 18                    | 46              | 26                                 |        | 10       |

<sup>1</sup> Includes 3 percent jarosite.

<sup>2</sup> Jarosite instead of gypsum.

<sup>3</sup> Siderite.

<sup>4</sup> Includes 18 percent beta-cristobalite.

<sup>5</sup> About half siderite, possibly manganiferous.

<sup>6</sup> The chemical analysis (table 7) reports 1.31 percent soluble sulfur.

Calcite, dolomite, gypsum, jarosite, pyrite, and clinoptilolite are minor minerals in some of the samples. Calcite in samples C886 and C880 reflect the presence of Foraminifera in the fraction coarser than 74 microns (table 4), but calcite was not found by X-ray methods in other samples with Foraminifera. The chemical analyses (see table 7) indicate that calcite is recognized consistently by X-ray methods only if carbon dioxide is reported in the analysis in amounts larger than about 2 percent. A carbon dioxide content of 2 percent is equivalent to a calcite content of about 4.5 percent. Dolomite amounts to 10 percent in sample C870. The mineral must be present as quite small crystals, since dolomite rhombs could not be recognized in the fraction coarser than 74 microns. On the basis of the X-ray analyses, estimates of about 7 and 4 percent dolomite were made for the two marlstone samples (C879 and C889), as compared to about 9 and 6 percent dolomite

calculated for these samples on the basis of other assumptions. (See p. 34.)

The X-ray estimates of abundance of sulfate and sulfide minerals only partly reflect the amounts of sulfur reported in the chemical analyses (table 7). Gypsum and jarosite together are estimated to amount to 5 percent in samples C871 and C872, which is in fairly close agreement with 3 percent acid-soluble sulfur as sulfur trioxide given in the chemical analyses. In sample C881, however, the X-ray analysis indicates about 4 percent gypsum to be present, although the sample contains only about 1 percent acid-soluble sulfur as sulfur trioxide. No sulfate minerals could be detected in the X-ray analysis of sample C890, which contains 1.31 percent acid-soluble sulfur as sulfur trioxide (table 7). Pyrite was estimated to be 2 percent from the X-ray traces of samples C884 and C885. The samples contain 0.66 and 0.49 percent, respectively, insoluble sulfur as sulfur; these figures calculate to about 1 percent pyrite in the rock. Pyrite was only tentatively identified in sample C891 for which 1.57 percent insoluble sulfur was reported; 1.57 percent insoluble sulfur calculates to about 3 percent pyrite in the rock. Jarosite is the only sulfate mineral in sample C891 recognized from the X-ray traces and is estimated to amount to 5 percent, although gypsum is evident in the sample and the acidic pH of the sample (table 20) suggests the presence of a soluble sulfate, such as melanterite.

Clinoptilolite, a calcium-sodium zeolite, is estimated from X-ray analyses to amount to 3 or 4 percent of some samples (table 5). Bramlette and Posnjak (1933) also found clinoptilolite in volcanic ash and bentonite, including a sample of the Pedro bentonite bed near the base of the Pierre shale on the west side of the Black Hills; Hey and Bannister (1934) later interpreted this material as being a high-silica heulandite. According to Mumpton (1958), heulandite and clinoptilolite give similar X-ray patterns, but heulandite undergoes a thermal transformation at about 230°C, whereas clinoptilolite remains stable to about 700°C. Mr. Schultz (oral communication, April 1959) reports that the common zeolite in the samples of the Pierre is of the thermally stable variety. Zeolites seem to be a common product of the alteration of volcanic material in a variety of situations (Bradley, 1929, p. 2-6; Boldyreva, 1953; Bramlette and Bradley, 1942, p. 31; Goldberg and Arrhenius, 1958, p. 154 and 161; Hay, 1957, p. 36; Keller, 1952, 1953; and Murray and Renard, 1891, p. 400-411).

Clinoptilolite in the samples of the Pierre is present in fresh samples at localities 8 and 9 and in weathered samples at localities 7, 8, and 10. It was found in both the core sample of the DeGrey member at locality 9

(sample C878) and the outcrop sample of the DeGrey member at locality 10 (sample C879), which suggests that the occurrence of clinoptilolite is independent of weathering. All these samples are highly bentonitic.

Bramlette and Posnjak (1933, p. 171) considered the clinoptilolite to be an intermediate state in the alteration of pyroclastic material to bentonite. Bradley considered the analcime in the Green River formation to be the result of diagenetic reactions between alkaline lake water and decomposed volcanic ash (1929, p. 4-6). The clinoptilolite in fresh samples of the Pierre seems best interpreted as a diagenetic mineral. There is no reason, though, why the clinoptilolite could not be an authigenic secondary mineral in some weathered samples, analogous to the occurrence of heulandite described by Gilbert and McAndrews (1948). The main requirements for the formation of authigenic zeolites seem to be a supply of reactive aluminum silicates and of alkali and alkaline-earth elements; both requirements could be met either under conditions of diagenesis or weathering.

The clay-mineral suite (table 5) consists predominantly of illite, montmorillonite, and a mixed-layer illite and montmorillonite, which makes up about half of the clay minerals in most samples. Illite is present in the samples in fairly uniform amounts, ranging from 10 to 30 percent. Montmorillonite is much more variable, ranging from 12 to 40 percent. Chlorite and kaolinite were found in nearly all samples.

Montmorillonite is more abundant in samples from the eastern facies belt than in samples from the western facies belt, as indicated by the following averages and ranges, in percent, given in the following table:

|                                   | Number of samples | Montmorillonite |       | Mixed-layer illite and montmorillonite |       | Illite  |       | Chlorite |       | Kaolinite |
|-----------------------------------|-------------------|-----------------|-------|--|-------|---------|-------|----------|-------|-----------|
|                                   |                   | Average         | Range | Average                                | Range | Average | Range | Average  | Range |           |
| Western and central facies belts. | 7                 | 21              | 12-36 | 51                                     | 45-57 | 20      | 16-30 | 3        | 0-7   | 5         |
| Eastern facies belt.              | 15                | 39              | 18-45 | 44                                     | 36-54 | 16      | 9-18  | 1        | ----- | 2         |

NOTE.—Averages do not include data for soillike weathering products, samples C874 and C883.

The data may be somewhat biased, because the western facies samples represent mostly the lower part of the Pierre-equivalent rocks and the eastern facies samples represent mostly the upper part of the Pierre. The one sample from the lowermost part of the Pierre shale in the eastern facies belt, which was included, contains relatively little montmorillonite compared to other eastern facies samples, but this may be a special case because the sample is so rich in organic carbon (table 7). Its exclusion from the averages would further

emphasize the eastward increase in montmorillonite.

The predominance of montmorillonite parallels the predominance of the finer sediment sizes in the eastern facies belt (see p. 17) and seems to account for the more highly bentonitic nature of the Pierre rocks in the eastern facies belt. These relations are consistent with the general setting of deposition of the Pierre, in which terrigenous sediments are more abundant in the western areas and there is a relative concentration of wind-transported volcanic material, and the resulting montmorillonitic alteration products, in the eastern rocks of the Pierre.

#### CHEMICAL COMPOSITION

##### AVERAGE COMPOSITION OF SELECTED SAMPLES OF PIERRE SHALE

The average composition of selected samples of the Pierre shale on an as-reported basis is shown in table 6. In making the average, 5 of the 22 samples shown in table 7 have been excluded. The two soillike weathering products C874 and C883 (see p. 28 and 30) were excluded, because they are not shale or claystone comparable to most of the other samples, although the composition of these two samples does not differ much from that of the claystone and shale. The two marlstone samples C879 and C889 have been excluded because they would weight the average composition unduly if they were included. The chemical composition of the clay fraction in these two samples, however, is very similar to that of other samples (p. 35). Sample C891 has been excluded because it differs considerably in sulfur content from the others and would unduly influence the average if it were included. In addition, this sample contains so much organic matter that the determinations for ferrous oxide and moisture are quite uncertain.

Marlstone and organic-rich samples should, of course, be included in any average that purports to represent the composition of the Pierre shale and equivalent rocks as a whole, but the number of samples analysed so far is too small for this purpose.

The standard deviations accompanying the average analysis of samples of the Pierre shale in table 6 indicate a fairly uniform composition for most of the major constituents. Some of the minor constituents, however, have quite a wide range. These minor constituents, in part, represent admixtures of nonclay material, either during deposition or diagenesis, such as calcium carbonate and pyrite (insoluble sulfur as sulfur in the analyses). Standard deviation is indicated by *s*. The formula (Dixon and Massey, 1951, p. 20) is

$$s = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N-1}}$$

TABLE 6.—Comparison of average composition, in percent, of 17 samples of Pierre shale and equivalent rocks with average compositions of montmorillonite and illite

[Pierre shale: 17 analyses from table 7, excluding C874, C879, C883, C889, and C891. Montmorillonite: 7 analyses quoted by Grim (1953, p. 371). Illite: 6 analyses quoted by Grim (1953, table D, analyses 1, 2, 5, 6, 7, and 8, p. 372)]

|   | Pierre shale     |                    | Montmorillonite    |         |         | Illite            |         |         |
|---|------------------|--------------------|--------------------|---------|---------|-------------------|---------|---------|
|   | Mean             | Standard deviation | Average            | Minimum | Maximum | Average           | Minimum | Maximum |
| SiO <sub>2</sub> .....                                | 59.68            | 3.49               | 52.37              | 49.91   | 57.55   | 50.83             | 47.55   | 53.12   |
| Al <sub>2</sub> O <sub>3</sub> .....                  | 15.40            | 1.52               | 18.31              | 15.96   | 20.14   | 27.04             | 21.67   | 32.45   |
| Fe <sub>2</sub> O <sub>3</sub> .....                  | 4.56             | 1.09               | 2.58               | .06     | 6.35    | 3.42              | .76     | 6.20    |
| FeO.....  | .96              | .64                | 1.50               | .26     | .95     | <sup>2</sup> 1.28 | .57     | 1.85    |
| MgO.....  | 2.11             | .47                | 3.93               | 2.49    | 6.53    | 2.61              | 1.32    | 4.48    |
| CaO.....  | 1.52             | 1.12               | 1.86               | .50     | 3.28    | .34               | .00     | .67     |
| Na <sub>2</sub> O.....                                | 1.09             | .42                | <sup>3</sup> 2.77  | .04     | 2.75    | .41               | .13     | 1.05    |
| K <sub>2</sub> O.....                                 | 2.49             | .26                | <sup>3</sup> 3.37  | .11     | .60     | 5.99              | 3.51    | 7.47    |
| H <sub>2</sub> O.....                                 | 3.73             | 1.09               | <sup>4</sup> 15.23 | 14.75   | 15.77   | <sup>5</sup> 2.38 | .....   | .....   |
| H <sub>2</sub> O+.....                                | 4.77             | .83                | <sup>2</sup> 7.85  | 7.46    | 8.53    | 7.03              | 6.03    | 7.88    |
| TiO <sub>2</sub> .....                                | .60              | .05                | <sup>4</sup> .21   | .10     | .32     | <sup>4</sup> .40  | .05     | .64     |
| CO <sub>2</sub> .....                                 | <sup>6</sup> .87 | 1.35               | .....              | .....   | .....   | .....             | .....   | .....   |
| P <sub>2</sub> O <sub>5</sub> .....                   | .15              | .04                | .....              | .....   | .....   | .....             | .....   | .....   |
| Acid-soluble S as S <sub>2</sub> O <sub>3</sub> ..... | .85              | .95                | .....              | .....   | .....   | .....             | .....   | .....   |
| Insoluble S as S.....                                 | <sup>7</sup> .21 | .17                | .....              | .....   | .....   | .....             | .....   | .....   |
| Cl.....   | <sup>8</sup> .01 | .....              | .....              | .....   | .....   | .....             | .....   | .....   |
| F.....  | .07              | .....              | .....              | .....   | .....   | .....             | .....   | .....   |
| MnO.....  | .19              | .39                | .....              | .....   | .....   | .....             | .....   | .....   |
| BaO.....  | .08              | .....              | .....              | .....   | .....   | .....             | .....   | .....   |
| Subtotal.....   | 99.34            | .....              | .....              | .....   | .....   | .....             | .....   | .....   |
| Less 0.....   | .07              | .....              | .....              | .....   | .....   | .....             | .....   | .....   |
| Total.....  | 99.27            | .....              | .....              | .....   | .....   | .....             | .....   | .....   |

- <sup>1</sup> Determined in only 3 samples.
- <sup>2</sup> Determined in only 5 samples.
- <sup>3</sup> Determined in only 6 samples.
- <sup>4</sup> Determined in only 4 samples.
- <sup>5</sup> Determined in only 1 sample.
- <sup>6</sup> Determined in only 16 samples.
- <sup>7</sup> Determined in only 14 samples.
- <sup>8</sup> Determined in only 11 samples.

where  $X$  = determined value for individual sample;  $\bar{X}$  = arithmetic mean of values; and  $N$  = number of samples.

#### MAJOR CONSTITUENTS

The major constituents of the 22 basic samples of the Pierre shale and equivalent rocks were determined by modifications of the conventional methods of silicate-rock analysis. (See Schlecht and Stevens, 1951, p. 12-22.) The analyses are shown in table 7.

Duplicates of samples C877 and C875 were submitted for analysis to the rock-analysis laboratory at Denver, Colo. They were designated C892 and C893, respectively, to hide their identity. The original field samples were crushed by hand until the largest pieces in the samples were about half an inch in diameter. Each sample was then quartered, and opposite quarters combined, to make two samples. Each of the resulting samples had about equal amounts of large pieces and fine dust. The results of the two independent analyses of each field sample are shown in table 8.

The differences between the duplicate analyses, on the as-reported basis, fall well within the limits for the analyses of standard granite sample G-1 and standard diabase sample W-1 (Dennen, Ahrens, and Fairbairn, 1951, figs. 1 and 2, p. 32). The largest differences

TABLE 7.—Chemical analyses of 22 basic samples of shale and marlstone from Pierre shale and equivalent rocks

[See table 1 for location and description of samples. Results are given in percent. Analyses by Marjorie K. Balazs]

|  | Locality 1          |                     |                     |                                 | Locality 2             | Locality 3          | Locality 4                       | Locality 5                            | Locality 6                             | Locality 7                             |
|--|---------------------|---------------------|---------------------|---------------------------------|------------------------|---------------------|----------------------------------|---------------------------------------|--|--|
|  | C871                | C872                | C873                | C874                            | C875                   | C870                | C876                             | C877                                  | C886                                   | C887                                   |
|  | Shale from Claggett | Shale from Claggett | Shale from Claggett | Soillike material from Claggett | Claystone from Bearpaw | Shale from Claggett | Shale from Mitten member, Pierre | Claystone from Unnamed member, Pierre | Shale from Virgin Creek member, Pierre | Shale from Virgin Creek member, Pierre |
| SiO <sub>2</sub> .....                           | 55.32               | 54.84               | 58.27               | 58.94                           | 61.16                  | 58.97               | 57.68                            | 58.09                                 | 56.20                                  | 62.88                                  |
| Al <sub>2</sub> O <sub>3</sub> .....             | 16.39               | 16.40               | 17.31               | 16.77                           | 16.23                  | 17.93               | 17.93                            | 16.36                                 | 15.19                                  | 14.77                                  |
| Fe <sub>2</sub> O <sub>3</sub> .....             | 5.10                | 5.01                | 6.17                | 5.74                            | 3.10                   | 3.23                | 5.39                             | 5.97                                  | 4.58                                   | 5.03                                   |
| FeO <sup>1</sup> .....                           | 1.24                | 1.21                | .45                 | .20                             | 2.04                   | .90                 | .59                              | .47                                   | .74                                    | .52                                    |
| MgO.....   | 1.91                | 2.06                | 1.45                | 1.37                            | 1.92                   | 3.52                | 1.72                             | 1.74                                  | 2.27                                   | 1.86                                   |
| CaO.....   | 1.25                | 1.11                | .23                 | .90                             | .71                    | 4.30                | .78                              | .95                                   | 3.46                                   | .76                                    |
| Na <sub>2</sub> O.....                           | .90                 | .75                 | .72                 | .82                             | 1.57                   | .72                 | .69                              | .68                                   | 1.92                                   | .65                                    |
| K <sub>2</sub> O.....                            | 2.21                | 2.36                | 2.23                | 2.30                            | 2.67                   | 2.41                | 2.66                             | 2.90                                  | 2.50                                   | 2.30                                   |
| H <sub>2</sub> O.....                            | 3.98                | 4.74                | 4.81                | 4.84                            | 2.84                   | 2.73                | 4.42                             | 5.52                                  | 3.95                                   | 4.63                                   |
| H <sub>2</sub> O+.....                           | 6.16                | 6.28                | 5.68                | 5.99                            | 4.59                   | 3.50                | 5.98                             | 4.88                                  | 3.47                                   | 4.80                                   |
| TiO <sub>2</sub> .....                           | .66                 | .66                 | .70                 | .66                             | .63                    | .56                 | .69                              | .65                                   | .63                                    | .60                                    |
| CO <sub>2</sub> .....                            | .14                 | .04                 | .03                 | .02                             | .10                    | 4.63                | .08                              | .01                                   | 1.82                                   | .00                                    |
| P <sub>2</sub> O <sub>5</sub> .....              | .14                 | .14                 | .15                 | .13                             | .11                    | .19                 | .29                              | .15                                   | .14                                    | .10                                    |
| Acid-soluble S as SO <sub>3</sub> .....          | 3.00                | 3.03                | .46                 | .17                             | 1.07                   | .74                 | .02                              | .64                                   | 1.67                                   | .07                                    |
| Insoluble S as S.....                            | .10                 | .10                 | .00                 | .02                             | .64                    | .00                 | .04                              | .02                                   | .05                                    | .01                                    |
| Cl.....  | .00                 | .00                 | .00                 | .00                             | .00                    | .01                 | .00                              | .01                                   | .01                                    | .00                                    |
| F.....   | .06                 | .06                 | .06                 | .06                             | .05                    | .07                 | .07                              | .07                                   | .08                                    | .07                                    |
| MnO.....   | .03                 | .03                 | .03                 | .04                             | .03                    | .03                 | .02                              | .02                                   | .06                                    | .03                                    |
| BaO.....   | .04                 | .04                 | .05                 | .06                             | .05                    | .08                 | .07                              | .05                                   | .08                                    | .09                                    |
| Subtotal.....                                    | 98.63               | 98.86               | 98.80               | 99.03                           | 99.51                  | 99.37               | 99.12                            | 99.18                                 | 98.82                                  | 99.17                                  |
| Less O.....                                      | .05                 | .05                 | .03                 | .04                             | .18                    | .03                 | .04                              | .04                                   | .06                                    | .03                                    |
| Total.....                                       | 98.58               | 98.81               | 98.77               | 98.99                           | 99.33                  | 99.34               | 99.08                            | 99.14                                 | 98.76                                  | 99.14                                  |
| Total Fe as Fe <sub>2</sub> O <sub>3</sub> ..... | 6.48                | 6.35                | 6.67                | 5.96                            | 5.78                   | 4.23                | 6.05                             | 6.49                                  | 5.40                                   | 5.61                                   |
| Organic C.....                                   | <.5                 | <.5                 | 1.6                 | <.5                             | 1.0                    | <.5                 | <.5                              | <.5                                   | <.5                                    | <.5                                    |

|  | Locality 8                              |   |   |   |   | Locality 9                           |  |                                       | Locality 10                          |  |                                       |  |  |
|--|---|---|---|---|---|--------------------------------------|--|---------------------------------------|--------------------------------------|--|---------------------------------------|--|--|
|  | C881                                    | C882                                    | C883  | C884                                    | C885                                    | C878                                 | C879                                     | C880                                  | C888                                 | C889                                     | C890                                  | C891                                     |  |
|  | Claystone from Verendrye member, Pierre | Claystone from Verendrye member, Pierre | Soillike material from Verendrye member, Pierre | Claystone from Verendrye member, Pierre | Claystone from Verendrye member, Pierre | Claystone from DeGrey member, Pierre | Marlstone from Crow Creek member, Pierre | Claystone from Gregory member, Pierre | Claystone from DeGrey member, Pierre | Marlstone from Crow Creek member, Pierre | Claystone from Gregory member, Pierre | Shale from Sharon Springs member, Pierre |  |
| SiO <sub>2</sub> .....                           | 61.79                                   | 63.67                                   | 60.07   | 60.68                                   | 60.42                                   | 69.04                                | 27.96                                    | 58.90                                 | 59.81                                | 35.25                                    | 56.87                                 | 47.42                                    |  |
| Al <sub>2</sub> O <sub>3</sub> .....             | 14.32                                   | 14.70                                   | 15.06   | 14.46                                   | 14.11                                   | 12.37                                | 6.60                                     | 16.83                                 | 15.70                                | 9.76                                     | 15.92                                 | 12.81                                    |  |
| Fe <sub>2</sub> O <sub>3</sub> .....             | 5.44                                    | 5.71                                    | 5.67  | 3.28                                    | 3.18                                    | 2.92                                 | 1.21                                     | 3.80                                  | 4.95                                 | 3.78                                     | 4.73                                  | .67                                      |  |
| FeO <sup>1</sup> .....                           | .36                                     | .42                                     | .44   | 2.09                                    | 2.00                                    | 1.20                                 | 4.26                                     | 1.53                                  | .35                                  | .00                                      | .15                                   | 4.17                                     |  |
| MgO.....   | 2.14                                    | 1.84                                    | 2.09  | 2.14                                    | 2.18                                    | 1.70                                 | 2.89                                     | 2.69                                  | 2.27                                 | 2.00                                     | 2.39                                  | .84                                      |  |
| CaO.....   | .94                                     | 1.01                                    | 1.54  | 1.97                                    | 2.35                                    | .76                                  | 25.06                                    | .99                                   | 1.34                                 | 21.65                                    | 2.97                                  | 1.21                                     |  |
| Na <sub>2</sub> O.....                           | .82                                     | .70                                     | .70   | 1.38                                    | 1.42                                    | 1.34                                 | .53                                      | 1.38                                  | 1.19                                 | .64                                      | 1.72                                  | .83                                      |  |
| K <sub>2</sub> O.....                            | 2.31                                    | 2.57                                    | 2.35  | 2.50                                    | 2.46                                    | 1.98                                 | 1.25                                     | 2.70                                  | 2.60                                 | 2.18                                     | 3.05                                  | 2.89                                     |  |
| H <sub>2</sub> O.....                            | 4.18                                    | 2.66                                    | 4.49  | 1.80                                    | 1.90                                    | 2.94                                 | 1.43                                     | 4.30                                  | 4.68                                 | 2.71                                     | 3.31                                  | 2.88                                     |  |
| H <sub>2</sub> O+.....                           | 4.63                                    | 4.67                                    | 5.33  | 4.42                                    | 4.26                                    | 4.02                                 | 2.09                                     | 4.75                                  | 4.67                                 | 2.77                                     | 4.27                                  | 8.35                                     |  |
| TiO <sub>2</sub> .....                           | .57                                     | .58                                     | .56   | .58                                     | .55                                     | .48                                  | .28                                      | .56                                   | .57                                  | .37                                      | .56                                   | .50                                      |  |
| CO <sub>2</sub> .....                            | .03                                     | .05                                     | .31   | 1.82                                    | 2.40                                    | .29                                  | 24.07                                    | .38                                   | .27                                  | 17.35                                    | 1.80                                  | .05                                      |  |
| P <sub>2</sub> O <sub>5</sub> .....              | .12                                     | .12                                     | .17   | .17                                     | .21                                     | .07                                  | .26                                      | .11                                   | .13                                  | .23                                      | .13                                   | .12                                      |  |
| Acid-soluble S as SO <sub>3</sub> .....          | 1.10                                    | .29                                     | .10   | .26                                     | .12                                     | .12                                  | .04                                      | .09                                   | .50                                  | .18                                      | 1.31                                  | 4.85                                     |  |
| Insoluble S as S.....                            | .00                                     | .02                                     | .02   | .66                                     | .49                                     | .27                                  | .43                                      | .44                                   | .01                                  | .01                                      | .01                                   | 1.57                                     |  |
| Cl.....  | .01                                     | .01                                     | .02   | .02                                     | .04                                     | .01                                  | .02                                      | .03                                   | .01                                  | .02                                      | .01                                   | .13                                      |  |
| F.....   | .07                                     | .07                                     | .07   | .07                                     | .07                                     | .05                                  | .06                                      | .09                                   | .08                                  | .08                                      | .08                                   | .08                                      |  |
| MnO.....   | .09                                     | .07                                     | .25   | .96                                     | 1.12                                    | .11                                  | 1.35                                     | .09                                   | .25                                  | .79                                      | .33                                   | .02                                      |  |
| BaO.....   | .11                                     | .14                                     | .10   | .12                                     | .13                                     | .11                                  | .03                                      | .04                                   | .05                                  | .00                                      | .04                                   | .01                                      |  |
| Subtotal.....                                    | 99.03                                   | 99.30                                   | 99.34   | 99.38                                   | 99.41                                   | 99.78                                | 99.82                                    | 99.70                                 | 99.43                                | 99.77                                    | 99.65                                 | 89.40                                    |  |
| Less O.....                                      | .03                                     | .03                                     | .04   | .20                                     | .16                                     | .09                                  | .13                                      | .15                                   | .03                                  | .04                                      | .03                                   | .45                                      |  |
| Total.....                                       | 99.00                                   | 99.27                                   | 99.30   | 99.18                                   | 99.25                                   | 99.69                                | 99.69                                    | 99.55                                 | 99.40                                | 99.73                                    | 99.62                                 | 88.95                                    |  |
| Total Fe as Fe <sub>2</sub> O <sub>3</sub> ..... | 5.84                                    | 6.18                                    | 6.16  | 5.60                                    | 5.40                                    | 4.25                                 | 5.94                                     | 5.50                                  | 5.34                                 | 3.78                                     | 4.90                                  | 5.30                                     |  |
| Organic C.....                                   | <.5                                     | .8                                      | .9  | 1.1                                     | 1.3                                     | <.5                                  | 1.5                                      | <.5                                   | <.5                                  | <.5                                      | <.5                                   | 7.4                                      |  |

<sup>1</sup> A correction was made for FeO present as pyrite, based on percent insoluble S found. Determination of FeO uncertain because of organic material in shale.

TABLE 8.—Duplicate chemical analyses, in percent, of two samples of claystone, and related data

[An asterisk (\*) indicates that the sample is part of a basic set of 22 samples. Analyses by Marjorie K. Balazs]

|   | As reported |       |            |            |       |            | Recalculated to 100 percent excluding H <sub>2</sub> O— |        |            |            |        |            | Standard deviation <sup>1</sup> |
|---|-------------|-------|------------|------------|-------|------------|---|--------|------------|------------|--------|------------|---------------------------------|
|   | Locality 5  |       |            | Locality 2 |       |            | Locality 5  |        |            | Locality 2 |        |            |                                 |
|   | *C877       | C892  | Difference | *C875      | C893  | Difference | *C877   | C892   | Difference | *C875      | C893   | Difference |                                 |
| SiO <sub>2</sub> .....                  | 58.09       | 59.12 | 1.03       | 61.16      | 61.22 | 0.06       | 62.08   | 62.54  | 0.46       | 63.73      | 63.82  | 0.08       | 0.23                            |
| Al <sub>2</sub> O <sub>3</sub> .....    | 16.36       | 16.66 | .30        | 16.23      | 16.64 | .41        | 17.49   | 17.62  | .13        | 16.91      | 17.33  | .42        | .17                             |
| Fe <sub>2</sub> O <sub>3</sub> .....    | 5.97        | 5.65  | .32        | 3.10       | 2.58  | .52        | 6.38  | 5.98   | .40        | 3.23       | 2.69   | .54        | .17                             |
| FeO.....                                | 4.47        | 4.55  | .08        | 2.04       | 2.18  | .14        | .50   | .58    | .08        | 2.13       | 2.27   | .14        | .06                             |
| MgO.....                                | 1.74        | 1.71  | .03        | 1.92       | 1.89  | .03        | 1.86  | 1.80   | .06        | 2.00       | 1.97   | .03        | .04                             |
| CaO.....                                | .95         | .93   | .02        | .71        | .77   | .06        | 1.02  | .98    | .04        | .74        | .80    | .06        | .09                             |
| Na <sub>2</sub> O.....                  | .68         | .65   | .03        | 1.57       | 1.60  | .03        | .73   | .69    | .04        | 1.64       | 1.67   | .03        | .21                             |
| K <sub>2</sub> O.....                   | 2.90        | 2.92  | .02        | 2.67       | 2.66  | .01        | 3.10  | 3.09   | .01        | 2.78       | 2.77   | .01        | .21                             |
| H <sub>2</sub> O.....                   | 5.52        | 4.56  | 1.04       | 2.84       | 2.73  | .11        | .....   | .....  | .....      | .....      | .....  | .....      | .....                           |
| H <sub>2</sub> O+.....                  | 4.88        | 4.97  | .09        | 4.59       | 4.39  | .20        | 5.23  | 5.26   | .03        | 4.78       | 4.57   | .21        | .08                             |
| TiO <sub>2</sub> .....                  | .65         | .66   | .01        | .63        | .63   | .00        | .69   | .70    | .01        | .66        | .66    | .00        | .03                             |
| CO <sub>2</sub> .....                   | .01         | .02   | .01        | .10        | .10   | .00        | .01   | .02    | .01        | .10        | .10    | .00        | .21                             |
| P <sub>2</sub> O <sub>5</sub> .....     | .15         | .15   | .00        | .11        | .12   | .01        | .16   | .16    | .00        | .11        | .12    | .01        | .02                             |
| Acid-soluble S as SO <sub>3</sub> ..... | .64         | .49   | .15        | 1.07       | 1.12  | .05        | .68   | .52    | .16        | 1.11       | 1.17   | .06        | .....                           |
| Insoluble S as S.....                   | .02         | .01   | .01        | .64        | .66   | .02        | .....   | .....  | .....      | .....      | .....  | .....      | .....                           |
| Cl.....                                 | .01         | .01   | .00        | .00        | .00   | .....      | .....   | .....  | .....      | .....      | .....  | .....      | .....                           |
| F.....                                  | .07         | .07   | .00        | .05        | .06   | .01        | .....   | .....  | .....      | .....      | .....  | .....      | .....                           |
| MnO.....                                | .02         | .03   | .01        | .03        | .03   | .00        | .02   | .03    | .01        | .03        | .03    | .00        | .01                             |
| BaO.....                                | .05         | .03   | .02        | .05        | .03   | .02        | .05   | .03    | .02        | .05        | .03    | .02        | .....                           |
| Subtotal.....                           | 99.18       | 99.19 | .....      | 99.51      | 99.42 | .....      | 100.00  | 100.00 | .....      | 100.00     | 100.00 | .....      | .....                           |
| Less O.....                             | .04         | .03   | .....      | .18        | .19   | .....      | .....   | .....  | .....      | .....      | .....  | .....      | .....                           |
| Total.....                              | 99.14       | 99.16 | .....      | 99.33      | 99.23 | .....      | .....   | .....  | .....      | .....      | .....  | .....      | .....                           |

<sup>1</sup> Seven replicate analyses of a granite from Dennen, Ahrens, and Fairbairn (1951, table 17, p. 38).

between the duplicate analyses of the samples of Pierre shale amount to about 25 percent for H<sub>2</sub>O— and about 2 percent for silica and alumina, but the difference is much larger, of course, for constituents present in small amounts. For the most part, the differences between the duplicate analyses are decreased when the analyses are recalculated to 100 percent, after excluding H<sub>2</sub>O— (water lost at 105°–110°C. See table 8). The amount of change depends, of course, on the difference between the H<sub>2</sub>O— content of the original sample and its duplicate; and in the analyses considered here, the largest difference is shown by the duplicate pair of samples C877 and C892.

The gross composition of the samples of the Pierre is intermediate between that of the granite G-1 and that of the diabase W-1; but it approaches the composition of granite sufficiently for comparisons to be made concerning the precision of analysis. Dennen, Ahrens, and Fairbairn (1951, table 17, p. 38) report standard deviations based on seven replicate analyses of the granite G-1 from a single laboratory, excluding H<sub>2</sub>O— and recalculating to 100 percent; these standard deviations and comparable transformed analyses of the Pierre samples are shown in table 8. The differences between the duplicate claystone samples are not greatly different than the standard deviations for the analyses of G-1. Apparently chemical analyses have about the same degree of precision for claystone and shale as for the crystalline rocks.

The claystone, shale, and marlstone of this investigation still present problems in analysis, however, despite

the acceptable degree of precision indicated by the duplicate analyses. Samples of claystone and shale, finely ground for analysis, tend to adsorb and give off moisture with changes in laboratory temperature and humidity. Changes in weight from this cause can sometimes be detected within the time of weighing for the determination of H<sub>2</sub>O— (L. C. Peck, oral communication, 1957). In addition, the organic material in many of the samples may have supplied some of the material reported as H<sub>2</sub>O— and certainly supplied some of the material reported as H<sub>2</sub>O+. The analyses of these samples were made in Denver, Colo., during the winter months, and changes in humidity and their effect on H<sub>2</sub>O— probably were small; but the difference in H<sub>2</sub>O— in the duplicate pair C877 and C892 indicates that large differences can occur. This kind of uncertainty can be minimized, however, by comparing analyses on an anhydrous basis, as was done in recalculating the analyses.

The totals of the analyses and the amounts of ferrous oxide reported in table 7 are somewhat uncertain because of the presence of organic matter in many of the samples. Most of the samples contain less than 0.05 percent organic carbon, but other samples have from about 1 to 7 percent organic carbon. The effect of the organic carbon on the totals of the analyses in table 7 is particularly evident for sample C891, which contains 7.4 percent organic carbon and totals only 88.95 percent. The determination of ferrous oxide depends upon a titration involving an oxidizing agent that can be consumed by organic matter as well as by ferrous iron. Probably

the amount of ferrous oxide reported for most of the samples is too large, but the effect of organic matter is unpredictable. The determination of total iron as ferric oxide is not affected by organic matter, and percentages for total iron as ferric oxide are included in table 7 for convenience.

The amounts reported for acid-insoluble sulfur as sulfur include any insoluble sulfates in the sample, such as barite (L. C. Peck, 1958, oral communication). This introduces uncertainties in the reported amounts of both the insoluble sulfur and ferrous oxide that are difficult to evaluate, although barite has not been detected by X-ray or microscopic studies. Sulfur in organic material probably also would be reported as insoluble sulfur.

#### MODE OF OCCURRENCE

The major constituents of the samples given in the chemical analyses of table 7 and the average analysis of table 6 are, of course, found mainly in the clay minerals. Silica may occur as quartz or cristobalite as well as in the clay minerals, but almost all of the alumina occurs in the clay minerals. Both ferric and ferrous iron are primary constituents of clay minerals, but ferric iron can occur in various hydrated oxides and in jarosite or other sulfates. The ferrous iron can occur also in pyrite or in siderite, in organic material, and in detrital biotite. The alkali and alkaline-earth elements are essential constituents of clay minerals, but calcium and magnesium also occur in some samples as carbonates. Titanium could be present in very finely divided heavy minerals, but its even distribution suggests that it is in the structure of the clay minerals.

Phosphorus probably is chiefly in biogenic apatite, such as fish scales and bone and teeth fragments, but phosphorus, like titanium, is very evenly distributed throughout the samples and could well be an adsorbed constituent of clay. There is no evidence that the phosphorus occurs in detrital or authigenic apatite, but this possibility cannot be excluded, particularly in view of the volcanic origin of much of the material. Much of the fluorine no doubt occurs in biogenic phosphates, but some is an adsorbed constituent (p. 56). Chlorine is reported in only about half of the samples, and its mode of occurrence is not known. Some chlorine might be present in biotite. One sample (C891) contains 0.13 percent chlorine. This sample also contains the largest amount of organic carbon found, which is the only other unique characteristic noted.

Sulfur is present mainly as sulfide in fresh samples and in sulfates of calcium and iron in weathered samples. Sulfur also is a common constituent of organic material. Manganese could occur either in clay

structures or as the carbonate in fresh samples and as an oxide in weathered samples. The principal occurrence of manganese seems to be as the carbonate or as a replacing ion in calcium compounds, including calcium carbonate. Barium would be expected, perhaps, to occur chiefly as the sulfate barite. No barite has been found, and the barium in these samples probably replaces potassium in clay minerals, or substitutes for potassium in feldspar.

The samples thus consist mostly of clay minerals; fresh samples also contain various amounts of calcium, magnesium, iron and manganese carbonates, sulfide compounds, and organic materials, and weathered samples contain various amounts of calcium and magnesium carbonates, iron and calcium sulfates, iron oxides, and organic material. The analyses indicate that biogenic phosphate in the Pierre is not affected by weathering. The organic materials are affected by weathering and could have an effect on the occurrence of sulfur, iron, and some of the minor metallic elements.

#### STATISTICAL DISTRIBUTION

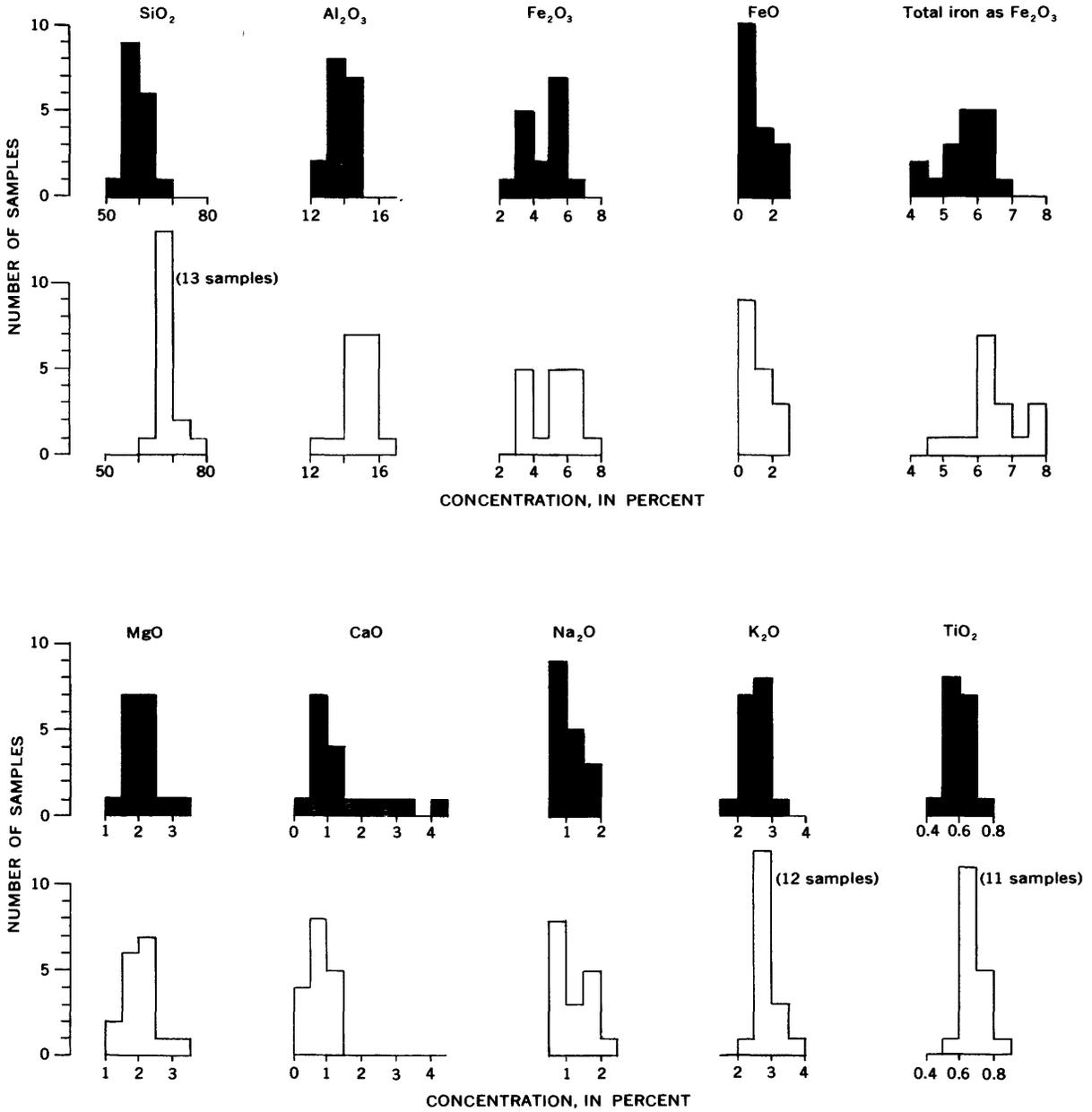
The distributions of the major constituents in 17 samples of the Pierre shale and equivalent rocks are shown by histograms in figure 6. As only 17 samples are involved, the histograms are not applicable to shale as a class of rocks, but the histograms do show the distribution pattern of the major constituents in the samples considered here.

The histograms are plotted in two forms: first, based on the amounts of the constituents as reported by the laboratory, and second, based on the amounts of the constituents after moisture and the components of calcite, dolomite, gypsum, and apatite were excluded from the analyses and each analysis was recalculated to 100 percent. The exclusion of these components is necessary before the distributions can be considered with respect to the clay mineral that makes up the shale and claystone.

Silica, alumina, magnesium oxide, potassium oxide, and titanium oxide, as shown on figure 6, have statistical distributions that are approximately normal on the as-reported basis, and the exclusion of the constituents of biogenic material and of secondary carbonate and sulfate has little effect on the distributions. For silica, the exclusion of the constituents of biogenic material decreases the standard deviation from 3.49 (table 11) for the as-reported analyses to 2.75 (table 12) for the recalculated analyses, but the standard deviations of alumina and the other oxides having a nearly normal distribution are not much changed by calculation.

Calcium oxide in the as-reported histogram has a markedly skewed distribution, resulting from the me-

GEOLOGIC SETTING AND CHEMICAL COMPOSITION OF PIERRE SHALE



EXPLANATION

 Histograms plotted from analyses as reported

 Histograms plotted from analyses recalculated to exclude moisture, CaO, MgO, and CO<sub>2</sub> as calcite and dolomite; CaO and SO<sub>3</sub> as gypsum, and CaO, F, and P<sub>2</sub>O<sub>5</sub> as apatite

FIGURE 6.—Statistical distribution of major constituents in 17 samples of the Pierre shale and equivalent rocks. Samples are those given in table 7, excluding samples C874, C879, C883, C889, and C891.

chance intermixture of calcium compounds of biogenic origin and clay minerals. Exclusion of these compounds from the analyses leaves a remainder of calcium oxide that represents the calcium bound in the clay minerals alone. The distribution of this clay-mineral calcium is approximately normal.

Ferric oxide has a very irregular distribution, and the exclusion from the analyses of biogenic constituents and secondary minerals does not have much effect on the distribution. The occurrence of ferric oxide in the samples is related, in part, to the degree of oxidation that the sample has undergone. The ferric oxide content as reported in the analyses also is related to the amount of ferrous oxide reported; and the amount of ferrous oxide is somewhat uncertain, as already pointed out (p. 24). The skewed distribution of ferrous oxide is partly the result of analytical uncertainties, but the distribution is the kind that would be expected for samples that have been oxidized to different degrees. The distribution of total iron as ferric oxide in the samples appears to be irregular, but it is more nearly normal than that of either one of the iron oxides alone. The distribution of total iron is somewhat changed by the exclusion of some constituents from the analyses, but the distribution still is approximately normal.

To a considerable extent, the iron content of the samples has two sources. Iron is a common constituent of montmorillonite, illite, and mixed-layer clay minerals making up the shale and claystone, and the range in iron content of these minerals may be large (Grim, 1953, p. 371-372). This iron is either relict from the original clay mineral or else enters the clay-mineral structure during the reconstitution of the clay minerals in the marine environment by ion exchange and perhaps by adsorption. However, during its formation, the rock may have iron added to it that is independent of the clay minerals and that reflects the environment of diagenesis through which the rock has passed. Pyrite and possibly siderite contain most of this additional iron. The combination of these two sources of iron should produce a kind of distribution that is not easily evaluated in terms of normality.

The distribution of sodium oxide is very skewed and differs markedly from that of potassium oxide. Both of the alkalies are essential constituents of the montmorillonite-illite clay minerals. The difference in distribution between the two probably is the result of weathering on the present land surface, sodium ions being much more easily displaced from the clay structure than potassium ions (Grim, 1953, p. 146).

#### RELATION OF CHEMICAL COMPOSITION AND CLAY MINERALS

Table 6 shows the average chemical composition of the Pierre shale and equivalent rocks and the average chemical composition of the clay minerals, montmorillonite and illite. The average chemical compositions of montmorillonite and illite are taken from Grim (1953, p. 371-372) and represent materials that are considered to be relatively pure samples of these minerals. The range of most of the constituents in the clay minerals is so large and the number of samples is so small that standard deviations were not calculated. The composition of clay minerals is not fixed in contrast to other minerals, and the averages in table 6 perhaps are not very meaningful, but some basis for comparison is needed.

The average chemical composition of the samples of Pierre shale is consistent with the mixture of montmorillonite and illite in various proportions and with some detrital quartz, as determined by X-ray analysis (table 5).

The average iron content of the Pierre samples, both ferric oxide and ferrous oxide, is larger than would be expected for montmorillonite and about that expected for illite. The average magnesium content of the samples is lower than that of the clay minerals. The reported average calcium content of the samples is lower than that expected for montmorillonite and higher than that for illite. When the analyses of the samples are recalculated to remove biogenic and secondary minerals, the remaining calcium (see table 12, p. 41), assignable to the clay minerals alone, is much less than that of the analyzed montmorillonite, and somewhat more than that of the analyzed illite. This comparative deficiency of magnesium and calcium in the samples of the Pierre is partly compensated for by larger amounts of sodium. The potassium content of the samples is about half that of illite and greatly exceeds that of montmorillonite, but is in keeping with the mixture of illite and montmorillonite that makes up the rock. Minor amounts of biotite and feldspar may contribute to some of the potassium in the samples. The titanium content of the samples is larger than that of either montmorillonite or illite.

#### CHANGES IN COMPOSITION ON WEATHERING

Knowledge of the changes in chemical composition of shale on weathering is useful in interpreting the significance of chemical analyses of surface samples. If the moderate degree of weathering that most exposed rocks undergo greatly alters the chemical composition

of the shale, samples of exposed rocks may not be suitable for geochemical study. It was not intended to study weathering as such; instead data were sought that would show the order of magnitude of change in chemical composition that takes place in rocks near the surface. Data were obtained from two localities with different conditions of weathering, and from samples from a core and from exposed rocks at the same stratigraphic positions as those obtained from the core. The data are considered on the basis of weight alone and not volume.

#### ROAD CUT IN FERGUS COUNTY, MONTANA

The first set of data is based on samples taken from a single bed in the Claggett shale in Fergus County, Mont. (loc. 1, pl. 1), that can be traced from the center of a road cut into a soillike weathering product on a hill slope. The relation of the samples and the analytical data are shown in figure 7. The road cut through the hill exposed three kinds of material. The core of the hill is made of soft black shale, in which joints and bedding planes are somewhat stained with iron oxides and coated with minute gypsum crystals. Surrounding this core is a zone of brownish-gray shale about 10 feet thick. The brownish-gray shale is markedly harder than the black shale in the core of the hill. Joints and bedding planes in the brownish-gray shale are stained with iron oxides, but little or no gypsum was observed. The outer zone of the hill, enveloping the zone of brownish-gray shale, is made up of brown clayey soillike material in which were scattered unoriented flakes of the hard shale. The soillike material appears to have formed by the disintegration of the brownish-gray shale, a process by which the hardest pieces of shale were not destroyed.

A bed of tuffaceous siltstone, about 0.1 foot thick, extends across the central core of black shale and the hard zone of brownish-gray shale into the soillike material. The bed of siltstone within the soil had slumped a little down the hill, but had not been displaced much. The bed of siltstone thus was used as a guide for obtaining samples from a single interval of shale that extends through each of the apparent zones of weathering. The samples were taken about 0.2 to 0.5 foot above the siltstone bed and 1 to 2 feet beneath the surface of the exposure. Each sample represents about 0.3 foot of shale.

The hard brownish-gray shale is characteristic of most of the outcrops of Claggett shale in central Montana, although perhaps more brown than is common. A few outcrops of the soft black shale were seen and appeared to be a less weathered form of the brownish-gray shale. The iron oxides and sulfates, and gypsum

were more abundant on the surface of the black shale than they were a foot or so beneath the surface. They thus seem to be the result of secondary concentration by evaporation of water moving to the surface.

The analyses of the samples of the three kinds of material exposed in the road cut are shown in figure 7 both as reported and after calculation to exclude moisture, biogenic carbonate, acid-soluble sulfur, and apatite. On the as-reported basis, the change in composition from the core of the hill to the soillike material seems to be large. The silica content increases about 3.5 percent, and the alumina content increases slightly. The relative amounts of ferric and ferrous oxides tend to change reciprocally. Sulfur in insoluble form (sulfide) parallels the change in reported ferrous oxide. The total iron content as ferric oxide is about uniform in the two core samples of black shale taken from the hill, is slightly larger in the brownish-gray shale, and decreases in the soillike material. The decrease of total iron in the surface material probably reflects removal of iron by leaching.

The total moisture in each sample is about 10 percent, but the  $H_2O-$  content increases and the  $H_2O+$  content decreases from the core of the hill outwards. The magnesium oxide, calcium oxide, and carbon dioxide contents decrease slightly from the core of the hill outwards, and the acid-soluble sulfur as sulfur trioxide decreases from 3.0 to 0.17 percent.

The amount of increase in silica and alumina from the core of the hill outwards is due largely to residual concentration resulting from the loss of the soluble constituents. When the analyses are recalculated to 100 percent after excluding moisture, carbon dioxide, calcium oxide to make calcium carbonate, and acid-soluble sulfur as sulfur trioxide, the amount of increase is made smaller. (No adjustment has been made for cations that accompany the acid-soluble sulfur as sulfur trioxide in recalculating the analyses, because the amount of iron sulfate and gypsum in the samples cannot be determined.) The silica-alumina ratio increases from about 3.36 in the core of the hill to 3.47 in the surface material (sample C874); this increase suggests a slight loss of alumina, perhaps because clay minerals were washed away from the weathered material on the hill slope and a residue somewhat enriched in detrital quartz was left.

The contents of magnesium and calcium still show a decrease from the core of the hill outwards, but the contents of sodium and potassium remain fairly constant. Sodium is the most readily exchangeable element in most montmorillonite, and it can be assumed that all the readily exchangeable sodium had been replaced before the samples had reached their present state of

CHEMICAL COMPOSITION

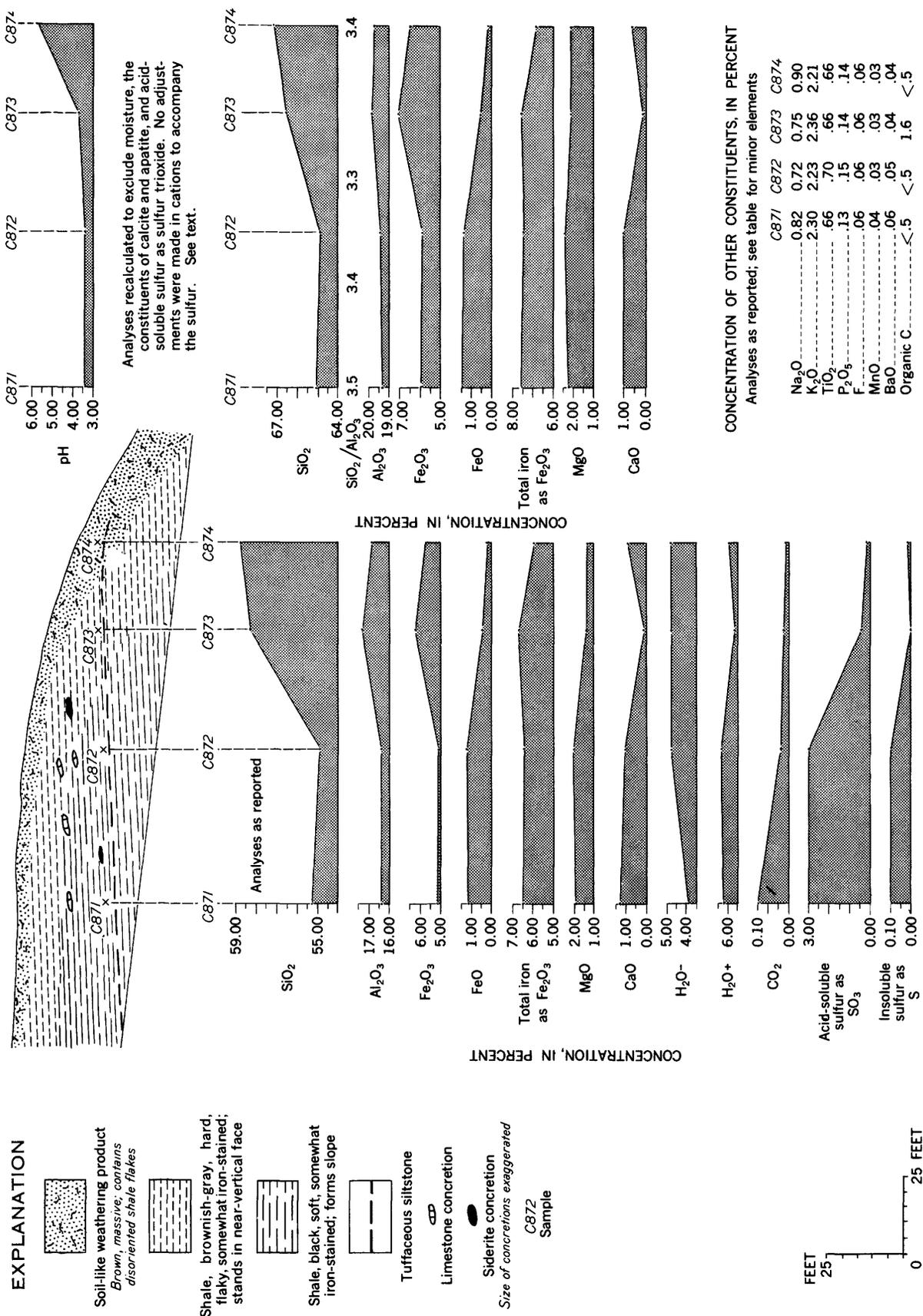


FIGURE 7.—Diagrams showing changes in chemical composition resulting from weathering of Claggett shale, locality 1, road cut in NW¼ sec. 31, T. 18 N., R. 19 E., Fergus County, Mont.

weathering. Magnesium and calcium are more difficult to replace and reflect the intensity of weathering by occurring in smaller amounts in the material that has been most weathered. The amounts of calcium would be smaller if a correction for gypsum could be made.

The pH profile (fig. 7; see also table 20) only partly reflects these supposed ion-exchange reactions. The low pH of the samples from the core of the hill indicates that part of the acid-soluble sulfur as sulfur trioxide in the samples can be readily hydrolyzed to make a slurry that is quite acidic. This suggests that some of the soluble sulfur is present in soluble sulfates of iron. The increase in pH from the core of the hill outward probably reflects the presence of decreasing amounts of soluble sulfur.

These changes in the major components of the rock do not explain sufficiently the different appearance of the three weathering zones. The only remaining component for which there are data is organic carbon. The samples from the core of the hill contain less than 0.5 percent organic carbon, which is the minimum amount detectable. (See p. 57.) The soillike material at the surface of the hill also contains less than 0.5 percent organic carbon. The hard brownish-gray shale, however, contains 1.6 percent organic carbon.

The nature of the compounds making up the organic material is speculative. It is possible that both the brownish-gray shale and the black shale contained about 1.0 percent organic carbon and that the organic materials have been leached from the shale in the core of the hill but not from the brownish-gray shale that borders the core. This explanation is unlikely because it contradicts our general understanding of weathering. It is also possible that during the formation of the soil-like material, reactions beneath this material resulted in stabilizing most of the organic material in what is now the brownish-gray shale. These reactions would have been taking place for a long time. When the road was cut through the hill about 3 to 5 years ago, the black shale was exposed. The organic material in the black shale was unstable and was removed by weathering from near the surface of the shale. An alternative explanation is that the organic material was concentrated in the brownish-gray shale, in part, by migration from the black shale. Evidence supporting any of these possibilities can be obtained only from detailed investigation of the organic substances involved.

#### SPILLWAY OF OAHE DAM, SOUTH DAKOTA

The spillway of the Oahe Dam in Stanley County, S. Dak., being excavated in August 1956 in the Verendrye member of the Pierre shale (loc. 8, pl. 1),

afforded another opportunity to sample a weathering profile. The relation of the samples and the analytical data are shown in figure 8. The spillway excavation was about 70 feet deep. The claystone at the bottom of the excavation had been exposed only a few days and was very dark gray to black. The color of the claystone became lighter toward the top of the excavation and had a somewhat brownish cast. At the top of the excavation was 3 to 5 feet of a soillike material that appeared to be in place and to be a residual weathering product of the claystone. Concretions in the claystone are rich in iron and manganese and were light colored at the bottom of the excavation, but became progressively more oxidized toward the top of the excavation, where they consisted entirely of dark-colored oxides of iron and manganese. The claystone in the spillway cut probably represents a completely gradational weathering profile from the black claystone at the bottom to the soillike material at the top.

Samples were collected near the bottom (C885, fig. 8), middle (C884), and top (C881) of the excavation. The uppermost sample was about 10 feet below the soil-like material and was about a foot above a fairly continuous zone of concretions parallel to a bedding plane. Sample C882 came from the same position as sample C881 relative to the zone of concretions, but about 40 feet to the side of the vertical line of samples. Sample C882 was only about a foot below the bottom of the soillike material. Sample C883 came from the soillike material, about 60 feet from sample C882, and seemed to be in the same position relative to the zone of concretions as samples C882 and C881. These samples were expected to show changes in weathering vertically across different beds and horizontally along one bed.

The analytical data for the Verendrye member of the Pierre shale shown in figure 8 show trends that seem to conflict with the trends indicated for the weathering profile of Claggett shale (fig. 7). The samples of the Verendrye have a somewhat different composition from the samples of the Claggett as they are higher in silica and carbon dioxide and lower in alumina than the Claggett. The contrast in degree of weathering also is larger for the samples of the Verendrye than for the samples of the Claggett. The freshest Claggett samples, for example, probably are much more weathered than the freshest Verendrye samples. The weathering situation of the sampled materials also is different. The soillike material formed on the Claggett lies on a slope that would permit relatively better drainage, and consequently more leaching and removal of constituents, than the gently irregular upland surface where

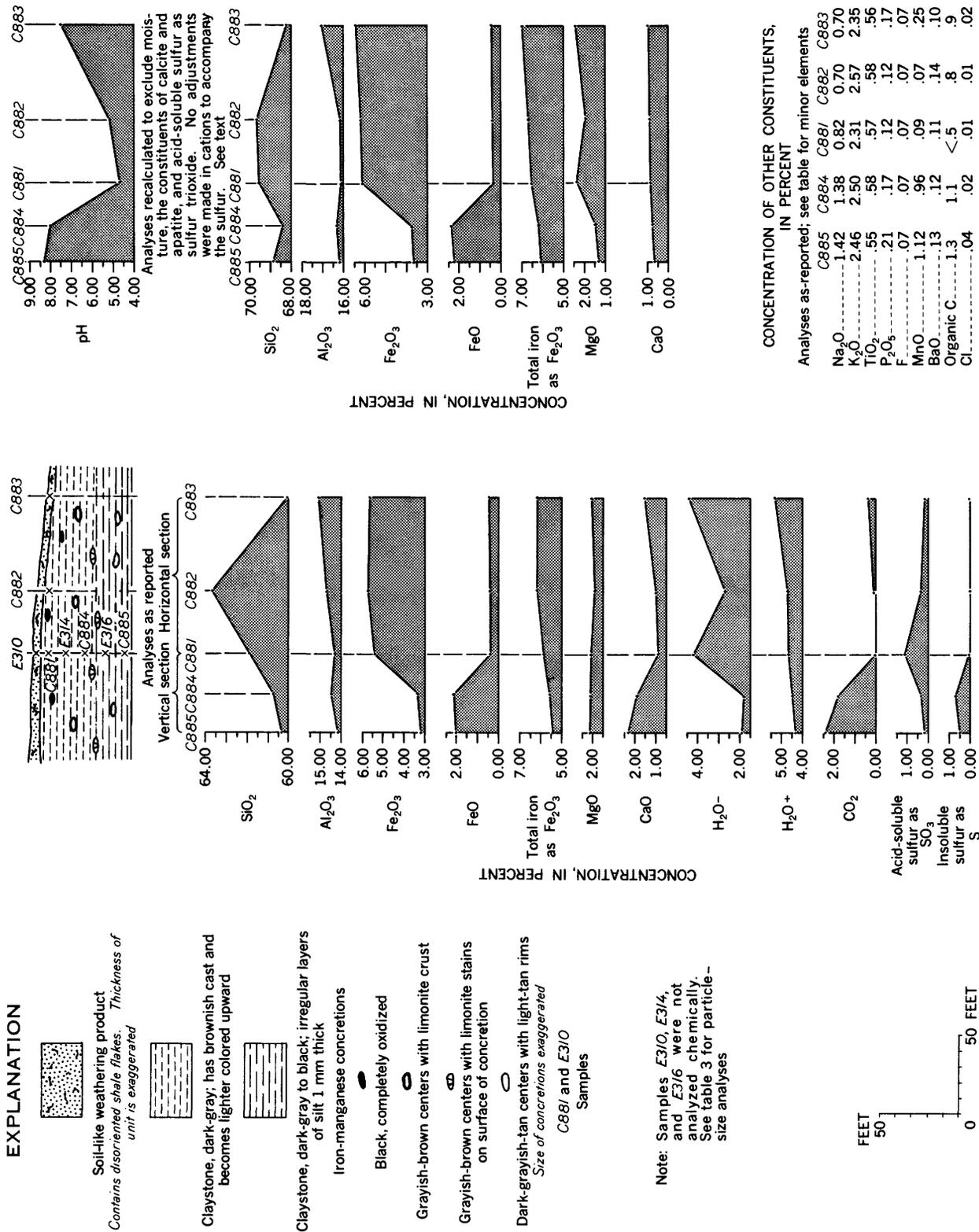


FIGURE 8.—Diagrams showing changes in chemical composition resulting from weathering of Verendrye member of Pierre shale, locality 8, spillway excavation, Omaha Dam, NE 1/4 sec. 81, T. 6 N., R. 30 E., Stanley County, S. Dak.

the soillike material on the Verendrye member was formed. In addition, the various beds of the Verendrye may have originally differed in chemical composition so that differences in composition shown by the vertical section may not be exclusively the result of weathering.

On the as-reported basis, the profile of the Verendrye shows a sharp increase in silica content and then a sharp decrease. The alumina content appears to be independent of the silica content. Ferrous oxide is most abundant in the freshest samples and ferric oxide in the most weathered samples; the total content of iron as ferric oxide shows a small but steady increase from the freshest material to the most weathered. The magnesium content is nearly uniform throughout the weathering sequence but the calcium content decreases sharply from bottom to top of the vertical profile and parallels a sharp decrease in carbon dioxide. Calcium increases slightly along the horizontal profile, because of the formation of small amounts of secondary calcium carbonate near the ground surface, as suggested by the small increase in carbon dioxide along the horizontal profile. The data for moisture show a very irregular distribution for which no explanation is apparent, except, perhaps, the uncertainty of the analyses. Sulfur in insoluble form and acid-soluble sulfur as sulfur trioxide show reciprocal relations suggesting oxidation of pyrite and formation of gypsum and other soluble sulfates in the intermediate part of the weathering sequence, and then leaching of these constituents at and near the ground surface. The sodium content of the samples decreases sharply in the freshest part of the weathering sequence and then is about uniform. The potassium content is almost uniform throughout the sequence, and so is the content of other elements, except manganese. Manganese shows a sharp decrease and then a small increase in the soillike material at the ground surface.

Calculation of the analyses to exclude carbon dioxide and calcium oxide to make calcium carbonate and acid-soluble sulfur as sulfur trioxide simplifies the interpretation of some of the trends noted in the analyses on the as-reported basis, and complicates others. No adjustment has been made for cations that accompany the acid-soluble sulfur as sulfur trioxide in recalculating the analyses, because the amount of iron sulfate and gypsum in the samples cannot be determined. The silica-alumina relations show differences in composition from sample to sample in the vertical weathering sequence that cannot be the result of weathering alone, but must be in part due to variations in original composition. In the horizontal weathering sequence, the ratio of silica to alumina of the soillike material is

markedly lower than for the two samples of the bed from which the surface material was derived. This implies an actual decrease in silica or increase in alumina that apparently cannot be explained by weathering. The soillike material (sample C883) contains more montmorillonite than mixed-layer illite-montmorillonite (table 5) and this is the only apparent mineralogical difference. An increase in the montmorillonite content would, however, be expected to increase the ratio of silica to alumina. Perhaps the basic assumption that the soillike material represents an in-place weathering product should be questioned. The data seem inconclusive.

The pH profile (fig. 8; see also table 20) shows that the freshest rocks are highly alkaline and this seems attributable to readily exchangeable sodium. The acidic part of the pH profile corresponds to the samples with relatively large amounts of acid-soluble sulfur as sulfur trioxide. The near-neutral pH of the soillike material seems to be caused mostly by the absence of any strong base or strong acid rather than by the presence of any particular ion or ions.

The distribution of the organic carbon content through the weathering profile suggests differences in composition from bed to bed for the vertical part of the profile. The horizontal profile for organic carbon, however, appears to show secondary enrichment of organic material in the weathered samples. This secondary concentration does not affect the appearance of the claystone in the same way that it does in the Claggett shale (fig. 7).

#### COMPARABLE CORE AND SURFACE SAMPLES

The relations between fresh and weathered material were investigated also by samples from a core hole at Oahe Dam, S. Dak., and samples from the outcrop at approximately the same stratigraphic position. U.S. Army Corps of Engineers core hole 2040 was drilled on the east side of the Missouri River, a thousand feet or so downstream from the axis of the dam (loc. 9, pl. 1). The samples were taken from core that had been lying on the ground for only about 8 hours. The samples came from depths of about 33 to 67 feet (fig. 9) and no signs of weathering could be recognized. The top of the Crow Creek member of the Pierre shale was at a depth of 50.5 feet; a fault cut the marlstone and reduced to about 1 foot its normal thickness of about 10 feet. There was no indication of any alteration of the marlstone near the slickensided fault surface. The DeGrey member of the Pierre shale (overlying the Crow Creek member), the Crow Creek member, and the underlying Gregory member were sampled from the core. The position of the samples is shown in figure 9.

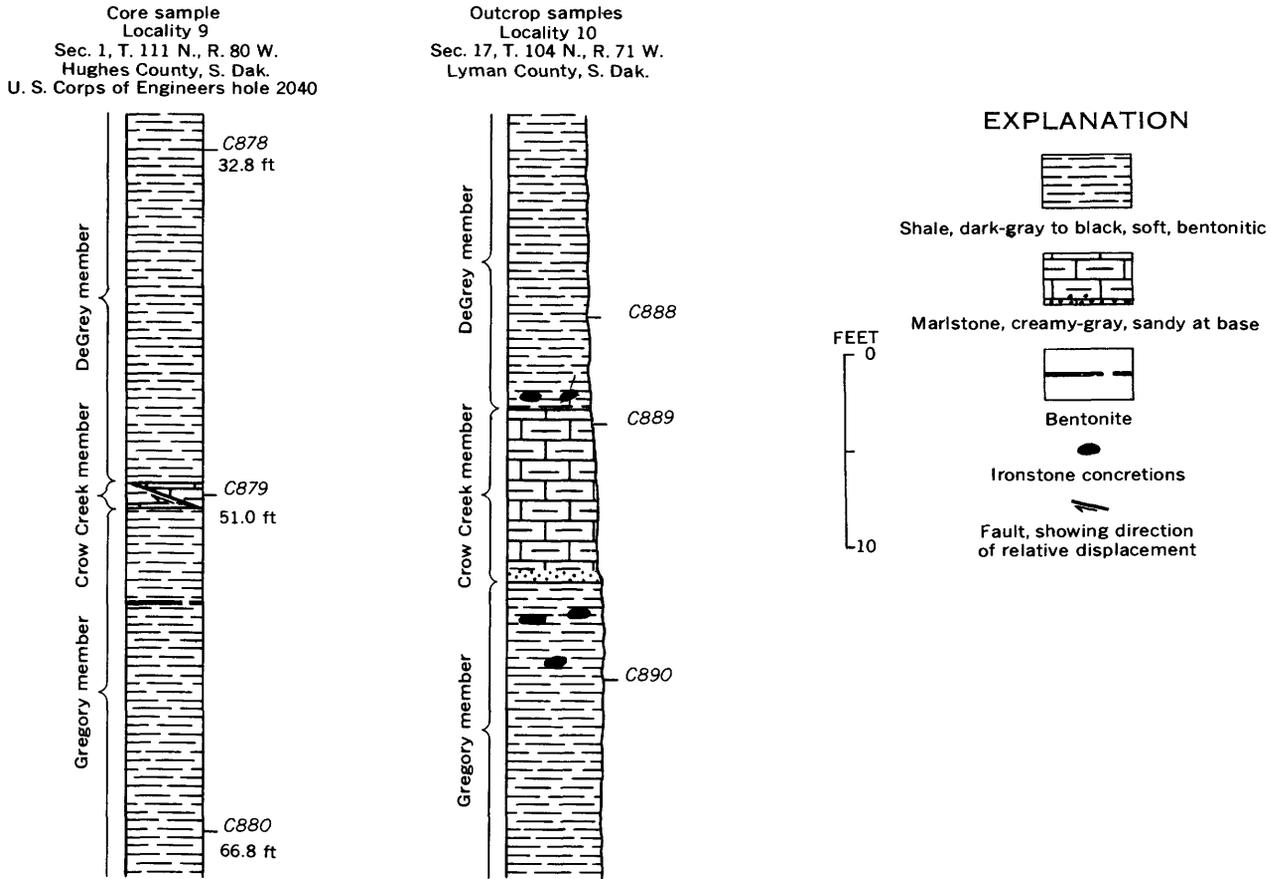


FIGURE 9.—Stratigraphic relations of samples of equivalent materials of the Pierre shale from core and outcrop.

These same stratigraphic units, at approximately the same position with respect to the Crow Creek member, were sampled from surface outcrops in Lyman County, near Chamberlain, S. Dak. (loc. 10, pl. 1). This locality is about 60 miles southeast of the core hole at Oahe Dam, and differences between analyses probably can be ascribed to actual changes in composition as well as to weathering. The stratigraphic section at locality 10 is shown in figure 9. The samples of the DeGrey and Crow Creek members were from a foot or so beneath the surface of natural outcrops; although the material obviously had been somewhat weathered, the claystone and marlstone were moderately hard when dug into, and appeared fresh. The sample of the Gregory came from the upper part of a steep road cut and had been exposed only several years. The sampled material was much less weathered than the claystone at the place where the cut intersected the hillsides. The samples from this locality represent the range of weathered material that normally is available for sampling throughout the area of the Pierre shale and equivalent rocks. The analyses of the samples are shown in table 9.

The analyses of the samples of the DeGrey (samples C878 and C888) differ significantly from each other.

TABLE 9.—Chemical analyses of core and outcrop samples from the Gregory, Crow Creek, and DeGrey members of the Pierre shale

[Stratigraphic sections shown in fig. 9]

|   | DeGrey                 |                           | Crow Creek             |                           | Gregory                |                           |
|---|------------------------|---------------------------|------------------------|---------------------------|------------------------|---------------------------|
|   | C878<br>Core<br>sample | C888<br>Outcrop<br>sample | C879<br>Core<br>sample | C889<br>Outcrop<br>sample | C880<br>Core<br>sample | C890<br>Outcrop<br>sample |
| SiO <sub>2</sub> .....                  | 69.04                  | 59.81                     | 27.96                  | 35.25                     | 58.90                  | 56.87                     |
| Al <sub>2</sub> O <sub>3</sub> .....    | 12.37                  | 15.70                     | 6.60                   | 9.76                      | 16.83                  | 15.92                     |
| Fe <sub>2</sub> O <sub>3</sub> .....    | 2.92                   | 4.95                      | 1.21                   | 3.78                      | 3.80                   | 4.73                      |
| FeO.....                                | 1.20                   | .35                       | 4.26                   | .00                       | 1.53                   | .15                       |
| MgO.....                                | 1.70                   | 2.27                      | 2.89                   | 2.00                      | 2.69                   | 2.39                      |
| CaO.....                                | .76                    | 1.34                      | 25.06                  | 21.65                     | .99                    | 2.97                      |
| Na <sub>2</sub> O.....                  | 1.34                   | 1.19                      | .53                    | .64                       | 1.38                   | 1.72                      |
| K <sub>2</sub> O.....                   | 1.98                   | 2.60                      | 1.25                   | 2.18                      | 2.70                   | 3.05                      |
| H <sub>2</sub> O.....                   | 2.94                   | 4.68                      | 1.43                   | 2.71                      | 4.30                   | 3.31                      |
| H <sub>2</sub> O+.....                  | 4.02                   | 4.67                      | 2.09                   | 2.77                      | 4.75                   | 4.27                      |
| TiO <sub>2</sub> .....                  | .48                    | .57                       | .28                    | .37                       | .56                    | .56                       |
| CO <sub>2</sub> .....                   | .29                    | .27                       | 24.07                  | 17.35                     | .38                    | 1.80                      |
| P <sub>2</sub> O <sub>5</sub> .....     | .07                    | .13                       | .26                    | .23                       | .11                    | .13                       |
| Acid-soluble S as SO <sub>3</sub> ..... | .12                    | .50                       | .04                    | .18                       | .09                    | 1.31                      |
| Insoluble S as S.....                   | .27                    | .01                       | .43                    | .01                       | .44                    | .01                       |
| Cl.....                                 | .01                    | .01                       | .02                    | .02                       | .03                    | .01                       |
| F.....                                  | .05                    | .08                       | .06                    | .08                       | .09                    | .08                       |
| MnO.....                                | .11                    | .25                       | 1.35                   | .79                       | .09                    | .33                       |
| BaO.....                                | .11                    | .05                       | .03                    | .00                       | .04                    | .04                       |
| Subtotal.....                           | 99.78                  | 99.43                     | 99.82                  | 99.77                     | 99.70                  | 99.65                     |
| Less O.....                             | .09                    | .08                       | .13                    | .04                       | .15                    | .03                       |
| Total.....                              | 99.69                  | 99.40                     | 99.69                  | 99.73                     | 99.55                  | 99.62                     |
| Organic C.....                          | <0.5                   | <0.5                      | 1.5                    | <0.5                      | <0.5                   | <0.5                      |
| pH.....                                 | 8.18                   | 7.70                      | 8.50                   | 8.18                      | 10.15                  | 8.23                      |

The core sample (C878) contains more silica and ferrous iron and less alumina than the surface sample (C888), and contains slightly more sodium. The contents of all other constituents are lower or about the same in the core sample than in the surface sample. The X-ray analyses (table 5) show that the core sample (C878) contains about 15 percent quartz and 18 percent beta cristobalite; the surface sample (C888) contains about 14 percent quartz and no beta cristobalite. Subtracting these amounts of silica, and the calculated amounts of calcium carbonate, calcium fluophosphate, calcium sulfate, and iron sulfide, from the analysis indicates that the samples are made up of about 65 percent and 84 percent clay minerals, respectively. (See table 10.)

TABLE 10.—*Calculated mineralogical and chemical composition, in percent, of claystone and marlstone from equivalent stratigraphic positions of members of the Pierre shale*

[See table 9 for original analyses]

|   | DeGrey      |                | Crow Creek  |                | Gregory     |                |
|---|-------------|----------------|-------------|----------------|-------------|----------------|
|   | Core sample | Surface sample | Core sample | Surface sample | Core sample | Surface sample |
|   | C878        | C888           | C879        | C889           | C880        | C890           |
| <b>Calculated mineralogical composition</b>                                 |             |                |             |                |             |                |
| CaCO <sub>3</sub> .....   | 0.5         | 0.6            | 38.0        | 32.8           | 0.9         | 1.6            |
| CaMg(CO <sub>3</sub> ) <sub>2</sub> .....                                   |             |                | 9.1         | 6.1            |             | 2.8            |
| Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>2</sub> .....        | .2          | .3             | .6          | .5             | .3          | .3             |
| FeCO <sub>3</sub> .....   |             |                | 5.7         |                |             |                |
| MnCO <sub>3</sub> .....   |             |                | 2.2         |                |             |                |
| MnO.....  |             |                |             | .8             |             |                |
| CaSO <sub>4</sub> .....   | .2          | .9             |             | .3             | .2          | 2.2            |
| FeS <sub>2</sub> .....  | .6          |                | .9          |                | .9          |                |
| SiO <sub>2</sub> :  |             |                |             |                |             |                |
| Quartz.....   | 15.0        | 14.0           | 12.0        | 8.0            | 18.0        | 15.0           |
| Beta cristobalite.....  | 18.0        |                |             |                |             |                |
| Clay minerals.....  | 65.5        | 84.2           | 31.5        | 51.5           | 79.7        | 78.1           |
| Total.....  | 100.0       | 100.0          | 100.0       | 100.0          | 100.0       | 100.0          |
| <b>Calculated chemical composition of clay minerals, excluding moisture</b> |             |                |             |                |             |                |
| SiO <sub>2</sub> .....  | 62.0        | 61.7           | 57.7        | 58.9           | 58.2        | 59.5           |
| Al <sub>2</sub> O <sub>3</sub> .....  | 21.3        | 21.2           | 23.9        | 21.1           | 23.9        | 22.6           |
| Fe <sub>2</sub> O <sub>3</sub> .....  | 5.0         | 6.7            | 4.4         | 8.2            | 5.4         | 6.7            |
| FeO.....  | 1.6         | .5             | .9          |                | 1.5         | .2             |
| MgO.....  | 2.9         | 3.1            | 3.3         | 2.9            | 3.8         | 2.5            |
| CaO.....  | .4          | .7             | 2.4         | 2.1            | .4          | .4             |
| Na <sub>2</sub> O.....  | 2.3         | 1.6            | 1.9         | 1.4            | 2.0         | 2.4            |
| K <sub>2</sub> O.....   | 3.4         | 3.5            | 4.5         | 4.7            | 3.8         | 4.3            |
| TiO <sub>2</sub> .....  | .8          | .8             | 1.0         | .8             | .8          | .8             |
| MnO.....  | .2          | .3             |             |                | .1          | .5             |
| BaO.....  | .2          | .1             | .1          |                | .1          | .1             |
| Total.....  | 100.1       | 100.2          | 100.1       | 100.1          | 100.0       | 100.0          |
| SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub> ratio.....                 | 2.91        | 2.91           | 2.41        | 2.79           | 2.44        | 2.63           |
| Organic carbon (percent total rock) <sup>1</sup> .....                      | <0.5        | <0.5           | 1.5         | <0.5           | <0.5        | <0.5           |

<sup>1</sup> Reported percentages (not calculated).

The chemical composition of the clay minerals, also shown in table 10, can now be compared without the masking effect of other mineral components. The silica content of the clay minerals in the core sample of the DeGrey member is about the same as in the surface sample, and the silica-alumina ratios are identical. The total iron content of the core and surface samples is

about the same, and ferrous oxide is a minor constituent in the surface sample compared to the core sample, as expected. The contents of magnesium, titanium, manganese, and barium in the calculated clay minerals from the two samples do not differ significantly. The calcium content of the core sample, however, is lower than that of the surface sample and the sodium content is much higher. Taken together, these relations suggest that the fresh material represented by the core sample contains a large amount of exchangeable sodium that in weathering is partly replaced by calcium. The relations may, however, indicate a real difference in composition.

The two analyses of marlstone samples, C879 and C889, are quite different. Calculation of a mineralogical composition, partly indicated by X-ray analyses and partly assumed, facilitates the comparison of the rock composition, and the method of calculating the mineralogical compositions needs more discussion for this pair of samples than for the preceding pair.

The X-ray analyses (table 5) indicate that the rocks are predominantly clay mixed with calcite and relatively small amounts of quartz and dolomite. These data can only be used as a preliminary guide to the calculation of the mineralogical composition of sample C879 because the analysis reports much more carbon dioxide than can be combined with the calcium oxide to form calcite. The clay minerals require both magnesium and calcium, so not all these oxides in the analysis can be applied to calcite or dolomite. The ratios between calcium oxide and magnesium oxide and alumina in the average analyses of claystone and shale of the Pierre and equivalent rocks (table 6) were applied to the alumina reported for sample C879 to determine the amount of calcium oxide and magnesium oxide to be reserved for clay minerals. The calcium oxide and magnesium oxide not assigned to clay minerals was then combined with carbon dioxide to make calcium carbonate and magnesium carbonate. Magnesium carbonate and calcium carbonate were combined to make dolomite and then set aside; the remaining calcium carbonate was set aside as calcite. Not all the carbon dioxide was accounted for by these calculations. Part of the remaining carbon dioxide was combined with all the manganese oxide to make manganese carbonate, but some carbon dioxide still remained. This was combined with ferrous oxide, after the reported amount of ferrous oxide had been corrected for the iron in pyrite, based on insoluble sulfur in the analyses. A small amount of ferrous oxide was thus left as a clay-mineral constituent. The small amount of acid-soluble sulfur as sulfur trioxide in sample C889 was then combined with calcium oxide to form calcium sulfate. The

amount of quartz indicated by the X-ray analyses was subtracted from the amount of silica to obtain a figure for silica in the clay minerals.

This procedure for calculating the mineralogical composition of the samples is quite arbitrary, and the results only partly agree with the X-ray analyses (table 5). Feldspar, indicated by X-ray analysis to be present in small amounts in most of the samples, has been ignored in the calculations. Biotite, found in the fraction coarser than 74 microns, also has been ignored. The amount of quartz determined by X-ray analysis is accepted and used because there seems to be no reasonable way to estimate the amount of quartz indirectly. The total clay contents of the samples indicated by X-ray analysis agree fairly closely with the calculated clay-mineral contents. The amount of calcite calculated for sample C879 agrees closely with the amount determined by X-ray analysis, but the amount of calcite calculated for sample C889 differs by 5 percent from that determined by X-ray analysis. Although dolomite can be identified by the X-ray analysis, the amounts estimated to be present are somewhat smaller than those calculated. The presence of manganese carbonate, as such, and pyrite is not implied by the X-ray data, but iron carbonate is reported in sample C879. The manganese carbonate and iron carbonate may occur together as an isomorphous mixture.

The occurrence of iron and manganese carbonates in the core sample is reasonable, but it should be recognized that their occurrence is problematical. The determination of ferrous oxide is quite uncertain in sample C879 because it contains about 1.5 percent organic carbon. Most unweathered clay minerals contain much more ferrous oxide than is available for the clay minerals calculated for sample C879. (See table 6.) Hewett (1930) pointed out that manganese-iron carbonate minerals form abundant concretions in the upper part of beds called the DeGrey member by Crandell (1950) and called the Oacoma zone of the Sully member by Searight (1937, p. 23-24). These carbonate concretions weather to oxides of iron and manganese. The assignment of manganese in the core samples to carbonate, where there is sufficient carbon dioxide and manganese, and to oxides in the surface samples, is consistent with other data. In addition, the assignment of manganese and iron largely to carbonate minerals in sample C879 is necessary to account for the amount of carbon dioxide in the analysis. The amount of carbon dioxide in the standard rock analysis is confirmed by the independent determination of mineral carbon shown in tables 9 and 18 (p. 57). Where manganese is present in relatively small amounts, it has been left in oxide form in the composition of the clay mineral.

The two marlstone samples show some differences that seem to be original differences in composition and some that seem ascribable to weathering. The core sample C879 contains more calcite, dolomite, and quartz than the surface sample C889. The calculated composition of the clay minerals in the core sample differs from that of the surface sample in having a distinctly smaller silica-alumina ratio and in being deficient in iron. The organic carbon content of the core sample is comparatively high and is much larger than that of the surface sample, probably because of weathering of the surface sample. The core sample contains iron and manganese carbonates and pyrite, and the absence of these constituents in the surface sample is the result of weathering. The core sample contains a larger amount of manganese than the surface sample. Relatively small amounts of gypsum and manganese oxide can be calculated for the surface sample, but there is no way to estimate the amount of the iron in the oxide form in the surface sample, although some surely is present. All the ferric iron has been placed in the calculated composition of the clay minerals. The differences between the alkali and alkaline-earth elements in the calculated clay-mineral composition of the two samples may reflect ion-exchange reactions. However, if the amount of iron present as free oxides in the surface sample could be determined, the calculated composition of the clay minerals in the two samples probably would be very similar. The differences in calcite, dolomite, and quartz, and perhaps manganese are the only real original differences in composition of the two rocks that can be discerned.

The differences between the samples of the Gregory member show some of the same changes in composition as the other samples from localities 9 and 10. The most conspicuous difference in calculated minerals is the presence of more calcite in the surface sample (C890) than in the core sample (C880), and the presence of more dolomite than calcite in the surface sample. The constituents of pyrite in the core sample show up in the surface sample as gypsum and a somewhat larger iron content in the clay minerals. The figure for magnesium is larger in the calculated composition of the clay minerals in the core sample than in the surface sample, but those for both sodium and potassium are larger in the surface sample than in the core sample. The silica-alumina ratio of the surface sample of the Gregory member is larger than that of the core sample and thus parallels the relations between the clay minerals of the two samples of marlstone. The surface sample of the Gregory member is relatively little weathered, so these differences probably indicate actual

differences in composition instead of any real differences brought about by weathering.

#### CONCLUSIONS

The data from the two weathering sequences and from the drill core and surface samples of equivalent rocks lead to a few generalizations concerning the significance and interpretation of samples from surface outcrops. Much of the data presented here concerns the degree of weathering that has broken down the shale and claystone to the soil-like material of the northern Great Plains region. It is never necessary to sample such material for data on the chemical composition of the rock, because outcrops of less weathered material ordinarily are available and because material that has been only moderately weathered can be obtained by digging. The sample that is of most significance in an investigation such as this is what might be called a good geologic sample—the freshest material that can be obtained by digging in normal kinds of outcrops. At many places, recent road cuts and stream banks provide fresher samples than do ordinary outcrops on hillsides.

The major changes in composition that take place during weathering under the conditions prevalent in the northern Great Plains region are the result of hydration, oxidation, and ion-exchange reactions and evaporation of ground moisture in surface outcrops.

The hydration reactions involve chiefly the relative proportions of  $H_2O-$  and  $H_2O+$  in the samples. Air-dried samples show that the content of  $H_2O+$  is higher than  $H_2O-$  in the fresh material and about the same or lower than  $H_2O-$  in weathered material. There is no notable change in the total amount of moisture between fresh and weathered air-dried samples, although the fresh material may contain more total moisture in the ground. The changes in moisture content do not influence any geochemical comparisons of analyses, because such comparisons can be made on a moisture-free basis.

The oxidation reactions concern the relative proportions of ferric and ferrous iron and the relative proportions of insoluble sulfur as sulfur and acid-soluble sulfur as sulfur trioxide. The determination of ferrous iron is unreliable (see p. 24) in the presence of organic matter, and the effect of organic matter on the determination is unpredictable. In spite of this uncertainty, the occurrence of ferrous iron in samples is consistent with field observations on the freshness of the samples, ferrous iron is always reported for samples believed to be fresh and absent or reported in very small amounts for samples that are obviously weathered. The distribution of ferric iron is the inverse of the distribution of ferrous iron. The total iron content

is fairly uniform across most weathering profiles, but may decrease under outcrop conditions where leaching is possible; such situations can be avoided by selecting other sites for sampling.

Sulfide minerals, such as pyrite or marcasite, in the rock are oxidized to sulfate compounds at a very early stage in the weathering of an outcrop. Outcrops that appear to be relatively fresh may contain no discernible sulfide minerals for several feet from the surface of the outcrop. Pyrite is nearly always present in unweathered rocks of the Pierre shale and equivalent units. Insoluble sulfur reported as sulfide in an analysis implies a considerable degree of freshness in the sample, barite or other insoluble forms of sulfur not having been recognized. Both acid-soluble and insoluble forms of sulfur in an analysis indicate an intermediate degree of weathering. The amount of soluble sulfur reported in an analysis cannot ordinarily be used to estimate the amount of insoluble sulfur in the rock before weathering, because the common oxidation products of sulfide sulfur are quite soluble and may either be removed from the outcrop or concentrated in it. Sulfate ions brought near the surface of the outcrop by capillary movements of water form relatively insoluble calcium sulfate, if calcium ions are present.

Organic matter in the rock almost certainly is affected by oxidation near the ground surface. The nature of the organic matter may be greatly modified, but the amount of organic matter remains large enough for an organic-rich shale to be recognized. The high organic carbon content of the fresh marlstone, however, probably would not be deduced from the analysis of surface samples. There is some indication (fig. 7) that the organic material may be partly mobile and can be relatively depleted or concentrated by weathering. Not enough data are available to indicate a consistent pattern of behavior for organic matter.

Ion-exchange reactions in weathering processes are very complex and are influenced by a host of factors, whose individual significance is not yet generally agreed upon (Grim, 1953, p. 142–155). The approximate course of such reactions can be predicted, however. The most easily replaced exchangeable cations in the clay minerals will be the first to be lost in weathering. The major alkali and alkaline-earth elements in the order of replacing power are  $Na < K < Ca < Mg$  (Grim, 1953, p. 144). Thus, exchangeable sodium would be easily lost in weathering and would be replaced by magnesium if the weathering were intense and magnesium was available. Although, in general, potassium is more easily replaced than calcium, the close fit between the ionic diameter of potassium and the

cavity in the oxygen layer in layer clay minerals makes potassium relatively very difficult to replace from those minerals (Page and Baver, 1939, cited by Grim, 1953, p. 146-147).

Trends in changes of composition that parallel and diverge from the expectable ion-exchange reactions have been pointed out in the data presented on weathering profiles. Water, circulating slowly in the relatively recent past through material even as impermeable as shale, could have caused ion-exchange reactions that resulted in such changes. Such reactions are believed to be responsible for changes in composition of ground water, where near-surface water from a rock unit is relatively rich in calcium but water from depth in the same rock unit is rich in sodium the sodium having been derived by its replacement with calcium in the clay minerals of the aquifer (Foster, 1950, p. 38-39; Babcock, Visher, and Durum, 1952, p. 20-21). The clay minerals would be correspondingly enriched in calcium and magnesium.

Surface samples from the freshest outcrops available seem to be suitable for this kind of geochemical investigation. The greatest shortcoming of surface samples is the indeterminate amount of pyrite in the original rock. This is unfortunate, since the amount of pyrite could be used to estimate the intensity of the re-

ducing conditions through which the rock had passed. The distribution of organic matter in near-surface samples also is uncertain. The nature of the organic material certainly must undergo considerable change. Sufficient total organic material still remains in the rock, however, to serve as an approximate index to the reducing nature of the environments of deposition and diagenesis. The alkali and alkaline-earth elements are partly mobile under both deep and near-surface conditions, so absolutely fresh samples would offer no real advantage. The effect of other changes in composition during weathering can be eliminated or minimized by calculations.

COMPARISON WITH OTHER SHALES

Table 11 shows average compositions for five other groups of rocks that can be compared with the average composition of the Pierre shale. Standard deviations have been calculated for four of these groups. These groups of data are derived from the study of pelitic rocks by Shaw (1956), the analyses and compilation of analyses of lutites of Precambrian age by Nanz (1953), the massive study of the composition of clays from the Russian platform by Vinogradov and Ronov (1956), and the average shale of Clarke (1915).

TABLE 11.—Comparison of average composition, in percent, of Pierre shale and equivalent rocks with other pelitic rocks

[ $\bar{X}$ , arithmetic mean; *s*, standard deviation]

|  | a         |          | b         |          | c         |          | d         |          | e         |          | f         |
|--|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|
|  | $\bar{X}$ | <i>s</i> | $\bar{X}$ |
| SiO <sub>2</sub> .....                           | 59.68     | 3.49     | 61.17     | 3.84     | 56.30     | 4.92     | 61.54     | 4.68     | 52.21     | 6.37     | 58.38     |
| Al <sub>2</sub> O <sub>3</sub> .....             | 15.40     | 1.52     | 19.65     | 2.55     | 17.24     | 3.62     | 16.95     | 4.21     | 14.64     | 2.57     | 15.47     |
| Fe <sub>2</sub> O <sub>3</sub> .....             | 4.56      | 1.09     | 1.48      | .81      | 3.83      | -----    | 2.56      | 1.97     | 6.19      | .87      | 4.03      |
| FeO.....   | .96       | .64      | 5.33      | 1.20     | 6.27      | -----    | 3.90      | 2.25     | -----     | -----    | 2.46      |
| MgO.....   | 2.11      | .47      | 2.03      | .64      | 2.54      | 1.09     | 2.52      | 1.91     | 3.21      | 1.48     | 2.45      |
| CaO.....   | 1.52      | 1.12     | .38       | .28      | 1.00      | 1.06     | 1.76      | 2.03     | 7.22      | 4.47     | 3.12      |
| Na <sub>2</sub> O.....                           | 1.09      | .42      | 1.16      | .63      | 1.23      | 1.06     | 1.84      | 1.18     | .87       | .31      | 1.31      |
| K <sub>2</sub> O.....                            | 2.49      | .26      | 3.70      | .51      | 3.79      | 1.57     | 3.45      | 1.32     | 3.39      | .96      | 3.25      |
| H <sub>2</sub> O.....                            | 3.73      | 1.09     | .16       | .30      | .38       | -----    | 3.47      | 2.25     | 5.40      | 1.54     | 5.02      |
| H <sub>2</sub> O+.....                           | 4.77      | .83      | 3.19      | .87      | 3.31      | -----    | -----     | -----    | -----     | -----    | -----     |
| TiO <sub>2</sub> .....                           | .60       | .05      | .98       | .17      | .77       | -----    | .82       | .61      | .73       | .14      | .65       |
| CO <sub>2</sub> .....                            | 3.87      | 1.35     | .03       | -----    | .84       | -----    | 1.67      | 2.37     | 5.95      | 4.10     | 2.64      |
| P <sub>2</sub> O <sub>5</sub> .....              | .15       | .04      | .14       | .24      | .14       | -----    | -----     | -----    | -----     | -----    | .17       |
| Acid-soluble S as SO <sub>3</sub> .....          | .85       | .95      | -----     | -----    | .28       | -----    | -----     | -----    | .68       | 1.63     | .65       |
| Insoluble S as S.....                            | 5.21      | .17      | .05       | -----    | 1.06      | -----    | -----     | -----    | -----     | -----    | -----     |
| Cl.....  | 7.01      | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     |
| F.....   | .07       | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     |
| MnO.....   | .19       | .39      | .07       | -----    | .10       | -----    | -----     | -----    | -----     | -----    | Tr.       |
| BaO.....   | .08       | -----    | .05       | -----    | -----     | -----    | -----     | -----    | -----     | -----    | .05       |
| Subtotal.....                                    | 99.34     | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     |
| Less O.....                                      | .07       | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     | -----    | -----     |
| Total.....                                       | 99.27     | -----    | 99.57     | -----    | 99.08     | -----    | 100.48    | -----    | 100.49    | -----    | 99.65     |
| Total Fe as Fe <sub>2</sub> O <sub>3</sub> ..... | 5.63      | -----    | 7.40      | -----    | 10.80     | -----    | 6.89      | -----    | 6.19      | -----    | 6.76      |

<sup>1</sup> Adjusted from reported FeS<sub>2</sub> and FeO.

<sup>2</sup> Loss on ignition includes organic matter, total moisture, halides, and sulfides.

<sup>3</sup> 16 samples.

<sup>4</sup> Only 62 values for CO<sub>2</sub>.

<sup>5</sup> 14 samples.

<sup>6</sup> Adjusted from reported FeS<sub>2</sub>.

<sup>7</sup> 11 samples.

<sup>8</sup> Ba instead of BaO.

<sup>9</sup> Includes 0.37 percent C.

<sup>10</sup> Includes 1.18 percent C.

<sup>11</sup> Includes 0.81 percent C.

a. 17 analyses from table 7, excluding C874, C879, C883, C889, and C891.

b. 18 analyses of Devonian pelitic rocks recalculated from Shaw (1956, table 2, p. 922).

c. 33 analyses of Precambrian lutites from Nanz (1953, table 2, p. 57; *s* calculated from table 1, p. 53-54).

d. Average pelitic rock calculated by Shaw (1956, table 10, p. 928).

e. Average clay of the Russian platform recalculated from 16 averages for subdivisions of geologic periods based on 249 composite samples consisting of 6,769 individual samples (Vinogradov and Ronov, 1956, p. 6, 7).

f. Average shale of Clarke (1915, p. 23).

Shaw uses the term "pelite" to refer to the general class of fine-grained rocks; Nanz uses "lutite" for the same purpose. Both studies are based on samples of metamorphosed rocks ranging from slate to schist that are believed to have been originally clay or shale. Since these rocks can not now be called shale, the usage of the Shaw and Nanz is retained. Shaw's work included 18 samples of shale, slate, and related metamorphic rocks of the Littleton formation of Devonian age from New Hampshire, and the compilation of

analyses from the literature to characterize a "world" pelite. Vinogradov and Ronov presented analyses of about 200 composite samples that were based on more than 6,000 individual samples. The composite samples range in age from Precambrian to Quaternary. The standard deviations were calculated from the figures presented for 16 age groups, such as Precambrian, Cambrian, and Ordovician (Vinogradov and Ronov, 1956, p. 6-7). The average shale of Clarke is based on the analyses of two composite samples consisting of 51

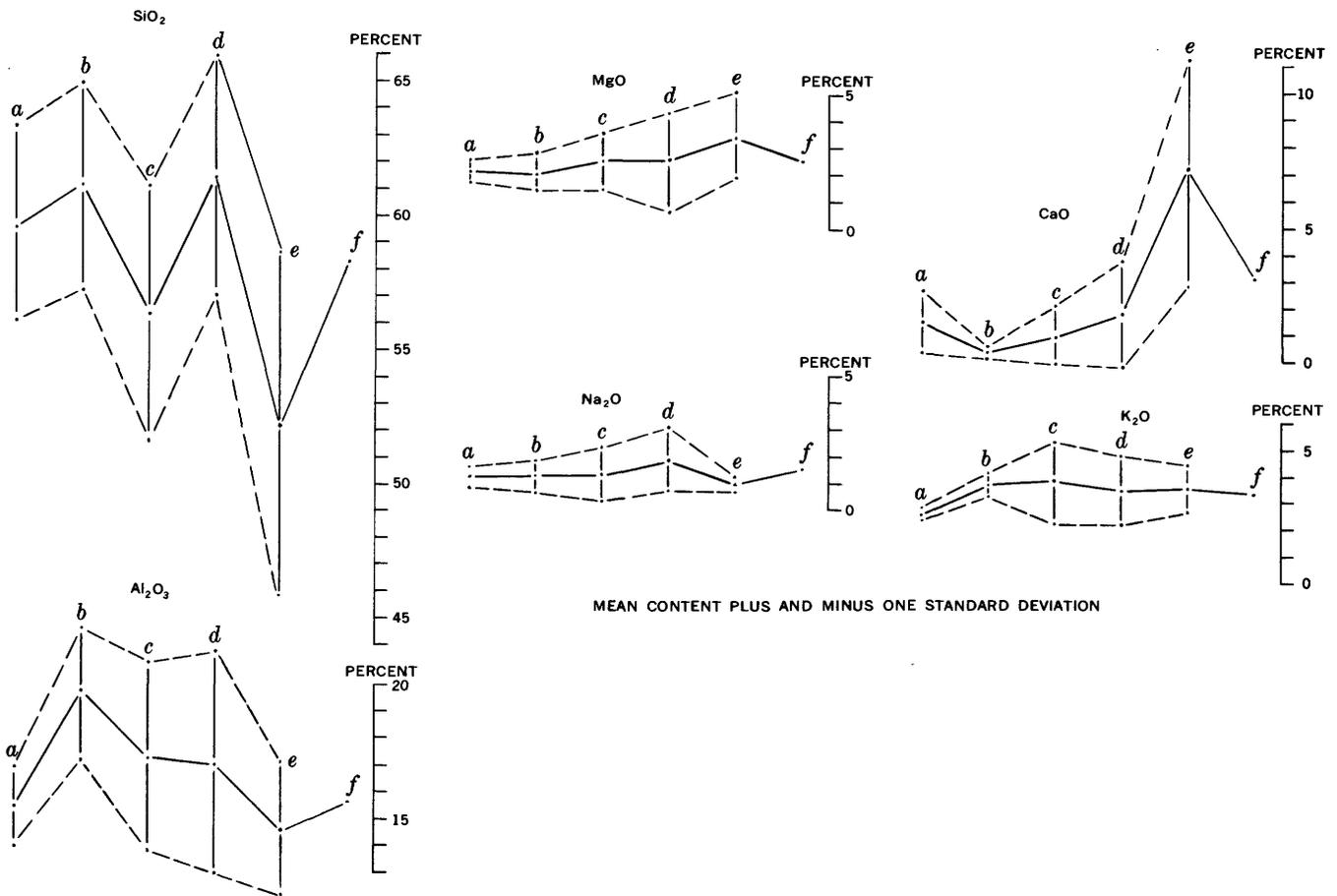


FIGURE 10.—Graphic comparison of average contents on as-reported basis of selected major elements in Pierre shale and equivalent rocks with other pelitic rocks. See table 11 for analytical data. *a*, 17 analyses of Pierre shale and equivalent rocks; *b*, 18 analyses of Devonian pelitic rocks; *c*, 33 analyses of Precambrian lutites; *d*, 155 analyses of pelitic rocks; *e*, 16 average analyses of clays from the Russian platform; *f*, average shale of Clarke.

shales of Paleozoic age and 27 shales of Mesozoic and Cenozoic age. The comparisons of the averages for selected major constituents are shown graphically in figure 10.

Most of the constituents of the Precambrian lutites and the world pelites have larger standard deviations than those of the Devonian pelites and the samples of the Pierre. Since the data on the Precambrian lutites and the world pelites are mostly compilations, there are two possible causes for the larger standard deviations. One of these is that the compilations include a much broader range of rock type than was included in the selected samples for the study of the Devonian pelites and the Pierre shale. The other is that the compilations include analyses made in different laboratories at different times, and probably with different methods. The analyses included in the averages thus are not certainly comparable.

The standard deviations of the Russian clays are both larger and smaller for different constituents than the standard deviations in the other groups of data. These differences seem to be best interpreted as the result of a wide range of clay types included in the averages. All the analytical work that provided the Russian data should be comparable within the Russian samples. There is no information, however, on the precision of the analyses.

The proportions of ferric and ferrous iron differ obviously between the groups of data. This difference in the state of oxidation is more likely to be related to the degree of weathering of the materials sampled than to the conditions of their origin. The average content of total iron as ferric oxide also is shown in table 11. The average total iron is smaller for the Pierre samples (5.63 percent) than for any of the other groups of data (6.19 to 10.80 percent). The total iron content of the Precambrian lutites is much larger than for any of the other groups of data. Inspection of data by Nanz (1953, table 1, p. 53-54) suggests that many of his samples represent materials specifically enriched in iron oxide and iron carbonate, and that the iron content is much larger than would be expected for clay minerals alone. The figures for total iron for the materials from which the other groups of data were derived also include some nonclay mineral iron, but the materials seem not to have been enriched in iron to the same extent as the Precambrian samples.

With respect to silicon, aluminum, calcium, potassium, and carbonate (carbon dioxide in the analyses), the six groups of data seem to differ considerably. The differences between the data from the Pierre shale and the other groups have been assessed by statistical tests following the procedures recommended by Shaw and

Bankier (1954). Such comparisons cannot be made with the average shale of Clarke, because standard deviations cannot be calculated. All tests have been carried out at the 5-percent significance level, which means that the differences found would occur by chance five times out of a hundred. The differences found for some of the major constituents between the samples of Pierre shale and the other groups of data are shown in the following table. Some of these differences, such as for magnesium oxide (see fig. 10), are not readily identifiable from inspection of the data.

*Statistical significance of differences between average composition of samples of Pierre shale and other rocks on as-reported basis*

[O, no significant difference at 5-percent level; X, difference significant at 5-percent level]

|                                      | Devonian pelites | Precambrian lutites | World pelites | Russian clays |
|--------------------------------------|------------------|---------------------|---------------|---------------|
| SiO <sub>2</sub> .....               | O.....           | X.....              | X.....        | X             |
| Al <sub>2</sub> O <sub>3</sub> ..... | X.....           | X.....              | X.....        | O             |
| MgO.....                             | O.....           | O.....              | X.....        | X             |
| CaO.....                             | X.....           | O.....              | O.....        | X             |
| Na <sub>2</sub> O.....               | O.....           | O.....              | O.....        | O             |
| K <sub>2</sub> O.....                | X.....           | X.....              | X.....        | X             |

Differences in amounts of detrital quartz, carbonate minerals, and moisture in the materials included in the averages could be responsible for some of the differences in most of the major constituents (Bramlette, 1946, p. 12; Shaw, 1956, p. 928). In addition to causing such apparent differences, the relative proportions of detrital quartz, carbonate minerals, and moisture also could mask real differences in clay mineral composition between the averages. Corrections for detrital quartz cannot be made without mineralogical data on the individual samples. The carbonate and moisture contents of the individual samples can be allowed for, however, by calculations. The calcium content is influenced also by the phosphorus present, and in samples that contain gypsum, it is influenced by the acid-soluble sulfur.

The objectives of the calculations are to remove independent variables, such as calcium carbonate and moisture, and to remove other constituents that are not believed to be part of the composition of the clay minerals themselves. The differences in composition after such calculations should be applicable to the interpretations of the clay mineralogy of the samples. The calculations involve arbitrary procedures and many assumptions concerning the mineralogy of the samples. General agreement on the procedures and assumptions probably would be impossible to reach. The results should be comparable enough for a preliminary examination of the data, and perhaps they could be used to find more effective means of investigating such problems.

The calculations on the individual analyses were carried out as follows:

1. Enough CaO is removed from the analysis to combine with the  $P_2O_5$  reported as apatite.
2. Acid-soluble sulfur as sulfur trioxide was reported in the analyses of the Pierre shale and equivalent rocks, the Precambrian lutites, and the Russian clays. Except for the samples of the Pierre, the minerals in which the acid-soluble sulfur occurs are unknown. In the Pierre samples, the acid-soluble sulfur is present in both iron sulfate minerals and gypsum, but the proportion of these minerals in each sample is unknown. For this reason, no adjustments have been made in cations that accompany the acid-soluble sulfur. The percentages shown for calcium oxide in the recalculated averages (table 12) therefore are somewhat too large.
3. Calculations based on the  $CO_2$  in the analyses involve several alternative treatments.

(a) For the Pierre samples: The amounts of dolomite and calcite reported by X-ray analysis were used as preliminary guides for the removal of MgO and CaO to combine with all the reported  $CO_2$ . For some of the samples, minor adjustments were necessary to avoid taking all the CaO. For most of the

samples, the amount of  $CO_2$  was small enough so that the correction took only a part of the CaO.

- (b) For the Devonian pelites, the  $CO_2$  content was so small that no correction was made for CaO, although the  $CO_2$  was eliminated from the analyses.
- (c) For the Precambrian lutites, amounts of  $CO_2$  larger than about 1 percent were reported for only four samples used in these calculations. For these four samples, the reported CaO was quite small and the reported FeO was quite large; therefore, all the  $CO_2$  was assigned to the FeO to make ferrous carbonate. (See table 12 for basis for excluding six samples from the recalculated average.)
- (d) For the Russian clays, CaO and MgO were removed from the analyses in amounts so that the resulting calcium carbonate and magnesium carbonate were in the ratio of 6 to 1, following the suggestion of Wickman (1954, p. 101). For the grouped data on the Lower Devonian and Upper Carboniferous samples (Vinogradov and Ronov, 1956, table 1), this resulted in the removal of all the CaO from the analyses, some  $CO_2$  still remaining. This remaining  $CO_2$  was then assigned to FeO to

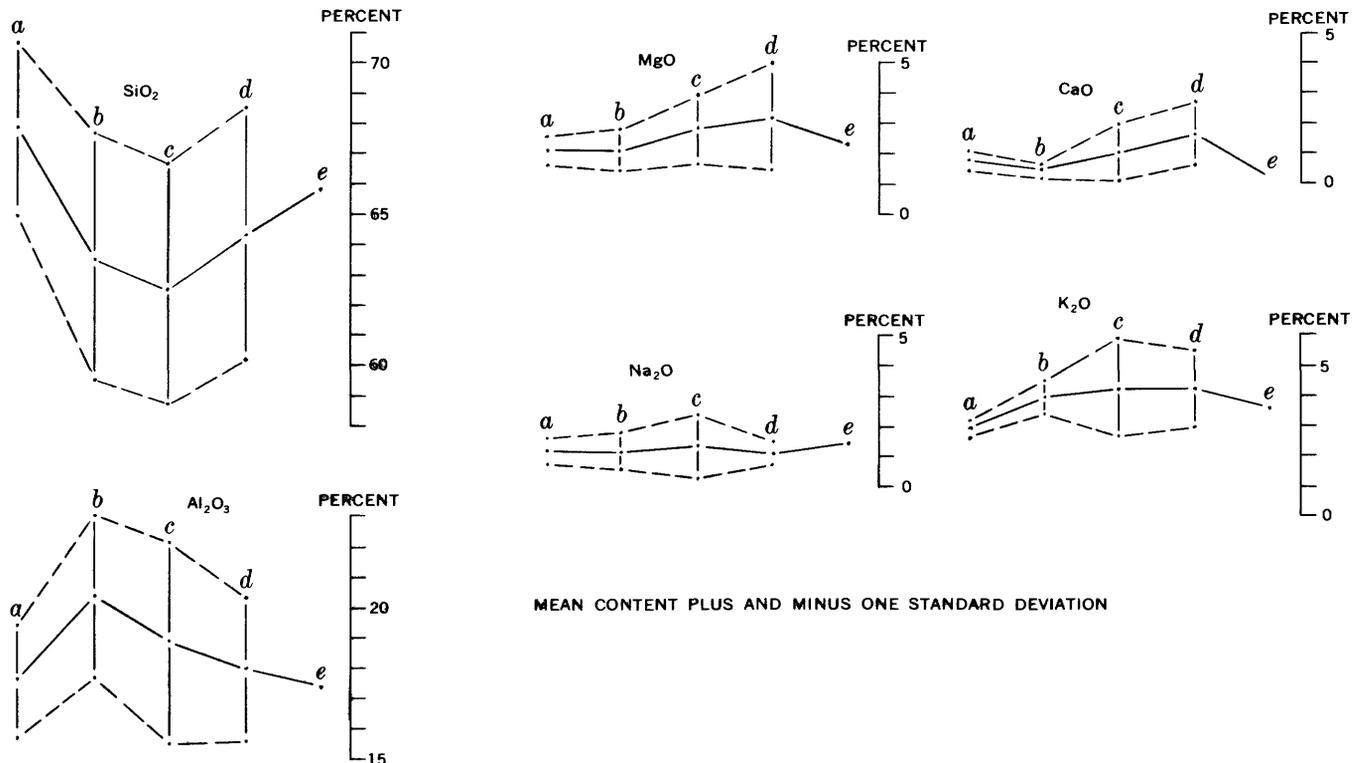


FIGURE 11.—Graphic comparison of average contents on recalculated basis of selected major elements in Pierre shale and equivalent rocks with other pelitic rocks. *a*, 17 analyses of Pierre shale and equivalent rocks; *b*, 18 analyses of Devonian pelitic rocks; *c*, 27 analyses of Precambrian lutites; *d*, 16 average analyses of clays from the Russian platform; *e*, average shale of Clarke. See table 12 for original data.

make ferrous carbonate. The amount of FeO necessary to combine with the remaining CO<sub>2</sub> as ferrous carbonate was then calculated and the reported amount for Fe<sub>2</sub>O<sub>3</sub> corrected accordingly.

4. A new total was made for each analysis and all constituents, except SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and TiO<sub>2</sub>, were eliminated. These constituents were then recalculated to approximately 100 percent.
5. The averages were then made for the recalculated analyses of each group, such as Pierre shale, Devonian pelites.

The resulting average analyses represent the composition of the original clay minerals more closely than the analyses on the as-reported basis. Minerals such as feldspar (either detrital or diagenetic), muscovite, biotite, and iron oxides, which might contribute important amounts of some constituents to the averages, have been ignored.

Table 12 gives the recalculated average chemical analyses and figure 11 shows graphically the similarities and differences between them. The world pelite given in table 11 and on figure 10 is not included because of the great amount of computations that would be involved in treating this average in the same way as the smaller groups of data. The average shales of Clarke (1915, p. 23) and Wickman (1954, p. 102) have been recalculated as though each were a single analysis; standard deviations cannot be calculated for these averages. The same statistical tests used to detect differences in the as-reported analyses reveal the following differences between Pierre samples and the other anhydrous carbonate-free average analyses:

*Statistical significance of differences between average composition of samples of Pierre shale and other rocks on recalculated basis*

[O, no significant difference at 5-percent level; X, difference significant at 5-percent level]

|                                      | Devonian pelites | Precambrian lutites | Russian clays |
|--------------------------------------|------------------|---------------------|---------------|
| SiO <sub>2</sub> .....               | X.....           | X.....              | X.....        |
| Al <sub>2</sub> O <sub>3</sub> ..... | X.....           | O.....              | O.....        |
| MgO.....                             | O.....           | X.....              | X.....        |
| CaO.....                             | X.....           | O.....              | X.....        |
| Na <sub>2</sub> O.....               | O.....           | O.....              | O.....        |
| K <sub>2</sub> O.....                | X.....           | X.....              | X.....        |

On the anhydrous carbonate-free basis, only three relations are different from the as-reported basis. The silica content of the samples of the Pierre is seen to be different from the silica content of the Devonian pelites. In alumina, the Pierre samples do not differ from the Precambrian lutites on the anhydrous carbonate-free basis; and in magnesia, they do differ. These three

TABLE 12.—Comparison of average composition, in percent, of Pierre shale and equivalent rocks with other pelitic rocks, excluding moisture, carbonate and phosphate minerals, and acid-soluble sulfur as sulfur trioxide<sup>1</sup>

[ $\bar{X}$  is arithmetic mean; *s* is standard deviation]

|  | a         |          | b         |          | c         |          | d         |          | e         | f         |
|--|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|-----------|
|  | $\bar{X}$ | <i>s</i> | $\bar{X}$ | <i>s</i> | $\bar{X}$ | <i>s</i> | $\bar{X}$ | <i>s</i> | $\bar{X}$ | $\bar{X}$ |
| SiO <sub>2</sub> .....                           | 67.92     | 2.75     | 63.61     | 3.98     | 62.56     | 3.87     | 64.37     | 3.95     | 65.89     | 61.49     |
| Al <sub>2</sub> O <sub>3</sub> .....             | 17.56     | 1.82     | 20.43     | 2.64     | 18.99     | 3.04     | 17.95     | 2.29     | 17.47     | 18.62     |
| Fe <sub>2</sub> O <sub>3</sub> .....             | 5.21      | 1.25     | 1.54      | .88      | 2.77      | 1.98     | 7.05      | 1.59     | 4.56      | 7.55      |
| FeO.....   | 1.09      | .72      | 5.54      | 1.26     | 5.30      | 3.74     |           |          | 2.78      |           |
| MgO.....   | 2.09      | .44      | 2.10      | .69      | 2.81      | 1.13     | 3.08      | 1.69     | 2.26      | 2.24      |
| CaO.....   | .75       | .29      | .44       | .28      | 2.99      | .97      | 31.53     | .95      | .19       | .23       |
| Na <sub>2</sub> O.....                           | 1.24      | .47      | 1.20      | .60      | 1.41      | 1.02     | 1.09      | .41      | 1.47      | 1.46      |
| K <sub>2</sub> O.....                            | 2.85      | .30      | 3.85      | .53      | 4.26      | 1.56     | 4.21      | 1.20     | 3.67      | 3.63      |
| TiO <sub>2</sub> .....                           | .68       | .08      | 1.01      | .18      | 4.87      | .47      | .90       | .17      | .74       | 1.08      |
| Total Fe as Fe <sub>2</sub> O <sub>3</sub> ..... | 5.70      | -----    | 7.70      | -----    | 8.66      | -----    | 7.05      | -----    | 7.65      | 7.55      |

<sup>1</sup> No adjustments were made in cations to accompany the sulfur. See p. 40.

<sup>2</sup> 26 values.

<sup>3</sup> 14 values.

<sup>4</sup> 23 values.

- a. 17 analyses of Pierre shale and equivalent rocks from table 7, excluding samples C874, C879, C883, C889, and C891. Percentage for CaO corrected for removal of P<sub>2</sub>O<sub>5</sub>.
- b. 18 analyses of Devonian pelitic rocks recalculated from Shaw (1956, table 2, p. 922). Correction for CaO and MgO on removal of CO<sub>2</sub> is insignificant 0.19 percent of the CaO is equivalent to 0.15 percent average P<sub>2</sub>O<sub>5</sub> content of 13 samples.
- c. 27 analyses of Precambrian slates recalculated from Nanz (1953, table 2, p. 57). Samples 20, 22, 25, 30-32, and 34-36 are excluded because of unacceptable total or extremely high content of Fe<sub>2</sub>O<sub>3</sub>. CaO and MgO not corrected for removal of CO<sub>2</sub>. 0.19 percent of the CaO is equivalent to 0.15 percent average P<sub>2</sub>O<sub>5</sub> content of 18 samples. FeO corrected for more than 1 percent CO<sub>2</sub> in 4 samples.
- d. 16 average analyses for subdivisions of geologic periods from Vinogradov and Ronov (1956, p. 8 and 7). CaO and MgO corrected for removal of CO<sub>2</sub> according to CaO-MgO ratio of 6 used by Wickman (1954, p. 101). Some average analyses contained so much CO<sub>2</sub> that a correction was required for FeO. CaO not corrected for removal of P<sub>2</sub>O<sub>5</sub>.
- e. Average shale of Clarke (1915, p. 23). CaO and MgO corrected for removal of CO<sub>2</sub> according to CaO-MgO ratio of 6 used by Wickman (1954, p. 101); CaO corrected for removal of P<sub>2</sub>O<sub>5</sub>.
- f. Average shale of Wickman (1954, table 5, p. 102); CaO corrected for removal of P<sub>2</sub>O<sub>5</sub>.

relations are the reverse of those shown on the as-reported basis.

The geochemical meaning of the differences on either the as-reported or the anhydrous carbonate-free basis is difficult to interpret clearly. Differences in the silica content of most shales certainly reflect differences in the amount of admixed detrital quartz, although secondary silica either as cristobalite or in other forms could be important. There is no way to work with such differences until data on the amount and form of quartz in a wide variety of analyzed shales are made available. The clay minerals could have an effect upon the silica content of an average shale, but the most common clay minerals have silica-alumina weight-percent ratios of less than 3 and the averages considered here have silica-alumina ratios of more than 3. Admixed detrital quartz probably has a much more important effect on the silica content of shales than the variation in composition of clay minerals.

The alumina in the average analyses on the anhydrous carbonate-free basis tends to be relatively low where the silica is relatively high (fig. 11). It can be inferred that the samples of the Pierre contain more detrital quartz or other discrete forms of silica than the Devonian pelites. The Devonian pelites are similar in

this respect to the Precambrian lutites. Furthermore, the silica-alumina relations are consistent with the general montmorillonite-rich nature of the Pierre samples and an assumed general illite-rich nature of the Devonian and Precambrian materials. The average composition of the Pierre samples has a lower magnesium content than the averages of the Precambrian lutites and Russian clays. The average composition of the Pierre samples has about the same amount of magnesium as the average Devonian pelite, but the Pierre has more calcium. No reason for these relations is immediately apparent, but the relation agrees with Shaw's conclusion that his rocks are poor in calcium compared to others (1956, p. 930). It is clear, though, that the Russian clays are rich in calcium, even after corrections have been made to remove calcium present as calcium carbonate; the reasons for this are not evident.

The sodium content of the averages is about the same. In the sedimentary cycle, sodium is concentrated in the oceans and does not form authigenic minerals in sedimentary rocks except under unusual conditions of infrequent occurrence (Clarke, 1924, p. 150). Variations in amounts of sodium in clay minerals because of ion-exchange reactions may be large (Grim, 1953, p. 370-373), but the possible effects of such variations are largely masked by the use of averages.

The potassium content in the average composition of the Pierre samples (2.85 percent potassium oxide) is significantly smaller than in the other averages. The other averages, ranging from 3.63 to 4.26 percent potassium oxide, do not differ much from each other, but a decrease in potassium content from older to younger rocks is suggested. This relation of the potassium in the average composition of the Pierre samples to that in older rocks is of interest because it agrees with the concept developed by Conway (1942, 1943, and 1945) concerning the decrease of the potassium content in the oceans throughout geologic time. Conway's reasoning was elegant (see Hutchinson, 1944) and complex, and need not be reviewed here. Most of his data concerning shale were based on Clarke's compilations (1904 and 1924). Conway postulated that the decrease in potassium was brought about by the development and proliferation of life in late Precambrian time, which led to conditions under which abundant glauconite formed and extracted potassium from sea water. Hutchinson (1944) pointed out that glauconite is not sufficiently abundant in shale to be quantitatively effective, although illite could serve this purpose. Hutchinson doubted that there is convincing evidence of any important changes in the rate of removal of potassium from the oceans with time and emphasized

the need for more chemical analyses of shales of different geologic ages.

Nanz (1953, p. 57-58) compared the average composition of the North American Precambrian lutites with the average compositions of shales of Paleozoic age and of Mesozoic and Cenozoic age (Clarke, 1915, p. 23). These comparisons showed that potassium as well as aluminum and total iron were progressively smaller in the younger samples and that silica became progressively more abundant. Nanz pointed out the similarity between these relations and the composition of successively coarser size fractions of clay (Grout, 1925, p. 402-403) and suggested the possibility that the younger samples of Clarke's averages were coarser grained than the older ones.

The large body of data of Vinogradov and Ronov (1956, p. 6) also shows a progressive decrease in the potassium content from older to younger shale. (See fig. 12.) The average potassium content for geologic periods plotted against geologic age shows a gradual decrease, although there are irregularities from period to period. Vinogradov and Ronov ascribe this trend to the greater availability of potassium-rich weathering products in early geologic time, because of the wide exposure of crystalline rocks. They pointed out that progressively smaller areas of crystalline rocks became available to supply these weathering products as sedimentation continued. The potassium-rich weathering products were derived from muscovite and potassium feldspar, and the products were sedimented as hydro-micas (illite). As areas of crystalline rocks decreased, and presumably as more and more sedimentary rocks were weathered, kaolinite and montmorillonite became predominant clay minerals.

This general sequence of illite being predominant in older rocks and montmorillonite in younger rocks has been discussed by Grim (1953, p. 356-357). This sequence is not uniformly applicable, however, and Weaver (1958, p. 273-309) has found abundant montmorillonite and mixed-layer montmorillonite-illite in rocks as old as Mississippian. Illite also is present in the samples of Pierre shale, even though montmorillonite may predominate in most samples. Although many similar exceptions to distribution of illite and montmorillonite are likely to be found, the differences in potassium content of shales of different ages suggests that illite, the clay mineral with the highest potassium content, actually is more abundant in older rocks than in younger rocks.

Illite is believed by some geologists (Grim, 1953, p. 352) to form from montmorillonite by diagenetic and postdiagenetic adsorption reactions accompanied by

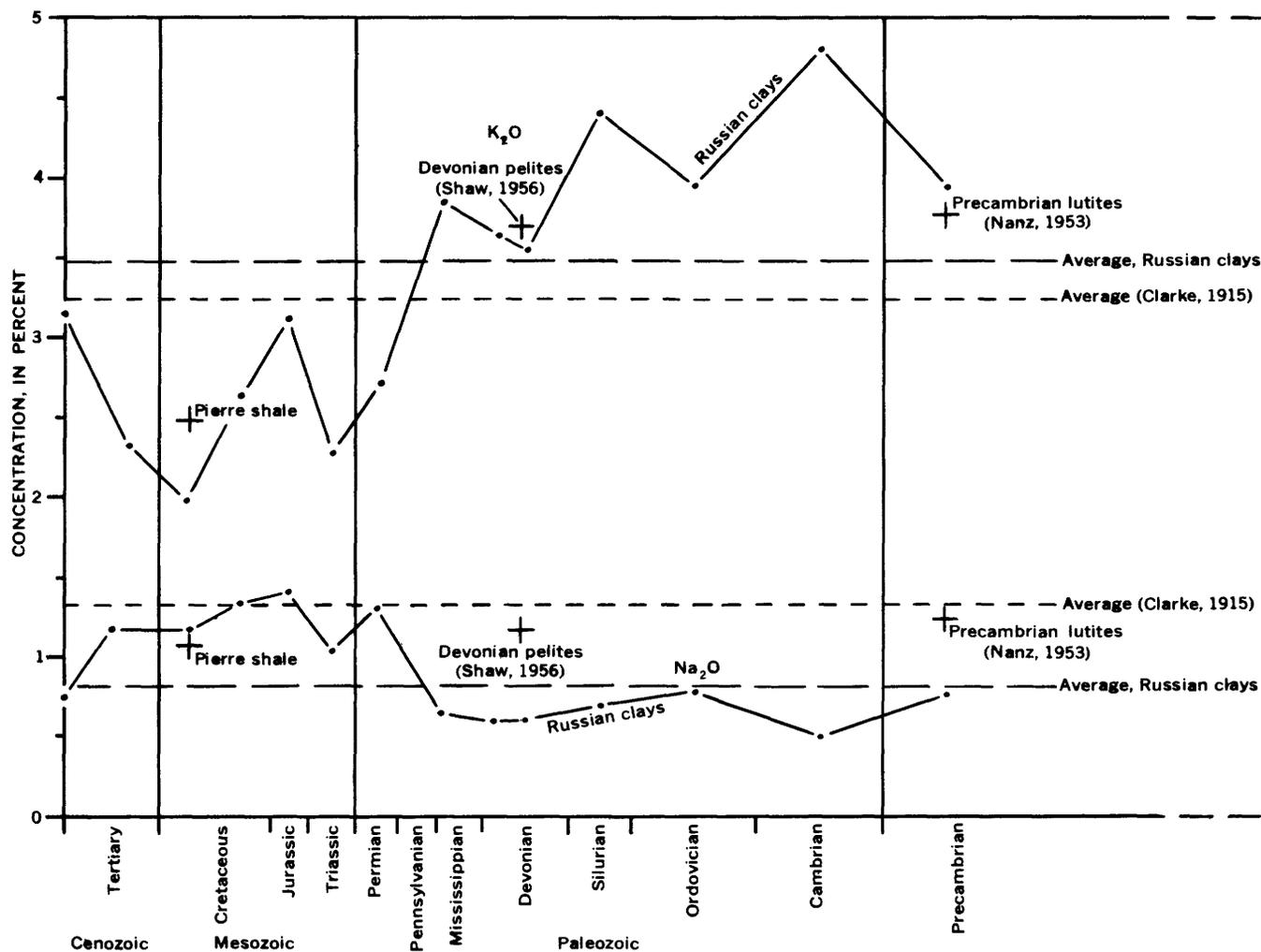


FIGURE 12.—Distribution in geologic time of potassium and sodium in Russian clays and some North American shales. (Modified after Vinogradov and Ronov, 1956.)

structural changes. Vinogradov and Ronov (1956, p. 9) consider that the potassium content of illite is "lattice-bound," and hence has to become part of the mineral during or before sedimentation. As only small amounts of potassium can be exchanged from samples of older clays, they doubt that diagenetic and post-diagenetic reactions can be effective. Foster (1954, p. 394) points out that structural changes are necessary to form illite from montmorillonite in addition to adsorption of potassium. In studies of the synthesis of muscovite, Yoder and Eugster (1955, p. 274-275) showed that illite has been applied to polymorphs of muscovite or interlayered muscovite and montmorillonite, and they suggest that muscovite (illite) grows in sediments by the reconstruction of montmorillonite and kaolinite. Zkhuz (1957) reports the diagenetic alteration of kaolinitic clays to montmorillonitic clays on the bottom of Lake Baikal, and that this represents one step of the reconstruction process.

The progressive decrease in the potassium content of clays with geologic time thus seems attributable to the prevalence of illite in the older clays. The illite may have been deposited as such and the potassium content of the clays thus is inherent, or the illite may have formed by diagenetic and some postdiagenetic exchange reactions. Neither of these possibilities seems to require unusual amounts of potassium in the water in which the clays were deposited. Much of the chemical data from which this decrease in potassium is interpreted, however, is based on metamorphosed rocks in which the potassium-bearing minerals now are muscovite and some biotite. It seems necessary to infer, therefore, that the mica-bearing rocks are metamorphic derivatives of potassium-rich shales, in which illite (sedimentary muscovite according to Yoder and Eugster, 1955, p. 252-254) was the predominant clay mineral.

Actually, the progressive decrease of potassium in

shales will be difficult to evaluate until there are more chemical analyses of rocks, ranging in age from ancient to young, that have demonstrably similar mineralogic composition. If many illitic shales of Cambrian age contain more potassium than many shales of Pennsylvanian age having about the same amount of illite and if these shales contain more potassium than similar illitic shales of Cretaceous age, then it may be possible to make meaningful statements concerning possible changes in the geochemical cycle of potassium.

#### REGIONAL VARIATION IN COMPOSITION

The variation in composition of major constituents for the Pierre shale and equivalent rocks is shown in table 13. Averages were calculated for the four geographic regions shown in plate 1. The samples are too few and not well enough distributed for conclusions to be drawn from the data, but some preliminary observations seem worthwhile. The similarity in composition from region to region is striking. This is partly the result of sampling, because only samples that consisted predominantly of clay were analyzed.

The data for the southern part of the western facies belt are the analysis of a single sample (C870), which differs somewhat from the others. The greater amount of admixed detrital quartz and relatively small amount of clay shown in X-ray analysis (table 5) is evident from the silica-alumina relations. In addition, the residual calcium content of the clay, after correction for dolomite, is higher than in the other samples. This sample comes from a relatively near-shore phase (Knappen and Moulton, 1931, p. 38-42) of the Claggett shale

TABLE 13.—Chemical composition of major constituents, in percent, of Pierre shale and equivalent rocks by geographic region, excluding moisture, carbonate and phosphate minerals, and acid-soluble sulfur as sulfur trioxide

[See pl. 1 for geographic regions.  $\bar{X}$  is arithmetic mean;  $s$  is standard deviation. No adjustments were made for cations that accompany the sulfur (see p. 40)]

|                                      | Western facies belt |                    | Central facies belt | Eastern facies belt | Average   |      |
|--------------------------------------|---------------------|--------------------|---------------------|---------------------|-----------|------|
|                                      | North-<br>ern part  | South-<br>ern part |                     |                     | 5         |      |
|                                      | 1                   | 2                  |                     |                     | $\bar{X}$ | $s$  |
| SiO <sub>2</sub> .....               | 65.94               | 71.62              | 65.93               | 68.52               | 67.92     | 2.75 |
| Al <sub>2</sub> O <sub>3</sub> ..... | 19.13               | 15.61              | 19.52               | 16.98               | 17.56     | 1.82 |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 5.60                | 3.95               | 6.47                | 4.73                | 5.21      | 1.25 |
| FeO.....                             | 1.41                | 1.08               | .61                 | 1.04                | 1.09      | .72  |
| MgO.....                             | 2.09                | 1.74               | 1.95                | 2.23                | 2.09      | .44  |
| CaO.....                             | .66                 | 1.31               | .63                 | .73                 | .75       | .29  |
| Na <sub>2</sub> O.....               | 1.12                | .87                | .78                 | 1.56                | 1.24      | .47  |
| K <sub>2</sub> O.....                | 2.76                | 2.91               | 3.17                | 2.85                | 2.85      | .30  |
| TiO <sub>2</sub> .....               | .76                 | .68                | .77                 | .64                 | .68       | .08  |

1. Average of basic samples C871, C872, C873, and C875.

2. Basic sample C870.

3. Average of basic samples C876 and C877.

4. Average of basic samples C878, C880, C885, C886, C887, C888, and C890.

5. Average of 17 samples of Pierre shale and equivalent rocks from table 12; includes all samples given in columns 1, 2, 3, and 4.

near the southernmost point that the Claggett has been recognized in Montana.

Other differences and similarities cannot be evaluated on the limited data.

#### MINOR CONSTITUENTS

The content of minor elements in the samples of the Pierre shale and equivalent rocks was investigated by semiquantitative spectrographic analysis for most elements and by chemical analysis for a few elements for which the minimum amount detectable spectrographically is inconveniently high. The analyses are given in three tables. Table 14 contains the spectrographic analyses. Major constituents were not determined spectrographically for the basic set of 22 samples, for which standard rock analyses are given in table 7, but were determined for the 45 additional samples for which semiquantitative spectrographic analyses provide the only information on chemical composition. Table 17 contains the chemical analyses for fluorine, zinc, arsenic, selenium, and uranium in the basic set of 22 samples. Table 18 contains the chemical analyses for carbon in the basic set of 22 samples and the 45 additional samples. The semiquantitative spectrographic data and the chemical data will be discussed separately.

#### REGIONAL VARIATION IN COMPOSITION

Before discussing the analytical data, it will be helpful to consider what is known of the general mode of occurrence and interrelations of minor constituents.

The mode of occurrence of minor elements in shales ordinarily is not directly determinable. The minor constituents are present in small amounts and are not known to form discrete compounds of their own, so that it is not feasible to separate, for example scandium-rich compounds for detailed study of scandium's mode of occurrence. Goldschmidt (1935) and later workers, such as Deul and Ansell (1956) and Degens, Williams, and Keith (1957, p. 2438-2441), have been able to show by indirect methods the concentration, or lack of it, of several minor constituents in the organic matter of coals and shales. Goldberg and Arrhenius (1958, p. 154-161) used chemical methods to fractionate samples of pelagic sediments and were able to distinguish elements that are concentrated or depleted in one fraction or another. Until techniques of this kind have been applied to a much greater variety of material, consideration of the mode of occurrence of minor constituents must be based on the data that show the abundance of these constituents in different kinds of rocks and their general geochemical characteristics, and the reactions and processes that are likely to affect them.

TABLE 14.—*Semiquantitative spectrographic analyses for minor elements in 67 samples from Pierre shale and equivalent rocks, and some older shales of Cretaceous age*

Analyses by Paul Barnett. See table 1 for location and description of samples, table 16 for minimum amounts detectable, and table 18 for chemical analyses for carbon. An asterisk (\*) indicates that the sample is part of the basic set of 22 samples (see p. 13), for which chemical analyses for major constituents are shown in table 7 and chemical analyses for As, F, Se, U, and Zn are shown in table 17]

Explanation of numerals and symbols <sup>1</sup>

|         |               |         |              |        |               |        |                             |
|---------|---------------|---------|--------------|--------|---------------|--------|-----------------------------|
| 16..... | >10.0 percent | 11..... | 0.3 percent  | 6..... | 0.007 percent | 1..... | 0.00015 percent             |
| 15..... | 7.0 percent   | 10..... | .15 percent  | 5..... | .003 percent  | d..... | Barely detected; concentra- |
| 14..... | 3.0 percent   | 9.....  | .07 percent  | 4..... | .0015 percent |        | tion uncertain              |
| 13..... | 1.5 percent   | 8.....  | .03 percent  | 3..... | .0007 percent | x..... | Looked for but not found    |
| 12..... | .7 percent    | 7.....  | .015 percent | 2..... | .0003 percent | n..... | Not looked for              |

| Locality (see pl. 1) | Sample | Li | Be | B | Na | Mg | Si | Al | K  | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Ga | Sr | Y | Zr | Nb | Mo | Ag | Ba | La | Ce | Nd | Yb | Pb |   |   |
|----------------------|--------|----|----|---|----|----|----|----|----|----|----|----|---|----|----|----|----|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|---|---|
| 1                    | *C871  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 5  | 6  | 4  | 7  | 4 | 7  | 3  | x  | x  | 8  | 5  | 7  | x  | 2  | 3  |   |   |
|                      | *C872  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 5  | 6  | 4  | 7  | 4 | 6  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 5  |   |   |
|                      | *C873  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 4  | 5  | 6  | 3  | 6 | 4  | 7  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 4 |   |
|                      | *C874  | x  | 1  | 5 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 8  | n  | 4  | 5  | 6  | 3  | 6  | 4 | 7  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 4  |   |   |
| 2                    | *C875  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 5  | 5  | 4  | 6  | 5 | 7  | 3  | x  | x  | 9  | 5  | 6  | 6  | 2  | 4  |   |   |
|                      | *C870  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 3  | 5  | 5  | 3  | 7 | 4  | 7  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 4 |   |
| 3                    | C896   | x  | 1  | 6 | 12 | 13 | 16 | 14 | 13 | 14 | 4  | 11 | 7 | 6  | 8  | 14 | 3  | 5  | 5  | 3  | 7  | 4 | 7  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 3  |   |   |
| 4                    | *C876  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 4  | 5  | 6  | 4  | 6 | 4  | 6  | 3  | x  | x  | 9  | 5  | 6  | x  | 2  | 4 |   |
|                      | C933   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 13 | 4  | 11 | 7 | 6  | 8  | 14 | 4  | 5  | 5  | 3  | 7  | 5 | 7  | 3  | x  | x  | 9  | 5  | 6  | d  | 2  | 4  |   |   |
| 5                    | *C877  | x  | 1  | 6 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 4  | 5  | 6  | 4  | 7 | 4  | 6  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 4 |   |
| 6                    | *C886  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 8  | n  | 4  | 4  | 6  | 6  | 4  | 7 | 4  | 7  | 3  | x  | x  | 9  | 5  | 6  | n  | 2  | 4 |   |
| 7                    | *C887  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 7  | n  | 4  | 4  | 6  | 6  | 3  | 7 | 4  | 7  | 3  | x  | x  | 9  | 5  | 6  | n  | 2  | 4 |   |
| 8                    | *C881  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 9  | n  | 4  | 4  | 6  | 6  | 3  | 7 | 4  | 7  | 4  | x  | x  | 10 | 5  | 6  | x  | 2  | 4 |   |
|                      | *C882  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 9  | n  | 4  | 4  | 5  | 6  | 3  | 7 | 4  | 7  | 3  | x  | x  | 10 | 5  | 6  | x  | 2  | 4 |   |
|                      | *C883  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 10 | n  | 4  | 4  | 6  | 6  | 4  | 7 | 5  | 7  | 3  | x  | x  | 9  | 5  | 7  | 6  | 2  | 4 |   |
|                      | *C884  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 12 | n  | 4  | 4  | 6  | 6  | 4  | 7 | 5  | 6  | 3  | x  | x  | 9  | 5  | 7  | 6  | 2  | 4 |   |
|                      | *C885  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 12 | n  | 4  | 4  | 6  | 6  | 4  | 7 | 5  | 6  | 3  | x  | x  | 9  | 5  | 6  | 6  | 2  | 4 |   |
| 9                    | *C878  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 9  | n  | 4  | 4  | 6  | 6  | 3  | 7 | 4  | 6  | 3  | x  | x  | 9  | 5  | 6  | 6  | 2  | 4 |   |
|                      | *C879  | x  | d  | 5 | n  | n  | n  | n  | n  | n  | 3  | n  | 6 | 5  | 12 | n  | 4  | 5  | 4  | d  | 9  | 4 | 6  | x  | x  | x  | 7  | 5  | 6  | n  | 1  | 3  |   |   |
|                      | *C880  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 9  | n  | 4  | 4  | 6  | 6  | 4  | 7 | 5  | 7  | 4  | x  | x  | 8  | 5  | 6  | 6  | 2  | 5 |   |
| 10                   | *C888  | x  | 2  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 10 | n  | 4  | 4  | 6  | 6  | 4  | 7 | 5  | 7  | 3  | x  | x  | 8  | 5  | 7  | n  | 2  | 4 |   |
|                      | *C889  | x  | 1  | 5 | n  | n  | n  | n  | n  | n  | 3  | n  | 6 | 6  | 12 | n  | 4  | 4  | 5  | 5  | d  | 9 | 4  | 6  | x  | x  | x  | 7  | x  | n  | 1  | 3  |   |   |
|                      | *C890  | x  | 1  | 7 | n  | n  | n  | n  | n  | n  | 4  | n  | 7 | 6  | 11 | n  | 4  | 4  | 6  | 6  | 4  | 7 | 4  | 6  | 3  | x  | x  | 8  | 5  | 7  | x  | 2  | 4 |   |
|                      | *C891  | x  | d  | 7 | n  | n  | n  | n  | n  | n  | 3  | n  | 8 | 6  | 6  | n  | 2  | 5  | 6  | 3  | 6  | 4 | 6  | 3  | 6  | d  | x  | 8  | x  | n  | 2  | 4  |   |   |
| 11                   | C910   | x  | 1  | 6 | 13 | 13 | 16 | 15 | 13 | 11 | 5  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | x  | 2  | 3  |   |   |
|                      | C911   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 11 | 5  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | x  | 2  | 3  |   |   |
|                      | C912   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 11 | 5  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | x  | 2  | 3  |   |   |
| 12                   | C913   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 10 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 5 | 7  | 4  | x  | x  | 9  | 5  | 6  | 7  | 6  | 2  | 3 |   |
| 13                   | C914   | x  | 1  | 6 | 13 | 13 | 16 | 15 | 14 | 10 | 5  | 11 | 8 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 5 | 7  | 4  | x  | x  | 9  | 5  | 6  | 7  | 6  | 2  | 4 |   |
| 14                   | C899   | x  | 1  | 5 | 12 | 13 | 16 | 15 | 13 | 11 | 4  | 11 | 8 | 6  | 8  | 14 | 4  | 4  | 5  | 6  | 4  | 7 | 5  | 6  | 3  | x  | x  | 9  | 5  | 6  | 6  | 3  | 4 |   |
|                      | C900   | x  | 1  | 5 | 13 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 8  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | d  | 2  | 4  |   |   |
|                      | C901   | x  | 1  | 5 | 13 | 13 | 16 | 15 | 13 | 13 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 5  | 3  | 7  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | x  | 2  | 4  |   |   |
| 15                   | C902   | 7  | 1  | 7 | 11 | 12 | 16 | 15 | 14 | 9  | 4  | 11 | 8 | 7  | 5  | 13 | 3  | 5  | 6  | 4  | 6  | 5 | 7  | 4  | x  | x  | 9  | 6  | 6  | 7  | 6  | 2  | 3 |   |
|                      | C903   | 7  | 1  | 7 | 11 | 12 | 16 | 15 | 14 | 12 | 4  | 11 | 8 | 7  | 6  | 14 | 3  | 5  | 6  | 4  | 7  | 5 | 7  | 4  | x  | x  | 9  | 6  | 6  | 7  | 6  | 2  | 4 |   |
|                      | C904   | 7  | 1  | 7 | 11 | 12 | 16 | 15 | 14 | 10 | 4  | 11 | 8 | 7  | 5  | 13 | 3  | 5  | 6  | 4  | 6  | 5 | 7  | 4  | x  | x  | 9  | 6  | 6  | 7  | 6  | 2  | 4 |   |
| 16                   | C905   | x  | 1  | 6 | 12 | 12 | 16 | 15 | 13 | 11 | 4  | 11 | 8 | 7  | 6  | 14 | 4  | 4  | 5  | 4  | 6  | 5 | 7  | 3  | x  | x  | 9  | 5  | 6  | 6  | 2  | 4  |   |   |
| 17                   | C909   | x  | 1  | 7 | 11 | 12 | 16 | 15 | 13 | 10 | 4  | 11 | 8 | 6  | 6  | 14 | 4  | 5  | 5  | 3  | 6  | 5 | 7  | 4  | x  | x  | 9  | 6  | 6  | 7  | 6  | 2  | 3 |   |
| 18                   | C898   | x  | 1  | 4 | 13 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 7  | 8  | 14 | 4  | 4  | 5  | 3  | 8  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | 6  | 2  | 3  |   |   |
| 19                   | C908   | x  | 1  | 6 | 12 | 12 | 16 | 15 | 13 | 10 | 5  | 11 | 8 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 4 | 7  | 3  | x  | x  | 9  | 5  | 6  | d  | 2  | 3  |   |   |
| 20                   | C907   | x  | 5  | 7 | 11 | 12 | 16 | 15 | 13 | 11 | 4  | 11 | 8 | 6  | 6  | 14 | 3  | 5  | 5  | 4  | 7  | 4 | 7  | 4  | x  | x  | 9  | 5  | 6  | 7  | 6  | 2  | 3 |   |
| 21                   | C906   | x  | 1  | 6 | 13 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 5  | 4  | 7  | 4 | 7  | 3  | x  | x  | 8  | 5  | 6  | x  | 2  | 3  |   |   |
| 22                   | C918   | x  | 1  | 5 | 13 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 4  | 5  | 4  | 7  | 4 | 7  | 3  | x  | x  | d  | 9  | 5  | 6  | d  | 2  | 4 |   |
|                      | C919   | x  | 1  | 5 | 13 | 13 | 16 | 15 | 13 | 13 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 5  | 4  | 8  | 5 | 7  | 3  | x  | x  | 9  | 5  | 6  | d  | 2  | 4  |   |   |
|                      | C920   | x  | 1  | 6 | 13 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 6  | 8  | 14 | 4  | 5  | 5  | 4  | 7  | 5 | 7  | 3  | x  | x  | d  | 8  | 5  | 6  | d  | 2  | 4 |   |
|                      | C921   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 5  | 3  | 8  | 5 | 7  | 3  | x  | x  | x  | 8  | 5  | 6  | d  | 2  | 4 |   |
|                      | C922   | x  | 1  | 5 | 13 | 13 | 16 | 15 | 13 | 12 | 4  | 11 | 7 | 6  | 8  | 14 | 4  | 4  | 5  | 3  | 8  | 5 | 7  | 3  | x  | x  | x  | 8  | 5  | 6  | d  | 2  | 4 |   |
|                      | C923   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 11 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 6  | 4  | 7  | 5 | 7  | 3  | x  | x  | x  | 8  | 5  | 6  | d  | 2  | 4 |   |
|                      | C924   | x  | 1  | 6 | 12 | 12 | 16 | 15 | 13 | 11 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 4  | 5  | 6  | 4  | 7 | 4  | 7  | 3  | x  | x  | x  | 8  | 5  | 6  | d  | 2 | 4 |
|                      | C925   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 14 | 13 | 4  | 11 | 7 | 6  | 8  | 14 | 4  | 6  | 5  | 4  | 7  | 5 | 7  | 3  | x  | x  | d  | 8  | 5  | 6  | n  | 1  | 4 |   |
| 23                   | C926   | x  | 1  | 5 | 12 | 13 | 16 | 14 | 13 | 15 | 3  | 10 | 6 | 5  | 8  | 13 | 2  | 3  | 5  | 2  | 7  | 4 | 6  | d  | x  | x  | d  | 8  | 5  | n  | x  | 4  | 4 |   |
| 24                   | C915   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 14 | 11 | 5  | 11 | 8 | 7  | 6  | 14 | 4  | 5  | 6  | 4  | 7  | 4 | 7  | 4  | x  | x  | 9  | 5  | 6  | d  | 2  | 4  |   |   |
| 25                   | C916   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 11 | 4  | 11 | 8 | 6  | 7  | 14 | 4  | 4  | 5  | 6  | 4  | 7 | 4  | 6  | 4  | x  | x  | 9  | 5  | 6  | d  | 2  | 4 |   |
| 26                   | C917   | x  | 1  | 6 | 11 | 12 | 16 | 15 | 13 | 11 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 5  | 3  | 7  | 4 | 7  | 4  | x  | x  | 9  | 5  | 6  | d  | 2  | 3  |   |   |
| 27                   | C931   | x  | 1  | 6 | 11 | 12 | 16 | 15 | 13 | 11 | 5  | 11 | 8 | 6  | 7  | 14 | 4  | 4  | 5  | 6  | 3  | 7 | 4  | 7  | 3  | x  | x  | d  | 9  | 5  | 6  | d  | 2 | 4 |
|                      | C932   | x  | 1  | 6 | 12 | 13 | 16 | 15 | 13 | 14 | 4  | 11 | 7 | 6  | 7  | 14 | 4  | 5  | 5  | 3  | 8  | 5 | 6  | 3  | x  | x  |    |    |    |    |    |    |   |   |

The different modes of occurrence of minor constituents in the Pierre shale and equivalent rocks are summarized in table 15. The table is based primarily on Krauskopf's discussion of the four general processes by which minor constituents can be deposited in sedimentary rocks (1955) and the factors that control the concentrations of some minor elements in sea water (1956). Data compiled by Rankama and Sahama (1950) also have been used. Krauskopf (1955, p. 428-448) identifies four different processes, but he points out that the last three of the following processes are not sharply separated: Mechanical enrichment; precipitation of insoluble compounds such as hydroxides, carbonates, sulfates, and sulfides; adsorption by and substitution in clays, oxides, carbonates, and sulfides; and organic reactions.

For each of the minor constituents table 15 suggests the different modes of occurrence that are believed to be appropriate for the Pierre shale and equivalent rocks, and an attempt is made to identify the mode or modes of occurrence that are the most important in these rocks. Manganese, for example, is believed to occur in the Pierre primarily as a substituted ion in carbonates and as an adsorbed ion in clays; manganese also occurs as a carbonate in its own right in fresh samples and as an oxide in weathered samples, but these are minor modes of occurrence. Occurrences of any of the elements as adsorbed or replacing ions in oxides refer chiefly to weathered samples. The elements shown as occurring in organic material are those for which this association has been pointed out many times.

TABLE 15.—Different modes of occurrence of minor constituents in Pierre shale and equivalent rocks

[Symbols: X, important mode of occurrence; x, minor mode of occurrence; and (?), of doubtful application to samples of the Pierre. Compiled chiefly from Rankama and Sahama (1950) and Krauskopf (1955; 1956)]

| Elements    | Mechanical enrichment | Precipitation |                    |                    |     | Adsorption and substitution |        |            |          | Organic material |
|-------------|-----------------------|---------------|--------------------|--------------------|-----|-----------------------------|--------|------------|----------|------------------|
|             |                       | OH-1          | CO <sub>3</sub> -2 | SO <sub>4</sub> -2 | S-2 | Clays                       | Oxides | Carbonates | Sulfides |                  |
| Be          |                       | x             |                    |                    |     | X                           | x      |            |          |                  |
| B           | ?                     |               |                    |                    |     | X                           |        |            |          |                  |
| Sc          |                       |               |                    |                    |     | X                           |        |            |          |                  |
| Ti          | ?                     |               |                    |                    |     | X                           |        |            |          |                  |
| V           |                       |               |                    |                    |     | X                           |        |            |          |                  |
| Cr          |                       | x             |                    |                    | x   | X                           |        |            |          | x                |
| Mn          |                       | x             | x                  |                    |     | x                           |        | X          |          |                  |
| Co          |                       |               |                    |                    |     | x                           | x      |            | X        | x                |
| Ni          |                       |               |                    |                    |     | x                           | x      |            | X        | x                |
| Cu          |                       |               |                    |                    | x   | X                           | x      | x          | X        | x                |
| Zn          |                       |               | x                  |                    |     | X                           | x      |            | X        | x                |
| Ga          |                       |               |                    |                    |     |                             |        | x          |          |                  |
| As          |                       |               |                    |                    |     |                             | x      |            | X        | X                |
| Se          |                       |               |                    |                    |     |                             | x      |            | X        | X                |
| Sr          |                       |               |                    |                    |     |                             |        | X          |          |                  |
| Rare earths | ?                     |               | x                  |                    |     | X                           |        |            |          |                  |
| Zr          | ?                     |               |                    |                    |     | X                           |        |            |          |                  |
| Mo          |                       |               |                    |                    |     |                             | x      |            |          | X                |
| Ag          |                       |               |                    |                    | x   |                             |        |            | X        | x                |
| Ba          |                       |               |                    |                    |     | X                           | x      |            |          |                  |
| Pb          |                       |               |                    |                    | x   |                             | x      |            |          |                  |
| U           |                       |               |                    |                    |     | X                           |        |            | x        | X                |

The four processes identified by Krauskopf (1955, p. 428-448) will be reviewed briefly for their application to the Pierre rocks; Krauskopf's discussion should be referred to for details.

Mechanical enrichment probably does not need to be considered with respect to the samples of the Pierre, because of the very great predominance of clay-sized material in the samples. Significant amounts of detrital ilmenite or zircon, for example, do not seem expectable. Biotite, however, is a possible mechanical source of minor constituents in the samples, because much of it could have been transported by the wind to the site of deposition. In addition, relatively large flakes of biotite are sedimentationally equivalent to clay-sized material and can be transported with clays. Except in a few thin beds of bentonite, biotite hardly amounts to one percent of the rock, and its contribution to the minor constituents of the claystone and shale would scarcely be detectable. Biotite containing one percent fluorine and amounting to one percent of the rock would contribute only 0.01 percent fluorine to the composition of the rock.

Precipitation involves the forming of an insoluble compound from two or more ions. The process is controlled by several variables, but chiefly requires that the ions concerned are present in greater concentration than the solubility concentration of their combined form under the physical and chemical conditions at a given place and time. Temperature, pressure, Eh and pH of the system, and concentration of other ions are examples of the factors included under "physical and chemical conditions at a given place." As pointed out by Krauskopf (1955, p. 441; 1956, p. 31-32), however, these conditions of precipitation appear to have occurred infrequently in the environments of deposition and diagenesis of sedimentary rocks (except for evaporites), and then only for a few elements. Sulfides of copper, zinc, lead, cobalt, and nickel might be expected in black shale, such as that in the Sharon Springs, but pyrite is the only sulfide that has been recognized. The strontium (0.07 percent, table 14, samples C879 and C889) in the samples of marlstone from the Crow Creek member might be ascribable to strontium carbonate, a compound that is very insoluble.

Adsorption, as used by Krauskopf (1955, p. 441-442), refers to the attraction of ions to solid surfaces in contact with a solution. Thus, certain kinds of coprecipitation, occlusion, ion exchange, and isomorphic substitution are included. Adsorption is most effective in materials approaching colloidal size, and is generally considered to be the most important process affecting the minor element content of shales. In the absence of positive data suggesting some other mode of occur-

rence, adsorption seems to be the process most likely responsible for observed concentrations. All the minor elements in the Pierre shale and equivalent rocks could be emplaced in the shale by adsorption, although the occurrence of some of the elements is influenced by organic matter and organic processes.

Organic processes are second only to adsorption in affecting the minor element content of most shales. Minor elements can be concentrated in the protoplasm and skeletal structures of many kinds of animals and plants. The minor elements can thus be concentrated in any deposit in which the organic matter and hard parts of animals and plants can be accumulated and preserved after death. Some of the organic compounds resulting from the decay or alteration of this organic matter can react with ions in their environments to further concentrate certain elements in organometallic complexes. Many organic compounds also are good adsorbants. In addition to forming actual organometallic compounds or adsorbing ions from solution, organic matter also influences the content of minor elements of shales by affecting the Eh and indirectly the pH of the environments of deposition and diagenesis, so that inorganic adsorption processes can operate or be more effective or so that precipitation of insoluble compounds can take place.

In summary, mechanical enrichment is not an important factor in the study of the minor constituents of the Pierre shale and equivalent rocks, because the samples analyzed contain very little detrital material that could contribute significant amounts of minor constituents. Precipitation as insoluble hydroxides may be a minor factor in the occurrence of beryllium, chromium, and manganese; insoluble carbonates of manganese, zinc, and strontium may occur. Barium sulfate and the sulfides of chromium, copper, zinc, molybdenum, silver, and lead are possible modes of occurrence of these elements. Adsorption or replacement of ions in clay minerals can account for the occurrence of most of the elements, and adsorption or replacement in iron and manganese oxides in weathered samples is a factor in the retention in the rock of a number of elements. Carbonates contain chiefly manganese and strontium as substituting ions, but some zinc may also be present. Cobalt, nickel, copper, arsenic, selenium, and silver, and perhaps uranium, are common substituting ions in sulfides. These same elements plus molybdenum generally are concentrated in organic-rich rocks and may participate in organometallic compounds. Vanadium and zinc may also occur in organic compounds, but the Pierre samples afford no clear evidence of such occurrence.

## SPECTROGRAPHIC DATA

### ANALYTICAL METHODS

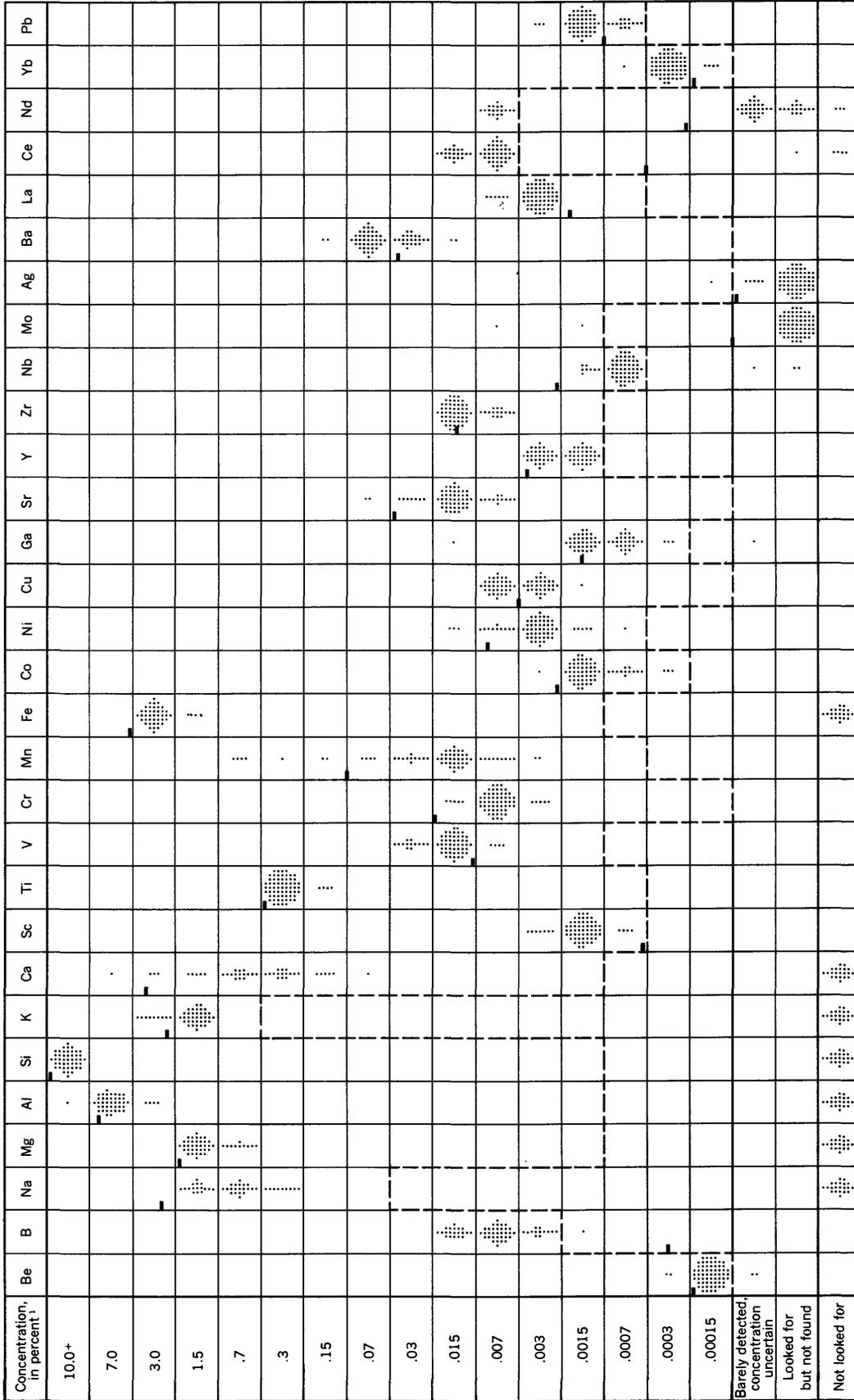
Semiquantitative spectrographic analysis is useful for the exploration of the distribution of minor elements in rocks, because more than 60 elements commonly can be determined from the photographic record of a single arcing (Waring and Ansell, 1953). The intensity of selected lines for each element on the photographic plate are compared visually with prepared standards. P. R. Barnett, who made the analyses reported here, and A. T. Myers (written communication, March 1959) have supplied the following information concerning the analyses of the Pierre shale and equivalent rocks:

The results of analysis for 58 elements in the samples of Pierre shale are reported in ranges, each power of ten being divided into three ranges. The ranges are bounded by multiples of the progression 1,  $\sqrt[3]{10}$ ,  $\sqrt[3]{100}$ , 10 (or about 1, 2, 5, 10). The approximate mid-points of the ranges, 1.5, 3, and 7, are the figures used in reporting results and these figures mean that the amount of an element in a sample may be expected to lie between 1.0 and 2.1, between 2.1 and 4.6, etc. Also, in a series of reported results, at least 60 percent are expected to lie within the correct range. Most of the uncertainty in the technique comes from those samples that contain an amount of an element close to the boundary of a range. Although detailed statistical studies are not available, and there can be some variation from element to element, it is believed that the errors are normally distributed and that about 20 percent of the results will be one range too high and 20 percent one range too low. For most elements, amounts in the ranges above that containing the minimum detectable amount are likely to be more reliable than those at or near the minimum detectable amount. At the opposite end of the scale of ranges of concentration, the sub-divisions, although of the same relative reliability, are so large in the absolute sense, that they have limited usefulness.

The minimum amounts detectable by the semiquantitative method are shown in table 16.

### STATISTICAL DISTRIBUTION

The semiquantitative spectrographic analyses given in table 14 are compiled on figure 13 to show the distribution of the elements found in the samples of Pierre shale and equivalent rocks, and some older Cretaceous shales. Each dot in the block for a spectrographic range and an element represents a sample for which the indicated spectrographic range was reported. The positions of the dots within the blocks have no significance; the dots in each block simply were arranged in a symmetrical pattern. The elements are arranged from left to right in order of increasing atomic number. A heavy dash along the left side of the column for each element indicates the crustal abundance of that element



<sup>1</sup>Percentages shown are approximate midpoints of arbitrary ranges of content; the ranges are bounded by multiples of the progression 1.0, 2.1, 4.6, and 10.0. At least 60 percent of the reported results are expected to be in the correct range.

EXPLANATION

- Semi-quantitative spectrographic analyses
- Lower limit of sensitivity of semi-quantitative spectrographic analysis
- Crustal abundance (Mason, 1958, p. 44)

FIGURE 13.—Distribution of elements in 67 samples of the Pierre shale and equivalent rocks and some older shales of Cretaceous age, as determined by semi-quantitative spectrographic analyses. See table 14 for analytical data.

TABLE 16.—Minimum amounts detectable, in percent, by semi-quantitative spectrographic analysis of samples of Pierre shale and equivalent rocks

[Revised January 1957 by U.S. Geological Survey laboratory in Denver, Colo. The minimum amounts detectable for B, Ce, Ga, La, Nb, Nd, Pb, and Sc are somewhat smaller for the samples of Pierre shale and equivalent rocks than those for other rocks]

|                 |                 |               |
|-----------------|-----------------|---------------|
| Ag..... 0.00005 | Hf..... 0.05    | Rh..... 0.005 |
| Al..... .001    | Hg..... 1.0-0.1 | Ru..... .005  |
| As..... .05     | In..... .001    | Sb..... .01   |
| Au..... .003    | Ir..... .005    | Sc..... .0005 |
| B..... .002     | K..... .5       | Si..... .001  |
| Ba..... .0001   | La..... .0005   | Sm..... .01   |
| Be..... .0001   | Li..... .01     | Sn..... .001  |
| Bi..... .001    | Mg..... .001    | Sr..... .0001 |
| Ca..... .001    | Mn..... .0005   | Ta..... .05   |
| Cd..... .005    | Mo..... .001    | Te..... .08   |
| Ce..... .005    | Na..... .05     | Th..... .05   |
| Co..... .0002   | Nb..... .0005   | Ti..... .0005 |
| Cr..... .0001   | Nd..... .005    | Tl..... .01   |
| Cu..... .00005  | Ni..... .0005   | U..... .05    |
| Dy..... .05     | Os..... .005    | V..... .001   |
| Er..... .005    | P..... .1       | W..... .01    |
| Fe..... .001    | Pb..... .0005   | Y..... .001   |
| Ga..... .0002   | Pd..... .0005   | Yb..... .0001 |
| Gd..... .005    | Pt..... .003    | Zn..... .02   |
| Ge..... .0005   | Re..... .005    | Zr..... .001  |

(Mason, 1958, p. 44). The dashes are plotted in their approximately correct positions with reference to the midpoints of the ranges along the left side of the diagram.

Figure 13 shows that most of the minor constituents, present in the samples of Pierre shale and equivalent rocks in amounts larger than the lower limit of detectability for the respective elements, occur in surprisingly narrow ranges. Almost half of the elements are reported in only one or two semiquantitative spectrographic ranges, and a third are reported only in three ranges. Calcium and manganese occur in seven and eight ranges, respectively, and have the widest distribution of content of any of the elements. Nickel occurs through five ranges, and boron, cobalt, strontium, and barium occur through four ranges. The distributions of these elements imply that shales such as these are quite uniform in composition without much differentiation in the content of minor elements with respect to mineralogic and bulk chemical composition. For molybdenum, silver, and neodymium the amount detectable is so large compared to the amounts present in the samples that only a few positive amounts are reported and little can be learned concerning their distribution.

In comparison with the crustal abundance of the elements, the amounts in the samples of Pierre shale and equivalent rocks agree generally with what has been previously known about the enrichment and de-

pletion of elements in shales (Rankama and Sahama, 1950, p. 226). Some of the differences from the data of Rankama and Sahama are to be expected, because the estimates of crustal abundance of certain elements have been revised. (See Mason, 1958, p. 44.)

Boron is considerably more abundant in the samples of Pierre shale and equivalent rocks than in the earth's crust. The abundance of boron in marine shales was pointed out by Goldschmidt and Peters in 1932 (Goldschmidt, 1954, p. 285) and later studied by Landergren (1945). Scandium is definitely enriched in the Pierre samples. Both lanthanum and cerium also seem to be enriched in the Pierre samples. The figures for crustal abundance of lanthanum and cerium in sedimentary rocks (Goldschmidt, 1954, p. 74-75) are based on very few analyses, and the significance of the difference is difficult to evaluate because of the semiquantitative nature of the data from the Pierre samples.

The data shown on figure 13 indicate that sodium, calcium, chromium, manganese, iron, strontium, yttrium, and niobium are depleted in the samples of the Pierre relative to their crustal abundance. Of these elements, only chromium and yttrium have relations different from those shown in the data of Rankama and Sahama (1950, p. 226). Chromium has been considered to be enriched in shales and the yttrium content of igneous rocks and shales has been thought to be about the same. The crustal abundance of yttrium used here, 0.004 percent (Mason, 1958, p. 44), is about a third higher than the previously generally accepted abundance of 0.0028 percent.

The abundance of the remaining 15 elements given in figure 13 does not seem to differ much from their crustal abundance. Some of this similarity undoubtedly is due to the semiquantitative nature of the data. Even so, it is surprising that aluminum, potassium, and copper, for example, do not show the expected enrichment in shales. It also is surprising that titanium, vanadium, and zirconium do not show the expected depletion in shales. Although these differences can be pointed out, the present data do not seem to provide a basis for interpreting them.

The ranges through which most of the elements occur in the rock types in this group of samples are so narrow that little difference is shown in the content of the minor elements. The marlstone samples (C879 and C889) differ sharply from the shale samples and contain about 30 percent calcium carbonate. The content of the minor elements in the marlstone samples must be increased about 50 percent to make them comparable to those in carbonate-free shale. Such calculations cannot be carried out with semiquantitative analyses, but even on an approximate basis it can be seen (table 14)

that the marlstone samples contain relatively more manganese, strontium, and probably cobalt than the shale samples. This implies that these elements are associated with the carbonate fraction of the marlstone.

Sample C891 shows that the organic-rich shale of the Sharon Springs member differs from other rock types by its molybdenum content of about 0.007 percent. This sample contains more than 7 percent organic carbon and the largest amounts of arsenic and selenium reported, 41 and 50 parts per million, respectively (table 17). The relations of molybdenum, arsenic, and selenium are discussed on pages 16 and 17. The other sample for which molybdenum was reported is C927, which contains about 0.0015 percent. This sample comes from the Belle Fourche shale, which is a conspicuously black shale among the shale units of Cretaceous age older than the Pierre, although the sample contains less than 0.5 percent organic carbon. This sample also is one of four in which about 0.015 percent lithium was found. Lithium, however, was not found in sample C891.

#### COMPARISON WITH OTHER SHALES

The 67 samples of Pierre shale and equivalent rocks, and some older shales (table 14), provide data that should indicate a reasonable approximation of the range of concentration of minor constituents in these rocks. The data represent a maximum stratigraphic range and a reasonable sampling of geographic range. Lithologic types of shale also are apparently reasonably well represented. Very few samples of rock containing large admixtures of detrital quartz and of carbonate are included. In the following discussion, this group of samples will be referred to as the Pierre samples.

The content of minor constituents of the Pierre samples will be compared with that of two other groups of samples similar in number and analyzed by similar techniques. The first of these is the semiquantitative spectrographic analyses of 82 samples of the Sharon Springs member of the Pierre shale presented by Kepferle (1959, p. 596, 601). The other is the quantitative spectrographic analyses of 63 samples of shale and pelitic schists presented by Shaw (1954, p. 1159-1162). As has been pointed out, the Sharon Springs member of the Pierre shale is relatively rich in organic matter, compared to other units in the Pierre, and the organic matter is distributed somewhat uniformly. Kepferle's study of the Pierre was limited mostly to central South Dakota from the east side of the Black Hills to the Missouri River, although some of his samples came from adjacent parts of Nebraska. His data, therefore, are based on a relatively homogeneous group of samples with respect to lithologic character and stratigraphic

position, and the samples came from a fairly small geographic area. This group of samples will be referred to as the Sharon Springs samples.

Shaw's samples all came from rocks in New Hampshire identified as the Littleton formation, a unit composed of dark-colored shale and slate and of equivalent metamorphic schist and gneiss whose metamorphic grade is as high as that of the sillimanite zone. This unit is believed to be of Devonian age. Shaw believed that his data also represented a reasonably uniform group of samples from a small geographic area.

The data from the 67 samples of Pierre shale and equivalent rocks, from Kepferle's 82 samples of the Sharon Springs member of the Pierre, and from Shaw's 63 samples of the Littleton formation are shown on figure 14. Only the 23 elements for which Kepferle had compiled histograms are shown. The average content and the range found by Shaw for 12 elements are shown by line conventions. In addition, the crustal abundances (Mason, 1958, p. 44) also are shown.

The differences in minor constituents between the heterogeneous material of the Pierre samples and the homogeneous material of the Sharon Springs samples seem remarkably small. Most of the elements in the Sharon Springs samples have about the same ranges of concentration as those in the Pierre samples. Manganese has a wider range of concentration in the Pierre samples than in the Sharon Springs samples, and also has a distinct bimodal distribution. Gallium also has a slightly wider range in the Pierre samples. In contrast, cobalt, copper, strontium, molybdenum, yttrium, and ytterbium all have distinctly wider ranges of concentration in the Sharon Springs samples. The cobalt, copper, and molybdenum seem to be associated with the organic matter in the Sharon Springs samples and a wider range thus would be expected. The Sharon Springs also is rich in fish bones and scales. This would imply a variable but fairly high phosphate content with which yttrium and ytterbium could be associated (Arrhenius, Bramlette, and Picciotto, 1957).

The ranges of those elements studied by Shaw are comparable to the ranges of the same elements in the Pierre and Sharon Springs samples and, except for copper and lead, tend to be narrower than in the shales of Cretaceous age. The extremely wide range of copper in Shaw's samples, from about 0.00015 to about 0.07 percent, and the somewhat smaller range of lead, from about 0.0015 to about 0.003 percent, seem to imply that these samples differ considerably in mode of occurrence of copper and lead from the Cretaceous shales, or that these elements may have been redistributed during the metamorphism undergone by the rocks of the Littleton formation.

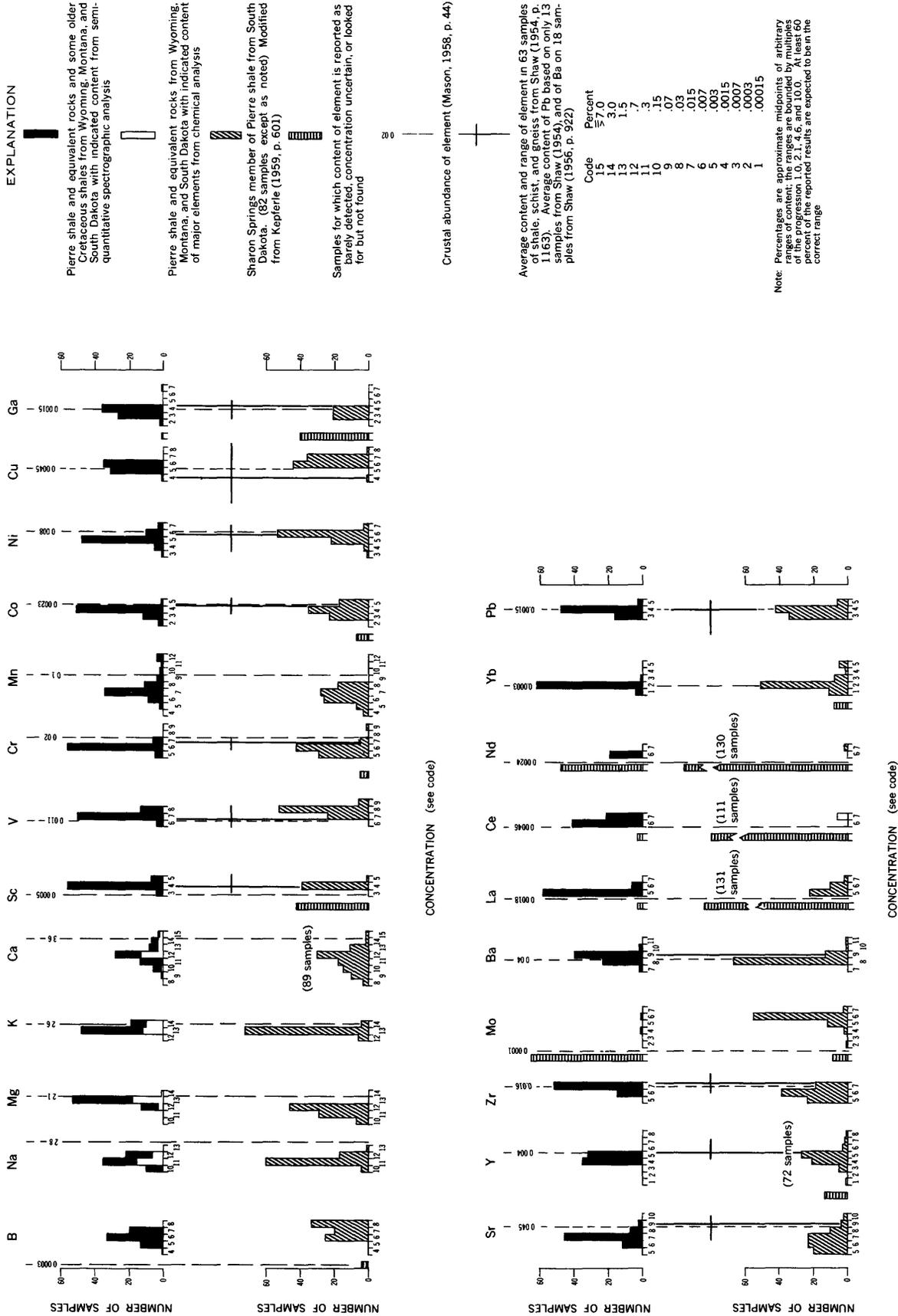


FIGURE 14.—Histograms showing distribution of elements in 67 samples of the Pierre shale and equivalent rocks and some older shales of Cretaceous age, as compared with crustal abundance and other data.

With respect to average content of the elements, the histograms indicate that the differences between the Pierre and Sharon Springs samples are few, and for the most part concern those elements that tend to be concentrated in organic-rich rocks. The Sharon Springs samples are enriched in boron, vanadium, nickel, copper, and molybdenum; the molybdenum content is particularly large. The two Pierre samples that contain detectable amounts of molybdenum are both relatively rich in organic matter. The Pierre sample that contains 0.007 percent molybdenum also contains 50 parts per million selenium and 41 parts per million arsenic. (See sample C891, table 17.) The Sharon Springs member of the Pierre shale is generally enriched in selenium and arsenic (Moxon, Olson, and Seairight, 1939, p. 39-40; Moxon and others, 1944, p. 78). Unusually high concentrations of uranium also are found in the Sharon Springs (Tourtelot, 1956, p. 66-68; Kepferle, 1959, p. 585-592).

The Pierre samples contain larger amounts of magnesium, gallium, probably strontium, and barium than the Sharon Springs samples. Lanthanum, cerium, and neodymium also seem to be present in larger amounts in the Pierre samples than in those of the Sharon Springs, but this probably is the result of improvements in analytical techniques between the time the Sharon Springs samples and the Pierre samples were analyzed (P. R. Barnett, oral communication, 1958). The single sample (C891, table 5) of Sharon Springs for which the clay minerals have been determined contains 18 percent montmorillonite. If this relatively small amount of montmorillonite is characteristic of the Sharon Springs, then the shale of the Sharon Springs would be expected to contain less magnesium and aluminum, and therefore gallium, than the montmorillonite-rich Pierre samples. Barium probably is higher in the Pierre samples because of greater adsorption on clay minerals.

No differences are noted in the content of the other elements between the Pierre samples and those of the Sharon Springs, or else the differences are so slight that their significance cannot be determined from the data available.

The average contents of samples from both the Pierre and Sharon Springs compare very closely with the averages of the elements determined by Shaw (1954, p. 1175). The largest differences are in copper and strontium, copper being lower and strontium being higher in Shaw's material than in the shales of Cretaceous age. Both copper and strontium are mobile during weathering, but if this is a factor, it would seem that copper was more affected than strontium in the shale samples. The relatively wide range of strontium in

the Cretaceous samples could be the result of weathering. The strontium content of the Pierre samples is related to the calcium content (see p. 59), but this does not seem to be true for Shaw's samples. It is curious that the Pierre samples contain more calcium and less strontium than Shaw's samples. The vanadium content of the Pierre samples is about the same as the average of Shaw's samples, but the vanadium content of the Sharon Springs samples is distinctly higher. Some minor differences in content, such as the content of chromium, between Shaw's mean and the mean content of the sample of the Pierre and Sharon Springs cannot be evaluated on the basis of the data available.

#### STRATIGRAPHIC AND GEOGRAPHIC VARIATION

Plate 3 presents the data, arranged by stratigraphic zone, from the semiquantitative spectrographic analyses in table 14 and from some of the chemical analyses in table 7. The zones are: A, Cretaceous rocks older than the Pierre shale and its equivalents; B and C, the *Baculites obtusus* s. l. and *Baculites compressus* s. l. zones of the Pierre shale and its equivalents; and D, the uppermost part of the Pierre shale and equivalent rocks. The *B. compressus* s. l. zone is represented by a total of 37 samples (table 2). Only 25 samples were used for plate 3, so that the group of samples would be about the same size as that for the *B. obtusus* s. l. zone. The 12 samples excluded were selected at random. Only the *B. obtusus* s. l. and *B. compressus* s. l. zones are represented by a sufficiently large group of samples, and the semiquantitative analyses do not permit any detailed interpretation.

The only positive differences in content between stratigraphic zones are for manganese and calcium, and it seems clear that the samples from the *Baculites compressus* s. l. zone contain more of these elements than the samples from the *Baculites obtusus* s. l. zone or the pre-Pierre rocks. Other elements for which the distributions suggest that the samples from the *B. compressus* s. l. zone are likely to have larger amounts are nickel, strontium, and possibly yttrium. Elements for which the distributions suggest that the samples from the *B. obtusus* s. l. zone are likely to have larger amounts are scandium, vanadium, and gallium, and possibly chromium and copper. The older shales of Cretaceous age may be richer in vanadium, chromium, and possibly boron than the Pierre rocks. For all the other elements, the distributions in the stratigraphic zones are so uniform that no inferences can be made.

None of these differences seem to be particularly interrelated. No reason is apparent why rocks that contain relatively larger amounts of scandium and vanadium in a given stratigraphic zone should also

contain relatively smaller amounts of nickel and strontium. The relations between calcium and manganese and between calcium and strontium have a certain coherency. Both manganese and strontium can replace calcium in carbonate and sulfate minerals (Rankama and Sahama, 1950, p. 648 and 480). Perhaps it is not surprising that manganese and calcium seem to show the most sharply defined differences by stratigraphic zone. These two elements really are the only ones that have a large enough range of content in the samples for such differences to be clearly revealed.

Plate 4 shows similar data on distribution of elements by geographic region. The geographic regions are defined on p. 9 and shown on plate 1. The columns from 1 to 4 show the sample data for each element from the northern and the southern parts of the western facies belt, and from the central and the eastern facies belts, respectively. Geographic variation in content of minor elements must be estimated from the different or similar distributions of samples in each column. Individual responses to this kind of diagram are likely to differ widely.

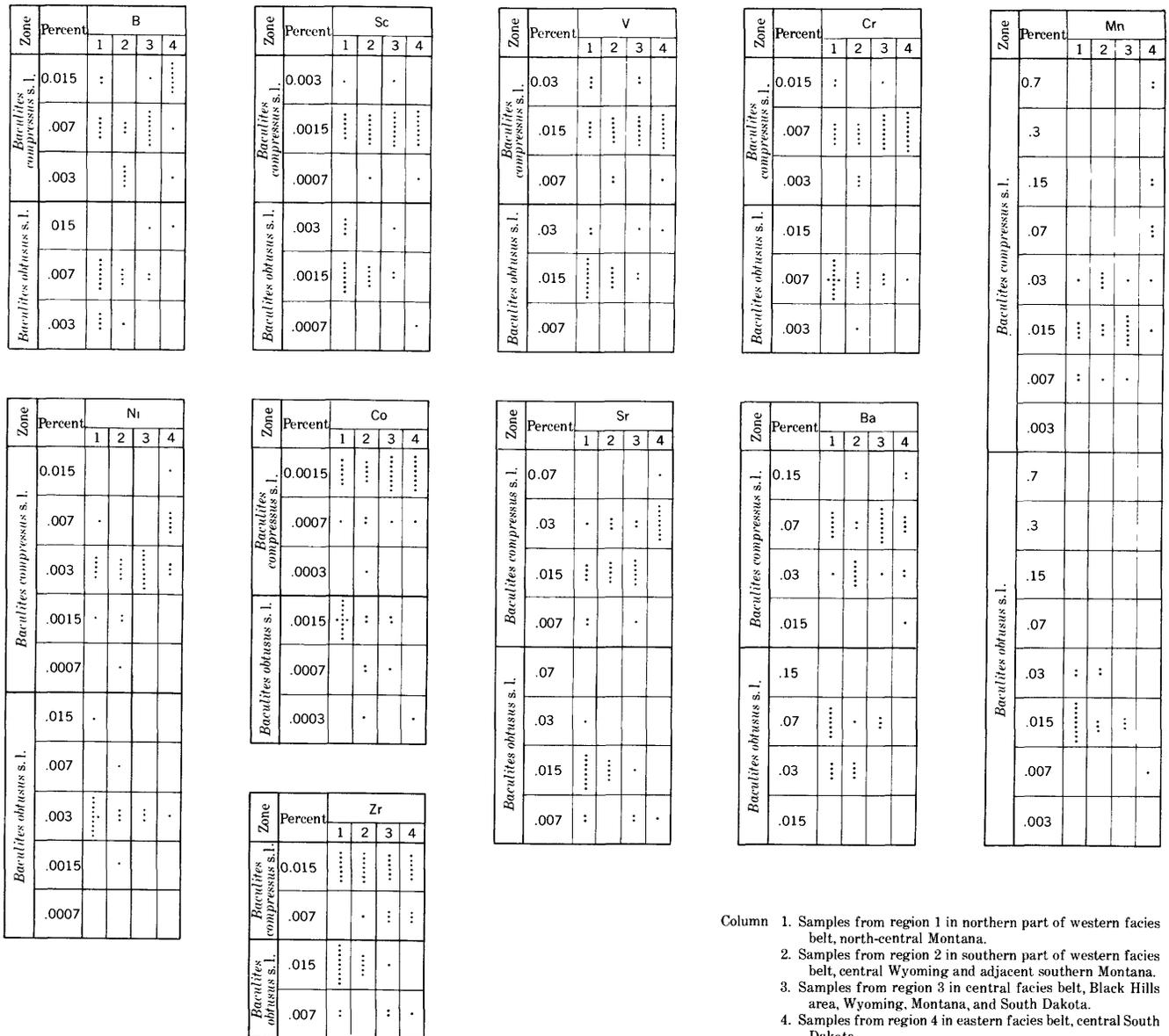
As in the distribution by stratigraphic zone (pl. 3), manganese and calcium show the largest differences from region to region. Strontium seems to be somewhat similar in distribution to calcium. The average content of these elements increases markedly from west to east, and the average contents of samples from the southern part of the western facies belt seem to be higher than of those from the northern part of the belt. Manganese shows these relations more sharply than calcium or strontium. This pattern of general increase from west to east is repeated by boron and nickel. For these two elements, however, the average contents of the samples from the southern part of the western facies belt seem to be lower than in the northern part. The average contents of vanadium, chromium, and copper in the samples from the northern part of the western facies belt seems to be higher than in the samples from the southern part. The average contents for these elements do not increase eastward, however, or else increase only enough to make the content of the samples in the eastern facies belt about the same as for those in the northern part of the western facies belt. The scandium content appears to decrease from west to east. Lanthanum appears to be high in the northern part of the western belt and relatively low but uniform elsewhere. The data for the other elements do not show any recognizable differences.

Except for calcium and manganese, no apparent coherence can be noted in the geographic distribution of the elements. For instance, no general reason is known why the boron content of samples should increase as the

scandium content decreases. Perhaps this apparent lack of coherence is not surprising, since the differences are identified by rather subjective handling of semi-quantitative data. Even though there is no basis for interpreting the differences observed, the coincidence between the distribution of the differences and certain features of the paleogeography of Pierre deposition suggests that the differences are real and offers hope that additional data will lead to their understanding.

During much of Pierre time, particularly for those units represented by the samples, the paleogeography of Pierre deposition was very similar to that shown by Reeside (1957, fig. 19, p. 537) for the Verendrye and Virgin Creek members of the Pierre shale and their equivalents. During this time, marine rocks, mostly shale, were deposited much farther to the west in Montana than they were in Wyoming. Samples from the southern part of the western facies belt, mostly from Wyoming and adjacent southern Montana (pls. 1, 4), thus represent relatively near-shore environments, and the samples from the northern part of the western facies belt represent open-sea environments some distance from shore. The samples from the central and eastern facies belts therefore represent open-sea environments even farther from shore, although the position of the eastern facies belt in relation to the eastern shore of the Pierre sea is not known. These relations suggest that the near-shore environment has a strong influence on the minor element content of shales deposited there. The influence of the open sea, however, seemingly is affected by characteristics, such as rate of accumulation, that can not yet be discriminated. Boron and nickel, for instance, are each more abundant in the shale deposited in the eastern open sea than in the western. The salinity of the sea water and the intensity of the reducing conditions that the shale passed through during diagenesis no doubt are important factors, but their effects cannot be evaluated.

Figure 15 shows the distribution of some of the elements by both stratigraphic zone and geographic region. The elements shown, except cobalt, barium, and zirconium, are those whose differences have been pointed out either between stratigraphic zones or geographic regions. Cobalt, barium, and zirconium, are included as representative of elements for which no trends in distribution could be seen on the basis of the data given on plates 3 and 4. The number of samples available from each zone for this kind of two-fold comparison is very unequal. The *Baculites obtusus* s. l. zone, for example, is represented by only one sample in the eastern facies belt (column 4), whereas the *Baculites compressus* s. l. zone is represented by nine. The *B. obtusus* s. l. zone



Column 1. Samples from region 1 in northern part of western facies belt, north-central Montana.  
 2. Samples from region 2 in southern part of western facies belt, central Wyoming and adjacent southern Montana.  
 3. Samples from region 3 in central facies belt, Black Hills area, Wyoming, Montana, and South Dakota.  
 4. Samples from region 4 in eastern facies belt, central South Dakota.

FIGURE 15.—Distribution of selected elements in the Pierre shale and equivalent rocks by stratigraphic zone and geographic region.

as a whole is represented by 20 samples and the *B. compressus* s. l. is represented by 33.

For the most part, figure 15 shows that the differences in content between geographic regions are found chiefly in the samples from *B. compressus* s. l. zone and consist of an eastward increase in the content of certain elements. This is particularly evident for boron, nickel, and manganese, but is also apparent for strontium. On the basis of available data, scandium seems to decrease eastward in both stratigraphic zones. The diagrams for vanadium and chromium do not show any trends in distribution.

**CHEMICAL DATA**

**FLUORINE, ZINC, ARSENIC, SELENIUM, URANIUM, AND EQUIVALENT URANIUM**

Chemical analyses for fluorine, zinc, arsenic, selenium, and uranium are shown in table 17, together with measurements of the radioactivity of the samples reported as percentage of equivalent uranium. Equivalent uranium expresses the radioactivity of a substance in terms of the amount of uranium in equilibrium with its daughter products that would produce a measured radioactivity. The statistical distributions of these elements are shown in figures 16 and 17.

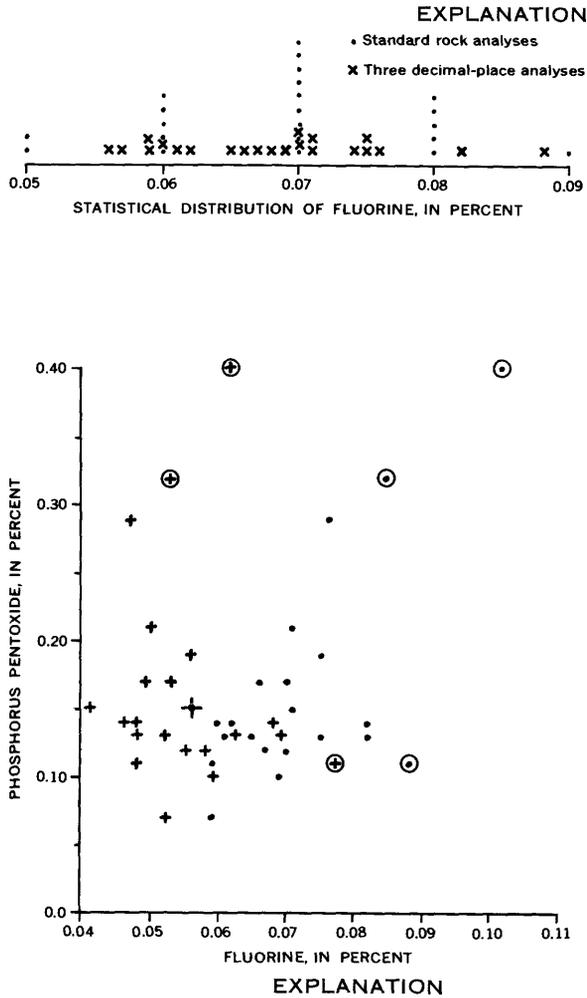


FIGURE 16.—Statistical distribution of fluorine in 22 samples of the Pierre shale and equivalent rocks and the fluorine-phosphorus relations.

The fluorine analyses in table 17 probably are accurate to a third decimal place and thus give more detailed information on the distribution of fluorine in the samples than the two-place analyses in the standard rock analyses in table 7. The agreement between the two sets of fluorine analyses is close if the three-place analyses are rounded off to two figures. Only sample C889 has a difference of more than 0.01 percent. The fluorine distributions for both sets of analyses are plotted in figure 16. The two-place determinations of the standard rock analyses show a very normal distribution for

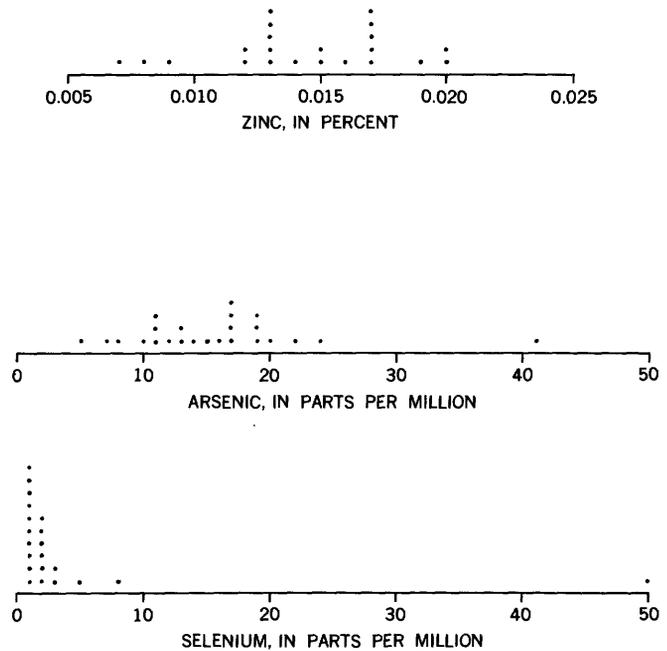


FIGURE 17.—Statistical distribution of zinc, arsenic, and selenium in 22 samples of the Pierre shale and equivalent rocks. See table 17 for analytical data.

TABLE 17.—Chemical analyses for fluorine, zinc, arsenic, selenium, and uranium in 22 basic samples of shale and maristone of Pierre shale and equivalent rocks

[Results are given in percent, except as noted. See table 1 for location and description of samples and table 7 for standard rock analyses. Analyses for F by R. P. Cox; for Zn by J. S. Wahlberg; for As by C. Huffman and J. P. Schuch; for Se by G. T. Burrow; for U by H. H. Lipp and J. P. Schuch; and for eU by C. G. Angelo]

| Locality (See pl. 1) | Sample    | F     | Zn    | As (ppm) | Se (ppm) | U     | eU    |
|----------------------|-----------|-------|-------|----------|----------|-------|-------|
| 1                    | C871..... | 0.062 | 0.013 | 17       | 1        | <.001 | 0.001 |
|                      | C872..... | .060  | .012  | 17       | 1        | ^/    | .003  |
|                      | C873..... | .056  | .012  | 19       | 1        | ^/    | .001  |
| 2                    | C874..... | .061  | .013  | 17       | 1        | ^/    | .001  |
|                      | C875..... | .059  | .013  | 10       | 1        | ^/    | .002  |
|                      | C870..... | .075  | .013  | 13       | 1        | ^/    | .001  |
| 3                    | C876..... | .076  | .019  | 11       | 5        | ^/    | .001  |
|                      | C877..... | .071  | .016  | 22       | 8        | ^/    | .001  |
|                      | C886..... | .082  | .015  | 7        | 3        | ^/    | .002  |
| 4                    | C887..... | .069  | .017  | 11       | 2        | ^/    | .001  |
|                      | C881..... | .067  | .017  | 13       | 1        | ^/    | <.002 |
|                      | C882..... | .070  | .014  | 12       | 2        | ^/    | .002  |
| 5                    | C883..... | .066  | .015  | 14       | 2        | ^/    | <.001 |
|                      | C884..... | .070  | .017  | 16       | 2        | ^/    | .003  |
|                      | C885..... | .071  | .017  | 19       | 2        | ^/    | .002  |
| 6                    | C878..... | .059  | .013  | 15       | 1        | ^/    | .001  |
|                      | C879..... | .068  | .007  | 17       | 1        | ^/    | <.001 |
|                      | C880..... | .088  | .020  | 24       | 1        | ^/    | <.001 |
| 7                    | C888..... | .065  | .020  | 5        | 3        | ^/    | .002  |
|                      | C889..... | .057  | .009  | 11       | 2        | ^/    | <.001 |
|                      | C890..... | .075  | .017  | 8        | 2        | ^/    | .002  |
| 8                    | C891..... | .074  | .008  | 41       | 50       | .001  | .004  |

fluorine and have an average content of 0.069. The three-place analyses show a much more continuous kind of distribution, and the average content of 0.068 is very close to that of the standard rock analyses. Because the three-place analyses for fluorine offer somewhat more detailed information, they will be used in the following discussions.

Figure 16 shows the relation between the phosphorus content from the standard rock analyses of the Pierre

samples (table 7) and the three-place fluorine analyses in table 17. The phosphorus pentoxide and fluorine contents of the two marlstone samples, C879 and C889, and the organic-rich sample, C891, have been calculated to carbonate-free and organic matter-free bases, respectively. The diagram suggests that the fluorine content of shales is directly related to the phosphorus content in samples that contain more than about 0.25 percent phosphorus pentoxide. Fluorine in fluorapatites ordinarily is present in amounts approximating one tenth of the phosphorus pentoxide in the apatite. Very finely divided apatite contains considerable adsorbed fluorine in addition to the normal amount bound in the lattice (Hendricks and Hill, 1950, p. 734-735).

Assuming that the phosphorus in the Pierre samples is present in normal apatite, all the samples contain considerable excess fluorine, as is typical of marine phosphorites (Altschuler, Clarke, and Young, 1958, p. 75). The relation between phosphorus and excess fluorine also is shown in figure 16. The confused relations between phosphorus and total fluorine and phosphorus and excess fluorine reflect the occurrence of fluorine in both phosphate compounds and clay minerals. The fluorine content of the clay minerals is the result of a complex interaction of such factors as the capacity for adsorption of fluorine and perhaps phosphorus by the clay minerals in the samples and the chemical characteristics of the system in which the adsorption took place. Unfortunately, no regularities in the distribution of phosphorus and fluorine can be observed between samples with a relatively high content of organic matter, reflecting more intense reducing conditions in the environments of deposition and diagenesis, and samples with a relatively low content of organic matter.

The zinc content of the samples in the basic set of 22 samples ranges from 0.007 to 0.020 percent. The distribution appears to be nearly normal (fig. 17), and the mean content is 0.014 percent. The crustal abundance of zinc is 0.0065 percent (Mason, 1958, p. 44); so zinc is fairly concentrated in the shale of these samples. Zinc ordinarily occurs as a sulfide or carbonate. Deul (1956) and Degens and others (1957, p. 2438-2440) found zinc to be concentrated in the organic fraction of sedimentary rocks. Degens and others also found that zinc is more concentrated in the organic fraction of marine shales than of non-marine ones. Krauskopf (1956, p. 24) concluded that adsorption of zinc on hydrated iron and manganese oxides, apatite, clay, and organic matter probably was the main process that regulated the occurrence of zinc in sea water. The zinc content of the two marlstone samples C879 and C889 and the sulfide-rich organic-

rich sample C891 are the lowest found in the samples analyzed for this study. Adsorption on clay minerals thus probably accounts for the occurrence of zinc in the Pierre samples.

Arsenic was found in all samples in amounts ranging from 5 to 41 ppm (parts per million). The statistical distribution of the amounts (fig. 17) is fairly normal between 5 and 24 ppm, and the average content of the 21 samples in this range is 14 ppm. The sample containing 41 ppm comes from the organic-rich Sharon Springs member (sample C891). These data are in general agreement with the data of Moxon and others (1944, p. 73), who reported 62 samples of Pierre shale to contain 2 to 24 ppm arsenic and to average 10 ppm, and 10 samples of the Sharon Springs and Mobridge members of the Pierre shale to contain 27 to 64 ppm; the average of all their samples is 14 ppm. Onishi and Sandell (1955, p. 21) considered  $10 \pm 5$  ppm as the most reasonable amount for the average arsenic content of shales, with somewhat larger amounts in shales that are rich in organic matter and pyrite.

Selenium also was found in all samples. The statistical distribution is markedly asymmetrical. The average content of all the samples is 18 ppm, but if sample C891 containing 50 ppm is excluded from the average, the average content becomes 2 ppm. The sample containing the largest amount of selenium comes from the Sharon Springs member of the Pierre shale. Moxon, Olson, and Searight (1939, p. 39-57) found selenium in 210 of 259 samples of Pierre shale in South Dakota. The average content of the 259 samples is 6 ppm. Their data also indicate that the Sharon Springs member has an average content of 10 ppm (60 samples), and that the rest of the Pierre shale has an average content of 5 ppm (199 samples). Large amounts of selenium and arsenic occur together in the organic-rich samples of the Sharon Springs member, but the calcareous Mobridge member, which was identified at that time as the Interior member (Moxon, Olson, and Searight, 1939, p. 23 and 52-57), contains relatively large amounts of selenium, but very little arsenic.

The uranium content of the samples in table 17 is uniformly 0.001 percent or less, although the equivalent uranium content of some of the samples is larger than this, and is as much as 0.004 percent in one sample C891. Beers and Goodman (1944, p. 1247-1252) pointed out that shales containing relatively abundant organic matter and pyrite are likely to contain uranium. This relation has been noted by many workers (McKelvey and Nelson, 1950, p. 38; Bates and Strahl, 1957; and others), but the exact nature of the association is not yet understood completely.

Bates and Strahl (1957, p. 1312) suggest that the uranium in the Chattanooga shale was precipitated from sea water in a reducing environment but they could not determine whether the uranium was present in an organouranium compound as suggested by Breger and Schopf (1955, p. 292). Adsorption of uranium on clay minerals is possible in the laboratory (Davey and Scott, 1956; Goldsztaub and Wey, 1955), but this has not been demonstrated conclusively to be effective in nature.

The Sharon Springs member of the Pierre shale is rich in organic matter and has been found to contain uranium throughout a large area in the Great Plains region (Tourtelot, 1956, p. 63-68; Kepferle, 1959; Landis, 1959). The very low amount of uranium (0.001 percent) in the sample from the Sharon Springs member (C891 in table 17) probably can be explained by leaching as suggested by Tourtelot and by Kepferle. The uranium content of this sample probably approached 0.004 percent before weathering. A sample from a different bed at this same locality (loc. 10, pl. 1) contained 0.01 percent uranium (Tourtelot, 1956, loc. 1). Although the determination of equivalent uranium content is not precise at the low levels of concentration found in the Pierre samples, it is probable that the uranium content of the other samples was more than 0.001 percent before weathering.

CARBON

Analyses of 67 samples for total carbon and carbonate carbon are given in table 18. The analyses were made by measuring the carbon dioxide evolved when the sample is dissolved in hot hydrochloric acid; this carbon dioxide is calculated as carbonate carbon. Another portion of the sample is then oxidized with sodium peroxide in a small bomb. The contents of the bomb are dissolved in hydrochloric acid, and the resulting carbon dioxide is measured; this carbon dioxide is calculated as total carbon. The difference between the amounts reported for total carbon and for carbonate carbon is reported as organic carbon. About 0.03 percent carbonate carbon and about 0.5 percent total carbon can be detected. Preliminary data suggest that the determination of total carbon is accurate to within 1 unit in the first decimal place and the determination of carbonate carbon is accurate within 1 unit in the second decimal place (I. C. Frost, oral communication, 1959).

The relations between carbonate carbon and organic carbon are shown in figure 18. Of the 67 samples, 29 contain 0.5 percent total carbon or less; therefore, organic carbon is reported only as less than 0.5 percent. As these samples also contain less than 0.1 percent carbonate carbon, they are plotted as a single

TABLE 18.—Chemical analyses for carbon, in percent, in 67 samples of shale and marlstone from the Pierre shale and equivalent rocks, and some older shales of Cretaceous age

[See table 1 for location and description of samples, table 7 for standard rock analyses. Analyst, J. P. Schuch. Total carbon and carbonate carbon were determined by a rapid method; organic carbon was obtained by difference. An asterisk (\*) indicates that the sample is one of the basic set of 22 samples (see p. 13)]

| Locality (see pl. 1) | Sample | Total carbon | Carbonate carbon | Organic carbon |
|----------------------|--------|--------------|------------------|----------------|
| 1                    | C871*  | <0.5         | <0.03            | <0.5           |
|                      | C872*  | <0.5         | <0.03            | <0.5           |
|                      | C873*  | 1.7          | <0.03            | 1.6            |
|                      | C874*  | <0.5         | <0.03            | <0.5           |
|                      | C875*  | 1.1          | <0.03            | 1.0            |
| 2                    | C870*  | 1.7          | 1.3              | 0.4            |
| 3                    | C896*  | 2.0          | 1.2              | 0.8            |
| 4                    | C876*  | <0.5         | <0.03            | <0.5           |
|                      | C933*  | <0.5         | <0.03            | <0.5           |
| 5                    | C877*  | <0.5         | <0.03            | <0.5           |
| 6                    | C886*  | 0.6          | 0.5              | 0.1            |
| 7                    | C887*  | 0.5          | 0.3              | 0.2            |
| 8                    | C881*  | <0.5         | <0.03            | <0.5           |
|                      | C882*  | 0.9          | 0.7              | 0.2            |
|                      | C883*  | 1.0          | 0.7              | 0.3            |
|                      | C884*  | 1.6          | 0.52             | 1.1            |
|                      | C885*  | 1.9          | 0.5              | 1.4            |
|                      | C879*  | 1.9          | 0.5              | 1.4            |
| 9                    | C880*  | 6.6          | 6.6              | 0.0            |
|                      | C888*  | 5.5          | 0.09             | 5.4            |
| 10                   | C889*  | 5.3          | 5.2              | 0.1            |
|                      | C890*  | 7.5          | 7.5              | 0.0            |
|                      | C891*  | 7.5          | 0.03             | 7.4            |
| 11                   | C910   | <0.5         | <0.03            | <0.5           |
|                      | C911   | <0.5         | <0.03            | <0.5           |
|                      | C912   | <0.5         | <0.03            | <0.5           |
| 12                   | C913   | <0.5         | <0.03            | <0.5           |
| 13                   | C914   | 1.3          | <0.03            | 1.3            |
| 14                   | C899   | 0.9          | <0.03            | 0.9            |
|                      | C900   | 1.0          | <0.03            | 1.0            |
|                      | C901   | 0.6          | 0.2              | 0.4            |
| 15                   | C902   | 0.7          | 0.1              | 0.6            |
|                      | C903   | 0.5          | 0.1              | 0.4            |
|                      | C904   | 0.7          | 0.1              | 0.6            |
| 16                   | C905   | 0.5          | 0.1              | 0.4            |
| 17                   | C909   | 0.9          | 0.1              | 0.8            |
| 18                   | C898   | 0.7          | 0.2              | 0.5            |
| 19                   | C908   | 1.3          | 0.1              | 1.2            |
| 20                   | C907   | 0.5          | 0.1              | 0.4            |
| 21                   | C906   | 0.5          | 0.1              | 0.4            |
| 22                   | C918   | 0.5          | 0.1              | 0.4            |
|                      | C919   | 0.5          | 0.1              | 0.4            |
|                      | C920   | 1.3          | 0.5              | 0.8            |
|                      | C921   | 0.6          | 0.2              | 0.4            |
|                      | C922   | 1.0          | 0.1              | 0.9            |
|                      | C923   | 0.5          | 0.1              | 0.4            |
|                      | C924   | 0.5          | 0.1              | 0.4            |
|                      | C925   | 0.9          | 0.3              | 0.6            |
| 23                   | C926   | 3.1          | 3.0              | 0.1            |
| 24                   | C915   | 2.4          | 0.1              | 2.3            |
| 25                   | C916   | 1.0          | 0.1              | 0.9            |
| 26                   | C917   | 0.6          | 0.1              | 0.5            |
| 27                   | C931   | 0.5          | 0.1              | 0.4            |
|                      | C932   | 0.5          | 0.1              | 0.4            |
| 28                   | C927   | 1.1          | 0.7              | 0.4            |
|                      | C928   | 0.5          | 0.1              | 0.4            |
|                      | C929   | 0.5          | 0.1              | 0.4            |
|                      | C930   | 0.5          | 0.1              | 0.4            |
| 29                   | C935   | 1.5          | 0.4              | 1.1            |
| 30                   | C934   | 1.8          | 0.4              | 1.4            |
| 31                   | C936   | 1.0          | 0.2              | 0.8            |
|                      | C937   | 1.1          | 0.2              | 0.9            |
|                      | C938   | 0.5          | 0.1              | 0.4            |
| 32                   | C895   | 1.7          | 1.3              | 0.4            |
| 33                   | C894   | 0.7          | 0.1              | 0.6            |
| 34                   | C897   | 0.5          | 0.1              | 0.4            |

point at the 0.5-0.1-percent intersection. Of the remaining 38 samples, 18 contain less than 0.1 percent carbonate carbon; organic carbon accounts for nearly all the carbon in the 18 samples. These samples are plotted along the 0.1-percent line for carbonate carbon. Another 11 of 38 samples contain less than 0.5 percent organic carbon and carbonate carbon accounts for nearly all the carbon in the samples. These samples are plotted along the 0.5-percent line for organic carbon. The remaining 9 samples contain measurable amounts of both carbonate and organic carbon.

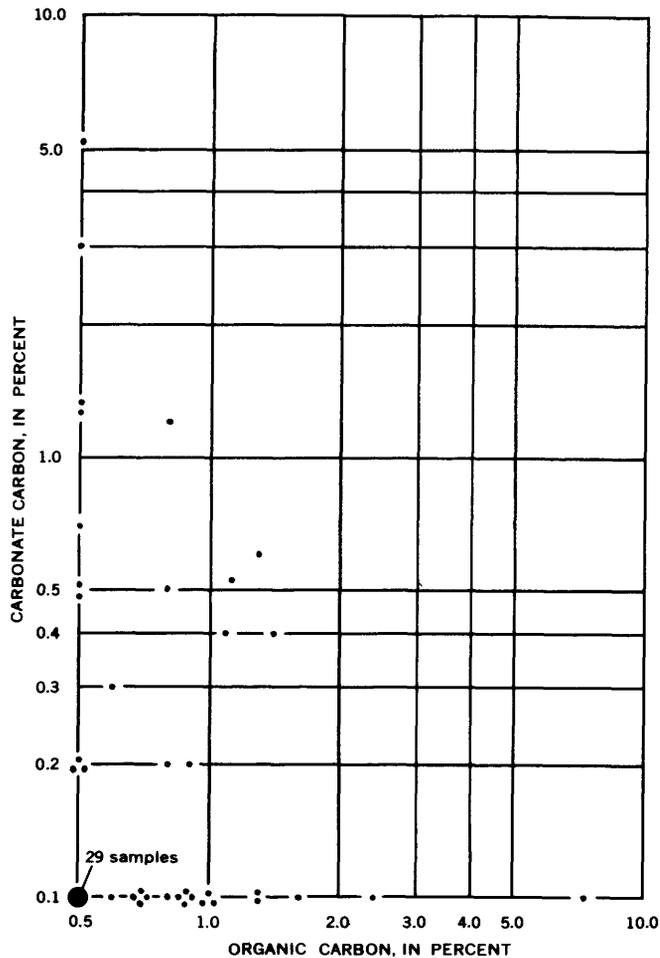


FIGURE 18.—Relations between carbonate and organic carbon in 67 samples of Pierre shale and equivalent rocks, and some older shales of Cretaceous age. See table 18 for analytical data.

The samples that contain more than about 1 percent organic carbon, and undetectable amounts of carbonate carbon, are characterized for the most part by conspicuously dark-gray to black colors. The weathered Claggett shale of sample C873 with 1.6 percent organic carbon, however, is grayish brown. The samples that contain more than 0.5 percent carbonate carbon, and undetectable amounts of organic carbon, are medium to light gray. The samples with detectable amounts of both carbonate and organic carbon are mostly dark gray; none is conspicuously black.

Weathering may destroy some kinds of organic matter, judging from the analyses of weathered and unweathered samples of the Crow Creek member. (See fig. 9.) Some kinds of organic material may be redeposited in weathered material according to the interpretation of the weathering profile of the Claggett shale as discussed on p. 30. A somewhat similar redeposition of organic compounds also is suggested

by sample C934 (table 18). This sample is medium-gray claystone that is exposed in the walls of a trench silo. The appearance of the sample does not suggest that it contains as much as 1.4 percent organic carbon. The sample has been in contact with the organic fermentation products of silage formation, and the high organic content may thus be completely secondary and not at all related to the nature of the rock. The minor element content of the claystone was not noticeably affected (table 14).

#### INTERRELATIONS

The interrelations of some of the elements have been discussed in preceding sections in connection with their distribution in the Pierre samples. For some of the elements no further discussion is needed, but for some of them, mostly the highly dispersed ones whose mode of occurrence is indefinite, a statistical approach is helpful in recognizing interrelations.

Correlation statistics give an objective basis for discussion of the association of elements. They seem thus to be a better approach to the problems of association than scatter diagrams, which are interpreted subjectively by each individual with little agreement among individuals. The statistical significance of correlation coefficients depends on both the number of samples and the ranges of concentration through which the compared elements occur. The 67 samples are sufficient for this study. The very small ranges of concentration of most of the elements (fig. 13) are unfortunate. The semiquantitative nature of most of the analytical data is no bar to the use of correlation statistics, because, for ease of handling, most large bodies of quantitative data are grouped for statistical study. The semiquantitative spectrographic analyses have already grouped the data. The uncertainty in the analyses would have little effect on the correlation statistic unless the uncertainty should be concentrated in either the high or low end of the ranges of concentration, which is believed to be unlikely. (See p. 47.)

The Stuart modification of the Kendall correlation coefficient  $t_c$  (Stuart, 1953) is probably the most usable and easily handled statistic for the ranked data discussed here, and does not require the assumption of a normal distribution of the data (T. G. Lovering, oral communication, 1959). The Stuart-Kendall correlation coefficient ranges from almost +1.0 for elements that are directly proportional to each other (a positive correlation) to nearly -1.0 for elements that are inversely proportional to each other in their occurrence (a negative correlation). Correlation coefficients near 0 indicate that the two elements are independent of each other in their occurrence. The statistical signifi-

cance of a coefficient can be determined at a given probability and depends in part on the number of samples involved. Correlation coefficients smaller than  $\pm 0.14$  have no statistical significance at the probability of 95 percent in the present study; that is, a coefficient of this size has no significance 95 times out of 100. It is doubtful that a correlation coefficient of less than  $+0.50$  has a clear-cut meaning geologically with respect to the two elements from which the coefficient is derived. Correlation coefficients smaller than  $\pm 0.50$  are useful, however, because they indicate a tendency toward positive or negative correlation and provide a basis for comparing the relative strengths of correlation.

Correlation coefficients were calculated for most of the minor constituents that occur in three or more spectrographic ranges (table 14 and fig. 13). Coefficients were not calculated between some pairs of elements, each of which occur in only three ranges; one

of these ranges includes the majority of the samples. The correlation coefficients are shown in table 19. The largest negative correlation coefficient is  $-0.44$ , between calcium and vanadium, and the next largest is  $-0.41$ , between manganese and vanadium. Positive correlation coefficients are smaller, in general, and the largest is  $+0.40$ , between scandium and gallium. The figures in the second decimal places probably are not significant. The scatter diagrams for the pairs of elements giving these larger correlation coefficients, and some smaller coefficients, are shown in figure 19. The correlation coefficients and scatter diagrams in themselves do not offer convincing proof of any associations between elements nor do they suggest any associations that were not expected.

The correlation coefficients are in agreement with the generalization that these rocks are made up chiefly of clay minerals intermixed with different amounts

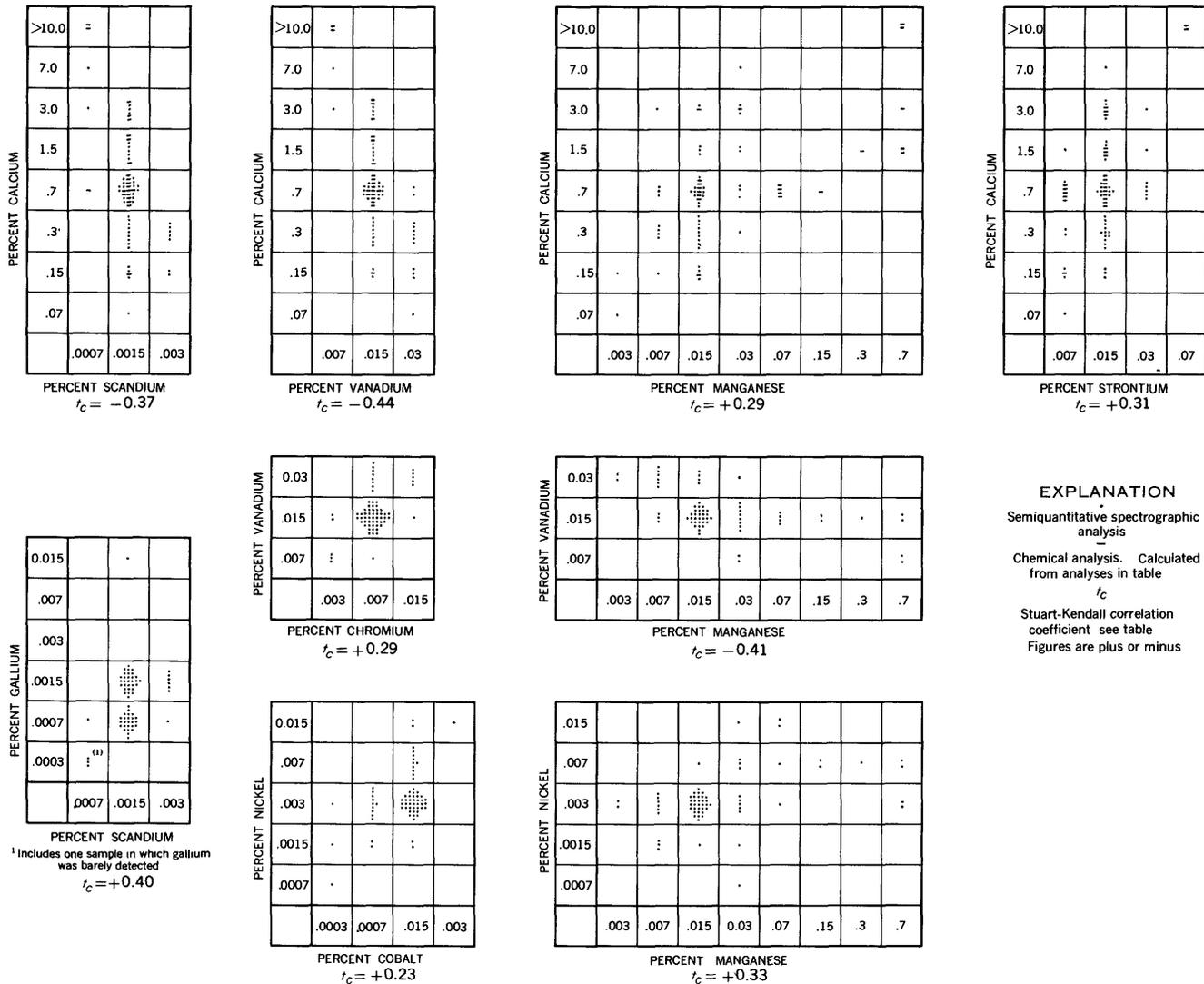


FIGURE 19.—Diagrams showing relations between selected elements.

TABLE 19.—*Stuart-Kendall correlation coefficients  $t_c$  for selected minor constituents in the Pierre shale and equivalent rocks calculated from data in table 14*

[Symbols: ns, correlation coefficient  $t_c$  not significant at 95 percent level; nc, correlation coefficient not calculated]

|         | Ca    | Sc    | V     | Mn    | Co    | Ni | Ga | Sr |
|---------|-------|-------|-------|-------|-------|----|----|----|
| Sc..... | -0.37 |       |       |       |       |    |    |    |
| V.....  | -0.44 | +0.20 |       |       |       |    |    |    |
| Cr..... | ns    | ns    | +0.29 |       |       |    |    |    |
| Mn..... | +0.29 | ns    | -0.41 |       |       |    |    |    |
| Co..... | ns    | nc    | ns    | +0.24 |       |    |    |    |
| Ni..... | ns    | ns    | ns    | +0.33 | +0.23 |    |    |    |
| Ga..... | -0.23 | +0.40 | +0.24 | ns    | ns    | ns |    |    |
| Sr..... | +0.31 | ns    | nc    | +0.23 | nc    | ns | ns |    |
| Ba..... | ns    | +0.22 | +0.23 | -0.20 | nc    | ns | ns | nc |

of calcium carbonate. Calcium is positively correlated with manganese and strontium. Each of these elements forms an insoluble carbonate and, in addition, manganese and strontium can replace calcium in calcium carbonate (Rankama and Sahama, 1950, p. 648, 480). The strontium probably was biologically incorporated in aragonitic shells that converted to calcite; although the resulting calcite can contain notable amounts of strontium, some strontium appears to be lost during this conversion (Odum, 1957, p. 45). Strontium mobilized during the conversion of aragonite to calcite may have formed strontium carbonate and remained in the rocks. During weathering, manganese in manganese carbonate, calcite, and siderite readily forms insoluble oxides and probably is not moved far from its primary occurrence. Calcium is negatively correlated with scandium and gallium, which commonly accompany aluminum, and with vanadium, which commonly accompanies organic matter but which also can occur in clays (Rankama and Sahama, 1950, p. 599-601).

Manganese is negatively correlated with barium, and positively correlated with strontium, because, as previously mentioned, manganese accompanies calcium and strontium in the carbonate fraction of the Pierre rocks, whereas barium is associated with the potassium-bearing clay fraction of the rocks. The positive correlations between manganese and cobalt and nickel do not seem explainable in terms of the assumed primary occurrence of these elements in the Pierre rocks. Both cobalt and nickel may occur either as sulfide minerals in the organic-rich rocks or as contaminants in pyrite. The fact that the amount of cobalt is smaller than that of nickel in the samples of the Pierre (fig. 13) is characteristic of the occurrence of these elements in sedimentary pyrite (Fleischer, 1955, p. 1004). Cobalt and nickel also can occur as part of the organic matter itself. These primary modes of occurrences of cobalt and nickel are antithetical to the primary occurrence of manganese in the Pierre rocks. The manganese oxides, and possibly some of the iron oxides, formed during present weathering of carbonate compounds, probably

adsorbed cobalt and nickel that were released by oxidation of pyrite or organic matter. Cobalt and nickel thus tend to be retained in the sample in amounts approximately related to the amount of manganese in the sample (Rankama and Sahama, 1950, p. 650). The weak positive correlation between cobalt and nickel probably simply reflects the similarity in behavior of these elements in the hydrolyzates.

The positive correlation between scandium and vanadium, scandium and gallium, and scandium and barium agrees with the classification of these elements, except barium, as typical of shales or hydrolyzates (Goldschmidt, 1937, p. 665; Gordon and Murata, 1952, p. 176). Both scandium and gallium are similar to aluminum in geochemical behavior. Vanadium occurs in shales either as an adsorbed cation on the clay minerals or with a claylike structure of its own, as in the mineral roscelite. Vanadium may occur in shales also as part of the organic matter. Barium does not form insoluble hydroxides, but it proxies for potassium in many minerals and is readily adsorbed by clays, in which it replaces potassium (Rankama and Sahama, 1950, p. 483).

Vanadium and chromium are typical of shales (Rankama and Sahama, 1950, p. 599-602 and 623) and have a positive correlation. Chromium follows iron and aluminum in the weathering cycle and presumably can replace either of these elements in clay minerals. Chromium hydroxide is very insoluble and the formation of this compound is suggested by Krauskopf (1956, p. 14 and 29) as a possible mechanism for regulating the amount of chromium in sea water. The relatively strong negative correlation between vanadium and manganese is due to the same causes as the negative correlation between calcium and vanadium. Vanadium, gallium, and barium are associated with each other in clay material rich in aluminum and potassium.

The data on arsenic, selenium, molybdenum, and uranium, the elements most prominently associated with organic-rich rocks, are too few (tables 14 and 17) for statistical study. The positive association between these elements and organic matter, however, seems clear. Both arsenic and selenium are much higher in sample C891 (table 17) than in the other samples, and this sample contains 7.4 percent organic carbon, the largest amount found (table 18). This sample also is one of the only two in the entire set of 67 samples in which molybdenum is present in amounts greater than 0.001 percent, the limit of detection for molybdenum by the semiquantitative spectrographic method. The other sample (C927, table 14) in which molybdenum was reported contains 0.0015 percent molybdenum and

less than 0.5 percent organic carbon. These relations suggest that organic material strongly influences the occurrence of arsenic, selenium, and molybdenum when the organic content is above 3 to 5 percent, the uncertain range reflecting the lack of carbon in this range in the samples analyzed (table 18). Where the organic carbon content is less than 3 to 5 percent, the occurrence of arsenic, selenium, and molybdenum is influenced by other factors that cannot be identified from these data.

The manner of association of arsenic, selenium, molybdenum, and uranium with organic matter is not at all certain. As to uranium, Bates and Strahl (1957, p. 1311-1312) concluded that most of this element in the Chattanooga shale is present as atoms randomly distributed through the matrix, although some is contained in organic-pyrite-clay complexes. Breger and Schopf (1955), however, concluded that the uranium in coalified wood in the Chattanooga shale was adsorbed by the wood when it entered the marine environment and that an organouranium compound was formed. Molybdenum is a common constituent of petroleum and seems to be present in organometallic compounds (Rankama and Sahama, 1950, p. 628). Data are lacking on the mode of occurrence of arsenic and selenium in organic-rich rocks, although the concentration of these elements in such rocks is evident (Moxon, Olson, and Searight, 1939, p. 33-58). Molybdenum, arsenic, and selenium commonly occur in sulfides such as pyrite (Fleischer, 1955, p. 1008, 999, and 1006). Williams and Byers (1934) found 205 ppm selenium in a concretion of pyrite from the Pierre shale in northeastern Nebraska, and Coleman and Delavaux (1957, p. 519-520) reported an average of 140 ppm selenium for five samples of pyrite and marcasite from the Mancos shale of Cretaceous age. The Mancos is widely exposed in western Colorado and is similar in age and general characteristics to the Pierre shale. The difficult problem of separation of sulfide minerals and organic matter from rocks without seriously altering the character of the organic matter for analysis of both constituents for elements such as arsenic, selenium, molybdenum, and uranium, must be solved if the relations between these elements and organic-rich rocks are to be understood.

Copper, zinc, and silver commonly are recognized as being associated with organic material in rocks. The data from the Pierre samples are inconclusive in this respect. Copper (table 14) is found in such a narrow range of concentration (from about 0.003 to 0.007 percent) that no relations with other elements or other rock characteristics are evident. The data on zinc (table 17, 22 samples ranging from 0.007 to 0.020 percent) are very few so that it is not surprising that relations with other elements are not evident. The limit of de-

tectability for silver is 0.0005 percent (table 16), so that the fact that traces of silver were reported for only 6 samples (table 14) suggests that these shales of Cretaceous age actually contain very little silver. This contrasts with the seeming widespread occurrence of silver in similar shales of Paleozoic age (Tourtelot, 1956, p. 74-75). No explanation is apparent, however.

No relations are apparent among the elements beryllium, boron, titanium, the rare earths, zirconium, and lead.

#### INTERRELATED CHEMICAL AND PHYSICAL CHARACTERISTICS

Interrelated chemical and physical characteristics investigated for this report include the pH of a slurry of the sample, and the liquid and plastic limits or Atterberg limits. The data are shown in table 20.

#### DATA ON pH OF SAMPLES

The pH measurements were made by Joseph Sharps (written communication, Dec. 1958), who has supplied the following information on the determination:

Distilled water was added to a portion of the sample crushed to minus 40 mesh to make a slurry that was slightly wetter than the liquid limit of the sample. Thus, the amount of water added varies with the liquid limit. Only enough water was added to each sample to allow the slurry to flow freely around the electrodes of the pH meter. The slurry set over night and the pH was measured with a standard laboratory type pH meter with glass electrode-calomel electrode couple. The instrument was calibrated against a solution of known pH. It is not likely that the second decimal place is significant.

The pH values range from 1.91 to 10.15 and the distribution of pH in the samples is shown in figure 20. The values of the sample with the highest pH and the one with the lowest pH are isolated; the remainder of the samples are divided into two groups of about equal number. The pH of one group is acidic to slightly acidic and ranges from about 3.3 to 5.7; the other group is mildly alkaline and the pH ranges from about 7.5 to 8.5.

The explanation of the pH of a slurry of rocks such as these is not clear cut (Thorne and Seatz, 1955, p. 220; Lyon and Buckman, 1937, p. 247-248). The pH results from a complex interaction of the acidic and basic ions that hydrolyze in the slurry. The combination of a weak base, such as iron, and a strong acid, such as sulfuric, results in an acidic pH, whereas a strong base, such as one of the alkali or alkaline-earth elements, and a weak acid, such as carbonic, results in an alkaline pH. The combination of a strong base and a strong

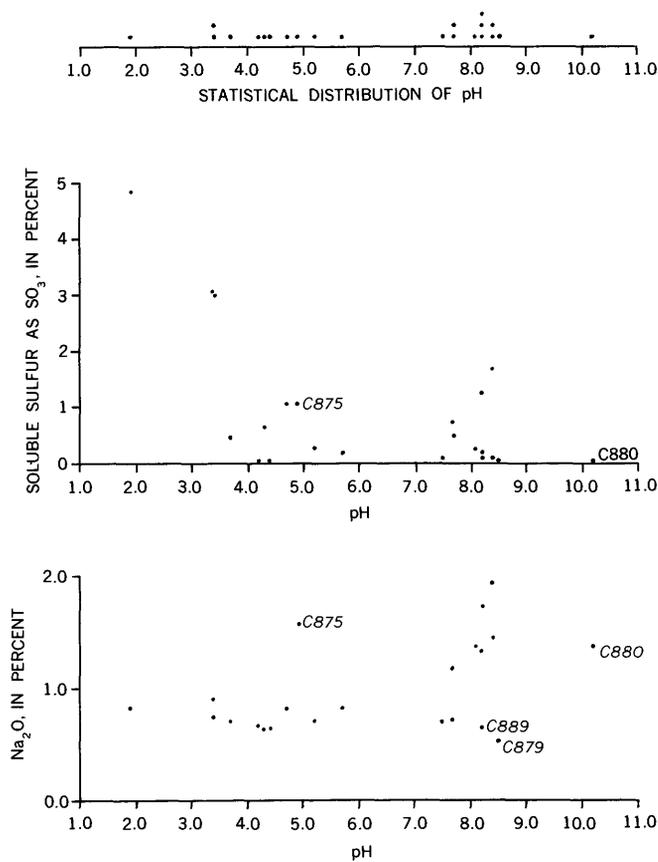


FIGURE 20.—Statistical distribution of pH in 22 basic samples of Pierre shale and equivalent rocks and the relation of pH to soluble sulfur and sodium oxide in the analyses in table 7.

acid results in an intermediate pH. The samples for which the slurry pH was determined consist of mixtures of such compounds. The possible causes for the pH values measured for the samples of Pierre shale

TABLE 20.—Slurry pH, liquid and plastic limit, and plasticity index of 22 basic samples of Pierre shale and equivalent rocks

[See table 1 for location and description of samples. Determinations by Joseph Sharps]

| Locality (see pl. 1) | Sample | pH    | Liquid limit | Plastic limit | Plasticity index |
|----------------------|--------|-------|--------------|---------------|------------------|
| 1                    | C871   | 3.37  | 56.3         | 31.6          | 24.7             |
|                      | C872   | 3.35  | 54.0         | 32.7          | 21.3             |
|                      | C873   | 3.67  | 52.4         | 38.1          | 14.3             |
|                      | C874   | 5.70  | 61.2         | 30.7          | 30.5             |
|                      | C875   | 4.92  | 46.0         | 22.9          | 23.1             |
| 2                    | C876   | 7.65  | 36.6         | 22.9          | 13.5             |
|                      | C877   | 4.22  | 54.0         | 33.1          | 20.9             |
| 3                    | C878   | 4.25  | 61.4         | 35.7          | 25.7             |
|                      | C879   | 8.37  | 101.3        | 33.6          | 67.7             |
| 4                    | C880   | 4.41  | 65.2         | 42.0          | 23.2             |
|                      | C881   | 4.72  | 75.9         | 38.8          | 37.1             |
| 5                    | C882   | 5.15  | 68.3         | 39.9          | 28.4             |
|                      | C883   | 7.50  | 88.1         | 38.2          | 49.9             |
| 6                    | C884   | 8.07  | 113.5        | 36.9          | 76.6             |
|                      | C885   | 8.38  | 112.0        | 34.9          | 77.1             |
| 7                    | C886   | 8.18  | 93.0         | 39.7          | 54.7             |
|                      | C887   | 8.50  | 89.6         | 20.1          | 40.5             |
| 8                    | C888   | 10.15 | 132.0        | 62.0          | 70.0             |
|                      | C889   | 7.70  | 113.0        | 40.5          | 72.5             |
| 9                    | C890   | 7.18  | 94.4         | 27.9          | 66.5             |
|                      | C891   | 8.23  | 101.5        | 35.3          | 66.2             |
|                      | C892   | 1.91  | 50.2         | 35.6          | 14.6             |

and equivalent rocks are many. Hydrolyzable sulfate compounds, however, seem the most obvious explanation for the acidic pH values found, and hydrolyzable alkali and alkaline-earth compounds seem the most likely explanation for the alkaline pH values found.

The relations between pH and acid-soluble sulfur compounds and between pH and sodium oxide are shown in figure 20. The acidic pH values have a roughly linear relation to the amount of acid-soluble sulfur as sulfur trioxide in the sample. The alkaline pH values have no direct relation to the acid-soluble sulfur, and some samples have an alkaline pH even though they contain more than 1 percent acid-soluble sulfur. The soluble sulfur reported in the analysis of these samples thus may not be a readily hydrolyzable form or else the effect of the sulfur is counteracted by the presence of a strong base. The alkaline pH values have a rough positive relation with the amount of sodium oxide in the sample, except in the two marlstone samples, C879 and C889. The alkaline pH values, of course, reflect only the loosely held hydrolyzable sodium in the samples, so a better relation with the total sodium in the sample probably is not to be expected. The very alkaline pH of sample C880 probably means that a very large part of the sodium in the sample is hydrolyzable; the sample is from a core, so a large amount of hydrolyzable sodium is possible. As expected, the acidic pH values do not seem to have any relation with the sodium oxide reported in the analyses. The anomalous position of sample C875 on the graph for sodium oxide probably means that most of the sulfate in the sample is readily hydrolyzable, but that very little of the sodium is.

The two marlstone samples, C879 and C889, have very alkaline pH values that do not seem to be related to the sodium oxide content of the sample. These samples are very rich in calcium carbonate, whose hydrolysis produces an alkaline reaction.

ATTERBERG LIMITS

The Atterberg limits consist of a liquid limit and the plastic limit. These limits are empirical and can be defined only in terms of the methods of their determination. The liquid limit, for instance, is the water content in percentage of dry weight at which two sections of a pat of material of a specified size barely touch each other, but do not flow together in a standard instrument when subjected to sharp blows from below (Terzaghi and Peck, 1948, p. 32). The plastic limit is the water content at which the material being tested begins to crumble when rolled out into thin threads (Terzaghi and Peck, 1948, p. 33). For many engineering purposes, it is convenient to use the plasticity

index, which is the numerical difference between the liquid and plastic limits. The determinations shown in table 20 were made according to the standards established by the American Society for Testing Materials (1950, liquid limit, standard D 423-39, p. 56-58, and plastic limit, standard D 424-39, p. 59-60).

The liquid and plastic limits and the plasticity index often are combined in a plasticity chart (Casagrande, 1947, p. 801) for the classification of soils and predicting some aspects of their engineering behavior. The chart was designed mostly for use with true soils and other unconsolidated materials, so that the classification is not necessarily applicable to material such as the Pierre shale. The chart (fig. 21) is a convenient way to compare data on different kinds of material and may be of use to those working with the engineering characteristics of shales. Both the plastic limit and the liquid limit are plotted against the plasticity index. Also shown for comparison, however, are the fields that are occupied on the chart by only the liquid limits of some other kinds of clayey rocks.

The plastic limit of the Pierre samples ranges from 20 to 62 (table 20), but most of the samples have plastic limits of 30 to 40. The liquid limits have a much wider range, from about 36 to 113, and are the major cause of variation in the plasticity index. The liquid limits of the samples generally are much higher than those for the kaolin-type clays, glacial clays, and gumbo clays reported by Casagrande (1947, p. 803), but are not

as high as those for bentonite. The liquid limits of the Pierre samples reported here fall mostly within the field of the liquid limits determined for about 120 samples from the Gregory, Crow Creek, and DeGrey members of the Pierre shale in core holes drilled by the U.S. Army Corps of Engineers at the Oahe Dam. The liquid limits for the Pierre samples fall both above and below the *A* line, which is an empirical boundary generally separating typical inorganic clays above the *A* line from plastic soils containing organic colloids below the *A* line (Casagrande, 1947, p. 801). This separation applies mostly to true soils and other unconsolidated materials; its application to materials like the Pierre shale is uncertain.

Only a few regularities can be distinguished between general lithologic characteristics and the liquid and plastic limits. The samples that were recognized in the field as being bentonitic (table 1) are among those with the largest plasticity indexes and liquid limits. Although the samples with the highest plasticity indexes and liquid limits (C885 and C884) were not specifically identified in the field as being bentonitic, the Verendrye member as a whole is bentonitic. These two samples are very fresh. The sample with the highest liquid limit (C880) comes from a core, but a surface sample (C888) has a higher plasticity index and a very high liquid limit. The two marlstone samples have quite different positions on the chart (fig. 21). Mineralogically and chemically the two samples are quite similar (table 10), but the surface sample (C889) contains about 50 percent clay and the core sample (C879) contains only 30 percent clay. The greater clay content and the surface weathering are the only apparent factors that would account for the higher plasticity index and liquid limit of the surface sample. The samples with low plasticity indexes and liquid limits include those from the Claggett formation and Sharon Springs member of the Pierre shale that contain organic carbon. Other samples with similar amounts of organic carbon, however, fall much higher in the diagram.

The data derived from the weathering sequences (see figs. 7, 8) are summarized in the following table. The samples are arranged in order of apparent increase in weathering at each locality.

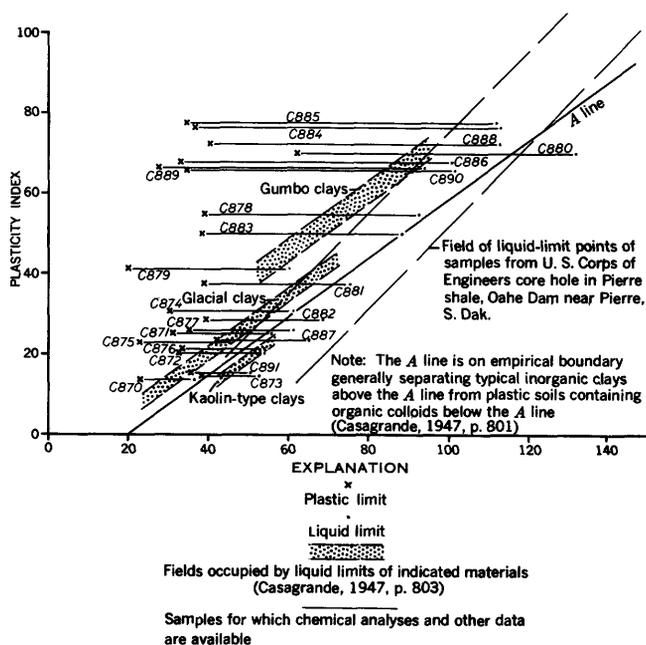


FIGURE 21.—Liquid limits and plastic limits plotted against plasticity indexes for 22 basic samples of Pierre shale and equivalent rocks, and other data. See table 20 for analytical data.

| Locality 1 |              |               |                  | Locality 8 |              |               |                  |
|------------|--------------|---------------|------------------|------------|--------------|---------------|------------------|
| Sample     | Liquid limit | Plastic limit | Plasticity index | Sample     | Liquid limit | Plastic limit | Plasticity index |
| C871       | 56.3         | 31.6          | 24.7             | C885       | 112.0        | 34.9          | 77.1             |
| C872       | 54.0         | 32.7          | 21.3             | C884       | 113.5        | 36.9          | 76.6             |
| C873       | 52.4         | 38.1          | 14.3             | C881       | 75.9         | 38.8          | 37.1             |
| C874       | 61.2         | 30.7          | 30.5             | C882       | 68.3         | 39.9          | 28.4             |
|            |              |               |                  | C883       | 88.1         | 38.2          | 49.4             |

These data suggest that the relatively extreme weathering that produced the soillike material at each of the localities (samples C874 and C883) increased the liquid limit and the plasticity index, but not the plastic limit, compared to the direct parent material (samples C873 and C882). At locality 8, however, this increase in liquid limit and plasticity index in the surface material still leaves these measures of physical characteristics much smaller than in the unweathered material (samples C885 and C884) at the locality. The relatively low plasticity index of the freshest samples at locality 1 suggest that these samples actually are somewhat weathered.

The characteristics of plasticity and moisture content measured by the Atterberg limits are obviously most highly developed in clays and, in fact, are almost the primary characteristics that distinguish clays from other sedimentary rocks (Grim, 1953, p. 1). Variations of these characteristics according to the type of clay

have long been recognized. The unusual thixotropic properties of bentonite, for example, indirectly indicated by the liquid limit, are the characteristic that first called attention to the material. Swelling bentonite and montmorillonite clays have the largest plastic and liquid limits of all clays (Casagrande, 1947, p. 804). The layerlike structure of most clay minerals and their capacity for ion-exchange reactions probably account for the ability of clay rocks to adsorb water and for their plasticity, as well as other unusual characteristics.

Montmorillonite is a prominent mineral component of the Pierre samples, although mixed-layer illite-montmorillonite is predominant in most samples (table 5). Figure 22 shows the relations between the liquid limits (table 20) and the montmorillonite content, and other characteristics of the samples. The liquid limit appears to have a straight-line relation with the percentage of montmorillonite determined by X-ray methods, although the points are fairly well dispersed around the

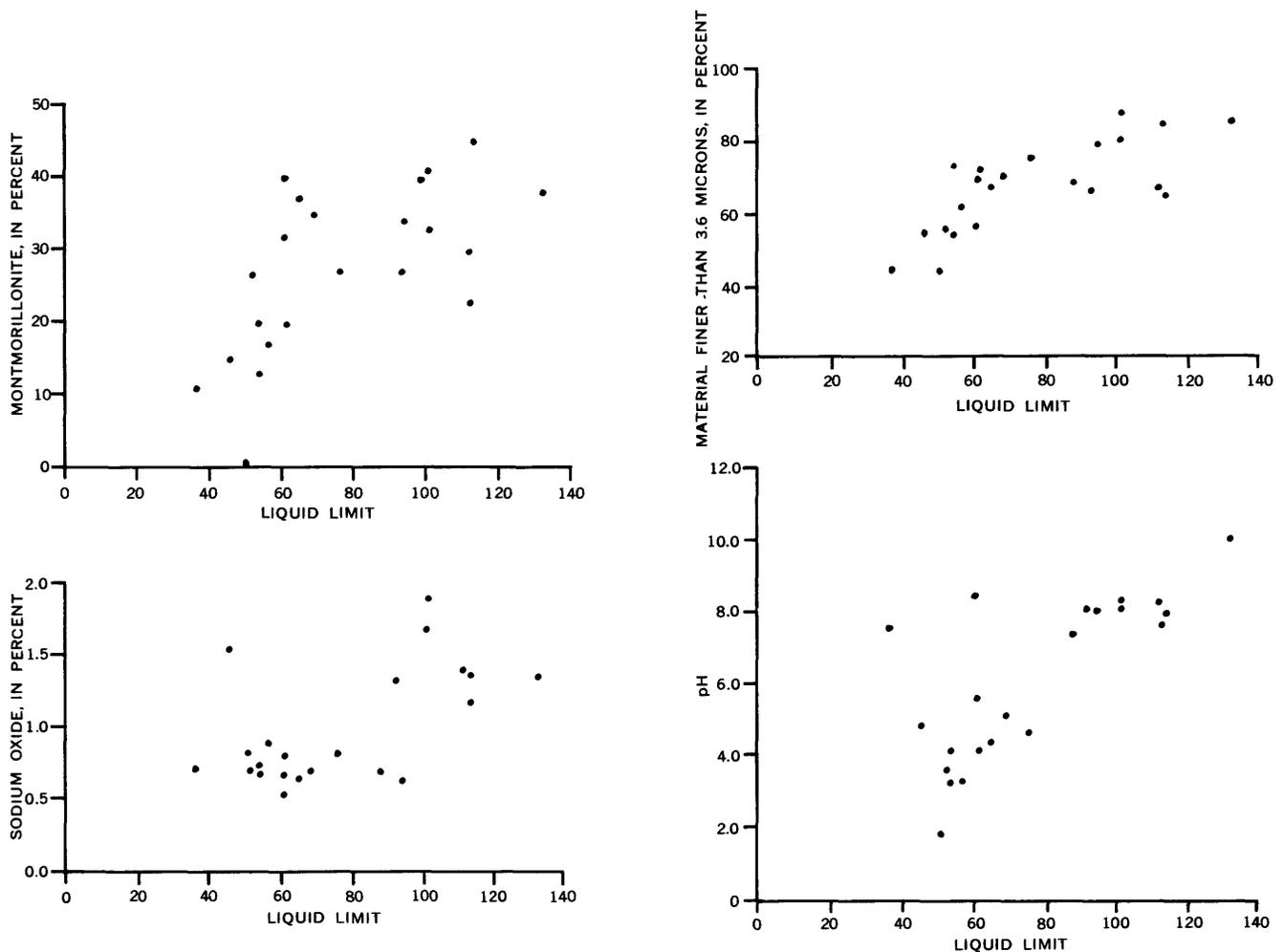


FIGURE 22.—Relation between liquid limit and content of montmorillonite, percentage of material finer than 3.6 microns, sodium oxide, and pH for the 22 basic samples of Pierre shale and equivalent rocks.

trend line. A similar direct relation between liquid limit and the percentage of material finer than 3.6 microns given in the size analyses (table 3) also is shown in figure 22. The trend suggested by the scatter diagram appears to be a curve with the importance of the relation decreasing markedly when the fraction finer than 3.6 microns exceeds 80 percent. The amount of clay-sized material in the samples, and the amount of montmorillonite in the clay thus are important in governing the liquid limit and plasticity index of the samples.

The liquid limit of montmorillonite is very sensitive to the exchangeable ions held by the clay mineral. Grim (1944, p. 269) pointed out that montmorillonite with sodium as the principal exchangeable ion has very large liquid limits. More recently, White (1958, p. 44), in a detailed study of the water-sorption properties of homoionic clay minerals, found that prepared sodium-saturated montmorillonite has larger Atterberg limits than montmorillonite saturated with any other cation, except lithium. No data are available on the amounts of exchangeable cations in the samples of Pierre shale, but figure 22 shows a rough relation between the liquid limits and the content of sodium. The percentages of sodium oxide from the rock analyses (table 7) include both the sodium that was exchangeable on the clay minerals and the sodium that was not exchangeable. The scatter diagram suggests that the samples differ in the amount of exchangeable sodium as compared to the total amount of sodium, although the exchangeable sodium in most samples must be a fairly large proportion of the total sodium. The liquid limit also seems to be directly related to the pH of the samples, as shown in figure 22. This is not surprising, however, since the highly alkaline pH of some samples seems attributable to hydrolyzable, and hence exchangeable, alkali and alkaline-earth elements among which sodium would play an important part.

Factors other than exchangeable sodium in the sample must also influence the Atterberg limits because some of the weathered samples (C874, C883, C889, and C890) have relatively high limits under situations where exchangeable sodium would not be expected to be preserved. Differences in clay-mineral content of the samples might affect the Atterberg limits for the marlstone samples (C879 and C889), as mentioned previously, but the other weathered samples do not seem to differ significantly in clay-mineral content from their unweathered or less weathered counterparts. Each of these samples, except C874 contains a greater amount of material finer than 3.6 microns (table 3) than their unweathered counterparts. The ease or difficulty of disaggregation may be one of the factors influencing

the Atterberg limits. Weathering seems to make the claystone and shale more responsive to the disaggregation procedures used in size analyses (p. 18). No other factors are discernible from the present data.

#### SUMMARY

The chemical and mineralogical composition and physical characteristics of the Pierre shale and equivalent rocks are being investigated to shed light on the geologic and chemical processes involved in the accumulation of shale, the predominant sedimentary rock in the earth's crust. The Pierre shale and equivalent rocks are a thick stratigraphic unit that occurs throughout the western interior region from northern Montana to northern New Mexico and from eastern North and South Dakota, Nebraska, and Kansas to western Montana and Wyoming, and central Utah and northeastern Arizona. This gross stratigraphic unit is composed mostly of clayey rocks relatively free from coarse material and also low in chemical precipitates and biogenic sediments. This report presents the data on samples of marine shale from widely separated localities in Montana, Wyoming, and South Dakota to measure the range in variation in chemical and mineralogical composition and related characteristics in the northern area of occurrence of the Pierre shale and its equivalents. Subsequent investigations will be concerned in detail with the composition of shale in geographic regions from east to west that represent different conditions of deposition.

The Pierre shale and equivalent rocks in the northern part of the western interior region are divided into three facies belts. The eastern facies belt lies in central South and North Dakota where the Pierre consists entirely of marine shale with minor amounts of marlstone. The central facies belt lies in the western Dakotas and adjacent Wyoming and Montana where the marine shale contains minor amounts of sandstone. The western facies belt consists of alternate sequences of marine shale and nonmarine rocks in its eastern part and entirely of nonmarine rocks rich in volcanic material in its western part; it is made of the Eagle, Claggett, Judith River, and Bearpaw formations in Montana; parts of the Cody and Baxter shales and Mesaverde group in Wyoming; and the Livingston, Two Medicine, and St. Mary River formations in western Montana. For the purposes of this report, the western facies belt is divided into northern and southern parts. A wide variety of rock types with known stratigraphic positions and relations thus are available for study.

Standard rock analyses for a set of 22 basic samples are given together with chemical analyses and semi-quantitative spectrographic analyses for minor ele-

ments, size analyses, X-ray mineralogical determinations, and measurement of slurry pH, liquid limit, and plastic limit. Semiquantitative spectrographic analyses for a set of 45 supplemental samples also are included. The samples were selected to obtain data on composition by stratigraphic zone and geographic region. The zones of *Baculites obtusus* s. l., *Baculites compressus* s. l., and *Baculites clinolobatus* were used to divide the samples into three groups from the lower to the upper part of the Pierre shale and equivalent rocks. The facies belts were used to group the samples by geographic region.

The geochemical system examined includes the weathering and erosion of source rocks in the land areas adjacent to the sea in which the Pierre and equivalent rocks were deposited, the transport of these materials to the sea, and deposition and diagenesis on the ocean floor. Several cycles of deposition and erosion probably occurred during the transportation of the material from the source area across wide coastal plains and into the sea. Although a heterogeneous mass of material was delivered to the landward margin of the coastal plain, clay-sized particles were the predominant material passed on to the sea. Volcanic material was available on land for erosion and weathering, but large amounts also were delivered aerially to the sea. In accumulating on the sea floor, the clay minerals became mixed with different amounts of organic matter and with calcium carbonate from plankton, such as Foraminifera and coccolithophorids. The amount of organic matter and calcium carbonate found in shale today is primarily a function of conditions under which these materials could be preserved on the original sea floor. The clay moved from an oxidizing environment in its source area on the land to its depositional site on the floor of the Pierre sea through a series of environments that tended to be increasingly reducing and alkaline. The composition of clay probably changed during transportation. On the sea floor, the clay entered a reducing environment and underwent further considerable chemical change. Following a period of relatively quiescent conditions that nevertheless may have greatly affected the composition of the shale because of its great length and because of the effects of loss of water and of compaction, the shale was uplifted and returned to the generally alkaline and oxidizing conditions of the zone of weathering near the present surface. Minor alternations between oxidizing and reducing conditions and variations in pH, within this major cycle of oxidizing, reducing, and then again oxidizing conditions, probably are characteristic of the geochemical history of shale in the Great Plains region.

The 22 basic samples selected for rock analysis consisted of 8 samples of flaky dark-gray to black shale, 10 of light-gray to dark-gray massive claystone, 2 of marlstone, and 2 of soil-like products of weathering. Of these samples, 13 were from the *Baculites compressus* s. l. zone and 9 from the *Baculites obtusus* s. l. zone. The 45 samples that were analyzed only by semiquantitative spectrographic methods included 2 from the *Baculites clinolobatus* zone, 24 from the *B. compressus* s. l. zone, 13 from the *B. obtusus* s. l. zone, and 6 from rock units older than the Pierre shale; all 45 samples consisted of shale and claystone. Most of the claystone samples were somewhat bentonitic, and the shale samples come from units that also contain beds of bentonite.

The 22 basic samples contain from 35 to 90 percent material finer than about 1/256 mm (about 4 microns) and average 70 percent. The average amount of material finer than 1 micron is about 50 percent, and the average of material coarser than 74 microns is less than 5 percent. Samples from the western and central facies belts average about 60 percent and 42 percent finer than about 4 and 1 microns, respectively, and samples from the eastern facies belt average 75 and 53 percent. The clays deposited far from the western shore of the Pierre sea thus were finer grained than those deposited near the shore. Weathered samples generally have smaller median diameters than fresh samples. Probably this is the result of weathering, which caused the samples to disaggregate more readily in the process of size analysis, rather than an actual decrease in grain size from weathering alone.

The material coarser than 74 microns consisted mostly of clay aggregates bound with iron or manganese oxides, although in one sample the aggregates were bound with organic matter. Quartz, feldspar, and biotite were present in most samples. Pyrite was present only in the freshest samples; gypsum and the iron-oxide aggregates were present in the weathered samples. Foraminifera were found only in samples from the eastern facies belt.

X-ray mineralogical determinations of the whole rock indicated 8 to 27 percent quartz in the samples, and one sample contained 18 percent beta cristobalite. Feldspar ranged from 1 to 5 percent in 20 samples, and was undetected or questionably detected in 2 samples. Calcite amounted to about 38 percent in the two marlstone samples, and 4 percent in a sample rich in Foraminifera. Dolomite amounted to about 2 percent in the marlstone samples and 10 percent in a claystone sample. Carbonate minerals in amounts of less than 2 percent were not detected by X-ray methods.

Gypsum, jarosite, and pyrite were detected in a few samples, but the determinations did not agree very closely with the chemical analyses. Clinoptilolite was found in 8 of the 22 samples, in which it seems to be a diagenetic mineral resulting from the alteration of volcanic material.

The clay fraction of the samples consisted predominantly of mixed-layer illite-montmorillonite in amounts ranging from about 36 to about 57 percent; for most samples, montmorillonite was the next most abundant mineral in amounts ranging from about 10 to 47 percent. Illite was the next most abundant mineral in 17 samples. Chlorite was found in 16 samples in amounts ranging from barely detectable to 7 percent. Kaolinite was detected in 21 samples in amounts ranging from barely detectable to 10 percent. Montmorillonite is present in larger amounts in samples from the eastern facies belt than in samples from the western and central facies belts.

The average composition and standard deviation (indicated by parentheses) of 17 of the 22 samples, excluding the 2 marlstone samples, the 2 weathered products, and 1 sample very rich in organic matter is:  $\text{SiO}_2$ , 59.68 (3.49);  $\text{Al}_2\text{O}_3$ , 15.40 (1.52);  $\text{Fe}_2\text{O}_3$ , 4.56 (1.09);  $\text{FeO}$ , 0.96 (0.64);  $\text{MgO}$ , 2.11 (0.47);  $\text{CaO}$ , 1.52 (1.12);  $\text{Na}_2\text{O}$ , 1.09 (0.42);  $\text{K}_2\text{O}$ , 2.49 (0.26);  $\text{H}_2\text{O}-$ , 3.73 (1.09);  $\text{H}_2\text{O}+$ , 4.77 (0.83);  $\text{TiO}_2$ , 0.60 (0.05);  $\text{CO}_2$  (determined in only 16 samples), 0.87 (1.35);  $\text{P}_2\text{O}_5$ , 0.15 (0.04); acid-soluble S as  $\text{SO}_3$ , 0.85 (0.95); insoluble S as S (determined in only 14 samples), 0.21 (0.17); Cl (determined in only 11 samples), 0.01; F, 0.07;  $\text{MnO}$ , 0.19 (0.39);  $\text{BaO}$ , 0.08. Most of these elements occur in the clay minerals themselves, but silica is present as quartz or cristobalite, and some of the iron and manganese, as well as calcium and magnesium, occur as carbonates. Iron also occurs in pyrite, and sulfur occurs in either pyrite or in sulfate minerals. The statistical distributions of most of the elements are approximately normal, although sodium and calcium have markedly skewed distributions. After recalculating the analyses to exclude moisture, calcium carbonate of biogenic origin, calcium phosphate, and acid-soluble sulfur as sulfur trioxide, the distribution of calcium approaches normality, but the shape of the sodium distribution is unchanged.

The average composition of the analysed samples agrees fairly closely with the mineralogical composition of the samples.

The suitability of surface samples for this kind of study was investigated by sampling two weathering sequences that showed progressive change from nearly fresh shale to residual soil-like products of weathering. The changes are considered on the basis of weight.

A part of the organic matter in the rock is lost in weathering. Sulfide sulfur in the fresh shale is oxidized to sulfate sulfur in the weathered material, but the sulfate sulfur is likely to be concentrated in the weathered material by the evaporation of ground moisture carrying soluble compounds to the surface of the outcrop. Ferrous iron in the fresh material becomes ferric iron in the weathered material, but there may be little change in total iron along the weathering sequence. Part of the sodium is lost with weathering and may be partly replaced by calcium or magnesium in ion-exchange reactions. Some calcium is added to the weathered material by accumulation of calcium carbonate near the surface. Total water remains about the same along the weathering profile, but the amount of  $\text{H}_2\text{O}+$  increases with weathering and the amount of  $\text{H}_2\text{O}-$  decreases. Except for organic matter, sulfide sulfur, and sodium, these kinds of changes can be allowed for by recalculation of the analyses. Analyses of samples weathered to different degrees thus can be compared.

The average composition of the 17 samples of Pierre shale differs in relatively minor ways from the average compositions of other shales, such as Shaw's Devonian pelites (1956), Nanz' Precambrian lutites (1953), the clays of the Russian platform (Vinogradov and Ronov, 1956), and the average shale of Clarke (1915). Differences in silica, alumina, and potassium are most apparent. The Pierre average contains both more and less silica and alumina than the average compositions of the other shales, because of different amounts of detrital quartz in the samples making up the averages and probably because of different original clay minerals. The silica content of all the averages ranges from about 52 to 62 percent and the alumina content ranges from about 15 to 20 percent. No mineralogical data are available on the rocks included in the other averages, which are based on rocks ranging from clay to schist.

The Pierre average contains 2.49 percent potassium oxide, and the other averages of potassium oxide range from 3.25 to 3.79 percent. This relatively low potassium oxide content of the average composition of the Pierre agrees with the apparent decrease in potassium content of shales with decreasing geologic age, as pointed out by Nanz and Vinogradov and Ronov. The Pierre average contains more calcium than that of the Devonian pelites, and much less calcium than that of the Russian clays, but does not differ from the other averages. Recalculating the averages to exclude moisture and assumed carbonate minerals does not make the averages agree much more closely. These recalculations emphasize, however, that the clays of the Russian platform are very rich in calcium, containing about 1.5

percent calcium oxide compared to about 0.75 percent for the samples of the Pierre.

The average contents of major constituents in the Pierre samples are strikingly similar when the samples are grouped by geographic region.

The minor element content of the 67 samples was investigated by semiquantitative spectrographic analyses for many elements. Chemical analyses for total carbon and mineral carbon, with the difference between these amounts interpreted as organic carbon, also were made of the 67 samples. Chemical analyses for fluorine, zinc, arsenic, selenium, and uranium were made of the basic set of 22 samples.

The minor elements determined spectrographically occur in surprisingly narrow ranges of concentration, the highest reported amount for about half of the elements being no more than about twice the lowest reported amount. Only calcium and manganese have ranges of as much as several percent. Compared with generally accepted concentrations for the crustal abundances of the elements, boron, scandium, lanthanum, and cerium are enriched in the Pierre samples; the enrichment of boron is the most conspicuous. Sodium, calcium, chromium, manganese, iron, strontium, yttrium, and niobium are depleted in the Pierre samples relative to crustal abundances. The other elements occur in the Pierre samples in about the same amounts as in the earth's crust.

The Pierre samples are believed to represent a reasonable approximation of the range of minor constituents to be found in these rocks, and to include a fair sampling of the stratigraphic and geographic extent of the Pierre as well as of the types of shale included in the unit. The minor-element content of this group of samples differs only in a few respects from that of a nearly similar number of samples from the organic-rich unit at the base of the Pierre in South Dakota (Kepferle, 1959). Boron, vanadium, nickel, copper, and molybdenum are enriched in the organic-rich samples, which also contain abnormal amounts of arsenic, selenium, and, locally, uranium. Magnesium and gallium, and probably strontium and barium, are somewhat relatively enriched in the Pierre samples as compared with the organic-rich samples. Other elements occur in about the same amounts in both groups of samples.

Differences in minor element content by stratigraphic zone and geographic region are difficult to evaluate because of the relatively few samples and the semiquantitative nature of the analyses. Distribution diagrams suggest, however, that calcium and manganese are present in larger amounts in the *Baculites compressus* s. l. zone than in the *B. obtusus* s. l. zone; and that nickel, strontium, and, possibly, yttrium are likely to be present

in larger amounts in the *B. compressus* s. l. zone. Scandium, vanadium, and gallium, and, possibly, chromium and copper, are likely to be present in larger amounts in the *B. obtusus* s. l. zone than in the *B. compressus* s. l. zone. These differences do not seem to be particularly interrelated and no explanation is apparent now.

With respect to geographic region, calcium, manganese, and strontium are present in larger amounts in the samples from the eastern facies belt; boron and nickel seem to be distributed similarly. Scandium and lanthanum seem to be present in larger amounts in samples from the western facies belt than in the eastern. Vanadium, chromium, and copper seem to occur in larger amounts in the samples from the northern part of the western facies belt than in the other geographic regions.

The average fluorine content of the basic set of 22 samples is 0.068 percent. Part of this fluorine probably is adsorbed on clay minerals, and the remainder occurs in finely divided apatite.

The average zinc content of the 22 samples is 0.014 percent, a concentration that is about twice as great as that of the crustal abundance. Zinc probably is adsorbed on clay minerals rather than being present in either sulfides or carbonates.

The average arsenic content of 21 samples in which arsenic ranged from 5 to 24 ppm is 14 ppm. One sample, not included in the average, contained 41 ppm arsenic. This sample is very rich in organic matter. The average selenium content of 21 samples is 2 ppm, excluding the sample rich in organic matter that contains 50 ppm selenium. Uranium was found in the 22 basic samples in amounts less than 10 ppm, but abnormal amounts of uranium are known to be present in other samples from the organic-rich unit. The association of these elements and molybdenum, copper, and nickel, is characteristic of organic-rich shales, either because they form organometallic compounds or because they form sulfide minerals. The lack of evidence of concentration of vanadium in the organic-rich Pierre rocks seems anomalous.

Of the 67 samples analyzed for forms of carbon, 29 samples contain less than 0.5 percent total carbon, the lower limit of detection. Of the remaining 38 samples, 18 contain less than 0.1 percent carbonate carbon, and organic carbon ranges from about 0.6 to nearly 8 percent; another 11 samples of the 38 contained less than 0.5 percent organic carbon, and carbonate carbon ranges from about 0.2 to 5 percent. The remaining nine samples contain measurable amounts of both organic and carbonate carbon. These nine samples include marlstones as well as shales. All samples that contain more

than about 1 percent organic carbon are very dark in color. No information is available on the nature of the compounds in which the organic carbon occurs.

The pH values measured in slurries of each of the samples range from about 1.9 to 10.2, although most samples fell in the range of about 3 to 8.5. Alkaline pH values seem to correlate with the hydrolyzable alkali and alkaline-earth contents of the samples, and acidic pH values seem to correlate with hydrolyzable sulfate compounds.

The plastic limit of the Pierre samples ranges from 20 to 62, with most of the samples falling in the range of 30 to 40. The liquid limit has a much wider range, from about 36 to 113. These ranges are characteristic of natural clays of mixed mineralogy. The figures for liquid limits seem to be directly proportional to both the amount of montmorillonite in the samples and to the pH produced by the sample, although scatter diagrams of these relations show considerable spread around the central trend. The liquid limits also are proportional to the amount of material finer than about 4 microns in the samples, but does not seem to be related to the amount of sodium oxide reported in the analyses. No regularities could be made out between the plastic limit and other characteristics of the samples.

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