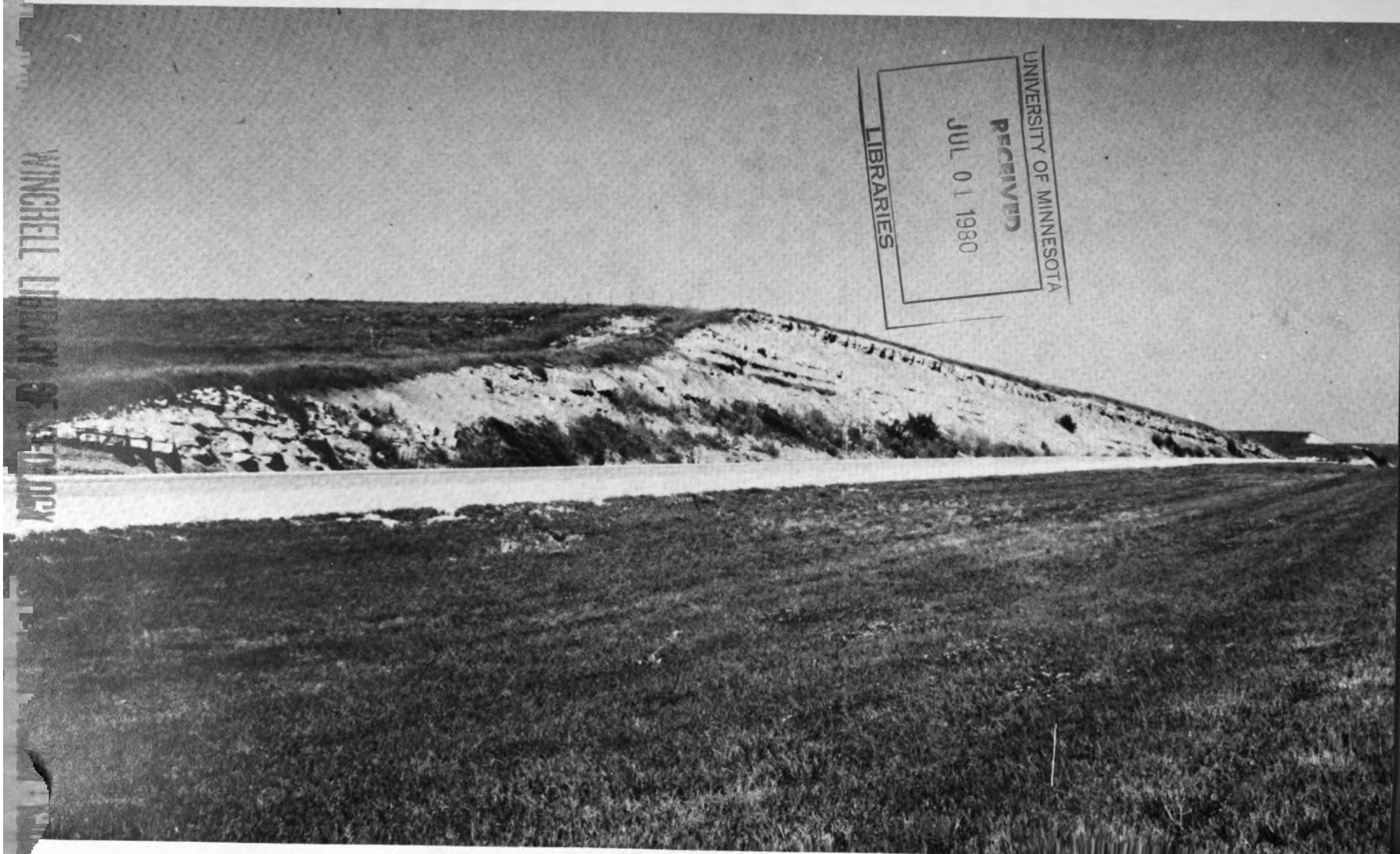
Geochemistry, Mineralogy and Petrology of Upper Paleozoic Shales of Kansa

Bulletin 217

John Cubitt



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BULLETIN 217

The Geochemistry, Mineralogy and Petrology of Upper Paleozoic Shales of Kansas

By

John M. Cubitt

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EXECUTIVE SUMMARY

Upper Pennsylvanian and Lower Permian deposits outcrop along a north-south section in eastern Kansas and underlie all of western Kansas. Within the 2000 feet of limestones, shales, and sandstones that constitute this division of the stratigraphic column are preserved large deposits of oil and gas that have been exploited since the turn of the century. The economic importance of these units has required that a comprehensive understanding of the nature, distribution, and origin of these Upper Paleozoic rocks be obtained. Consequently, detailed stratigraphical, petrological, and paleontological studies of Upper Pennsylvanian and Lower Permian deposits systematically evolved, resulting in the development of the cyclic sedimentation concept by R. C. Moore in the 1930s. This concept revolutionized thoughts and approaches to Upper Paleozoic sediments to the point that by the 1960s cyclic sedimentation was accepted internationally as a frequently occurring sedimentary process.

Nevertheless, results of research did not always support the application of cyclic successions to all sections of the Upper Pennsylvanian and Lower Permian. In particular, lithologies within the Kansas City and Lansing Formations revealed alternations of limestones and shales that contrast markedly with cyclic sequences reported by Moore from the same units. One of the major differences in the results has been attributed to the sampling techniques employed. Moore was primarily concerned with the faunal characteristics of carbonate sediments whereas other workers also examined the lithologies developed in the intervening poorly exposed clastic sediments. Doubt was thus cast on many of the cyclic sequences reported by Moore within the remainder of the Upper Pennsylvanian and Lower Permian. Concern was also expressed that identification and interpretation of subsurface cyclic sequences could now be considered only tentative and the speculated distribution of possible reservoir rocks was open to question. In an attempt to solve some of these questions and provide a set of reference information for later studies, a detailed geochemical, mineralogical, and petrological study of Upper Pennsylvanian and Lower Permian shales was undertaken.

Shale samples were collected from every clastic unit in the Upper Pennsylvanian and Lower Permian with the exception of the Auburn and Winzeler Shales (Wabaunsee Group) and the Seminole Formation (Pleasanton Group). To establish the mineralogical variation within the shales, samples were examined by quantitative X-ray diffraction. Results indicate the presence of quartz, calcite, dolomite, feldspar, chlorite, kaolinite, and illite within the majority of samples with subsidiary proportions of pyrite, gypsum, jarosite, and several expanding clay minerals. The geochemical variation was determined by emission spectrometric analysis of six major oxides and 20 trace elements within the shales. The siting of certain trace elements within the minerals was confirmed using electron spin resonance. Finally, numerous thin sections were made to examine petrological variation within the shales.

Analysis of the multitude of raw data revealed the presence of the following six major clastic facies: (1) a sandstone and siltstone facies corresponding to deltaic deposits, (2) a clayey shale facies corresponding to prodelta marine muds, (3) a black shale facies deposited in reducing conditions, (4) a calcareous grey shale facies that represents open-marine, shallow-water deposition, (5) shale partings in limestones, and (6) red and purple shales common to Lower Permian strata. For ease of interpretation, facies (1) and (2) can be combined to form "outside shales" and (3) and (4) combined to form "inside shales."

Stratigraphically, these facies were found to be distributed in a number of zones.

1. In the Pleasanton, Kansas City, and Lansing Groups, there are regular alternations of limestones and inside shales separated into formations by thick beds of deltaic outside shales.
2. The succeeding Douglas Group, however, appears to contain only outside shales.
3. The Shawnee Group reverts to the limestone-inside shale alternation with outside shales separating limestone formations.

4. The Upper Pennsylvanian culminates in the Wabaunsee Group with outside shales and occasional limestones.
5. In the Admire, Council Grove, and Chase Groups of the Lower Permian, a general increase in the carbonate content is manifest in the development of calcareous outside shales (red and purple shale facies) separating the alternations of inside shales and limestones. Towards the top of the division evaporites are developed, although the geochemical data showed no evidence for increasing salinity.

Within the Pleasanton, Kansas City, and Shawnee Groups, Fourier analysis of the stratigraphical distribution of quartz, Al_2O_3, CaO, MnO, Ba, Cr, Ni, Mo, Cu, and Ga indicate the presence of 70-foot cycles in the shales that may be accounted for by orogenic events in the Ouachita foldbelt.

A multivariate statistical analysis elucidated the geochemical and mineralogical evolution of the Upper Pennsylvanian and Lower Permian shales and indicated that the stratigraphical variation in the mineralogical and geochemical data is controlled by nine components—a carbonate component, a black shale component, a clay mineral component, a dolomite component, a shallow versus deep water environment component, a manganese component, and three uninterpretable components. These carbonate and black shale factors may be related to the orogenic controls of outside and inside shales and, similarly, the manganese component is related to marine conditions of the inside shales. The dolomite component indicates that diagenetic activity has affected the shales particularly in the Lower Permian.

In conclusion, therefore, the research conducted has shown that the concept of cyclic sedimentation proposed by Moore is not conclusively supported by mineralogical, geochemical, or petrological data from the Upper Pennsylvanian and Lower Permian shales of Kansas. However, a simplification of the clastic classification to three components—calcareous marine shales, restricted marine black shales, and finally, deltaic and prodeltaic shales, sandstones, and siltstones suggests cycles at approximately 70-foot intervals in the Pleasanton, Kansas City, Lansing, and Shawnee Groups.

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JOHN M. CUBITT[1]

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INTRODUCTION

The Upper Carboniferous (Pennsylvanian) and Permian stratigraphy of Kansas has been extensively studied in the past 100 years, culminating in the development of the revolutionary concept of cyclic sedimentation by R. C. Moore in the 1930s. From a detailed examination of the lithology and paleontology of limestones in eastern Kansas, the repetitive sequence of characteristic fossiliferous limestones was accounted for by cyclic changes in sedimentary environments. This concept has developed dramatically in the past 15 years with applications to many different stratigraphic horizons and areas. For example cyclic sediments have been described from North America and Europe by Weller (1956, 1958, 1964), Read (1961, 1965, 1967, 1969), Merriam (1964), Duff *et al.* (1967), Read and Dean (1967, 1968, 1972), Reyment and Collinson (1971), Read and Merriam (1972), Mayers and Worsley (1973), Heckel (1978), and from Australia by Johnson and Cook (1973). It is notable that, although the concept has been widely accepted by geologists as a true representation of sedimentary processes, the original "ideal cyclic sequence" (Moore, 1936) is still being questioned.

Moore's ideal cyclothem, representative of much of the Upper Pennsylvanian and Lower Permian succession of Kansas (Moore, 1936, 1949, 1950, 1959), contains 10 lithological and paleontological units including six or more clastic units. Moore based this cyclothem on the occurrence of characteristic limestones—a molluscan limestone, a fusulinid limestone, and an algal limestone. However, the intervening poorly exposed shales have been studied only superficially and their mineralogy and petrology are largely unknown. It is on this point that the two serious alternatives to Moore's hypothesis seem to dwell (Davis and Cocke, 1972; Schwarzacher, 1967, 1969). These concepts are based on a three-state depositional system (limestone; thick, course, sandy, and silty shales; thin calcareous shales) which was developed from computer-oriented statistical analyses of detailed lithological and stratigraphical investigations.

As a further possibility, tectonic features of the Midcontinent suggest the presence of four possible shale facies—a clastic wedge lithology similar to Ferm's Appalachian facies (Ferm, 1973) derived from the Ouachita Mountains of Arkansas and Texas; a deltaic sandstone and siltstone facies derived from the lowlands to the east, northeast, and southeast of Kansas; a normal marine shale associated with fossiliferous marine limestones; and a marine black shale lithology.

In the light of the recent revival of interest in cyclic sedimentation, it is most important that the confusion surrounding the "classic" cyclic sequences of the Upper Pennsylvanian and Lower Permian of Kansas be removed and a hypothesis based on the regional tectonic framework of the U.S. Midcontinent

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established to account for the stratigraphic record during this period.

Therefore, a detailed study was conducted to determine the nature of the lithological variability in shales and relate this variability to known tectonic and environmental changes in Kansas during the Upper Pennsylvanian and Lower Permian. However, the poor exposure and monotonous nature of Carboniferous and Permian shales in Kansas hindered attempts to differentiate shale types in the field. The fine-grained nature of the shales also precluded detailed optical microscopic investigations of mineralogy and petrology. Instrumental techniques have, on the other hand, provided considerable information about the geochemistry and mineralogy of fine-grained clastics (Van Moort, 1972, 1973; Reimer, 1972) and their use has proved to be especially illuminating in the study of shales (Davis, 1967). Therefore, three techniques, X-ray diffraction providing details of the mineral composition of shales, emission spectroscopy providing trace element concentrations, and electron spin resonance revealing the structural positions of certain trace ionic constituents, were used to examine the mineralogy and geochemistry of the Carboniferous and Permian shales of Kansas.

From raw geochemical and mineralogical data, it was often impossible to differentiate shale types manually. However, with the aid of a computer, statistical analyses of the geochemical and mineralogical data revealed major variations among rock samples and consequently a classification of the shales was prepared. To relate this classification to field identifications, it was necessary to develop petrological and lithological classification by careful examination of thin sections and hand specimens. Fabric analysis using scanning electron microscopy provided additional information for distinguishing shale types (Gillott, 1969).

The three classifications of the Upper Pennsylvanian and Lower Permian shales of Kansas currently under examination (Moore, 1959; Schwarzacher, 1967, 1969; Davis and Cocke, 1972) are compared with the combined geochemical, mineralogical, and petrological classifications developed herein and any repetition of shale types based on the classification derived is explained in terms of the stratigraphy, tectonics, and paleogeography of the Midcontinent.

STRATIGRAPHY

The Upper Pennsylvanian. The Upper Pennsylvanian outcrops in Midcontinent North America from Iowa through Nebraska, Missouri, and eastern Kansas to Oklahoma and consists of approximately 650 m (2200 ft.) of alternating limestone and shale formations. The limestone formations with included thin shales average 5-15 m in thickness and generally contain abundant marine fossils; the intervening shale formations averaging 15-30 m are generally poorly fossiliferous.

The Upper Pennsylvanian stratigraphic section (Figure 1) consists of two Stages—the Missourian and Virgilian. The Missourian Stage lies unconformably on the Desmoinesian Stage of the Middle Pennsylvanian, and is subdivided into the Pleasanton, Kansas City, and Lansing Groups. Conformably overlying the Lansing are the Douglas, Shawnee, and Wabaunsee Groups of the Virgilian Stage.

At the base of the Missourian Stage of the Upper Pennsylvanian is the Pleasanton Group, which is composed of 10-45 m of shale with some sandstone, limestone, and coal (Jewett *et al.*, 1965). The irregular basal Hepler Sandstone Member rests in channels and is overlain by the South Mound Shale Member, the Checkerboard Limestone Formation, and the Tacket Formation. Shales are often rich in phosphate nodules (Runnels, 1949; Runnels *et al.*, 1953; Rose and Hardy, 1967) and organic material (Jewett, 1940). Some lenticular sandstones are present in the Tacket Formation and are locally known as the Knobtown sandstone and Charlton conglomerate (Branson, 1962b; Jewett *et al.*, 1965).

The Kansas City Group lying above the Pleasanton Group is characterized by six relatively thick, persistent limestone formations separated by six shale formations of variable thickness. Sandstones form a minor lithology in northern Kansas but thicken considerably towards Oklahoma (Schulte, 1959). Many of the limestones are algal, oolitic, and cross-bedded, locally thickening to form carbonate buildups (Hall, 1961; Merriam, 1963; Crowley, 1969; Hamblin, 1969; Heckel, 1972a, 1974, 1975a, 1975b, 1978). Thin discontinuous coal beds occur in the middle of the Kansas City Group and several "paper-thin" black shales act as marker horizons. This Group contains a number of limestones that wedge out in southern Kansas, e.g., in southern Allen County the Wyandotte Limestone pinches out, bringing the Bonner Springs Shale in contact with the Lane Shale to form a single inseparable unit termed the Lane-Bonner Springs Shale (Merriam, 1963). The Lane Shale has therefore been interpreted as a deltaic platform upon which the Wyandotte Limestone algal banks of eastern Kansas were formed (Crowley, 1969). Another deltaic clastic complex, the Bonner Springs Shale, then covered this buildup. Similar algal reefs have been

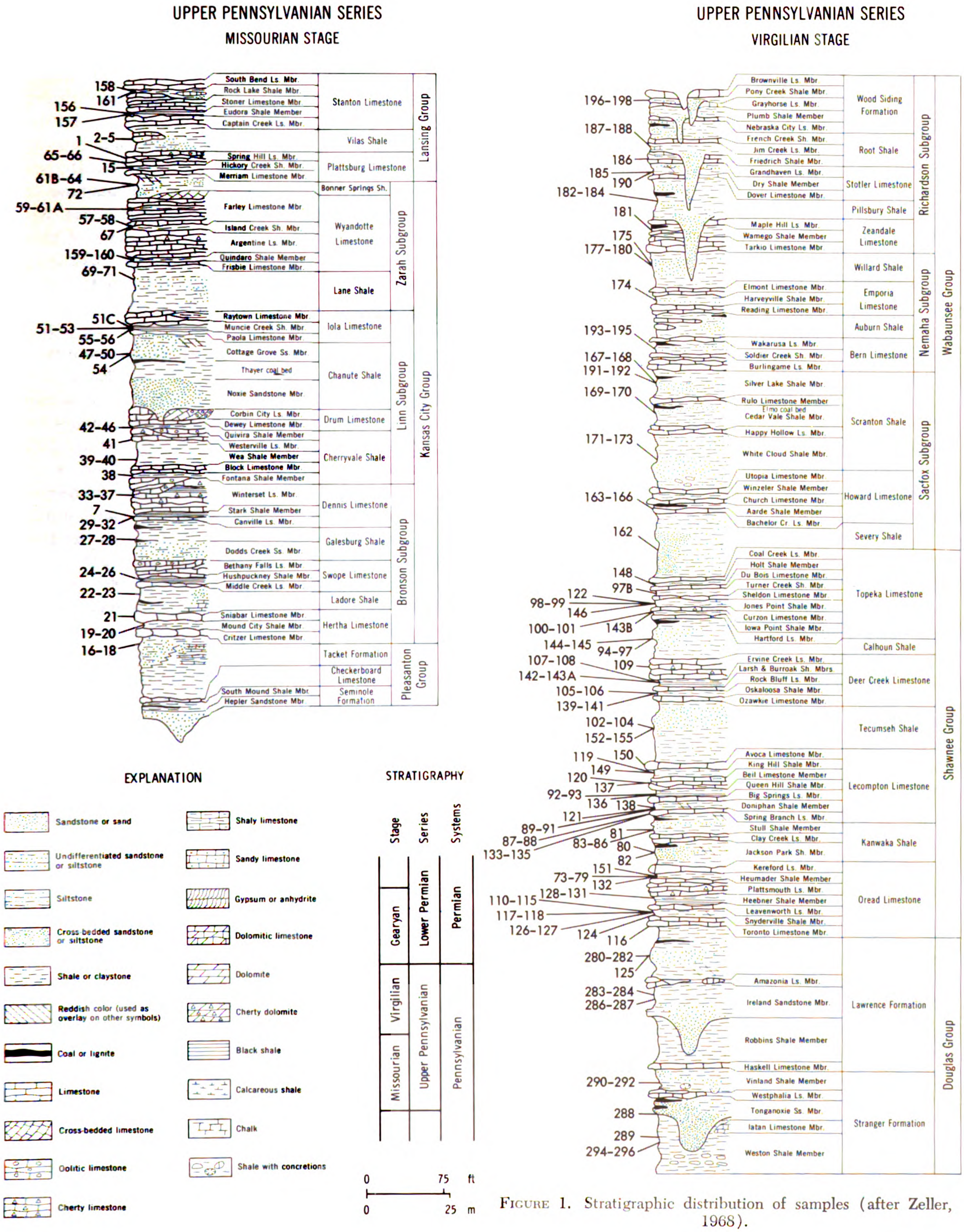

FIGURE 1. Stratigraphic distribution of samples (after Zeller, 1968).

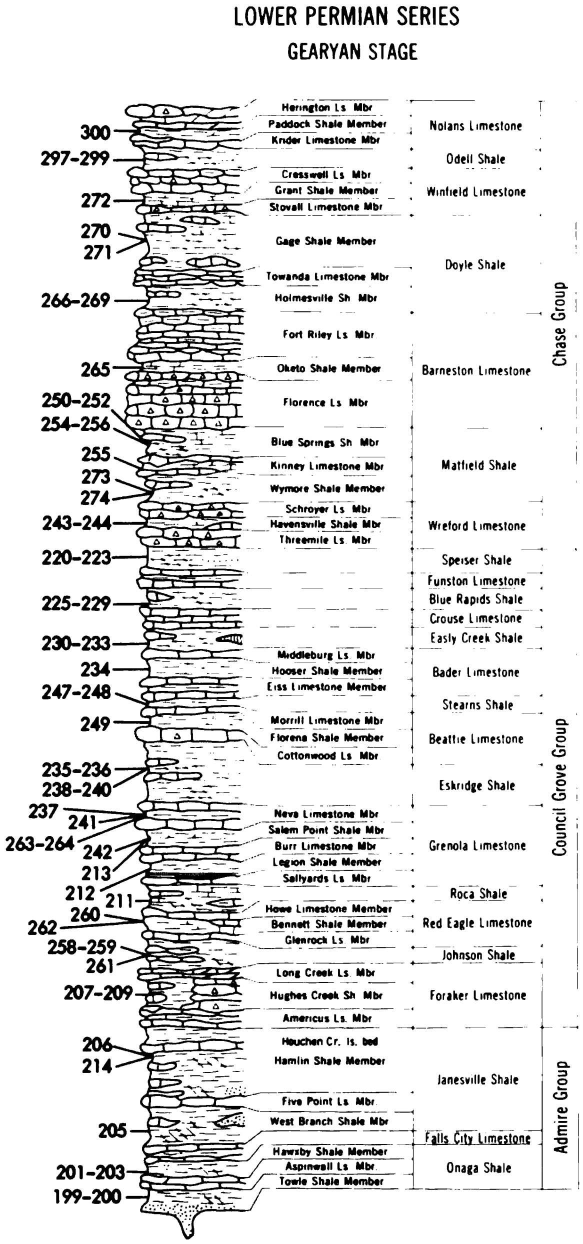

FIGURE 1. Continued.

reported in the underlying Iola (Heckel and Cocke, 1969), Dennis (Frost, 1968, 1975), Swope (Mossler, 1970, 1971, 1973; Scott, 1970), Cherryvale (Heckel and Cocke, 1969), and Hertha (Heckel and Cocke, 1969) Formations. Information on the intervening beds, with the exception of the Chanute Shale (Hall, 1961; Schulte, 1959), is minimal.

Conformably overlying the Kansas City Group is the Lansing Group consisting of two thick limestone formations separated by one shale formation. At the base, the Plattsburg Limestone consists of 7-28 m of limestone and shale, thickening towards the Oklahoma border. Algal buildups in the Plattsburg Limestone of southern Kansas have attracted much attention as possible oil traps (Davis, 1959; Harbaugh, 1959, 1960, 1964; Harbaugh *et al.*, 1965). The Vilas Shale Formation (Kinell, 1962) varies in thickness and lithology southwards, directly attributable to the surrounding marine banks (Harbaugh, 1959). It is generally a monotonous, unferruginous marine shale but locally beds of sandstone and fossiliferous sandy limestones are found (Zeller, 1968). The Lansing culminates with the Stanton Limestone Formation consisting of three limestone and two shale members (Russell, 1974). The Formation's most distinctive features are the algal buildups in the limestone members (Wilson, 1957a, 1957b, 1962; Heckel, 1972a, 1972b, 1974, 1975a, 1975b, 1978) and the Eudora black Shale Member comprising approximately one meter of greyish-black fissile shale with phosphate nodules overlain by 1-2 m of calcareous green-grey and dark grey shale and is recognized both in subsurface and outcrop (Murphy *et al.*, 1972; Heckel, 1975a, 1975b, 1978; Long, 1977). Trace fossils in the Rock Lake Shale indicate that the environment of deposition was represented by low wave energy euryhaline conditions (Hakes, 1975) and that the Rock Lake Shale marks a regressive phase before the transgressive South Bend Limestone.

The Douglas Group (O'Connor, 1963) consists largely of coarse shales and siltstones with occasional inpersistent thin limestones and local sandstone channels. A few thin coals make suitable marker horizons (e.g., Sibley coal beds). Beds in the group thicken from 80 m (260 ft.) in northern Kansas to 130 m (420 ft.) on the Kansas/Oklahoma border, but precise identification of horizons is problematic as distinguishing gross lithological characteristics are generally lacking and the lower boundary with the Lansing Group is often obscure (Ball, 1964). However, deltaic sandstone channels have been mapped in this Group by Winchell (1957), Sanders (1959), and Bower (1961). The Lawrence Shale Formation (Upper Douglas Group) was thought by Moore (1936, 1950) to represent a transgressive phase of sediment deposition. Faunal evidence now indicates that a restricted, marine environment existed and that no change from marine to non-marine can be inferred (Hakes, 1973). The Douglas Group is therefore considered to be a nonmarine phase separating the generally marine phases of the Lansing and Shawnee Groups.

The Shawnee Group consists of four limestone formations—Topeka, Deer Creek, Lecompton, and Oread Limestones—separated by thick shales and siltstones. Coals and sandstones are thin and of local occurrence only; e.g., the Elgin Sandstone (Brown, 1966, 1967) is a deltaic distributary complex that only outcrops in south-central Kansas. The thick limestone formations have been extensively described by Brown (1956), Perkins *et al.* (1962), Toomey (1964), Troell (1965, 1969), Galle and Waugh (1966), and Griesemer (1972) in terms of marine depositional environments, but the intervening Kanwaka, Tecumseh, and Calhoun Shale Formations are almost unknown (Hakes, 1975). Thin shales found in the limestone formations (Murphy *et al.*, 1972; Rowell, 1973; Von Bitter, 1972, 1973; Brondos, 1974; Long, 1977) are also poorly described with the exception of the Heebner Shale (Evans, 1967, 1968; Calder and Attaway, 1971), a paper-thin black shale lying between the Leavenworth and Plattsmouth Limestone Members. This is a very distinctive horizon and is consistently recognized both in outcrop and boreholes (Merriam, 1963). Shales of this type are recurrent features of the Kansas City, Shawnee, and Wabaunsee Groups and find extensive use as marker horizons (Moore, 1936, 1949, 1950, 1957).

The Wabaunsee Group conformably overlies the Shawnee Group and consists predominantly of shales and limestones with local sandstone lenses and several thin but persistent coal beds—the Nodaway and Elmo coals. The limestones are normally indistinguishable but the Dover, Zeandale, and Howard Limestones can be recognized by their lithology (Merriam, 1963). Channel sandstones occur in the Richardson Subgroup and often confuse the normal shale-limestone sequence (Mudge, 1956). A number of important underclays occur in association with the coals, e.g., Nodaway underclay (McMillan, 1956). The total group thickness is 165 m (540 ft.).

The Permian-Pennsylvanian boundary has been placed at the base of the Indian Cave sandstone of the Towle Shale Member (Zeller, 1968). This is unfortunately a poor choice of boundary as it is a channel sandstone of local importance only and is often difficult to recognize in the field. The Wellington Formation (Cimarronian Stage of the Lower Permian) has been suggested as an alternative by Branson (1960a, 1960b), and there has been recent palynological evidence for a Pennsylvanian-Permian boundary above the Eskridge Shale (Wilson, 1973). However, there is general agreement that little is to be gained by moving a boundary that has only reached reasonable stability in the past three decades.

The Lower Permian. The Lower Permian rocks of Kansas have been subdivided into two Stages, Gearyan (below), and Cimarronian (above). The Admire Group forms the lowest division of the Permian and consists of shale deposits with some thin limestones and coal beds. The sequence is similar to that of the underlying Wabaunsee Group and is difficult to differentiate on lithology alone. Conformably overlying the Admire Group is the Council Grove Group comprising approximately 100 m (325 ft.) of limestones and shales in 14 formations. The limestones are generally thinner and less massive than those in the overlying Chase Group, but they form a greater proportion of the total thickness than in the underlying groups. Another indication of changing sedimentary conditions is provided by the sudden increase in red and varicolored shales (Merriam, 1963). Together with cherty limestones, these characteristic sediments are interpreted by Moore and Merriam (1959) in terms of oscillating transgressions and regressions. This repetition is well developed in the Beattie Limestone (Walker, 1951; Imbrie, 1955; Imbrie *et al.*, 1959, 1964; Laporte, 1962; Elias, 1964; Laporte and Imbrie, 1964). The paleoecology of the Red Eagle Limestone has been interpreted in similar terms (McCrone, 1963) and the Eskridge Shale has been examined in connection with the Pennsylvanian-Permian boundary problem (Brookings and Chaudhuri, 1973) and depositional environments (Wells, 1950; Moore, 1957, 1959; Mudge and Yochelson, 1962; Cullers, 1974; Russell, 1974; Cullers *et al.*, 1975). Red shales, green shales, cherty and dolomitic limestones characterize and divide the Chase Group into seven alternating shale and limestone formations. There is a noticeable increase in the number of evaporite horizons, suggesting some restriction of the Kansas sea at this time. Little information is available, however, on horizons in the Chase Group (Murphy *et al.*, 1972), except those in the Wreford Limestone Formation, which have been examined paleontologically by Cuffey (1967), Newton (1970, 1971), Warner and Cuffey (1973), Bifano *et al.* (1974), and Lutz-Garihan (1974), sedimentologically by Hattin (1957) and Lutz-Garihan and Cuffey (1973), and geochemically by Cullers (1974) and Cullers *et al.* (1975).

CYCLICITY OF THE SEDIMENTS

R. C. Moore (1936, 1949, 1950, 1959, 1964) recognized repetitive associations of sediments in the Pennsylvanian and Permian stratigraphy of Kansas which he termed cyclothems and interpreted as recurrent transgression/regression sequences. The typical or "ideal" cyclothem (Figure 2) consists of 10 beds symmetrically developing from a non-marine sandstone or shale (0, 1a) up to a fusulinid limestone (5), representing the culmination of normal marine transgression, and then back to a non-marine shale and sandstone bed (9), representing the regressive marine

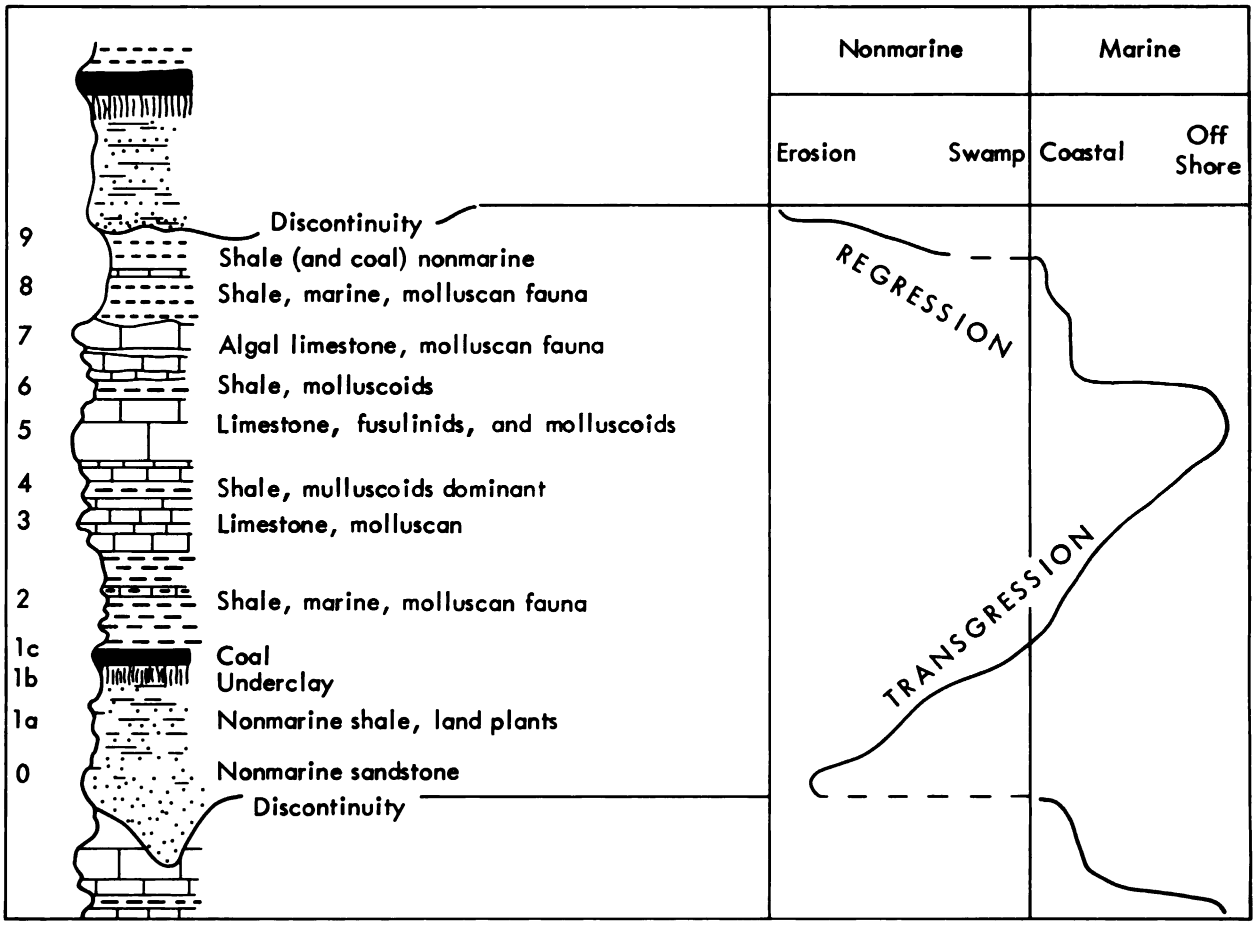

FIGURE 2. Diagrammatic section of Pennsylvanian rocks in Kansas showing the "ideal cyclothem" (after Moore and Merriam, 1959).

phase. This "ideal" cycle is characteristic of Wabaunsee Group sediments (Moore, 1949).

However, this is not a common occurrence in Kansas and a number of different cyclic sequences have now been recognized (Heckel, 1975a, 1975b, 1977; Heckel and Baesemann, 1975). In the Shawnee Group, for example, the most distinct cycle consists of a black shale followed by thick limestones separated occasionally by thin calcareous shales. Frequently, a thick, coarse, non-marine shale occurs between each group of thick limestones. The Lansing and Kansas City beds also contain cyclothems that bear no resemblance to the "ideal" cyclothem, and Abernathy (1937) noted little correlation between Cherokee cyclothems (Desmoinesian Stage) and the "ideal" cycle. However, recently Shannon (1978) recognized similarities in Cherokee cycles and clay mineral repetitions indicative of cyclic changes in depositional environments. In the Permian beds, cycles were recognized by Moore and Merriam (1959) and Elias (1937, 1964). The variation in Kansas cyclothems is summarized in Table 1 and it is clear that the "ideal" cyclothem is certainly not the typical cycle developed in Kansas. Merriam (1963) has pointed out that this variation is a result of the non-development of particular beds or their development and subsequent destruction. However, Branson (1962b) describes the situation more forcefully: "A general misconception of the nature of cyclical sediments has been widely held. An ideal cyclothem has not been found and in the Mid-Continent, no cyclothem approaches the ideal."

In comparison, Moore (1959) considered that the different Upper Pennsylvanian and Lower Permian sedimentary cycles recognized were minor variations of the "ideal" sequence. Repetitive occurrences of these cyclothem varieties were also noted and termed "cycles of cyclothems" or megacyclothems (see also Heckel, 1977, 1978). The Shawnee succession consists of two distinct cyclic sequences, a simple shale sequence which corresponds to one Wabaunsee cyclothem and the more common complex limestone-shale

TABLE 1. Variation in Kansas cyclothems.

PENNSYLVANIAN					LOWER PERMIAN
Desmoinesian		Missourian	Virgilian		
Cherokee	Marmaton	Kansas City and Lansing	Shawnee	Wabaunsee	
Shale, calcareous					
Limestone					
Shale, grey	Shale, grey to brown, or Limestone		Limestone	Limestone	Limestone
Shale, black	Shale, black, platey	Shale or Limestone with marine fossils	Shale, marine, black	Shale, marine	Shale, marine
Coal	Coal	Coal	Coal	Coal	
Underclay	Underclay	Underclay	Underclay	Underclay	(Evaporites)
Shale (sandy)	Shale (sandy, silty, and clayey)	Shale (sandy to clayey)	Shale, non-marine	Shale, non-marine	Shale, non-marine, red
Sandstone	Sandstone, non-marine	Sandstone, non-marine	Sandstone, non-marine	Sandstone, fine, micaceous	
Moore, 1949	Moore, 1949	Moore, 1949	Moore, 1936	Moore, 1950	Moore & Merriam, 1959

sequence which, with some imagination, corresponds to one or three Wabaunsee cycles. As a result, the Shawnee succession could represent a sequence of complex and simple cycles or megacyclothems.

Although some units, particularly limestones, can be traced from Oklahoma to Pennsylvania (Moore, 1959) and cover areas as large as 80,000 sq. mi. (Duff *et al.*, 1967), it is not easy to see how individual cyclothems and megacyclothems are delimited. Duff *et al.* have noted that units are not too infrequently assigned to different cyclothems in different studies, presumably indicating how incomplete the cyclothems are. This is further exemplified by the variation in the number and thickness of cyclothems recorded. Wanless (1950) recognized 25-30 cycles in Kansas, whereas Branson (1962b) identified 60 from the Oklahoma/Kansas border, 41 containing coals, and Merriam (1963) said that 85 cycles can be identified from the base of the Cherokee to the top of the Pennsylvanian system. In comparison, Kosanke *et al.* (1960) recognized only 37 from Illinois.

Schwarzacher (1969) analyzed the Kansas City and Shawnee cyclothems mathematically and developed a different classification of lithologies based on Merriam's (1963) original field descriptions. This cyclothem could be described as consisting of five limestone and one shale units in each cycle:

	EXAMPLE
LIMESTONE 5	Clay Creek
OUTSIDE SHALE	
LIMESTONE 4	Kereford
LIMESTONE 3	Ervine Creek
LIMESTONE 2	Leavenworth
LIMESTONE 1	Toronto
OUTSIDE SHALE	

"Limestone 1" to "Limestone 4" are separated by inside shales, of which the black shale following "Limestone 2" is the most characteristic. The reduction of the clastic beds from the "ideal" six or seven units to an outside/inside shale subdivision still preserves the cyclic nature of the sequence, and quantitative analysis revealed a 13-20 m (42-65 ft.) oscillation. This compares with a manual determination of 24.5 m (80 ft.) for the average cyclothem (Schwarzacher, 1969), the difference being attributed to the classification of the Douglas Group as an outside shale. Schwarzacher admits that this classification may be a mistake geologically but states there is no evidence for a missing cycle and it is obvious that the Douglas Group represents abnormal sedimentary conditions. Such irregularities are eliminated to an extent using the method of recurrent probabilities and it is for this reason that the reconstructed cyclothem is a valuable aid to interpreting the nature of the succession.

Nevertheless, Moore's cyclothem phases would be ideal lithological states if one were able to recognize the phases by their lithology and faunal characteristics. However, available descriptions do not allow such an identification, nor to the author's knowledge has such an attempt been successful. A less detailed classification is possible. By combining lithologies described as "yellowish shale, shales with plant fragments, silts, sands and sandstones" into one group and "grey fossiliferous shales, shales with predominantly molluscan fauna" and "black fissile shales" into a second group, two states can be obtained which closely resemble outside and inside shales. Thus a three-state system could be adopted consisting of limestone, outside shale, and inside shale (see Heckel, 1978).

Pearn (1964) distinguished only five lithologies in Pennsylvanian sediments which constituted a revised form of Moore's "ideal" cycle.

5. Limestone with fusulinids and molluscoids
4. Shale, molluscoids dominant
3. Limestone with molluscans
2. Shale, non-marine with coals, shale with molluscan fauna
1. Sandstone

Certain problems were recognized in classification by these five lithologies, yet it was noted that the average cyclothem observed in Kansas would be similar to that proposed by Moore (1959).

Davis and Cocke (1972), on the other hand, recognized 17 lithologies including nine clastic units in a study of Kansas City and Lansing Group cycles. Using a technique known as substitutability analysis, a classification procedure that groups states on the basis of their context in a sequence, it was concluded that lithologies must be grouped into fewer than eight states before any cyclic pattern emerges from the Upper Pennsylvanian succession. Further analysis revealed that the stratigraphical succession contains a pattern of alternating calcilutites, calcarenites, and marine shales. Sporadic incursions of coarser sediment may interrupt this pattern at any point. It may, therefore, be inferred that the various limestones and inside shale facies are interrelated and the occurrence of a specific lithological type at certain points within the sequence seems to have no great significance. In contrast, the coarser outside shales and siltstones seem to represent a clastic influx independent of the basic depositional pattern. Thus, Davis and Cocke infer that the limestone-inside shale depositional environment constitutes the normal sedimentation pattern with an occasional influx of coarser outside shales.

In recent studies of the Stanton Formation and the Shawnee Group in eastern Kansas, Heckel (1975a, 1975b, 1977, 1978) and Heckel and Baesemann (1975) have enlarged upon Moore's original concept of a typical cyclothem and have recognized a "basic cyclothem" consisting of an outside shale-limestone-core-shale (black)-limestone-outside shale sequence that is based upon detailed facies and paleontological analysis. Within this framework, black shales are recognized to be genetically distinct from the other shales on facies, conodont (Baesemann, 1973; Heckel and Baesemann, 1975), and geochemical evidence (Cubitt, 1975b) and are thought to have been formed during high sea-level periods when "a thermocline allowed prevailing trade winds to establish quasi-estuarine circulation cells resulting in depletion of bottom waters and concentration of phosphate" (Heckel, 1977, 1978). This contrasts with earlier visions of black shale formation that predominantly centered on a barred basin concept (Heckel, 1972a, 1972b). However, recent evidence from other Precambrian, Paleozoic, and Mesozoic epeiric and shelf seas suggest that tidal currents or progressive ventilation of the oceans may provide the mechanism for stagnation of bottom waters and development of black shale facies (Berry and Wilde, 1978; Klein and Ryer, 1978). The environment of deposition of these deposits remains problematic (see, for example, the alternative suggestions put forward by Heckel (1977, 1978) and Berendsen and Zeller (1978) for the depth of formation of black shales).

Moore's "ideal" cyclothem has, therefore, been questioned by detailed analysis of reported cyclic sequences. Yet there are many notable geologists who accept cyclic sedimentation without doubt. Zhemchuzhnikow (1958) wrote: "Those who accept rhythm in nature will find it when it is rather indistinct, and they will arrive at proper conclusions. Those who do not want to, will not find it even when it is obvious."

TECTONIC HISTORY OF MIDCONTINENT DURING THE UPPER PENNSYLVANIAN AND LOWER PERMIAN

Throughout the Pennsylvanian and Permian, Kansas was covered by a shallow epeiric sea (Heckel, 1972a, 1972b) and sediment was continually deposited in a number of broad, north-south trending anticlinal and synclinal structures (Figure 2). Local and external tectonic events affected the sedimentary succession throughout Kansas, and Weller (1956) went as far as to propose that cyclic patterns in Kansas sediments are a product of tectonism alone.

Structurally, Kansas is split into five regions (Merriam, 1963) that were active during the Pennsylvanian and Permian eras. The Forest City Basin (Anderson and Wells, 1968), occupying the northeast and eastern edge of the state, is a remnant of the earlier North Kansas Basin and has been a depositional area since the Arbuckle period (Lower Ordovician). It contains approximately 1300 m (4000 ft.) of Paleozoic sediments lying on Precambrian metamorphics with the greatest thickness of sediment recorded on the basin's western flank. The basinal axis, the Brownville Syncline (Condra, 1927) trends slightly east of north and lies close to the axis of the Nemaha Anticline, producing an asymmetrical basin profile.

The Nemaha structural zone was active during the Mississippian (Branson, 1962b; Merriam, 1963) and was block faulted down the east side (Berendsen, personal communication). Some sediments were eroded from the northern end and deposited along the eastern flank. The anticline separates the Forest

City Basin from the Salina Basin (Reed, 1954), a post-Mississippian syncline trending northwestwards and plunging northwards with the greatest thickness of sediment recorded in north-central Kansas. To the southwest of the Salina Basin lies an indistinct unnamed saddle (Merriam, 1963), delimiting the edge of the Sedgwick Basin. This shelf-like, northerly-plunging area in southern Kansas is a major pre-Desmoinesian, post-Mississippian structural feature. Southwards, sedimentary facies change and thicknesses increase as the Sedgwick Basin passes into the Anadarko geosynclinal Basin.

The extent of the Mississippian beds in Kansas outlines the northern-trending pre-Desmoinesian, post-Mississippian Central Kansas Uplift, and in the southwest lies a large shelf-like extension of the Oklahoma Anadarko Basin, the Hugoton Embayment (Maher and Collins, 1948). These areas separate the tectonically active Denver and Anadarko Basins, with sediments thickening considerably off the shelf (Denison, 1976; Rascoe, 1976). The Hugoton Embayment development was completed by the Mesozoic with a peak during the Desmoinesian.

Tectonic activity in these regions made a distinct impression on the sedimentary succession of Kansas but these effects were of minor significance in comparison to the tectonic activity in Kansas' neighboring states: in Oklahoma and Arkansas the Ouachita orogeny was reaching its peak in the Pennsylvanian and Permian; in Colorado, Idaho, and New Mexico the ancestral Rocky Mountains were developing rapidly; and in Missouri the Ozark Dome was shedding sediments into the epeiric sea covering Kansas.

Surrounding Kansas therefore during the Pennsylvanian and Permian was a series of mountain ranges stretching from the Ozarks of Missouri to the Black Hills of South Dakota (Figure 3). These were the major sources of sediment for the Kansas Basins, and tectonic events within the mountain regions produced dramatic changes in sediment deposition in the shelf seas of Kansas and Colorado (Figure 4).

Considering first the Ozark Dome of east-central Missouri, we find that the area remained a complex uplifted block of Precambrian and Cambrian igneous and sedimentary rocks from the early Paleozoic. Although channel sandstones are revealed in many Pennsylvanian deposits including Wabaunsee and Lower Permian sediments (Hinds and Greene, 1915; Mudge, 1956; Mudge and Yochelson, 1962), the Dome is considered to have been stable during this period (Elias, 1964) and sediments deposited in the Forest City Basin were predominantly silts and clays (Anderson and Wells, 1968).

To the south of the Ozark Dome lie the Ouachita Mountains (King, 1961; Morris, 1973; Gordon and Stone, 1973; Haley and Charles, 1973; Viele, 1973), an Arkansas range that developed during orogenic movements in the Mississippian, Pennsylvanian, and Permian Eras (Keller and Cebull, 1973). Structurally associated with the Ouachitas are the Arbuckle and Wichita Mountains of Oklahoma and the Amarillo Uplift of Texas. This chain of mountains forms one arm of the Ouachita-Appalachian tectonic region (Thomas, 1973) that has been interpreted in terms of the Dewey and Bird (1970) model for a thermally-driven cordilleran-type mountain belt by Keller and Cebull (1973), Rowett and Walper (1973), Walper and Rowett (1973), Cebull and Keller (1974), Cebull *et al.* (1974), Griffin (1974), Rowett (1974), Cebull *et al.* (1976), Thomas (1976), and Wickham *et al.* (1976). It is generally accepted that the Ouachita orogenic belt developed as the failed arm of a three-armed radial rift system (Hoffman *et al.*, 1974; Stewart, 1976) and represents a continent/arc collision (Walper and Rowett, 1973; Hatcher, 1973, 1974) marking an early event in the opening of a proto-Atlantic Ocean. Walper and Rowett also propose that the Ouachita orogenic belt is continued in the foldbelts of Mexico and Central America and that apparent offsets in the tectonic belt are manifestations of ancient transform faults (Cebull *et al.*, 1976).

In Colorado, northern New Mexico, and southern Idaho, a chain of mountains commonly known as the Ancestral Rocky Mountains developed in response to orogenic movements during the Late Devonian to early Mississippian or early Pennsylvanian interval. Sediments were shed into deep basins on either side of this chain during the Pennsylvanian and Permian Eras developing approximately 5000 m (16,250 ft.) of coarse clastics in the Denver Basin (Chronic, 1964). No easterly sediment transport directions have been recorded in west Kansas as the effects of the orogenic movements were limited to Colorado and little sediment reached Kansas.

The Ancestral Rockies are continued in Idaho by the Bighorn Mountains, a long sinuous mountain chain marking the western boundary of the Powder River Basin. Undulating deltaic lowlands persist from North Dakota to the Ozark Dome and form the boundary for the Powder River Basin, Denver Basin, and Kansas shelf sea. The lowlands were not tectonically active during the Pennsylvanian and Permian and supplied limited quantities of sediments to the basins (McKee and Crosby, 1975).

It would appear that the Kansas shelf sea was surrounded by lowlands and orogenic mountain belts.

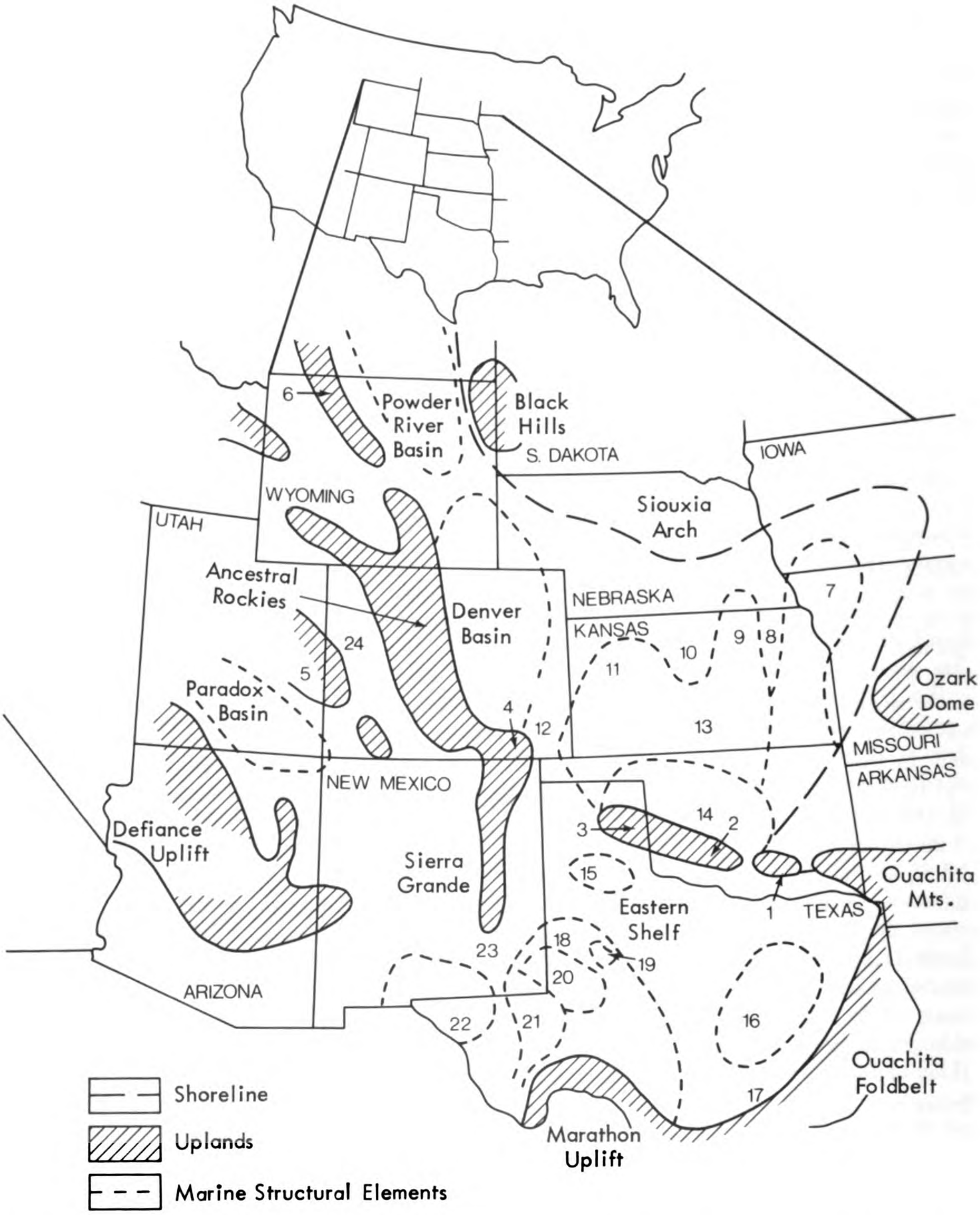

FIGURE 3. Tectonic features of the Midcontinent during the Upper Pennsylvanian and Lower Permian (information obtained from Flawn *et al.,* 1961; Branson, 1962b; Rascoe, 1962; Wilson, 1962; Merriam, 1963; McKee and Oriel, 1967; Clark and Stearn, 1968; Troell, 1969; Dott and Batten, 1971; Fagerstrom and Burchett, 1972; Heckel, 1972a, 1972b; Hills, 1972; Galloway and Brown, 1973; Lumsden *et al.,* 1973; Ross, 1973; Jacka, 1974; and Werner, 1974).

1. Arbuckle Mts.
2. Wichita Mts.
3. Amarillo uplift
4. Apishapa uplift
5. Uncompahgre uplift
6. Bighorn Mts.
7. Forest City basin
8. Nemaha Anticline
9. Salina Basin
10. Central Kansas uplift
11. Hugoton embayment
12. Dalhart basin
13. Sedgwick basin
14. Anadarko basin
15. Plainview basin
16. Fort Worth basin
17. Llano uplift
18. Midland basin
19. Scurry platform
20. Central basin platform
21. Delaware basin
22. Diablo platform
23. Northwestern shelf
24. Central Colorado trough

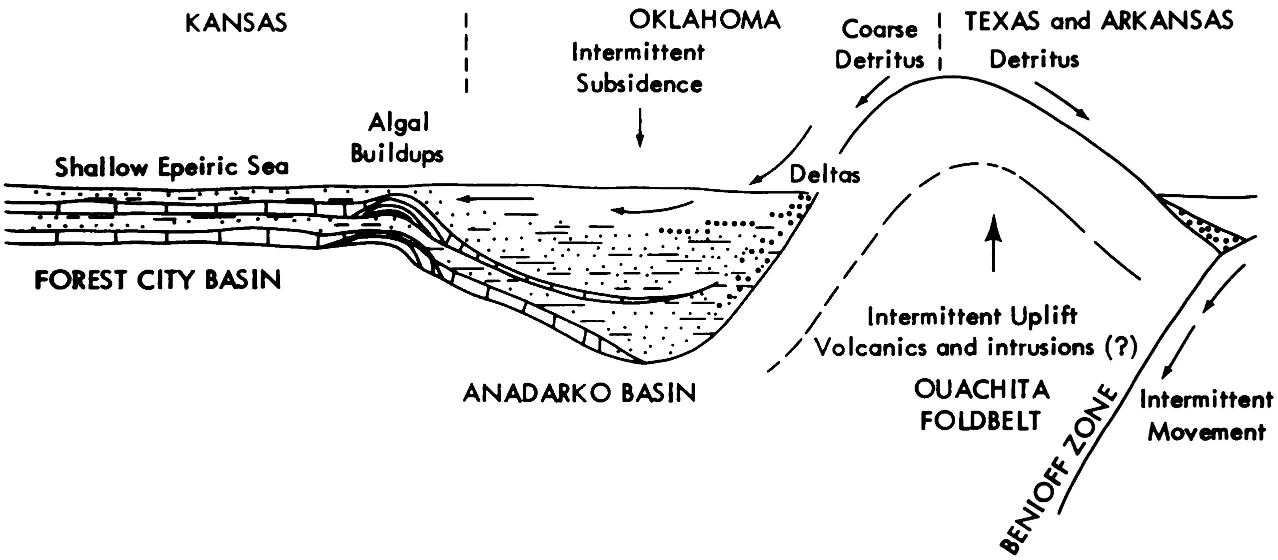

FIGURE 4. A schematic section illustrating detrital sediment buildup in Kansas with the orogenic development of the Ouachita foldbelt.

However, one narrow channel to the open marine seas in northwest Texas existed. The Dalhart Basin, separating the Amarillo Uplift and the Apishapa Uplift (part of the Ancestral Rockies), may have formed a shallow barrier bar during the Pennsylvanian and Permian and produced, in extreme conditions, a stratification of the seas in the Kansas area, anaerobic bottom waters, and the development of a black shale lithology (cf. Black Sea. sediments, Heckel, 1972a, 1972b).

To illustrate the tectonic development of the Midcontinent during the Pennsylvanian and Permian, three generalized paleogeographic maps are presented (Figures 5, 6, 7). Initially, in the early Paleozoic, a Benioff zone was instigated in the Gulf Coast region of Texas and slow movement of the oceanic plate down the Benioff zone resulted in the development of an orogenic zone in Arkansas, Texas, and Oklahoma. A shallow shelf sea extended northwards from the orogenic belt onto the stable cratonic continental crust of Kansas, with a deep subsiding basin, the Anadarko Basin, separating them. During the early Pennsylvanian, development of the orogenic belt reached its peak, as an "orogenic welt" arose and great thicknesses of flysch were deposited on the collapsing shelf (McBride, 1969). Some of these "clastic wedges" (Ferm, 1973) spread over the shelf, thinning rapidly northwards, and in the Forest City Basin, the thicker, coarser shales may represent the finer fraction of the "clastic wedge" lithologies. The flysch deposits were followed in the late Pennsylvanian/early Permian periods by a mollasse facies marking the cessation of subduction and orogenic activity. Subsequently, stabilization of the orogenic belt resulted in the disappearance of "clastic wedges" from Kansas and the development of evaporite/carbonate sedimentary sequences.

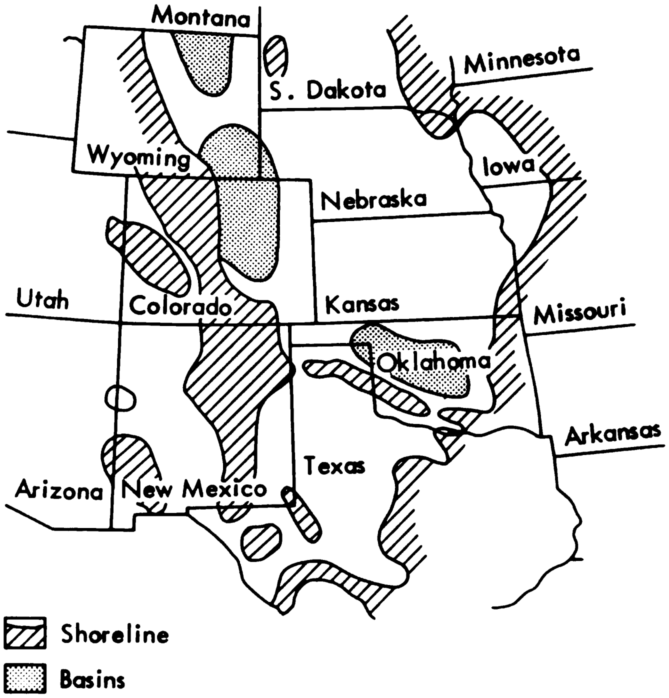

FIGURE 5. Upper Pennsylvanian (Missourian Stage) paleogeography of the Midcontinent (adapted from Sloss *et al.*, 1960; Rascoe, 1962; Wanless *et al.*, 1970; and Moore and Nelson, 1974).

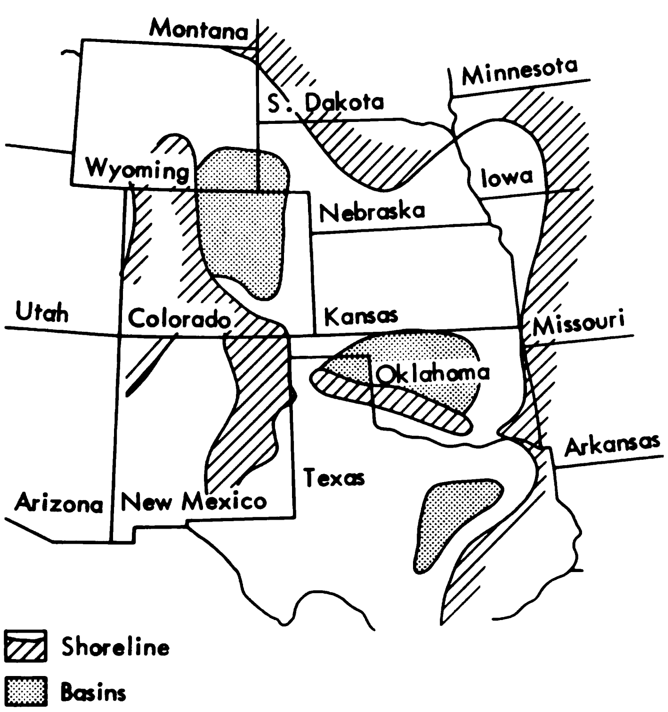

FIGURE 6. Upper Pennsylvanian (Virgilian Stage) paleogeography of the Midcontinent (adapted from Sloss *et al.*, 1960; Rascoe, 1962; Schubert, 1963; Clark and Stearn, 1968; Troell, 1969; Dott and Batten, 1971; Heckel, 1972b; and Moore and Nelson, 1974).

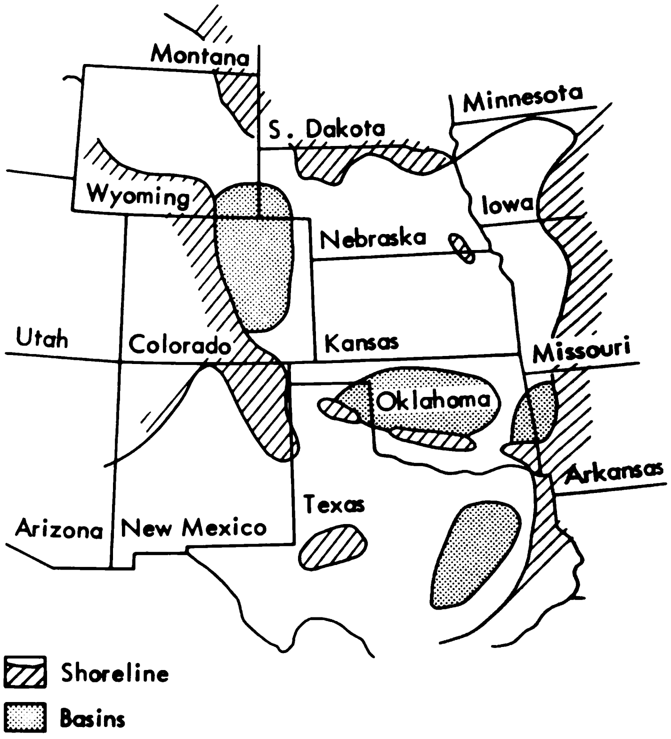

FIGURE 7. Lower Permian (Gearyan Stage) paleogeography of the Midcontinent (adapted from Sloss *et al.*, 1960; Rascoe, 1962; Schubert, 1963; Elias, 1964; McKee and Oriel, 1967; Hills, 1972; Ross, 1973; Seyfert and Sirkin, 1973; and Moore and Nelson, 1974).

Bott and Dean (1973) studied stress diffusion at plate boundaries and noted that movement along subduction zones was of cyclic nature, i.e., movement along the zones was possible only when frictional resistance was overcome by continually increasing pressure originating from the mid-ocean ridges. It is to be suspected that similar conditions existed in the Pennsylvanian and we can infer that the Ouachita Mountains development was cyclic and that the occurrence of thick, coarse "clastic wedge" deposits in Kansas is a reflection of this cyclic mountain building. This may account for the regular repetition of coarse clastics in the sedimentary succession. The excessively thick Douglas clastics may also be explained in terms of sudden large-scale orogenic movement (possibly, the culmination of the Pennsylvanian orogeny) in the Ouachita belt.

Thus, in Kansas during the early Pennsylvanian, it is speculated that the rise of the Ouachita system deposited thick clastics in the Anadarko Basin and, during sudden uplifts in the mountain chain as a result of cyclic subduction, clastic wedges spread out onto the shelf sea of Kansas. This situation predominated until orogenic movement ceased at the end of the Permian era.

The normal sedimentary deposits formed in the Kansas epeiric sea during the Pennsylvanian consisted of limestones alternating with thin, calcareous shales (Heckel, 1972a). Algal buildups of southern Kansas developed in response to subsidence in the Anadarko Basin. In comparison, the intervening clastics were deposited from deltas on the lowlands to the east and north of Kansas.

The orogenic belt of Colorado, New Mexico, and Idaho throughout this period was providing coarse clastic sediments for the Denver and Powder River Basins but had little direct effect on the sedimentary succession of Kansas. It did, however, complete a ring of land around Kansas, providing a classic epeiric sea setting for the Kansas shelf. The narrow Dalhart Basin separated the Ouachita and Rocky Mountains and may have formed a barred entrance to the Kansas sea. As a result, stratification of the epeiric sea may have occurred at a number of times during the Pennsylvanian (Heckel, 1972a), encouraging anaerobic conditions to prevail in the bottom waters and sediments of the sea. Black shales, a distinct lithology used as a marker horizon in the "ideal" cyclic sequences

(Moore, 1950), may be developed in these anaerobic conditions and are normally enriched in trace elements. Alternatively, the narrow basinal entrance may have provided suitable conditions for the development of quasiestuarine circulation cells (Heckel, 1978).

With the cessation of orogenic development in the Ouachitas at the beginning of the Permian (Figure 7), the paleogeographic conditions of the Midcontinent changed dramatically. Carbonate deposition increased and, towards the end of the Council Grove Group, evaporite sediments developed substantial thicknesses. The Amarillo Uplift-Wichita Mountains-Arbuckle Mountains belt became a series of islands (Rascoe, 1962) separating the Ouachita and Rocky Mountains, and the Kansas epeiric sea became a partially barred carbonate/evaporite basin similar to that of the Mediterranean during the Miocene (Hsu *et al.*, 1973). The tear-drop distribution of carbonate and evaporite sediments (McKee and Oriel, 1967, Figure 4) reflects the partially barred nature of the Kansas Permian sea.

To summarize, therefore, tectonic events in Oklahoma, Texas, and Arkansas have affected the Pennsylvanian and Permian sedimentary succession in Kansas and suggest a fourfold division of the clastic sediments. First, there are the carbonate-rich shales characteristic of "normal" carbonate/shale deposition in the Kansas epeiric sea. The second division is a variation of this theme—the distinctive black shale lithology characteristic of anaerobic bottom waters or upwelling phosphate-rich waters. Next, from the east came a number of deltaic channel sandstones, siltstones, and shales that were deposited in the Forest City Basin. Finally, thick, coarse clastic units are found at regular intervals up the Pennsylvanian stratigraphic section that are derived from the Ouachita tectonic belt of Oklahoma, Arkansas, and Texas.

SAMPLING PATTERN

Stratigraphically, each clastic horizon in the Upper Pennsylvanian and Lower Permian is not necessarily restricted to a unique lithology. In fact, in Moore's classification, two or even three lithological divisions of a cyclothem could be found in one clastic bed. As Moore based his conclusions on field and hand specimen evidence, it was concluded that lithologies, recognizably different in the field, should be sampled for mineralogical, petrological, and geochemical analysis. Samples were collected from horizons in the Tacket Formation (Pleasanton Group) and all clastic units up to the Paddock Shale Member of the Nolans Limestone (Chase Group); the distribution can be seen in Figure 1. The only exceptions were the Auburn and Winzeler Shales (Wabaunsee Group) where lack of surface exposure prevented adequate collection.

Samples collected for each horizon are considered representative of a single shale facies for many miles along the outcrop strike. Merriam (1963), for example, has commented on how it is possible to recognize single lithologies over remarkable distances in Kansas and how stable bed thicknesses are.

The distribution of sample collecting stations in eastern Kansas (Figure 8) was restricted to the Forest City Basin. A comparison of the sample distribution and Heckel's concept of facies belts within the Pennsylvanian (Heckel, 1978) indicates that the majority of samples were collected in the "open marine facies." However, adequate exposures in some cases could only be found in southern Kansas. In the latter situation, it should be noted that clastic deposits do coarsen and thicken southwards from south Kansas into the Anadarko Basin of Oklahoma implying that the south Kansas outcrops will not necessarily be representative of the normal Pennsylvanian and Permian sediments in the Forest City Basin. Interpretation of analytical results in succeeding sections will take this into consideration.

Outcrops of Pennsylvanian and Permian deposits are found along highways cutting east-west across the state (Plate 1). Samples collected from such exposures were extracted at a depth of six inches from the surface to obtain relatively unweathered sediments. Suitable samples were then thin-sectioned and analyzed by X-ray diffraction, emission spectroscopy, and electron spin resonance. Appendix 3 summarizes the sampling information in tabular form, recording sample number code, collecting station, and analyses performed on each sample.

Analyses were performed on a representative selection of sediments extracted from the total sample collection. This was considered necessary to establish overall trends and cycles throughout the stratigraphical section and avoid unnecessary noise caused by minor lithological variations. Therefore, only gross lithologies were analyzed for mineralogical and geochemical variations.

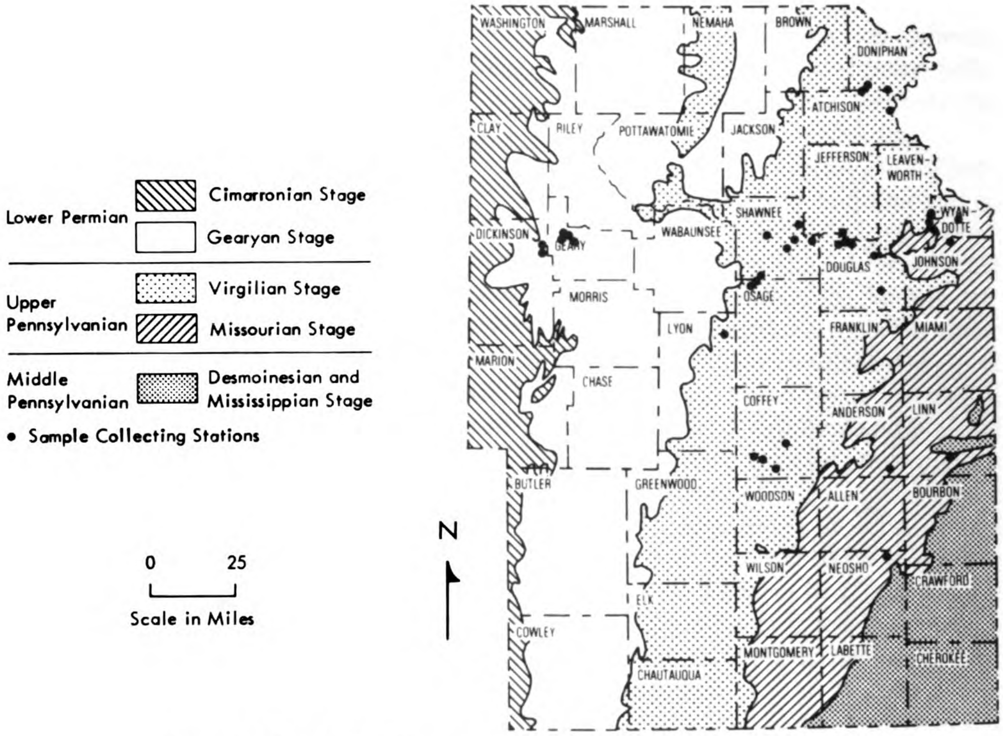

FIGURE 8. Distribution of sample-collecting stations in eastern Kansas.

Plate 1.A. Important outcrops of Shawnee Group beds on Interstate 70, west of Lawrence, Kansas.

Plate 1.B. Road cutting exposure of Vilas Shale near Altoona, Wilson County in southern Kansas.

MINERALOGY

INTRODUCTION

The objectives of this section are twofold—to determine the mineralogical nature of the Upper Pennsylvanian and Lower Permian shales of Kansas, and to observe and account for the stratigraphic distribution of the major mineral components. Using the X-ray diffraction techniques developed in Appendix 1 and discussed in Cubitt (1975a, 1975b), it is possible both to identify the minerals and to quantify the major components present in the shales. The resulting stratigraphic distribution of minerals throughout the Upper Pennsylvanian and Lower Permian shales can be plotted, analyzed, and interpreted in terms of changing tectonic and sedimentary environments. Similarly, any periodic elements detected in the mineral distributions can be examined and tested by statistical analysis.

ANALYTICAL EQUIPMENT AND TECHNIQUE

The equipment employed in the X-ray diffraction analysis consisted of a Norelco X-ray Diffractometer, wide-range goniometer, AMR3—202 LiF curved crystal monochromator, proportional counter, and pulse-height analyzer.

All shale samples were ground to less than 60 microns and prepared for X-ray diffraction analysis using the sample mounting procedure described in Appendix 1. Individual samples were then placed in the sample cavity of the Norelco Diffractometer and examined at $2°2\theta$/min. over a period of 30 minutes under standard conditions (Cubitt, 1975b). All major peaks were recorded within the range $2°2\theta$ to $60°2\theta$ and minerals present were identified.

X-RAY IDENTIFICATION AND CHARACTERISTICS OF MINERALS

The identification of minerals in the X-ray diffraction traces was primarily achieved by examining standard d-spacings in the ASTM Powder Data File. However, several clay minerals are not easily identified using this method and tests on the shale samples were required to establish the species present. The standard identification procedure for clay minerals (Carroll, 1970; Griffin, 1971) was therefore adopted.

1. *Position of main peaks.* This is of primary importance in the identification of minerals as each has a unique and characteristic set of peak positions.

2. *Effects of glycolation on peak positions.* Normally montmorillonite, illite, and the interstratified clay minerals are indistinguishable as major peak positions overlap, and minor peaks are inevitably lost in background noise. However, they may be differentiated by their swelling reactions in an atmosphere of ethylene glycol; illite does not respond to the organic reagent but swelling clays such as montmorillonite absorb the molecules, producing an expansion of the crystal lattice and a characteristic shift in major peak positions on the diffraction trace.

3. *Effects of heating on peak positions.* Heating clay minerals results in an initial loss of water from the crystal lattice, especially in the case of illite, and at higher temperatures volatilization of organic molecules from the interlayer sites. Other notable features include the breakdown of kaolinite to an amorphous state at 500-600°C and chlorite at 800°C. Each of these events is marked by a drop in height of the X-ray peaks on the diffraction trace. Table 2 illustrates the important role these effects play in the identification of clay minerals in shale samples.

The major mineral constituents of the shales were identified as quartz, calcite, dolomite, feldspar, illite, chlorite, and kaolinite. The following secondary minerals were also recorded: gypsum, jarosite, pyrite, mixed layered illite-montmorillonite, montmorillonite, and swelling chlorite. The feldspar minerals detected could not be individually identified although considerable effort was spent attempting to implement the X-ray and optical techniques of Goodyear and Duffin (1954), Smith (1956), Smith and Yoder (1956), and Wright (1968). These complicated and laborious procedures were discovered to be excessively time-consuming in sediment analysis and are considered appropriate only for igneous rock studies where considerable feldspar is often available. ASTM identification of feldspars also proved fruitless because it is essentially based not on the main peak positions, which occur within a very narrow range on the diffraction trace, but on secondary peaks. In all the shale samples studied, no secondary peaks were detected, presumably because the feldspar concentration is too low. Attempts at separating the feldspar

TABLE 2. Effects of test treatments on peak position of major minerals in the shale samples.

Mineral	Basal Spacings (001 Unless Stated Otherwise)	2θ Transformation on Main Peak	Effect of Glycolation on Peak Position	Effect of Heating on Peak Position
Quartz	3.34Å (101); 4.26Å (100)	26.66 20.85	none	none
Feldspar	3.30Å	27.70	none	none
Calcite	3.03Å (104)	29.47	none	none
Dolomite	2.88Å (104)	30.05	none	none
Chlorite	14.1Å + integral series of basal spacings	6.27	none	(001) increases in intensity; at 800°C shows wt. loss (Mg form)/collapse (Fe form)
Kaolinite	7.15Å; 3.75Å (002)	12.56	none	Becomes amorphous at 550-600°C
Illite	10Å (002) broad	8.70	none	(001) more intense as H_2O removed from structure

N.B. Disordered kaolinite shows broadening of X-ray peaks.

content from the other minerals were also inconclusive. Dr. McCaleb of Sun Oil Company kindly examined a number of shale samples with high peak area measurements of feldspar (e.g., samples 96 and 170). On the basis of automated X-ray diffractometer readings, they were found to contain approximately 20 percent orthoclase and little or no plagioclase feldspar. This result seems dubious in the light of petrological investigations of the shales, where distinct albite-twinned plagioclase laths were recognized. In this study, a decision was therefore made to employ the general term feldspar for the X-ray measurement taken.

X-RAY MEASUREMENTS MADE ON SHALE SAMPLES

The following X-ray measurements were taken on samples prepared using the technique described in Appendix 1. First, peak height readings were taken of the quartz (100) peak at 26.66°2θ, the calcite (104) peak at 29.47°2θ, the feldspar peak at 27.7°2θ, the dolomite (104) peak at 30.05°2θ, the kaolinite (001) peak at 12.36°2θ, the illite (001) peak at 8.70°2θ, and the chlorite (001) peak at 6.87°2θ. Then peak areas were calculated for the quartz (101) peak at 20.85°2θ, the calcite (104) peak, the dolomite (104) peak, and the feldspar peak at 27.7°2θ. Interference from other mineral peaks was negligible, therefore avoiding inconsistent peak area measurements. Finally, using the calibration charts for quartz, calcite, and dolomite developed by Cubitt (1975a), percentages were estimated. A feldspar calibration curve could not be established because of the identification problem mentioned previously, and no curves could be set up for clay minerals as variable crystallinity prevented exact matching of sample clay minerals and "spikes." The results of the X-ray diffraction analyses are presented in Table 3.

STRATIGRAPHIC DISTRIBUTION OF MINERALS

X-ray measurements described previously were taken on the major components of 127 clastic rock samples from the Upper Pennsylvanian and Lower Permian of Kansas (Table 3). The stratigraphic positions of these samples can be seen in Figure 1 and their geographic position will be found in Appendix 3. The results can be summarized as a statistical table (Table 4) and as a series of graphs (Figure 9) showing the mathematical distribution each mineral describes.

Quartz forms the major mineral component of most shales and varies from 14 to 96 percent as a unimodal population with a slightly skewed distribution. The tail towards the higher value end of the histogram is produced by a number of sandstones and siltstones with high quartz values.

Stratigraphically, the distribution of quartz in Upper Pennsylvanian and Lower Permian shales (Figure 10)[*] can be interpreted in terms of five zones. First the Pleasanton, Kansas City, and Lansing Groups are distinguished by samples with relatively low concentrations of quartz (from 17 to 57 percent) and large fluctuations in concentration between samples. Second, the Douglas Group clastics are rich in quartz

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[*] Note that the stratigraphic distributions illustrated, with the exception of Figures 21, 36, 44, 47, and 48 are calculated by averaging, for individual stratigraphic members, all included sample values. By carefully examining the mineralogical and geochemical results, most of the data variation was found to be between members rather than within members, allowing a certain degree of artistic license in illustrating the stratigraphic distributions. It is primarily for simplicity of illustration therefore that sample averages are employed. However, it should also be noted that interpretation of these distributions takes the generalization into account, and that the figures considered of major importance to the conclusions drawn in each chapter contain all sample values (Figures 21, 36, 44, 47, and 48).

TABLE 3. Results of X-ray diffraction analyses of Pennsylvanian and Lower Permian shales of Kansas.

	X-ray Diffraction Measurements														
	Quartz			Calcite			Feldspar		Dolomite			Kaolinite	Illite	Chlorite
Sample Number	Peak Area	Peak Height	Percent	Peak Area	Peak Height	Percent	Peak Area	Peak Height	Peak Area	Peak Height	Percent	Peak Height	Peak Height	Peak Height
16	10833.00	100.00	57.00	2387.00	7.00	3.00	6119.00	23.00	2547.00	7.00	5.00	21.00	32.00	22.00
19	7393.00	100.00	41.00	2941.00	7.00	4.00	4310.00	15.00	2811.00	5.00	6.00	28.00	33.00	21.00
20	8684.00	100.00	47.00	5475.00	21.00	8.00	4962.00	21.00	5135.00	18.00	11.00	15.00	22.00	18.00
21	4227.00	53.00	24.00	16629.00	64.00	23.00	2790.00	9.00	7786.00	36.00	17.00	10.00	14.00	15.00
23	4019.00	44.00	22.00	15358.00	48.00	21.00	2979.00	8.00	7551.00	28.00	16.00	7.00	13.00	14.00
24	7208.00	76.00	40.00	4043.00	7.00	6.00	4306.00	12.00	3405.00	11.00	7.00	10.00	18.00	15.00
25	6806.00	96.00	38.00	3387.00	7.00	5.00	4534.00	17.00	3248.00	7.00	7.00	17.00	33.00	16.00
26	8200.00	100.00	46.00	4036.00	12.00	6.00	5377.00	19.00	2758.00	5.00	6.00	12.00	31.00	21.00
27	4273.00	53.00	24.00	20557.00	85.00	28.00	2355.00	9.00	1532.00	4.00	2.00	7.00	11.00	15.00
28	7445.00	87.00	42.00	3743.00	9.00	6.00	5866.00	10.00	3391.00	8.00	7.00	6.00	30.00	24.00
7	9564.00	100.00	50.00	3965.00	8.00	6.00	4127.00	10.00	4113.00	7.00	9.00	7.00	17.00	16.00
31	6152.00	91.00	35.00	3371.00	8.00	5.00	4650.00	16.00	3402.00	7.00	7.00	20.00	32.00	18.00
32	6754.00	90.00	37.00	3692.00	8.00	6.00	6291.00	18.00	4071.00	8.00	8.00	14.00	27.00	17.00
34	6456.00	86.00	36.00	7012.00	10.00	10.00	4938.00	15.00	5283.00	7.00	11.00	16.00	28.00	17.00
36	5688.00	66.00	32.00	15487.00	65.00	21.00	4015.00	12.00	2194.00	10.00	4.00	14.00	17.00	13.00
35	2709.00	31.00	17.00	21779.00	89.00	29.00	1980.00	8.00	15858.00	85.00	35.00	4.00	9.00	11.00
38	6003.00	97.00	34.00	3950.00	10.00	6.00	4872.00	14.00	2889.00	7.00	6.00	17.00	32.00	20.00
40	6543.00	97.00	37.00	3154.00	7.00	4.00	4583.00	15.00	2884.00	5.00	6.00	25.00	44.00	27.00
41	4176.00	68.00	23.00	13700.00	71.00	19.00	3498.00	18.00	4197.00	10.00	9.00	18.00	24.00	17.00
43	5875.00	74.00	33.00	3498.00	6.00	5.00	4951.00	14.00	3544.00	6.00	7.00	12.00	26.00	18.00
46	6240.00	86.00	35.00	4619.00	11.00	7.00	5399.00	14.00	3664.00	10.00	8.00	19.00	30.00	19.00
47	6659.00	99.00	37.00	4771.00	13.00	7.00	4662.00	15.00	3672.00	6.00	8.00	19.00	33.00	20.00
48	7402.00	100.00	42.00	4319.00	12.00	7.00	4650.00	15.00	4707.00	12.00	10.00	17.00	42.00	19.00
54	7465.00	100.00	42.00	12815.00	65.00	18.00	3862.00	34.00	2314.00	5.00	5.00	11.00	23.00	11.00
50	4998.00	69.00	28.00	7128.00	25.00	11.00	4687.00	16.00	2992.00	4.00	6.00	6.00	16.00	19.00
53	4087.00	46.00	23.00	2408.00	7.00	3.00	6119.00	7.00	2037.00	4.00	4.00	8.00	15.00	16.00
69	6721.00	100.00	38.00	3097.00	8.00	4.00	3457.00	16.00	3402.00	7.00	7.00	36.00	37.00	20.00
70	8113.00	100.00	44.00	3856.00	7.00	6.00	6071.00	17.00	3083.00	5.00	6.00	36.00	32.00	20.00
71	8926.00	100.00	48.00	3547.00	12.00	6.00	6044.00	29.00	2544.00	7.00	5.00	23.00	36.00	25.00
160	5971.00	82.00	33.00	6066.00	28.00	9.00	4956.00	13.00	3098.00	7.00	6.00	17.00	26.00	22.00
67	6915.00	100.00	38.00	2528.00	6.00	4.00	4807.00	19.00	2465.00	8.00	5.00	49.00	60.00	28.00
61A	6259.00	96.00	35.00	7250.00	21.00	11.00	3201.00	15.00	2633.00	5.00	5.00	28.00	45.00	20.00
63	7075.00	100.00	39.00	2846.00	8.00	4.00	5380.00	12.00	2498.00	5.00	5.00	45.00	50.00	24.00
12	8009.00	100.00	44.00	3449.00	9.00	5.00	6140.00	31.00	3564.00	9.00	7.00	25.00	22.00	19.00
66	3043.00	27.00	18.00	3411.00	13.00	5.00	3411.00	4.00	21040.00	100.00	48.00	4.00	7.00	10.00
15	5257.00	66.00	29.00	13054.00	54.00	18.00	3201.00	10.00	2258.00	5.00	4.00	13.00	20.00	27.00
3	5598.00	83.00	31.00	2962.00	7.00	4.00	4098.00	10.00	2796.00	6.00	6.00	30.00	36.00	17.00
157	7387.00	88.00	41.00	2878.00	6.00	4.00	5270.00	15.00	2533.00	6.00	5.00	25.00	34.00	21.00
161	7398.00	92.00	41.00	4687.00	12.00	7.00	4773.00	16.00	2987.00	7.00	6.00	8.00	24.00	16.00
296	7748.00	99.00	43.00	4754.00	15.00	7.00	4754.00	15.00	2764.00	7.00	6.00	24.00	23.00	18.00
294	14173.00	100.00	75.00	2362.00	3.00	3.00	4047.00	21.00	2665.00	3.00	5.00	9.00	11.00	11.00
290	16877.00	100.00	85.00	2554.00	6.00	4.00	4648.00	17.00	2309.00	4.00	5.00	16.00	21.00	13.00

TABLE 3 (cont.). Results of X-ray diffraction analyses of Pennsylvanian and Lower Permian shales of Kansas.

	X-ray Diffraction Measurements													
	Quartz			Calcite			Feldspar		Dolomite			Kaolinite	Illite	Chlorite
Sample Number	Peak Area	Peak Height	Percent	Peak Area	Peak Height	Percent	Peak Area	Peak Height	Peak Area	Peak Height	Percent	Peak Height	Peak Height	Peak Height
284	6662.00	100.00	37.00	3894.00	7.00	6.00	4884.00	11.00	2653.00	6.00	5.00	25.00	27.00	18.00
287	7243.00	100.00	40.00	5447.00	16.00	8.00	7716.00	13.00	2378.00	5.00	5.00	20.00	28.00	15.00
281	10365.00	100.00	54.00	4128.00	14.00	7.00	5636.00	15.00	7719.00	22.00	17.00	17.00	21.00	13.00
125	13387.00	100.00	72.00	2521.00	5.00	4.00	5297.00	18.00	2312.00	4.00	5.00	25.00	33.00	20.00
116	6296.00	83.00	35.00	8079.00	20.00	12.00	4709.00	12.00	3378.00	8.00	7.00	22.00	20.00	21.00
110	6531.00	69.00	37.00	7709.00	23.00	11.00	2569.00	13.00	2906.00	4.00	6.00	9.00	12.00	17.00
112	11034.00	100.00	58.00	2449.00	6.00	4.00	4132.00	15.00	2300.00	5.00	5.00	27.00	29.00	19.00
128	6916.00	87.00	39.00	4201.00	8.00	7.00	4201.00	11.00	4522.00	10.00	9.00	15.00	27.00	20.00
130	4689.00	53.00	25.00	7536.00	23.00	11.00	2205.00	6.00	21035.00	100.00	46.00	7.00	15.00	12.00
79	4584.00	62.00	25.00	11418.00	47.00	16.00	4807.00	9.00	4767.00	13.00	10.00	15.00	24.00	18.00
151	6428.00	98.00	37.00	3359.00	7.00	5.00	4684.00	19.00	3713.00	7.00	8.00	38.00	48.00	23.00
82	6738.00	98.00	38.00	3691.00	7.00	6.00	4396.00	11.00	2658.00	6.00	5.00	20.00	23.00	22.00
80	6497.00	85.00	36.00	3675.00	7.00	6.00	4204.00	13.00	3744.00	6.00	8.00	24.00	36.00	27.00
81	5811.00	77.00	33.00	3252.00	7.00	9.00	4124.00	11.00	2976.00	8.00	6.00	22.00	31.00	28.00
85	11761.00	100.00	63.00	2265.00	6.00	3.00	9967.00	35.00	3224.00	4.00	7.00	13.00	26.00	12.00
135	3041.00	30.00	18.00	11092.00	42.00	16.00	2098.00	4.00	15074.00	57.00	33.00	7.00	12.00	13.00
121	18913.00	100.00	96.00	1982.00	6.00	3.00	1884.00	9.00	2225.00	4.00	4.00	9.00	10.00	16.00
138	5141.00	57.00	28.00	8205.00	26.00	12.00	4314.00	10.00	3965.00	8.00	8.00	8.00	24.00	17.00
136	6398.00	100.00	36.00	6203.00	20.00	9.00	4535.00	16.00	6232.00	24.00	13.00	14.00	29.00	20.00
137	4293.00	50.00	24.00	22244.00	74.00	30.00	4962.00	8.00	2253.00	7.00	4.00	9.00	16.00	14.00
149	8859.00	100.00	48.00	6228.00	17.00	9.00	5475.00	17.00	2939.00	6.00	6.00	13.00	21.00	14.00
150	8987.00	100.00	48.00	3375.00	7.00	5.00	6272.00	17.00	3236.00	7.00	7.00	9.00	20.00	25.00
152	7697.00	100.00	42.00	3417.00	7.00	5.00	4664.00	17.00	2846.00	6.00	6.00	12.00	28.00	20.00
153	7105.00	100.00	40.00	2680.00	7.00	4.00	5417.00	19.00	2525.00	7.00	5.00	54.00	62.00	26.00
155	9678.00	100.00	51.00	3356.00	5.00	5.00	5765.00	19.00	2639.00	5.00	5.00	17.00	33.00	20.00
105	7453.00	92.00	41.00	12790.00	61.00	18.00	1383.00	11.00	2268.00	4.00	4.00	15.00	14.00	13.00
107	7152.00	81.00	40.00	2988.00	7.00	4.00	4354.00	13.00	2761.00	12.00	6.00	20.00	25.00	15.00
109	2872.00	28.00	16.00	25017.00	94.00	34.00	1383.00	8.00	1564.00	4.00	2.00	7.00	12.00	11.00
94	4640.00	17.00	25.00	14627.00	100.00	20.00	2586.00	4.00	3332.00	21.00	7.00	6.00	10.00	9.00
96	9900.00	100.00	52.00	2218.00	6.00	3.00	8381.00	39.00	2431.00	7.00	5.00	19.00	40.00	20.00
97	6387.00	77.00	36.00	4265.00	8.00	7.00	4526.00	11.00	3037.00	7.00	6.00	25.00	33.00	28.00
144	8097.00	96.00	45.00	2903.00	5.00	4.00	5758.00	18.00	6417.00	20.00	14.00	33.00	39.00	22.00
101	7558.00	100.00	42.00	3851.00	13.00	6.00	4687.00	18.00	2734.00	7.00	5.00	33.00	40.00	33.00
122	4013.00	47.00	22.00	20978.00	89.00	28.00	5010.00	8.00	2023.00	4.00	4.00	10.00	18.00	14.00
97B	9859.00	100.00	51.00	5601.00	18.00	8.00	6164.00	23.00	2738.00	5.00	5.00	11.00	19.00	18.00
148	6906.00	76.00	38.00	3546.00	6.00	5.00	4534.00	15.00	3437.00	7.00	7.00	18.00	26.00	20.00
162	8976.00	100.00	48.00	2439.00	7.00	4.00	5974.00	27.00	2369.00	6.00	5.00	14.00	30.00	21.00
163	6131.00	39.00	35.00	3194.00	15.00	4.00	3020.00	6.00	2250.00	5.00	4.00	29.00	15.00	10.00
171	6364.00	100.00	36.00	2613.00	7.00	4.00	5244.00	16.00	2754.00	6.00	6.00	26.00	38.00	20.00
173	6566.00	99.00	37.00	3471.00	6.00	5.00	4875.00	14.00	2689.00	7.00	5.00	25.00	38.00	22.00
168	9848.00	100.00	52.00	2142.00	5.00	3.00	5926.00	38.00	2225.00	4.00	4.00	19.00	29.00	15.00
192	5964.00	77.00	34.00	6960.00	27.00	10.00	3543.00	18.00	17802.00	82.00	39.00	11.00	17.00	15.00

TABLE 3 (cont.). Results of X-ray diffraction analyses of Pennsylvanian and Lower Permian shales of Kansas.

	X-ray Diffraction Measurements														
	Quartz			Calcite			Feldspar		Dolomite			Kaolinite	Illite	Chlorite
Sample Number	Peak Area	Peak Height	Percent	Peak Area	Peak Height	Percent	Peak Area	Peak Height	Peak Area	Peak Height	Percent	Peak Height	Peak Height	Peak Height
194	6576.00	95.00	37.00	6106.00	6.00	9.00	5073.00	22.00	3146.00	4.00	6.00	13.00	15.00	15.00
176	4883.00	69.00	26.00	3093.00	7.00	4.00	4171.00	11.00	3315.00	6.00	7.00	31.00	31.00	23.00
180	7337.00	100.00	41.00	2865.00	7.00	4.00	4289.00	18.00	2531.00	7.00	5.00	28.00	43.00	20.00
181	8449.00	100.00	46.00	4470.00	14.00	7.00	5387.00	14.00	2900.00	6.00	6.00	15.00	18.00	22.00
184	9291.00	100.00	49.00	2378.00	8.00	3.00	7654.00	31.00	3003.00	6.00	6.00	28.00	32.00	18.00
185	8818.00	100.00	48.00	4376.00	21.00	7.00	6300.00	16.00	3350.00	7.00	7.00	14.00	16.00	14.00
186	6206.00	74.00	35.00	5102.00	14.00	8.00	6725.00	11.00	3308.00	5.00	7.00	9.00	13.00	22.00
187	3862.00	44.00	21.00	13433.00	44.00	19.00	2831.00	9.00	3925.00	10.00	8.00	7.00	19.00	14.00
197	5161.00	69.00	29.00	8779.00	29.00	12.00	3179.00	12.00	9916.00	38.00	22.00	11.00	19.00	15.00
200	6768.00	86.00	37.00	5293.00	12.00	8.00	5010.00	17.00	3134.00	5.00	6.00	13.00	22.00	20.00
205	7287.00	98.00	40.00	3470.00	8.00	5.00	5037.00	15.00	2823.00	7.00	6.00	24.00	35.00	22.00
206	3550.00	39.00	20.00	23486.00	88.00	32.00	1692.00	4.00	2019.00	4.00	4.00	7.00	11.00	11.00
208	2876.00	40.00	17.00	23180.00	96.00	31.00	6044.00	6.00	1771.00	4.00	3.00	8.00	13.00	13.00
209	3100.00	34.00	18.00	20590.00	88.00	28.00	2233.00	6.00	3692.00	14.00	8.00	9.00	16.00	14.00
261	3032.00	41.00	18.00	18205.00	66.00	25.00	2032.00	6.00	2503.00	8.00	5.00	10.00	13.00	14.00
262	4686.00	46.00	25.00	13612.00	56.00	19.00	3002.00	9.00	2637.00	6.00	5.00	8.00	13.00	16.00
212	4594.00	61.00	25.00	18711.00	100.00	25.00	2569.00	8.00	1776.00	4.00	3.00	7.00	20.00	15.00
213	3079.00	34.00	18.00	22979.00	98.00	31.00	5380.00	6.00	1581.00	4.00	2.00	7.00	13.00	12.00
264	4779.00	46.00	26.00	10649.00	35.00	15.00	3438.00	10.00	6009.00	17.00	13.00	8.00	13.00	14.00
237	2888.00	30.00	17.00	30646.00	100.00	41.00	1572.00	5.00	1546.00	5.00	2.00	5.00	11.00	11.00
235	3929.00	41.00	22.00	12965.00	43.00	18.00	2406.00	7.00	2110.00	4.00	4.00	6.00	15.00	13.00
238	7137.00	77.00	40.00	5783.00	19.00	9.00	4511.00	13.00	2908.00	4.00	6.00	6.00	21.00	17.00
249	3528.00	43.00	20.00	7200.00	29.00	11.00	1888.00	6.00	20020.00	100.00	44.00	6.00	12.00	13.00
248	5169.00	49.00	29.00	6163.00	24.00	9.00	3089.00	8.00	14905.00	54.00	33.00	6.00	12.00	14.00
234	2874.00	20.00	17.00	15325.00	70.00	21.00	1987.00	6.00	2148.00	4.00	4.00	9.00	11.00	20.00
230	5727.00	65.00	33.00	6515.00	18.00	10.00	4620.00	10.00	3077.00	6.00	6.00	5.00	20.00	18.00
226	5685.00	69.00	31.00	8599.00	32.00	12.00	3230.00	9.00	2626.00	5.00	5.00	5.00	16.00	13.00
227	8007.00	97.00	44.00	3179.00	6.00	4.00	3975.00	11.00	3013.00	5.00	6.00	5.00	20.00	17.00
221	6599.00	67.00	37.00	11286.00	40.00	16.00	3842.00	8.00	3363.00	7.00	7.00	5.00	16.00	13.00
222	2107.00	19.00	14.00	27611.00	100.00	37.00	1368.00	3.00	1341.00	4.00	0.00	4.00	8.00	10.00
243	5292.00	61.00	29.00	6564.00	22.00	10.00	3910.00	9.00	2999.00	6.00	6.00	8.00	23.00	31.00
244	5249.00	87.00	29.00	4849.00	9.00	7.00	6824.00	11.00	3907.00	8.00	8.00	6.00	30.00	22.00
273	4549.00	51.00	25.00	3597.00	6.00	6.00	2616.00	10.00	14651.00	62.00	32.00	7.00	12.00	16.00
253	3100.00	38.00	18.00	19456.00	73.00	26.00	1763.00	7.00	2795.00	10.00	6.00	8.00	15.00	12.00
251	4106.00	41.00	24.00	11884.00	37.00	17.00	2633.00	6.00	7477.00	21.00	16.00	8.00	16.00	13.00
256	7697.00	92.00	42.00	7854.00	24.00	11.00	3449.00	13.00	6091.00	26.00	13.00	9.00	15.00	12.00
265	3545.00	39.00	20.00	19237.00	66.00	17.00	2222.00	7.00	3521.00	11.00	7.00	10.00	16.00	16.00
268	6293.00	78.00	35.00	2830.00	7.00	4.00	3381.00	13.00	3895.00	14.00	8.00	11.00	29.00	17.00
270	7606.00	96.00	42.00	3524.00	11.00	6.00	4006.00	12.00	5358.00	21.00	11.00	9.00	19.00	15.00
272	4152.00	49.00	23.00	16211.00	59.00	22.00	2948.00	7.00	2192.00	4.00	4.00	7.00	15.00	19.00
298	8917.00	100.00	48.00	3439.00	7.00	5.00	4528.00	16.00	7104.00	28.00	15.00	9.00	15.00	16.00
300	4844.00	68.00	27.00	2465.00	5.00	5.00	3039.00	9.00	23333.00	100.00	52.00	6.00	16.00	16.00

TABLE 4. Summary statistics of X-ray diffraction measurements.

	X-RAY MEASUREMENTS														
Minerals	Quartz			Calcite			Feldspar		Dolomite			Kaolinite	Illite	Chlorite
Statistics	PH	PA	%	PH	PA	%	PH	PA	PH	PA	%	PH	PH	PH
Mean	76.8	6611.0	36.2	26.9	7648.0	10.9	13.6	4332.0	13.7	4351.0	9.1	15.5	28.8	17.6
Standard Deviation	25.1	2673.0	13.4	28.5	6546.0	8.6	6.8	1537.0	20.7	4148.0	9.4	10.0	10.9	4.7
Median	86.0	6476.5	36.5	12.5	5694.0	7.0	13.0	4251.0	7.0	3067.0	6.0	16.0	21.5	17.0
Minimum	17.0	2107.0	14.0	3.0	1982.0	3.0	3.0	1368.0	3.0	1341.0	0.0	4.0	7.0	9.0
Maximum	100.0	18913.0	96.0	100.0	30646.0	41.0	39.0	9967.0	100.0	23333.0	52.0	54.0	62.0	33.0

PH = peak height
PA = peak area
% = percent

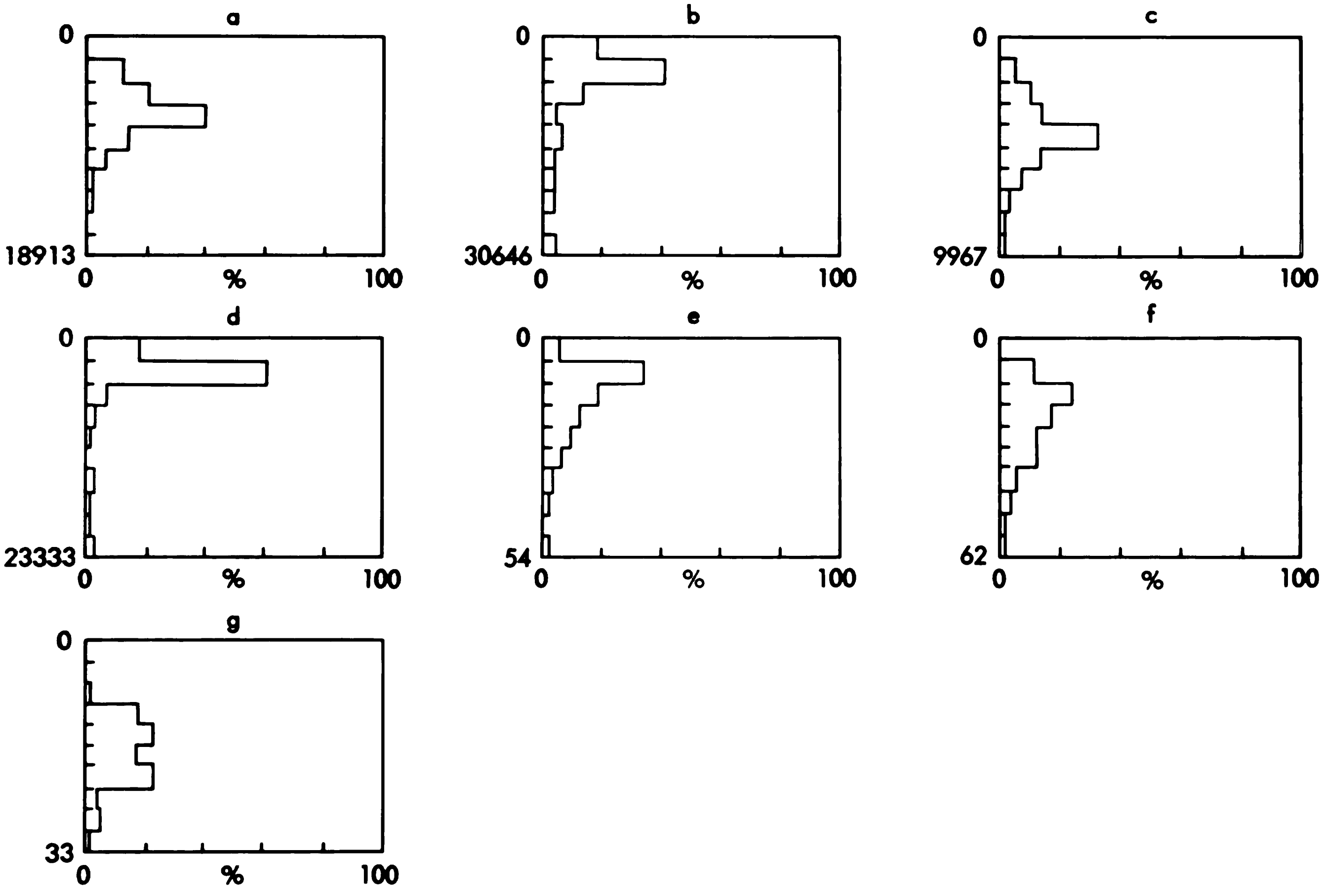

FIGURE 9. Histograms showing the variation and distribution of the major mineral components measured by X-ray diffraction (total samples = 128); peak areas for (a) quartz, (b) calcite, (c) feldspar, (d) dolomite; peak heights for (e) kaolinite (f) illite, and (g) chlorite. Vertical scale is 0 to maximum value in 10 divisions.

(up to 85 percent) as they consist mainly of coarse silts and sands, whereas the succeeding Shawnee Group shales are characterized by variable quartz concentrations (16 to 96 percent). The Wabaunsee shales have more stable quartz values (21 to 52 percent) indicating consistent environmental conditions, and a general tendency for smaller concentrations in the younger beds. This is reversed in the Lower Permian Groups where increased values are recorded in Chase Group samples. Nevertheless, the percentages determined are still low (14 to 48 percent).

Feldspar measurements of peak area (Figure 10) and peak height stratigraphically vary in a similar manner to the quartz distribution, indicating a detrital

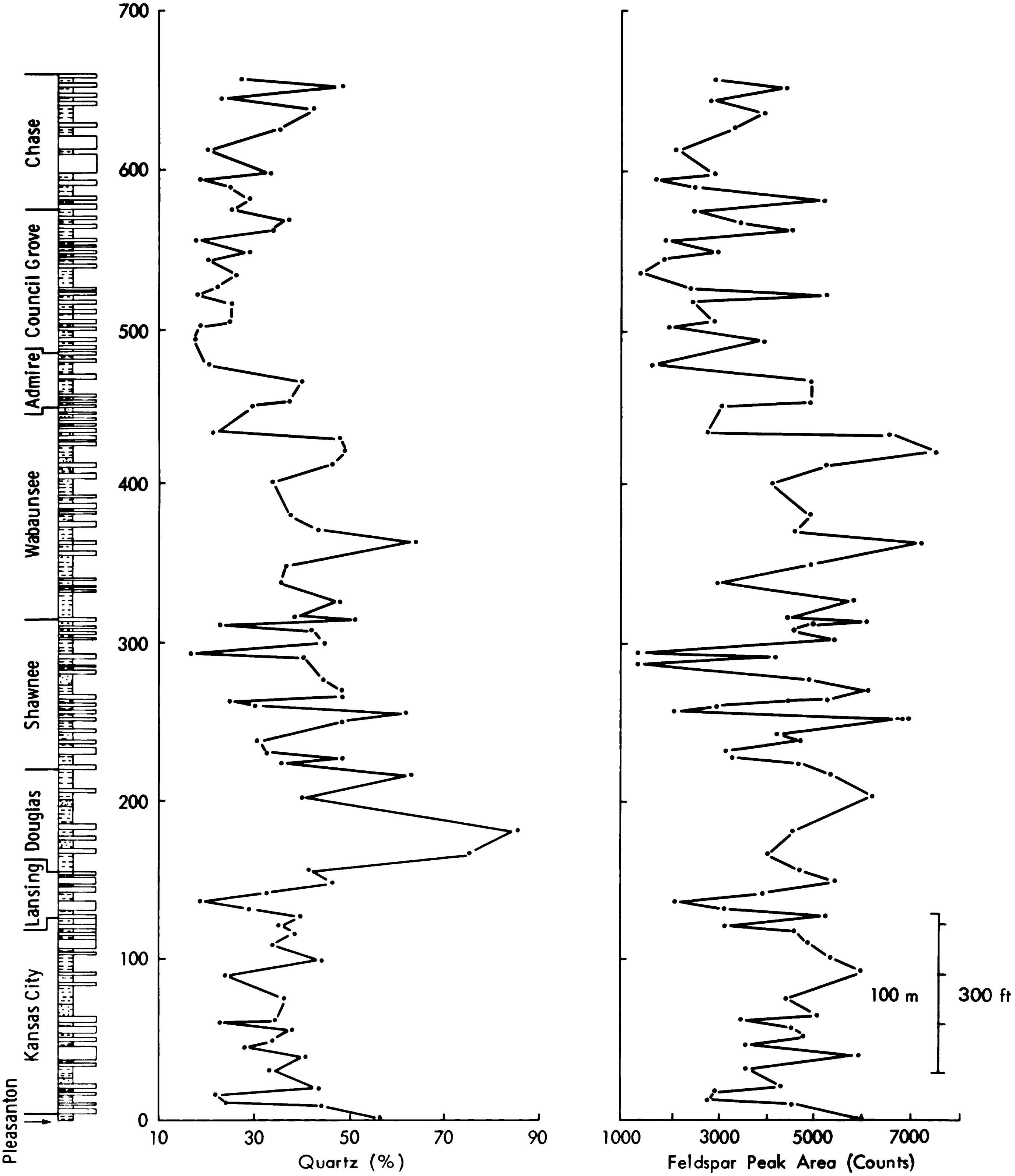

FIGURE 10. Distribution of quartz(%) and feldspar (peak area) in shales from the Upper Pennsylvanian and Lower Permian of Kansas.

association between the minerals. The graphs correspond within the Pleasanton, Kansas City, Lansing, Shawnee, and Lower Permian Groups, but the high quartz values in the Douglas samples are not present in the feldspar measurements.

Periods in which low quartz values are recorded such as the Shawnee, Lower Permian, Pleasanton, Kansas City, and Lansing Groups are marked by intensive carbonate generation. Both calcite and dolomite distributions (Figure 11) show low values in the Douglas and Wabaunsee Groups (averaging 5 to 10 percent carbonate), whereas calcite shows high concentrations in the Lower Permian, Upper Shawnee, and Kansas City Groups and dolomite has high values in the Lansing, Council Grove, and Chase Groups (Figure 11). Differences in the peak area histograms of these minerals (Figure 9) indicate a possible cause for the variation between carbonate stratigraphic distributions. The calcite histogram approximates to a "normal" curve (averaging 15 to 25 percent), whereas dolomite shows a bimodal histogram with one group of samples with low values (5 to 10 percent dolomite) and another with exceptionally high dolomite (50 percent average), indicating that the dolomite present may be of secondary diagenetic origin as opposed to the primary precipitated calcite. Petrological evidence supports this conclusion.

The three major clay mineral components have skewed (kaolinite and illite) or irregular bimodal histograms (chlorite). There is little evidence for stratigraphic control of clay mineral distributions (Figure 12), although in the Upper Kansas City Group, a series of high peak height values are recorded for all three clay minerals. One can also, by inspection of the data, note a similarity between the clay mineral distributions and a lack of similarity to other mineral distributions.

This association of minerals is supported statistically, in the similarity matrix (Table 5). Here we can see that quartz, feldspar, and clay minerals have high positive correlations and form one combination of minerals, whereas the carbonates have negative correlations with respect to the other minerals. High correlations are recorded between quartz and calcite; kaolinite, chlorite, and illite; and between illite and calcite. These are produced primarily by the inverse relationship between mineral groups characteristic of clastic and calcareous deposits, and by a close environmental relationship between the clays.

On examining the mineral distributions by eye, it is apparent that quartz and calcite show repetitive variability in a stratigraphic sense, i.e., there is a stratigraphic oscillation of peaks and troughs in the distribution of quartz and calcite in Upper Pennsylvanian and Lower Permian shales. This we can interpret in terms of changing sedimentary environments. For example, shales in the Pleasanton, Kansas City, and Lansing beds oscillate between calcite- and quartz-dominated mineralogies. This pattern is repeated in the Shawnee and to a minor extent in the Lower Permian. Between these oscillatory stratigraphic zones, there are beds of relatively quartz-rich shales, namely the Douglas and Wabaunsee Group clastics. It appears, therefore, that there are two cycles of events being recorded in the quartz and calcite mineral distributions, first a short-term, bed-by-bed oscillatory variation, and second a long-term group-by-group repetition.

The observed mineralogical periodicity in the sediments can be tested using a statistical procedure designed originally for wave-form analysis in electrical engineering, Fourier analysis (Preston and Henderson, 1964; Harbaugh and Merriam, 1968; Davis, 1973; Dunn, 1974). From this the natural cycles can be recognized. A series of computations have to be performed prior to the Fourier analysis, however, to transform the data into a suitable form for entry into the computer program. Initially, using a linear interpolation procedure (Davis, 1973), the data is changed from sample values with irregular depth in-

TABLE 5. Similarity matrix for the mineral distributions employing correlation coefficients. Note that although peak area measurements were used for quartz, calcite, feldspar, and dolomite, and peak heights for kaolinite, illite, and chlorite, the correlation coefficient is a unitless measure and as such the original measurement units have no influence on the similarities recorded. Only the lower half of the correlation matrix is reproduced as this is a mirror image of the upper half. Correlations significant at the 95 percent level are indicated by * and at the 99 percent level by **.

Mineral	Quartz	Feldspar	Calcite	Dolomite	Kaolinite	Illite	Chlorite
Quartz	1.00						
Feldspar	0.26**	1.00					
Calcite	–0.62**	–0.43**	1.00				
Dolomite	–0.20*	–0.21*	–0.03	1.00			
Kaolinite	0.20*	0.10	–0.32**	–0.24**	1.00		
Illite	0.26**	0.23**	–0.52**	–0.24**	0.73**	1.00	
Chlorite	0.16	0.14	–0.45**	–0.25**	0.48**	0.69**	1.00

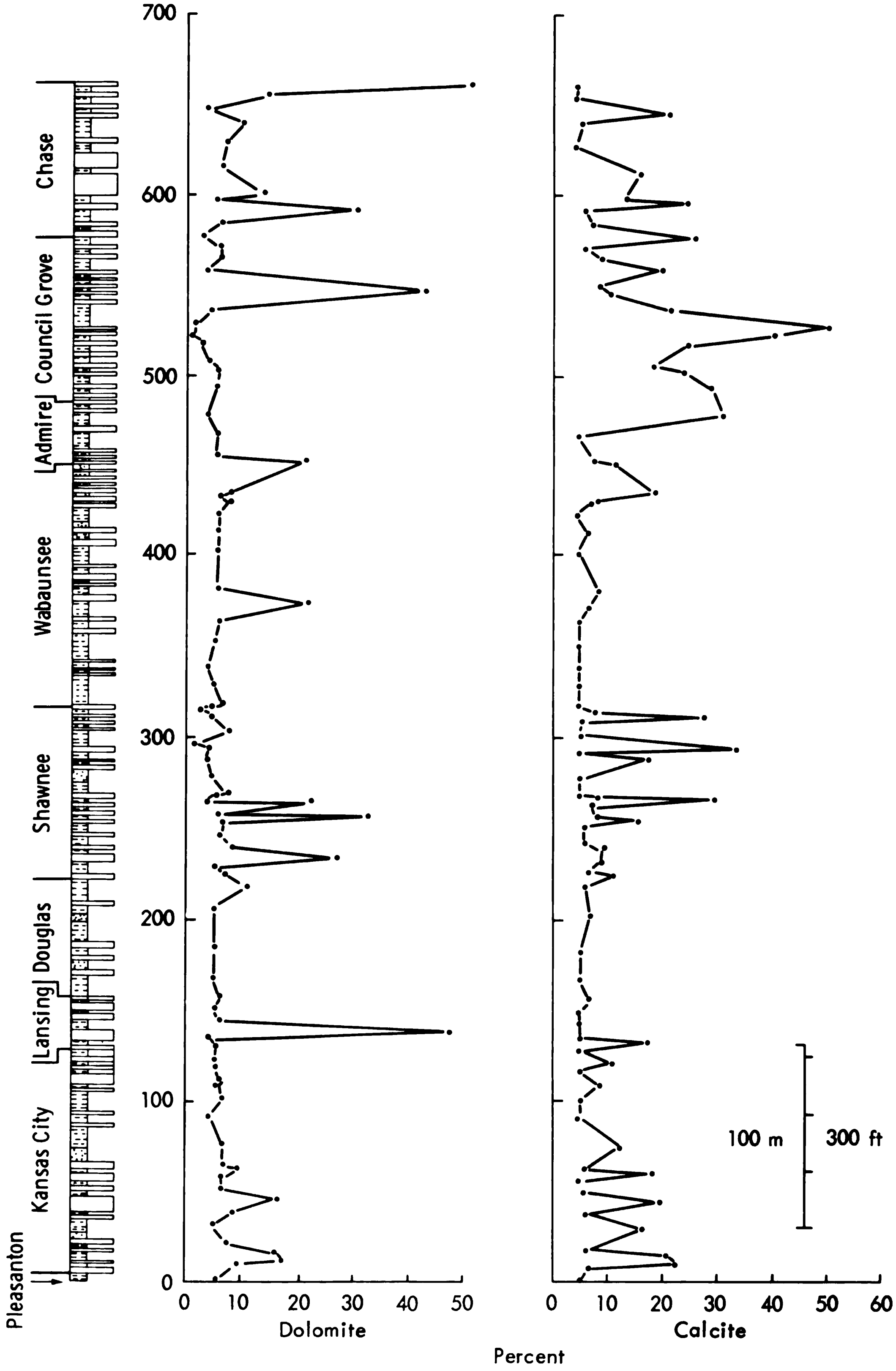

FIGURE 11. Variation of calcite and dolomite in Upper Pennsylvanian and Lower Permian shales of Kansas. Vertical scale matches that in Figure 10 allowing stratigraphic comparisons.

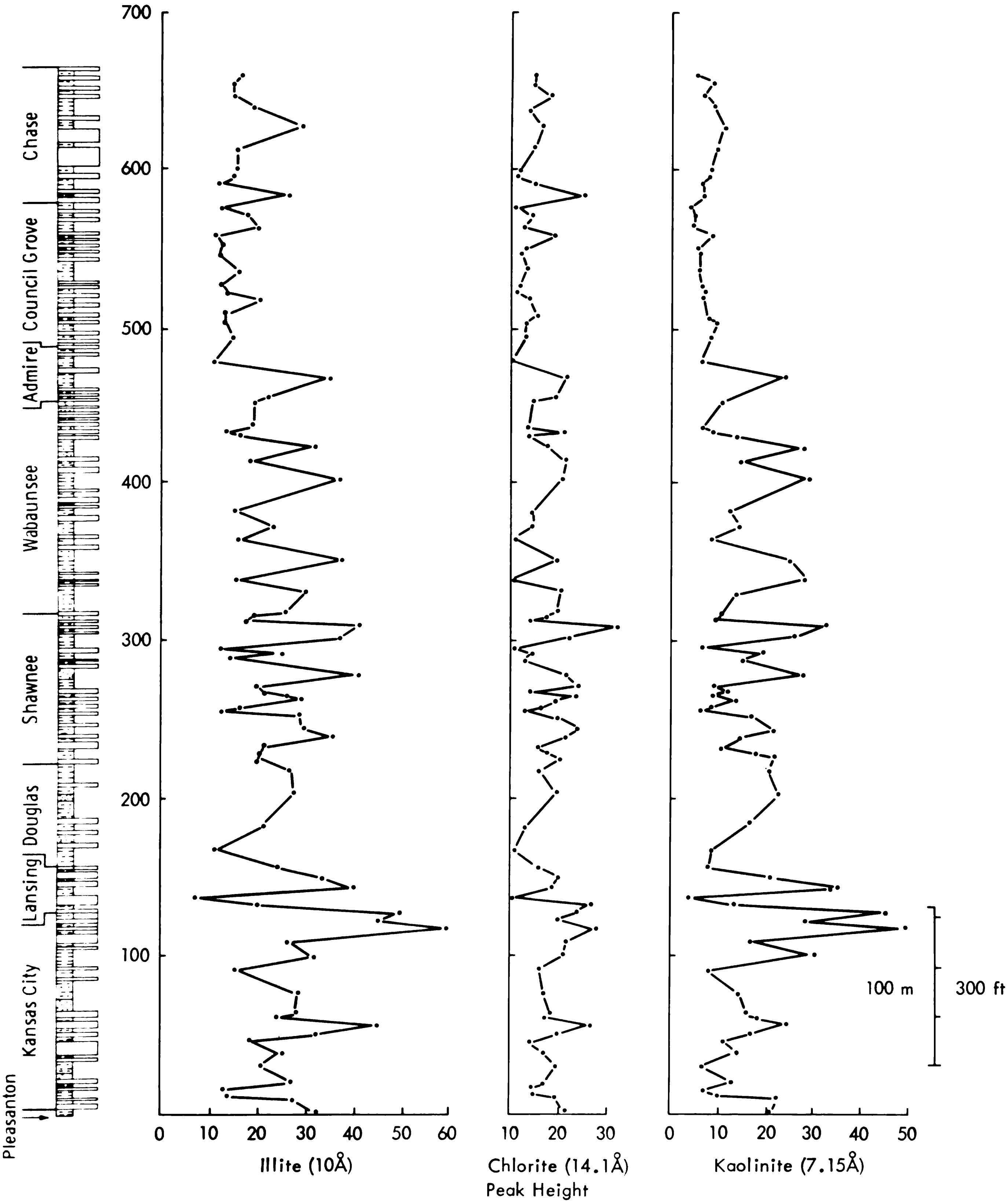

FIGURE 12. Variation in illite, chlorite, and kaolinite clay mineral peak heights from Upper Pennsylvanian and Lower Permian shales of Kansas. Vertical scale is identical to Figure 10 and 11 allowing stratigraphic comparisons.

tervals to a pattern of values taken at a constant depth interval. Ten feet (3.05 m) was chosen as the most practical equal spacing interval, as Schwarzacher (1967) has shown that the smallest lithological cycle occurs at intervals of 45 feet, and any larger interval would obscure these cycles. The total number of data points is, in this way, increased from 128 to 218. In the case of the quartz distribution shown in Figure 13A, it was noted that, although major peaks correspond to those in the raw data plot (Figure 10), it was possible that through this interpolation process there may have been a significant alteration of the data variability and trend. A linear regression analysis showed that, although the trend and goodness of fit measures had changed, the differences were acceptable, i.e., goodness of fit increased from .06 to .13 and the correlation coefficient from .26 to .37. The equal spaced data were then run through a Fourier analysis and the raw power spectrum calculated (Figure 14). It can be seen that the two main peaks corresponding to the third and seventh harmonics (multiples of the fundamental wavelength chosen, i.e., 10 feet), are indistinguishable from surrounding points. Noise in the equal spaced data may have produced this power spectrum fuzziness. An 11-term smoothing operation on the raw data, however, removed the short-term noise and revealed the power spectrum shown in Figure 14 (dashed lines). Features retained in the smoothed power spectrum include two main peaks at the third and seventh harmonics and subsidiary peaks at the fifth, 11th, 13th, and 14th. These indicate fundamental periodic elements in the quartz distribution with 30, 50, 70, 110, 130, and 140 foot intervals that may be explained in terms of oscillations in the quartz values of Pleasanton, Kansas City, Lansing, Shawnee, and Lower Permian shales.

Although these features were recognized initially in the quartz distribution, no evidence for these conclusions could be found in the power spectra of dolomite, feldspar, illite, chlorite, or kaolinite. In calcite's spectrum, on the other hand, a peak was developed at the seventh harmonic and a plateau at the third. However, the negative association of calcite with quartz in all these results may only be a reflection of the closed data set under examination (Vistelius and Sarmanov, 1961; Krumbein and Graybill, 1965; Chayes, 1971; Davis, 1973).

MULTIVARIATE STATISTICAL ANALYSIS OF THE MINERALOGICAL DISTRIBUTION

In the previous section we have noted how some minerals vary stratigraphically in relation to each other, and how some show periodic elements in their distributions. However, it is very rare in the earth sciences to find a single factor such as quartz percentage controlling the development of sedimentary environments. It is normally a combination of variables that produces the overall sedimentological effects, e.g., in Kansas an assemblage of mineral distributions may relate more approximately to the periodicity of shale deposition than to one mineral phase.

Multivariate classification techniques enable the investigator to quantify the relationships between variables and classify shale samples into groups dependent on the variable relationships. The distribution of individuals within the groups matched against depth can then be used to indicate stratigraphic divisions not previously noted and any repetition in the shale group associations.

With this in mind, an R-mode principal components analysis (Davis, 1973; Joreskog *et al.*, 1976) of the peak area measurements of quartz, calcite, feldspar, and dolomite and the peak heights of kaolinite, illite, and chlorite was performed. Three components were found to be significant (i.e., eigenvalues greater than one). The principal axis component loadings (Figures 15 and 16a) reveal similar relationships to the simple correlation coefficients. On the first component, the carbonate minerals have high positive loadings, whereas illite, chlorite, kaolinite, quartz, and feldspar have high negative loadings. This component can therefore be considered as an indicator of clastic or carbonate conditions of sedimentary deposition. Similarly, the second component's high positive loadings for quartz and feldspar and high negative loadings of calcite and clay minerals reflect the detrital versus nondetrital origin of most of the shales. Quartz and feldspar are commonly associated with detrital sediments, and calcite is normally a nondetrital mineral. It would seem at first glance unusual to note a connection between clay minerals and calcite, but it must be remembered that many of the thin shales occurring between limestones in the Kansas City and Shawnee Groups have high values for both calcite and clay minerals. Alternatively, this component may reflect the high quartz and feldspar content of some coarse shales, silts, and sandstones and corresponding lack of calcite and clay minerals in these samples. The high negative loading of dolomite on the final significant component represents the influence of the irregular dolomite distribution and may be an indicator of primary or secondary mineral origin. As noted previously, the irregular distribution of dolomitic shales indicates a diagenetic origin for the dolomite.

We can now express the variation of mineralogy

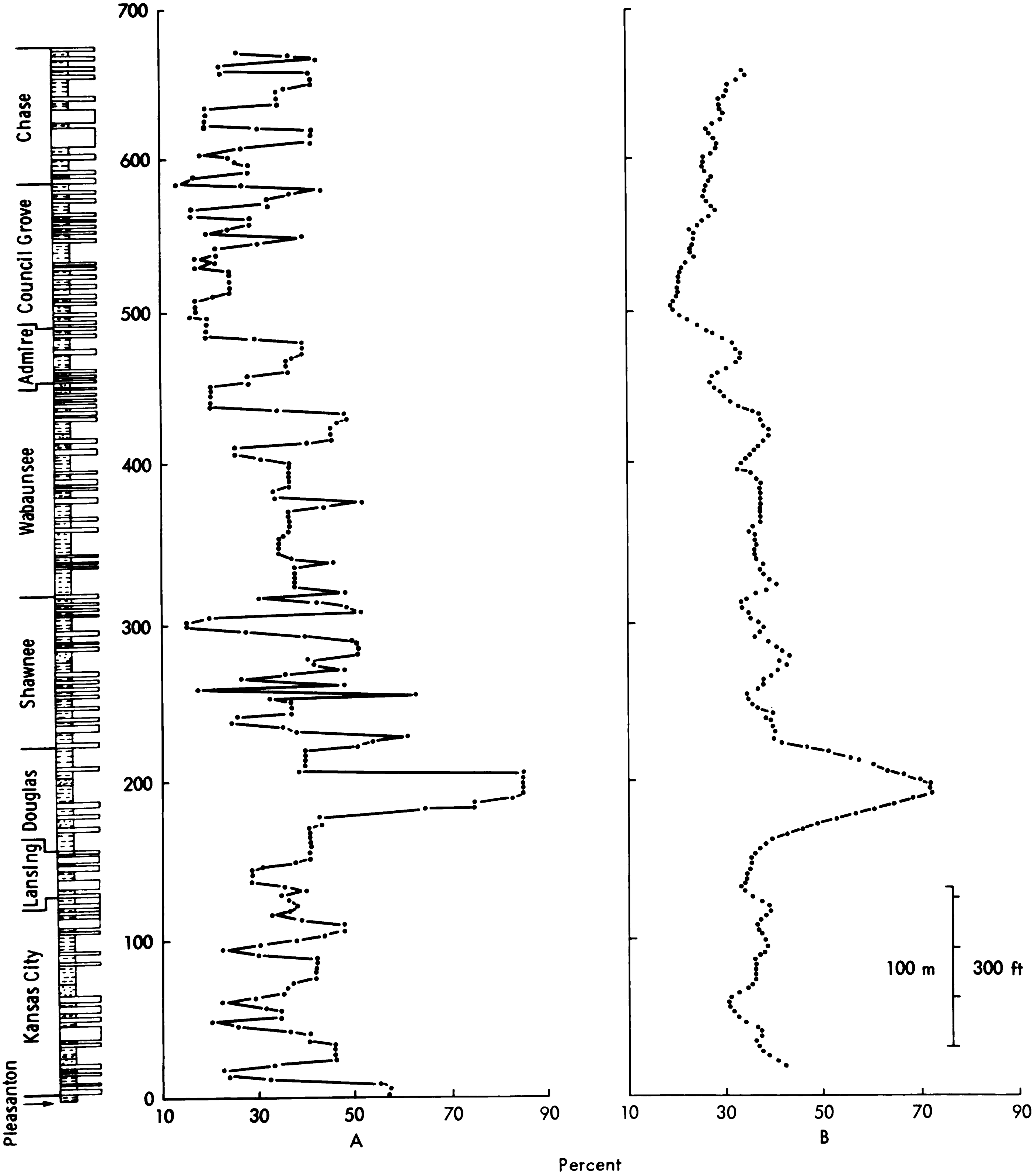

FIGURE 13. Distribution of quartz (in percent) after (a) equal spacing by a linear interpolation procedure, (b) equal spacing and smoothing (using an 11-term moving average equation). For a stratigraphical comparison see Figure 10.

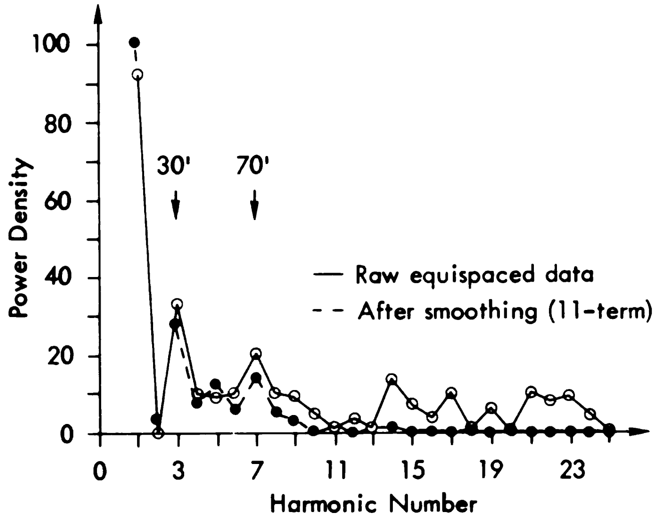

FIGURE 14. Power spectrum of quartz in the Upper Pennsylvanian and Lower Permian shales of Kansas. The fundamental wavelength chosen is 10 ft.

in the Kansas shales in terms of three geologically interpretable components. An attempt can, however, be made to clarify the geological interpretation of the components by emphasizing the loadings of the influential variables using varimax and promax rotation procedures (Imbrie and Purdy, 1962; Harman, 1967). With the component loadings matrix, we find that on varimax rotation there is an accentuation of the clay mineral loadings (Figure 16b) on Factor 1, and the quartz/calcite antipathy is weighted more strongly on Factor 2. The highlighting of known information has proved valuable but, with promax rotation (an oblique factor rotation) of the mineralogical data (Figure 16C), interpretation becomes a major problem. The results of promax rotation will therefore only be included for comparative purposes.

Having established the variable relationships, scores of samples on the components are calculated by Harman's short regression and square root method (Harman, 1967, pp. 362-369) and form the basis of the sample classification now undertaken. A Q-mode cluster analysis (Davis, 1973; Cubitt, 1975b), employing an agglomerative, polythetic unweighted pair-group algorithm with distance coefficients, arranges the samples on the basis of their scores on component axes into the hierarchical structure (dendrogram) shown in Figure 17. The dendrogram can be divided into eight clusters (labelled A to H) that represent natural subdivisions of the sample classification. However, before placing faith in these results, it is necessary to ensure that the groups of samples are not just a product of the clustering procedure but are unique subdivisions of the sample population. A multiple discriminant analysis (a procedure for statistically developing functions that maximize between group variation) of the raw mineralogical data, arranged in the same manner as the dendrogram, produces a distribution of groups shown in Figures 19 and 20. The mineralogical nature of the groups can be determined by superimposing the relative contribution of each variable to each axis (Figure 18) on the discriminant plot. H and G are, therefore, recognized as groups of highly dolomitic shales and D as more argillaceous than the others. On the other hand, quartz predominates in group C samples and calcite in E. A, B, and F appear to be intermediate groups in both Figures 19 and 20. Examining the raw mineralogical data, it is noticeable that samples in F are more akin to group E than to B or A. This is emphasized on the plot of first and third discriminant axes (Figure 20). For simplicity therefore E and F are combined.

A number of individuals from groups whose boundaries are closely related (i.e., A, B, and E) are also misplaced by the clustering algorithm. Manual examination of sample scores on the first three discriminant axes indicate that samples 281, 298, 270, 256, 79, 41, 136, and 197 should be attached to group E, while sample 20 is more naturally associated with group A.

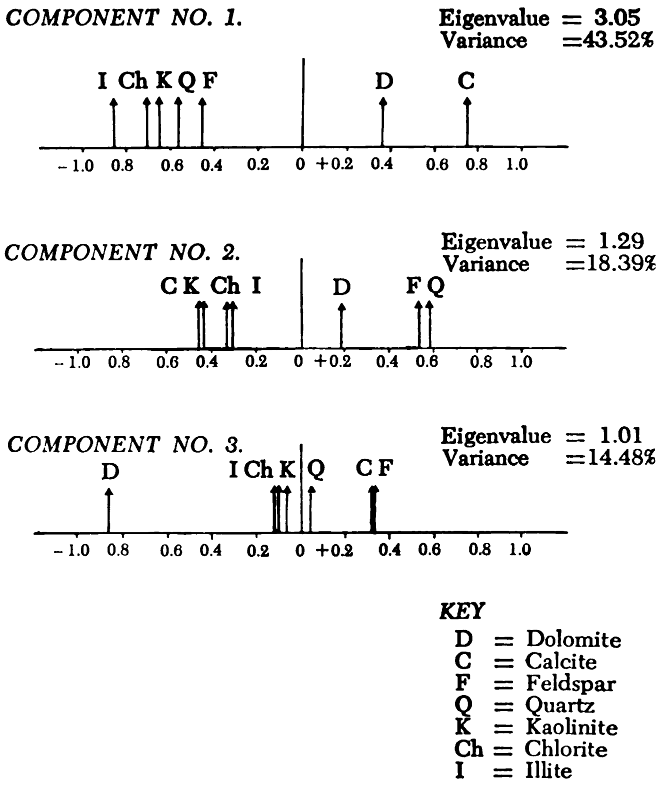

FIGURE 15. Principal axis loadings of the significant components (i.e., components with eigenvalues > 1.0).

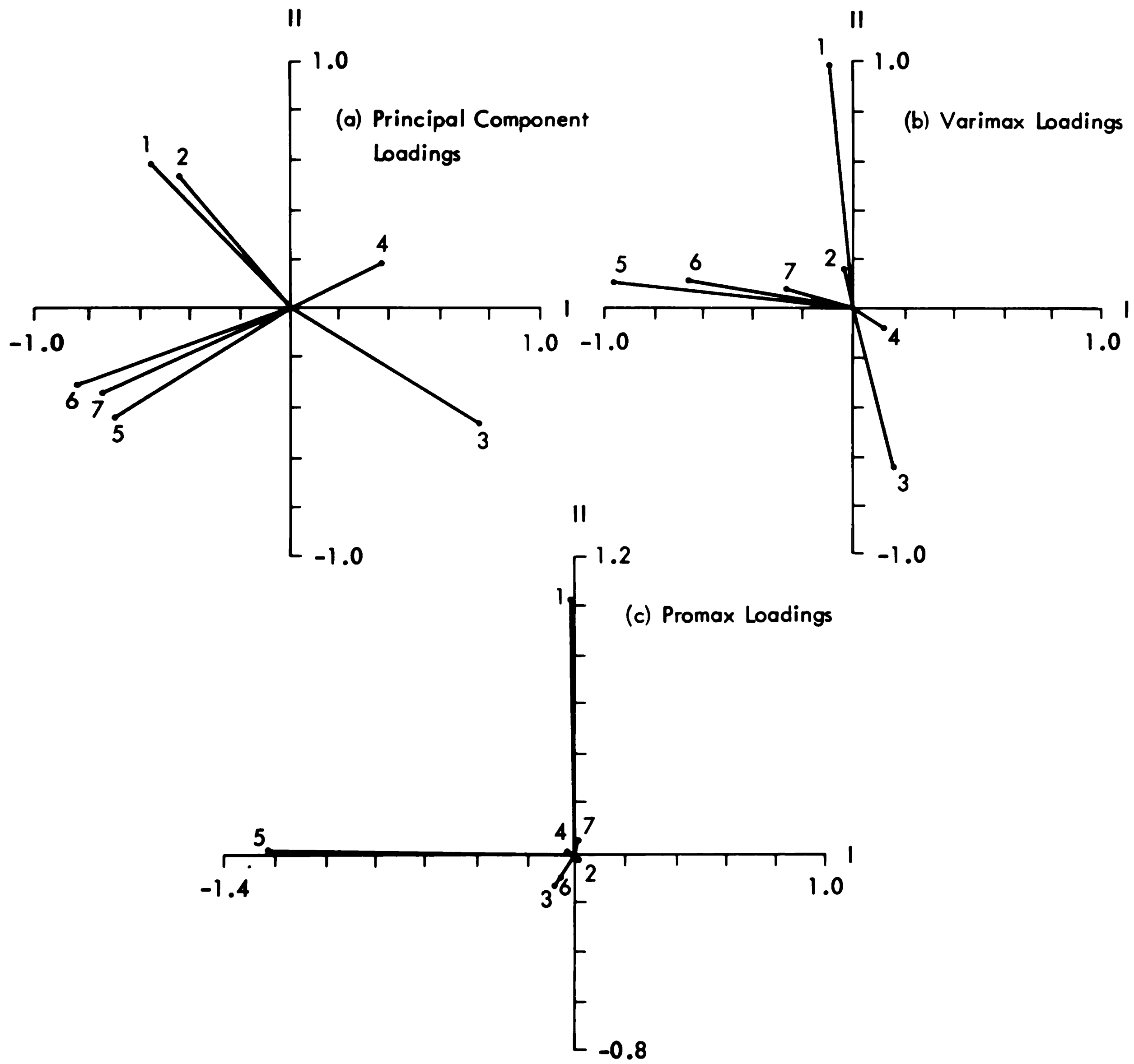

FIGURE 16. Plot of loadings on two components extracted from raw mineralogy data. Variables plotted are (1) quartz, (2) feldspars, (3) calcite, (4) dolomite, (5) kaolinite, (6) illite, (7) chlorite. Note that promax axes are not orthogonal (correlation = −0.0308) but, for simplicity, are drawn so.

On reallocation we can conclude that the seven groups established are now mineralogically distinct.

A plot of samples arranged according to their cluster analysis group against stratigraphic position (Figure 21) reveals seven zones in the Upper Pennsylvanian and Lower Permian stratigraphic column:

1. Pleasanton and Lower Kansas City Groups;
2. Upper Kansas City Group;
3. Lansing Group;
4. Douglas Group;
5. Shawnee Group (including the Upper Lawrence Formation of the Douglas Group);
6. Wabaunsee and Lower Admire Groups; and
7. Upper Admire, Council Grove, and Chase Groups.

Each division is characterized by differing mineralogical and sedimentological conditions. The Pleasanton and Lower Kansas City Groups, Lansing Group, and Shawnee Group zones show an alternation of calcite-(normally associated with limestones) and quartz-rich shales (predominantly clusters B, E, and A) indicating oscillating calcareous and noncalcareous environments. The noncalcareous sediments could have been derived from either the lowlands to the north and east of Kansas or from the Ouachita orogenic belt to the south. Source areas for the shales

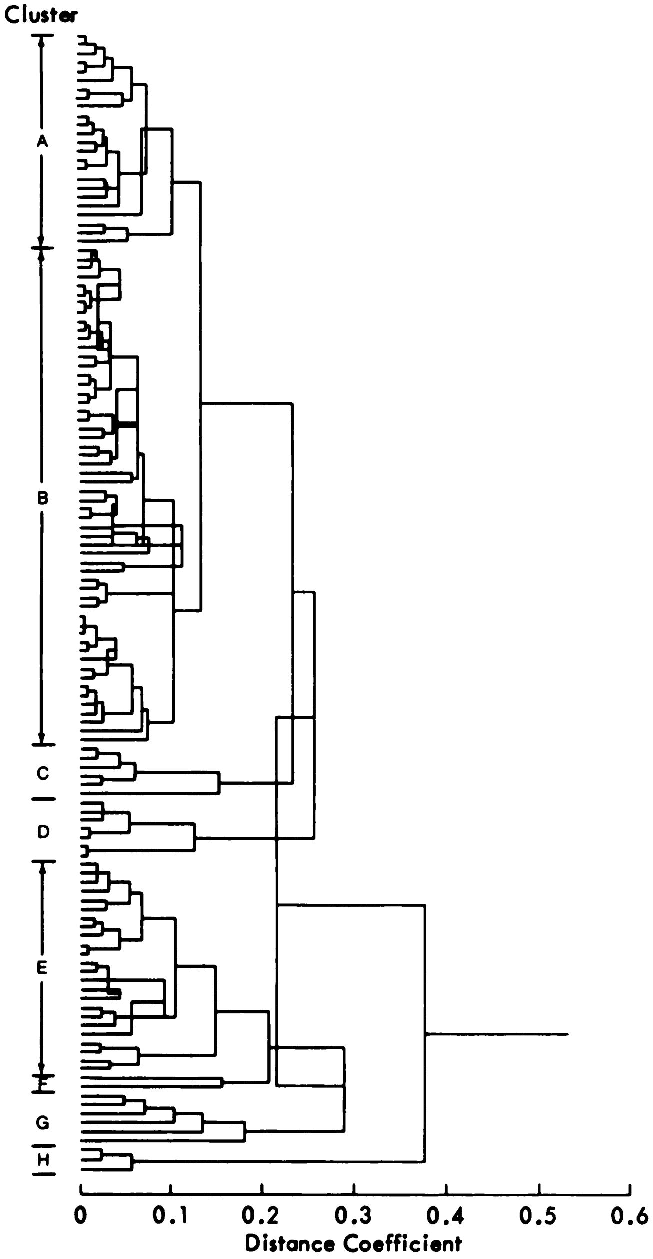

FIGURE 17. A dendrogram produced by a Q-mode cluster analysis of mineralogical data. Clusters produced are outlined on the left of the diagram. The reverse linkage is caused by the pair group method of clustering.

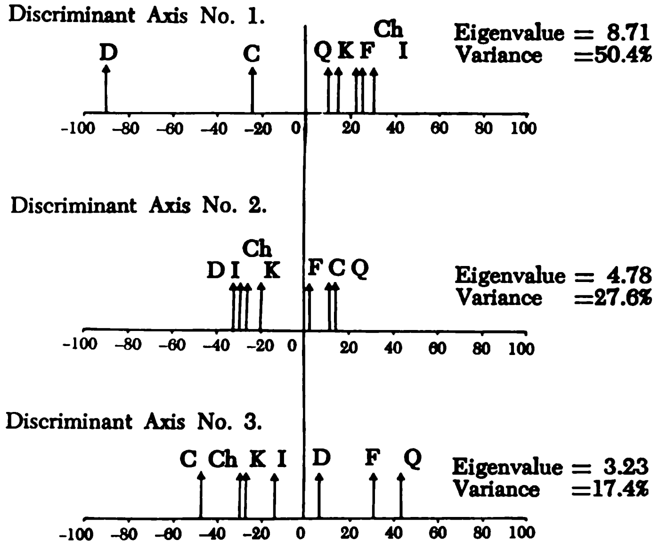

FIGURE 18. Loadings of variables on significant discriminant axes (i.e., eigenvalue > 1.0)—D = dolomite, C = calcite, Q = quartz, K = kaolinite, F = feldspar, Ch = chlorite, I = illite.

may be distinguished by comparing their geochemical and mineralogical results. On the other hand, the calcareous sediments were deposited at a time of predominantly limestone deposition and could represent either normal marine shales or the equivalent of limestone insoluble residues.

The Douglas and Wabaunsee Groups are dominated by shales that have quartz as the primary mineral component (clusters B and C). The Douglas Group shows the most extreme values of quartz content as the sediments are largely coarse siltstones and sandstones. The Wabaunsee also has coarse units but no samples are recorded in cluster C, unlike the Douglas or even the Shawnee Group.

In the Upper Admire, Council Grove, and Chase Groups, considerable periods of carbonate deposition (cluster E) are broken by an occasional quartz-rich shale (cluster B) or intermediate shale (cluster A), indicating an overall change in the sedimentary environment. The increase in carbonate formations is a product of the gradual restriction of the Kansas epeiric sea during Early Permian times (Heckel, 1972a) and is followed by a succession of evaporitic and calcareous beds in the Middle Permian. After establishing the nature of mineralogical variation with respect to stratigraphy, we can postulate a group-by-group control of sedimentary environments by local or regional tectonic events.

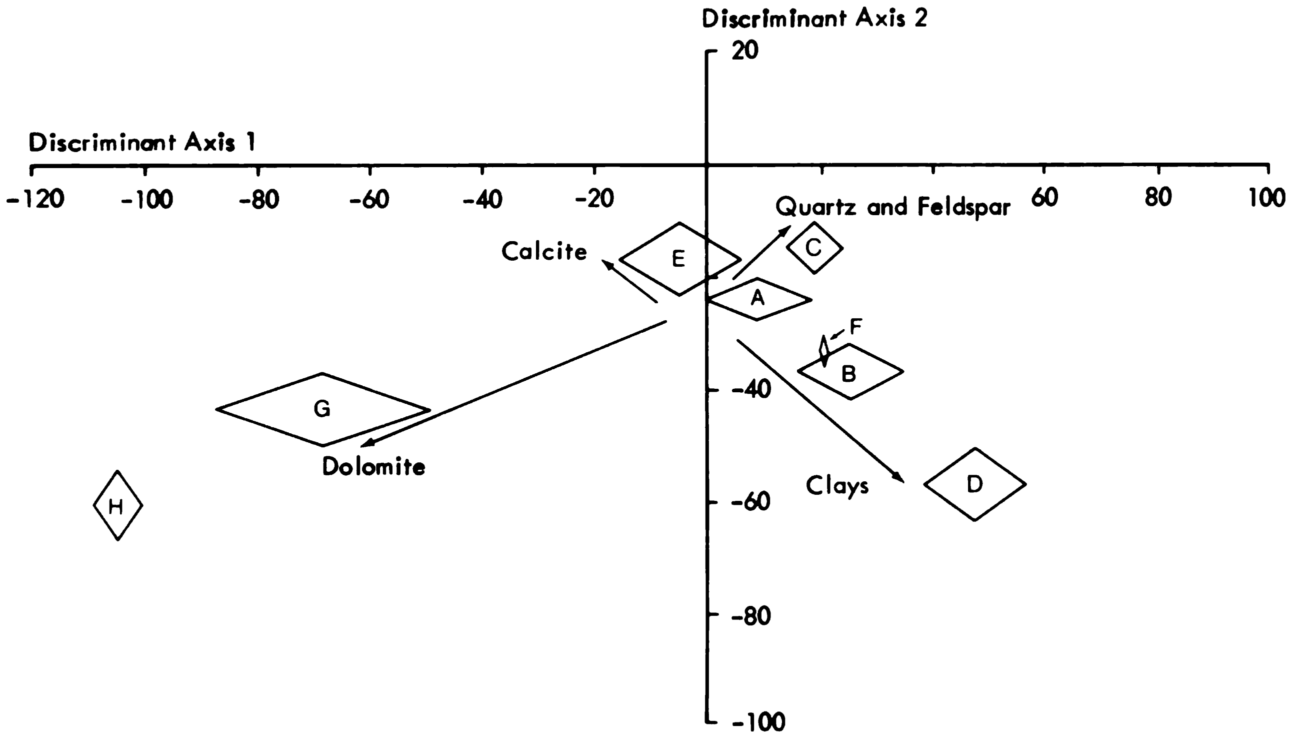

FIGURE 19. Distribution of cluster analysis groups on the first two discriminant axes. Primary mineralogical variation is superimposed for reference. Diamonds represent the mean of each group ± 1 standard deviation of each axis.

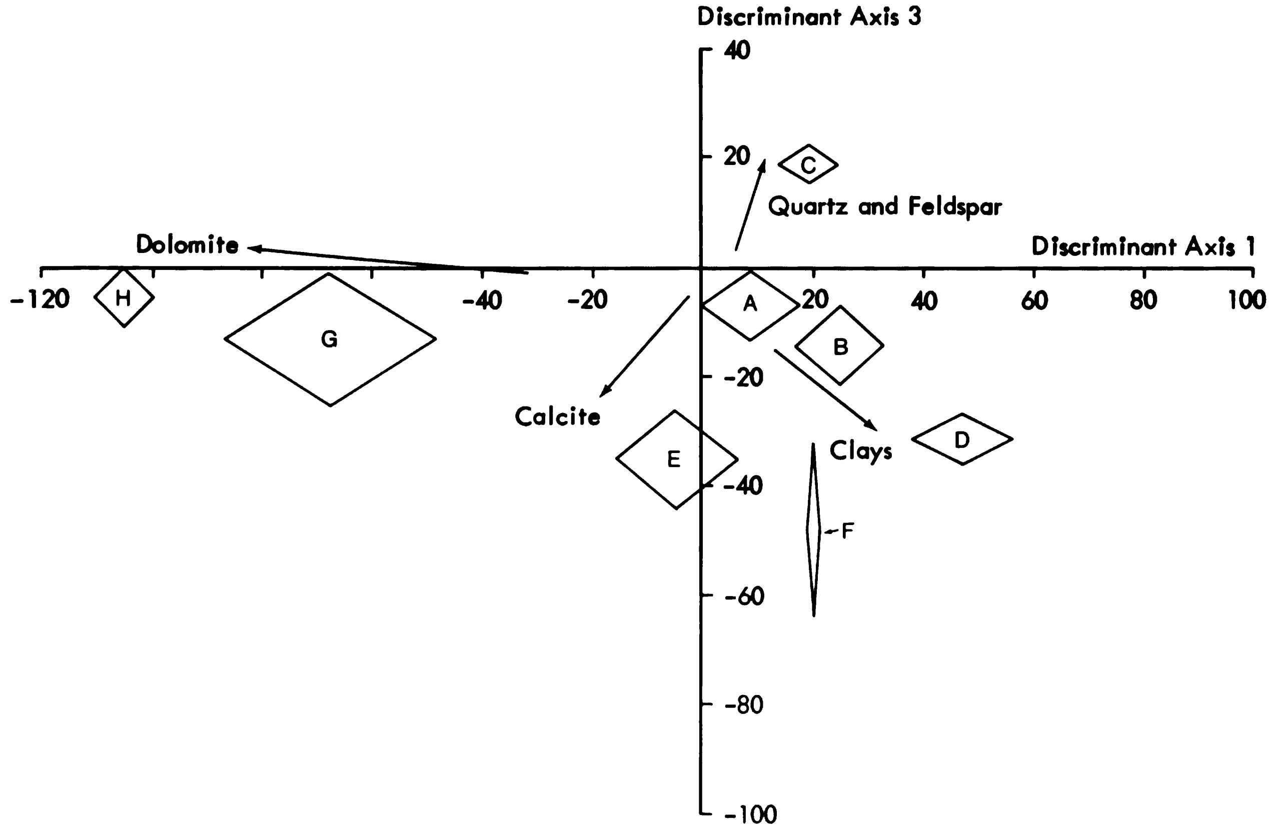

FIGURE 20. Distribution of cluster analysis groups on the first and third discriminant axes. Primary mineralogical variation is superimposed for reference. Diamonds represent the mean of each group ± 1 standard deviation on each axis.

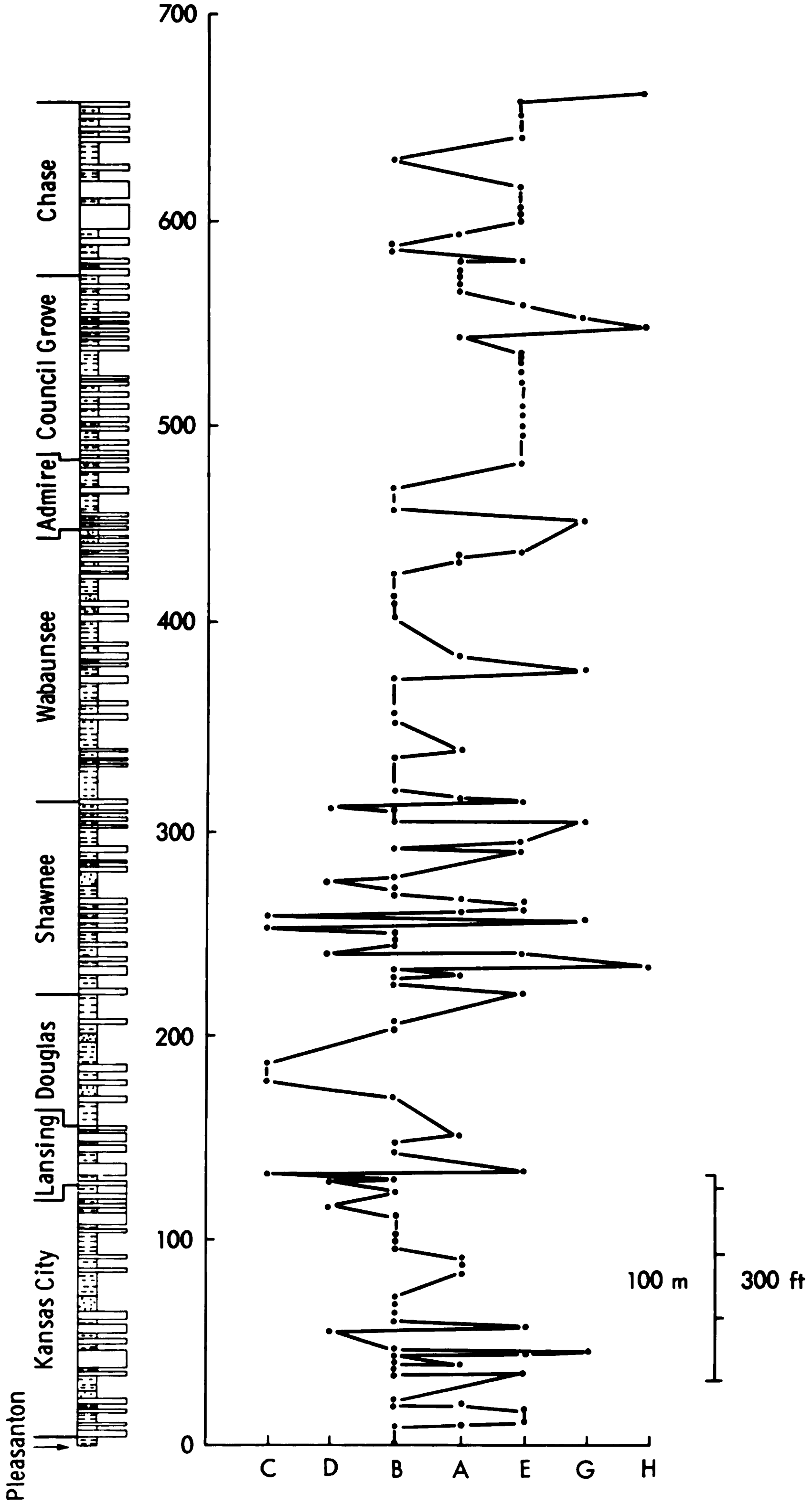

FIGURE 21. Stratigraphic distribution of samples arranged on a horizontal scale according to their cluster analysis class (Figure 17). The order of classes along the horizontal scale is arbitrary but may be interpreted as calcareous classes on the right and non-calcareous on the left.

EMISSION SPECTROSCOPY AND GEOCHEMISTRY

INTRODUCTION

Geochemistry of sediments is normally determined using X-ray fluorescence (XRF) or occasionally wet chemical methods, although exploration geochemists have in the past sacrificed the accuracy and sensitivity of XRF for the quantity of output obtained using emission spectroscopy. However, Davenport (1970) and Celenk (1972) have studied the problems associated with the emission spectroscopic analysis of rocks, stream sediments, and ore samples and have developed an efficient technique capable of handling many samples and producing results with an acceptable level of accuracy. A number of sedimentary rock analyses have subsequently been performed on the ARL 2900B direct reading spectrometer in the Geology Department at Leicester University, England, and the results have proved most successful (Celenk, 1972; Monteleone, 1973; Turner, 1973; Cubitt, 1975b).

Description of the Spectrometer. Analysis was performed on an ARL 2900B direct reading emission spectrometer with a D.C. arc source unit. The spectral lines for the elements sought are isolated from the remainder of the spectrum by passing the light, produced from the excitation of a sample, over a grating and receiving the resulting lines through a set of secondary slits. The intensities of the lines are measured electronically by photomultiplier tubes and their output is stored in a series of capacitors. A digital voltimeter reads the charge on the capacitors and a peripheral electric typewriter is used to obtain a printed copy of the readout. The optical characteristics of the spectrometer and details of the spectral lines are presented in Celenk (1972) and Cubitt (1975b).

Sample Preparation. As a result of orientation surveys performed by Celenk (1972), the following procedure was adopted for the geochemical analysis of sedimentary rocks. Samples were ground to pass through a 150 mesh sieve and preheated to 600°C, recording the percentage weight loss. One-hundred mg. of each sample was mixed with 150 mg. of buffer (a mixture of one part NaF to three parts "Magicoal" carbon powder), placed in a polystyrene vial containing a lucite ball and homogenized for one minute. The resulting mixture was then packed into a predrilled graphite electrode and heated by a Bunsen burner prior to arcing. During the arcing procedure, the filled electrode was used as an anode and a smooth, square-ended, graphite counter electrode was used as a cathode.

Calibration Standards. A set of synthetic bases, U.S. Geological Survey international standard rocks, and British Chemical Standards were analyzed for major and minor elements. The results determined the accuracy of the analytical method.

Mixtures of synthetic bases were prepared from "Specpure" Johnson and Matthey oxides, homogenized, and then fused in a muffle furnace at 950°C for three hours. The fused samples were ground and mixed with carefully weighed amounts of "Spec-Mix" (a mixture of 1.28 percent of each of the 49 element oxides), producing standards with 1000 ppm of all 49 element oxides. Stepwise dilution led to the preparation of further standards with 500, 250, 100, 50, 10, and zero ppm concentrations.

USGS and British Chemical Standards were used for calibration of major element oxides in the rock samples. Precise minor element values have not been recorded for these standards but a range of values is provided by the USGS and other organizations for comparative studies. With minor elements of values greater than 1000 ppm, care must be exercised as the synthetic bases may not be able to match the extremes in concentrations and the analytical results may be erroneous. However, using correction procedures (Celenk, 1972), extrapolation to higher concentrations can produce meaningful results.

Sensitivity, Precision, and Accuracy of the Procedure. Sensitivity of a method is defined as three times the standard deviation obtained by the repeated analysis of a sample containing zero ppm concentrations of the elements under examination (Cameron and Harton, 1967) and practically is the lowest possible concentration at which a particular trace element may be reliably detected. For the minor elements this value is less than 10 ppm except in the case of Zn (11 ppm) where, although two wavelengths were recorded, only one proved sensitive enough for normal analysis.

Precision of the analytical technique is expressed in terms of a coefficient of variation and indicates the reproducibility of the results. It is calculated using the equation: $P(\%) = (2 \times \text{standard deviation} \times 100)/\text{mean}$, and is found to be better than 20 percent for all elements.

By comparing the results obtained from this procedure with those calculated by Flanagan (1969), Celenk (1972) evaluated the accuracy of the method and concluded that the method was reasonably consistent, especially when the wide range of values quoted by Flanagan is taken into account.

Details of the precision and sensitivity for the method are presented in Table 6. Accuracies are calculated from data provided by Celenk (1972) and are reported in Table 7 (data were only available for MnO, Ba, Co, Cr, Cu, Ga, Li, Ni, Pb, Sr, V, Zn, Zr).

TABLE 6. Precision and sensitivity of spectroscopic technique.

	Precision (%)	Sensitivity (ppm)
Al_2O_3	8.8	
CaO	8.6	
Fe	10.9	
K_2O	17.7	
MgO	13.5	
SiO_2	8.0	
MnO	6.1	8
Ba	12.5	2
Be	6.2	1
Bi	8.6	1
Co	9.8	2
Cr	15.1	8
Cu	9.6	6
Ga	3.8	1
Ge	10.0	1
Li	5.6	2
Mo	15.2	6
Ni	10.9	9
Pb	15.6	8
Sn	17.5	4
Sr	9.0	1
V	11.8	3
Zn	14.1	11
Zr	18.0	8

RESULTS OF THE SPECTROSCOPIC ANALYSIS

One-hundred-twenty-six samples of Upper Pennsylvanian and Lower Permian shales from Kansas were analyzed using the previously described procedures (sample 170 was unavailable for geochemical analysis). The results are presented in Table 8. However, the following points should be borne in mind when examining Table 8. The results for Cd in the standards (see Cubitt, 1975b for complete tabulation) show anomalously high readings; those for Mo and Zn read slightly higher than normal; and the Fe, SiO_2 and Zr lines give low readings. Some care, therefore, must be taken in interpreting the results. It must also be remembered that the extrapolation procedure may overestimate any unusually high readings. Consequently, the value of 114 percent SiO_2 in sample 121 must be regarded sceptically. More realistic estimates for the few extreme major oxide values can be obtained from the mineralogical data.

Summary statistics for all the major and minor elements are presented in Table 9. Two extra parameters are included in the table, the percentage weight loss on ignition (Heat Loss) and the ratio of Mn to Fe.

Ag, Be, Bi, Ge, and Sn are only recorded in minor quantities in samples and therefore appear to have little influence on geochemical variation in the Upper Pennsylvanian and Lower Permian shales. Of the remaining elements and oxides, many show considerable numerical variation with standard deviations of the

TABLE 7. Accuracy of the spectroscopic technique.
A comparison of results obtained by Celenk (1972) employing the described equipment and technique to Flanagan's (1969) standardized analysis for rocks GSP-1, AGV-1, and PCC-1.

Standard Rock		MnO	Ba	Co	Cr	Cu	Ga	Li	Ni	Pb	Sr	V	Zn	Zr	Results by
GSP-1	RANGE	260–	855–	<3–	5–	15–	12–	–	3–	14–	148–	38–	54–	323–	Flanagan
		450	2000	22	18	54	35		25	80	400	67	340	685	1969
	MEAN	326	1360	8	13	35	19	36	11	52	247	52	143	544	
GSP-1	RANGE	205–	1029–	2–	B.D.–	23–	16–	9–	B.D.–	44–	168–	16–	23–	256–	Celenk
		297	1576	15	14	45	25	39	8	80	362	114	143	745	1972
	MEAN	261	1308	8	5	34	21	20	2	66	263	52	67	436	
AGV-1	RANGE	640–	1047–	10–	8–	52–	14–	–	11–	18–	348–	70–	64–	186–	Flanagan
		870	2700	30	45	83	24		27	48	1050	171	304	315	1969
	MEAN	728	1410	16	13	64	18	12	18	35	657	121	112	227	
AGV-1	RANGE	423–	900–	2–	B.D.–	48–	14–	B.D.–	B.D.–	18–	458–	46–	66–	129–	Celenk
		759	1431	20	11	78	22	17	18	53	858	272	141	342	1972
	MEAN	592	1134	0	4	65	19	6	6	37	618	83	101	194	
PCC-1	RANGE	610–	–	80–	1840–	5–	–	–	1750–	–	–	21–	24–	–	Flanagan
		1430		330	4780	6			3400			55	100		1969
	MEAN	889	7	112	3090	10	12	0	2430	13	<1	31	53	0	
PCC-1	RANGE	623–	B.D.–	88–	1830–	B.D.–	B.D.–	B.D.–	1528–	B.D.–	B.D.–	8–	22–	B.D.–	Celenk
		1126	13	173	3181	7	4	4	2950	21	2	34	128	24	1972
	MEAN	851	2	91	2169	7	1	0	1898	5	0	23	85	9	

B.D. = Below detection limit.

TABLE 8. Results of emission spectroscopic analysis of Upper Pennsylvanian and Lower Permian shales of Kansas.

	Sample Number	16	19	20	21	23	24	25	26	27	28	7	31	32	34	36	35	38	40	41	43	46
Major Oxides (Percent)	Al_2O_3	17.3	17.4	14.8	8.4	11.8	17.8	15.8	15.9	8.8	16.9	12.9	16.4	16.1	16.2	12.9	5.3	17.5	18.3	13.5	14.9	16.9
	CaO	0.4	0.4	7.2	21.5	19.5	0.9	2.0	2.9	22.4	0.1	0.1	3.4	2.5	4.2	16.5	29.4	2.0	0.3	14.5	0.4	2.8
	Fe Oxides	5.6	4.7	3.0	3.7	3.3	3.7	4.6	3.9	2.1	3.2	5.2	5.0	5.4	4.3	3.7	3.2	5.4	5.1	3.8	4.8	5.1
	K_2O	2.6	3.3	2.6	1.5	2.9	3.0	3.7	4.0	2.3	2.9	2.2	3.4	3.7	3.6	2.8	1.2	3.8	3.0	2.7	2.7	3.6
	MgO	2.0	1.8	3.0	5.2	3.3	1.8	2.1	2.0	1.3	2.0	1.1	2.8	2.3	3.0	2.0	13.8	2.6	2.0	2.5	1.9	2.6
	SiO_2	71.2	64.6	73.3	39.6	37.7	69.1	62.4	58.5	35.3	75.4	69.9	62.0	65.3	60.7	50.9	20.6	64.5	68.6	44.5	59.8	69.3
	Mn/Fe	0.5	0.5	1.6	1.7	2.0	0.3	0.6	0.7	1.3	0.4	0.1	0.6	0.6	0.6	1.0	2.5	0.7	0.5	1.1	0.0	0.4
Minor Elements and Oxides (PPM)	MnO	293.0	242.0	469.0	618.0	656.0	93.0	276.0	273.0	273.0	126.0	67.0	283.0	311.0	247.0	385.0	789.0	350.0	255.0	435.0	181.0	192.0
	Ag	0.0	0.0	0.0	1.0	0.0	18.0	1.0	0.0	2.0	0.0	16.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	1.0	6.0	0.0
	Ba	392.0	286.0	534.0	152.0	141.0	376.0	278.0	369.0	133.0	231.0	317.0	329.0	353.0	331.0	259.0	92.0	374.0	404.0	283.0	269.0	361.0
	Be	3.0	7.0	3.0	5.0	6.0	12.0	6.0	5.0	5.0	3.0	10.0	6.0	4.0	7.0	3.0	8.0	7.0	3.0	5.0	7.0	4.0
	Bi	0.0	1.0	0.0	3.0	2.0	2.0	1.0	0.0	4.0	0.0	2.0	1.0	2.0	1.0	1.0	3.0	1.0	0.0	1.0	1.0	0.0
	Cd	23.0	31.0	30.0	45.0	49.0	138.0	39.0	15.0	73.0	34.0	58.0	28.0	37.0	19.0	39.0	34.0	19.0	30.0	44.0	52.0	28.0
	Co	57.0	35.0	36.0	37.0	42.0	35.0	27.0	33.0	37.0	15.0	21.0	66.0	32.0	27.0	66.0	46.0	28.0	30.0	27.0	73.0	24.0
	Cr	109.0	109.0	124.0	76.0	78.0	1428.0	159.0	173.0	77.0	115.0	1064.0	339.0	137.0	197.0	95.0	38.0	110.0	124.0	108.0	482.0	199.0
Minor Elements (PPM)	Cu	23.0	40.0	21.0	9.0	16.0	134.0	41.0	32.0	15.0	22.0	118.0	61.0	57.0	27.0	22.0	8.0	33.0	37.0	23.0	99.0	20.0
	Ga	23.0	24.0	16.0	10.0	15.0	24.0	22.0	22.0	12.0	22.0	17.0	23.0	24.0	23.0	16.0	6.0	24.0	26.0	18.0	22.0	23.0
	Ge	1.0	1.0	0.0	3.0	3.0	1.0	1.0	1.0	7.0	0.0	1.0	1.0	2.0	1.0	2.0	5.0	1.0	0.0	1.0	1.0	1.0
	Li	64.0	35.0	21.0	32.0	30.0	45.0	52.0	42.0	75.0	46.0	43.0	70.0	62.0	63.0	41.0	37.0	63.0	75.0	43.0	47.0	51.0
	Mo	6.0	0.0	9.0	34.0	22.0	231.0	0.0	0.0	54.0	0.0	241.0	69.0	2.0	0.0	34.0	47.0	9.0	0.0	13.0	44.0	0.0
	Ni	68.0	66.0	61.0	39.0	39.0	363.0	136.0	109.0	45.0	40.0	239.0	321.0	97.0	125.0	140.0	29.0	73.0	76.0	73.0	661.0	122.0
	Pb	21.0	63.0	6.0	9.0	28.0	205.0	39.0	43.0	8.0	17.0	77.0	59.0	35.0	27.0	42.0	7.0	38.0	25.0	12.0	356.0	9.0
	Sn	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.0
	Sr	149.0	100.0	322.0	923.0	779.0	124.0	90.0	153.0	1471.0	132.0	95.0	211.0	205.0	190.0	925.0	682.0	158.0	111.0	362.0	77.0	154.0
	V	198.0	121.0	137.0	78.0	55.0	3607.0	204.0	205.0	85.0	109.0	2358.0	324.0	153.0	205.0	90.0	50.0	234.0	171.0	110.0	808.0	161.0
	Zn	286.0	161.0	158.0	38.0	71.0	816.0	515.0	154.0	40.0	153.0	697.0	468.0	209.0	335.0	97.0	0.0	207.0	239.0	156.0	873.0	235.0
	Zr	345.0	159.0	354.0	220.0	109.0	140.0	189.0	236.0	194.0	262.0	128.0	236.0	160.0	208.0	165.0	137.0	142.0	131.0	127.0	82.0	206.0
	Heat Loss (%)	4.1	7.4	6.9	2.5	9.0	29.9	4.4	6.6	7.0	4.9	25.0	8.7	4.5	4.9	8.1	0.1	4.5	4.0	7.9	15.0	6.1

	Sample Number	47	48	54	50	53	69	70	71	160	67	61A	63	12	66	15	3	157	161	296	294	290
Major Oxides (Percent)	Al_2O_3	16.7	16.2	8.9	14.2	12.1	17.7	16.6	17.3	15.0	16.1	17.0	17.7	16.2	6.7	13.5	18.8	15.6	17.0	18.5	9.0	14.4
	CaO	4.0	4.1	12.0	8.1	18.2	0.8	6.1	2.6	5.1	0.5	6.2	0.4	3.4	21.4	12.8	0.1	1.1	3.8	5.2	0.1	0.1
	Fe Oxides	4.0	4.5	2.8	4.6	3.4	5.4	5.4	4.6	4.3	5.3	5.1	5.9	4.7	5.4	3.8	7.0	5.8	5.0	4.7	2.6	4.4
	K_2O	3.3	3.4	1.1	3.1	2.8	2.9	2.1	2.6	2.2	3.6	3.6	3.5	2.7	1.1	2.0	4.6	4.9	3.8	2.9	0.5	2.1
	MgO	2.6	3.0	0.9	2.1	1.9	2.3	1.8	1.9	1.6	2.0	2.2	2.5	2.4	26.8	1.3	2.0	2.1	2.6	2.1	0.4	0.5
	SiO_2	58.3	60.9	67.2	49.6	43.9	59.5	66.1	67.6	53.3	59.7	61.3	61.0	65.3	26.9	44.5	59.2	57.6	66.2	67.5	89.0	69.7
	Mn/Fe	0.5	0.5	2.9	0.6	0.5	0.5	0.9	0.8	0.9	0.5	0.8	0.5	1.2	2.3	1.1	0.6	0.5	0.5	0.6	1.1	0.8
Minor Elements and Oxides (PPM)	MnO	185.0	227.0	821.0	269.0	172.0	255.0	492.0	350.0	382.0	252.0	419.0	279.0	570.0	1251.0	431.0	406.0	269.0	237.0	279.0	295.0	339.0
	Ag	3.0	0.0	0.0	11.0	2.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	46.0	0.0
	Ba	428.0	417.0	204.0	201.0	310.0	347.0	394.0	446.0	412.0	312.0	416.0	356.0	272.0	123.0	372.0	500.0	353.0	384.0	484.0	180.0	398.0
	Be	6.0	3.0	4.0	5.0	8.0	6.0	5.0	5.0	5.0	6.0	6.0	6.0	5.0	6.0	4.0	8.0	6.0	6.0	6.0	2.0	5.0
	Bi	0.0	0.0	0.0	1.0	2.0	1.0	0.0	0.0	0.0	1.0	1.0	2.0	0.0	2.0	1.0	2.0	3.0	1.0	1.0	0.0	1.0
	Cd	14.0	23.0	20.0	28.0	97.0	30.0	31.0	25.0	19.0	31.0	20.0	34.0	17.0	15.0	14.0	35.0	41.0	22.0	43.0	48.0	35.0
	Co	45.0	29.0	77.0	15.0	37.0	32.0	39.0	51.0	31.0	32.0	39.0	36.0	37.0	43.0	23.0	52.0	27.0	32.0	34.0	224.0	40.0
	Cr	165.0	149.0	51.0	97.0	566.0	95.0	86.0	109.0	117.0	106.0	119.0	110.0	94.0	35.0	107.0	143.0	169.0	127.0	113.0	40.0	80.0
Minor Elements (PPM)	Cu	9.0	12.0	13.0	25.0	58.0	37.0	28.0	22.0	49.0	23.0	22.0	7.0	37.0	6.0	31.0	35.0	63.0	30.0	26.0	5.0	27.0
	Ga	23.0	23.0	9.0	22.0	14.0	24.0	19.0	20.0	20.0	25.0	25.0	27.0	20.0	6.0	18.0	32.0	27.0	24.0	23.0	8.0	19.0
	Ge	1.0	1.0	1.0	2.0	2.0	1.0	1.0	1.0	0.0	1.0	1.0	2.0	1.0	2.0	1.0	3.0	3.0	1.0	1.0	0.0	1.0
	Li	37.0	37.0	18.0	27.0	32.0	83.0	63.0	61.0	25.0	72.0	66.0	87.0	44.0	15.0	38.0	113.0	68.0	28.0	59.0	6.0	33.0
	Mo	0.0	0.0	32.0	6.0	60.0	0.0	10.0	1.0	0.0	0.0	5.0	0.0	15.0	19.0	7.0	0.0	21.0	4.0	0.0	11.0	3.0
	Ni	99.0	94.0	44.0	49.0	249.0	50.0	53.0	69.0	83.0	56.0	75.0	53.0	62.0	43.0	61.0	109.0	106.0	59.0	58.0	22.0	27.0
	Pb	4.0	7.0	14.0	13.0	177.0	11.0	14.0	19.0	38.0	32.0	28.0	13.0	7.0	4.0	38.0	27.0	44.0	22.0	25.0	6.0	32.0
	Sn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Sr	186.0	307.0	259.0	367.0	731.0	110.0	211.0	169.0	124.0	92.0	324.0	119.0	198.0	301.0	129.0	257.0	136.0	254.0	233.0	68.0	118.0
	V	170.0	168.0	74.0	109.0	488.0	130.0	114.0	174.0	83.0	171.0	213.0	161.0	174.0	53.0	102.0	286.0	271.0	166.0	142.0	49.0	89.0
	Zn	213.0	255.0	86.0	140.0	909.0	226.0	217.0	266.0	268.0	243.0	250.0	207.0	197.0	0.0	183.0	323.0	430.0	200.0	210.0	108.0	200.0
	Zr	205.0	213.0	291.0	141.0	190.0	159.0	229.0	340.0	118.0	152.0	312.0	189.0	339.0	124.0	122.0	240.0	186.0	295.0	217.0	192.0	499.0
	Heat Loss (%)	4.6	6.4	2.0	8.5	4.8	2.9	4.8	3.4	8.2	3.1	4.5	2.0	3.8	0.9	5.7	6.0	7.0	7.1	3.9	2.0	0.5

	Sample Number	284	287	281	125	116	110	112	128	130	79	151	82	80	81	85	135	121	138	136	137	149
Major Oxides (Percent)	Al_2O_3	15.0	16.4	14.2	14.6	15.4	16.6	15.5	17.0	9.0	15.9	17.5	17.4	19.8	17.8	14.0	9.4	4.1	15.5	13.4	9.2	16.2
	CaO	1.2	4.7	8.8	0.1	4.1	8.5	0.8	4.2	16.2	14.1	1.1	1.5	1.1	0.3	0.1	17.1	0.1	8.2	7.6	20.8	5.3
	Fe Oxides	5.2	4.7	4.7	2.8	4.2	5.1	4.9	5.3	5.8	4.9	4.9	4.9	6.4	5.5	1.9	4.9	2.6	5.2	4.1	4.2	3.9
	K_2O	3.0	3.1	2.3	1.7	2.9	2.8	2.0	3.4	1.9	3.4	4.2	3.4	3.2	3.4	1.2	2.1	0.1	3.3	2.8	1.5	2.6
	MgO	1.6	1.7	3.6	0.7	2.0	2.5	1.1	3.0	7.4	3.6	2.4	1.8	2.0	1.9	0.6	6.0	0.3	2.3	2.8	1.4	2.2
	SiO_2	57.3	62.0	63.9	83.8	56.4	63.3	79.3	61.6	34.2	52.8	63.4	63.7	65.0	58.0	82.3	27.1	114.0	51.6	52.0	32.3	65.7
	Mn/Fe	0.4	1.9	1.2	0.2	0.9	0.7	0.6	0.5	1.4	1.2	0.4	0.7	0.4	0.4	0.5	2.0	0.3	0.8	0.8	2.2	0.9
Minor Elements and Oxides (PPM)	MnO	182.0	874.0	549.0	65.0	396.0	341.0	296.0	263.0	789.0	588.0	194.0	330.0	266.0	234.0	96.0	960.0	67.0	400.0	330.0	912.0	368.0
	Ag	1.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	1.0	0.0
	Ba	297.0	412.0	807.0	382.0	351.0	251.0	361.0	368.0	203.0	368.0	470.0	376.0	520.0	451.0	284.0	173.0	111.0	315.0	287.0	214.0	379.0
	Be	3.0	6.0	6.0	3.0	5.0	6.0	4.0	8.0	5.0	7.0	7.0	5.0	4.0	4.0	4.0	4.0	2.0	5.0	4.0	4.0	6.0
	Bi	0.0	1.0	1.0	0.0	1.0	1.0	0.0	2.0	4.0	2.0	1.0	1.0	1.0	1.0	0.0	3.0	0.0	1.0	1.0	4.0	0.0
	Cd	22.0	19.0	77.0	56.0	20.0	46.0	41.0	165.0	20.0	23.0	21.0	26.0	29.0	22.0	46.0	10.0	47.0	26.0	28.0	11.0	16.0
	Co	15.0	51.0	58.0	70.0	17.0	25.0	33.0	67.0	35.0	39.0	36.0	24.0	31.0	28.0	47.0	48.0	85.0	20.0	34.0	27.0	46.0
	Cr	82.0	103.0	91.0	101.0	152.0	99.0	94.0	1097.0	72.0	92.0	146.0	108.0	113.0	125.0	66.0	71.0	66.0	95.0	94.0	61.0	95.0
Minor Elements (PPM)	Cu	8.0	22.0	14.0	5.0	43.0	30.0	5.0	105.0	24.0	23.0	21.0	31.0	34.0	32.0	11.0	14.0	2.0	29.0	24.0	27.0	17.0
	Ga	20.0	23.0	16.0	15.0	27.0	22.0	17.0	21.0	12.0	20.0	27.0	26.0	28.0	28.0	12.0	12.0	3.0	22.0	17.0	12.0	19.0
	Ge	1.0	1.0	2.0	0.0	1.0	2.0	1.0	1.0	4.0	3.0	1.0	1.0	2.0	1.0	0.0	3.0	0.0	1.0	1.0	4.0	1.0
	Li	30.0	60.0	26.0	11.0	29.0	21.0	46.0	35.0	36.0	35.0	48.0	89.0	77.0	94.0	14.0	33.0	7.0	28.0	30.0	40.0	30.0
	Mo	0.0	29.0	8.0	11.0	0.0	6.0	0.0	174.0	34.0	27.0	0.0	0.0	0.0	3.0	0.0	26.0	0.0	17.0	2.0	39.0	13.0
	Ni	39.0	78.0	41.0	22.0	70.0	61.0	53.0	421.0	61.0	51.0	75.0	52.0	64.0	69.0	19.0	45.0	19.0	43.0	48.0	39.0	50.0
	Pb	4.0	14.0	17.0	15.0	15.0	18.0	9.0	184.0	33.0	20.0	22.0	12.0	23.0	18.0	21.0	14.0	7.0	47.0	30.0	37.0	9.0
	Sn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0	0.0	0.0	5.0	0.0	0.0	0.0	0.0	0.0
	Sr	114.0	198.0	571.0	390.0	181.0	404.0	98.0	136.0	524.0	427.0	195.0	135.0	167.0	175.0	68.0	509.0	21.0	227.0	217.0	438.0	162.0
	V	103.0	228.0	103.0	153.0	161.0	139.0	105.0	951.0	70.0	154.0	288.0	166.0	165.0	253.0	73.0	58.0	19.0	94.0	116.0	56.0	138.0
	Zn	182.0	198.0	135.0	161.0	247.0	129.0	190.0	903.0	59.0	192.0	220.0	260.0	198.0	317.0	117.0	52.0	44.0	194.0	121.0	51.0	190.0
	Zr	105.0	320.0	370.0	507.0	159.0	235.0	289.0	184.0	126.0	195.0	213.0	157.0	155.0	168.0	730.0	79.0	463.0	115.0	153.0	107.0	344.0
	Heat Loss (%)	4.3	1.9	7.4	3.0	6.0	7.9	3.9	11.6	10.5	7.1	3.1	6.9	5.0	6.4	2.4	15.5	0.5	8.3	4.8	10.5	3.9

	Sample Number	150	152	153	155	105	107	109	94	96	97	144	101	122	97B	148	162	163	171	173	168	192
Major Oxides (Percent)	Al_2O_3	17.1	18.4	17.1	17.0	10.2	16.2	8.4	7.1	15.6	20.2	17.0	16.3	12.1	14.2	17.7	15.5	13.1	18.3	19.8	15.4	8.3
	CaO	0.5	0.5	0.2	0.5	14.6	5.8	25.5	30.8	0.1	2.1	4.2	3.6	13.9	5.0	2.7	0.1	7.6	0.1	0.2	0.1	17.7
	Fe Oxides	4.1	5.9	5.7	7.2	2.9	5.3	6.0	3.9	4.3	5.9	5.2	4.8	4.4	3.6	5.2	7.1	10.3	9.6	6.6	6.1	5.4
	K_2O	3.0	3.4	2.7	2.2	1.4	3.1	1.4	1.8	2.1	3.6	3.4	2.8	3.0	2.4	3.2	2.2	3.4	3.5	2.4	1.7	1.7
	MgO	2.0	2.0	1.8	1.5	1.1	2.0	1.1	3.8	1.3	2.4	4.2	1.6	3.0	1.6	2.3	1.0	5.4	1.3	1.6	1.1	8.9
	SiO_2	70.2	67.4	57.3	72.9	48.8	55.1	21.7	14.6	68.4	65.5	56.7	59.6	51.9	66.6	58.9	71.2	54.5	65.2	67.9	76.5	46.7
	Mn/Fe	0.5	0.6	0.7	0.5	2.2	0.4	2.6	3.2	0.7	0.8	0.9	0.6	0.9	0.8	0.4	0.3	0.1	0.3	0.7	0.6	4.4
Minor Elements and Oxides (PPM)	MnO	218.0	374.0	417.0	344.0	624.0	185.0	1564.0	1264.0	317.0	469.0	465.0	292.0	374.0	301.0	229.0	179.0	136.0	289.0	449.0	347.0	2385.0
	Ag	0.0	0.0	0.0	0.0	0.0	2.0	2.0	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Ba	400.0	444.0	379.0	452.0	217.0	345.0	256.0	151.0	412.0	684.0	388.0	548.0	284.0	365.0	381.0	380.0	285.0	519.0	529.0	348.0	201.0
	Be	3.0	6.0	6.0	3.0	4.0	12.0	6.0	9.0	5.0	7.0	7.0	5.0	2.0	4.0	7.0	4.0	6.0	7.0	5.0	2.0	6.0
	Bi	0.0	1.0	0.0	1.0	1.0	3.0	6.0	8.0	0.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0	5.0	3.0	0.0	0.0	3.0
	Cd	23.0	37.0	34.0	27.0	14.0	168.0	5.0	47.0	25.0	19.0	14.0	31.0	22.0	27.0	56.0	38.0	25.0	40.0	26.0	19.0	9.0
	Co	16.0	36.0	28.0	55.0	49.0	63.0	52.0	53.0	70.0	73.0	59.0	29.0	32.0	29.0	31.0	41.0	24.0	40.0	31.0	149.0	74.0
	Cr	105.0	138.0	83.0	98.0	63.0	376.0	70.0	67.0	81.0	130.0	97.0	95.0	81.0	89.0	490.0	82.0	123.0	106.0	140.0	65.0	53.0
Minor Elements (PPM)	Cu	19.0	42.0	25.0	25.0	15.0	139.0	20.0	25.0	24.0	36.0	26.0	33.0	24.0	22.0	140.0	23.0	55.0	20.0	28.0	22.0	6.0
	Ga	24.0	25.0	24.0	22.0	11.0	24.0	12.0	12.0	19.0	28.0	24.0	26.0	15.0	19.0	26.0	20.0	23.0	27.0	26.0	17.0	9.0
	Ge	0.0	1.0	1.0	1.0	1.0	2.0	8.0	12.0	0.0	2.0	1.0	2.0	1.0	1.0	1.0	1.0	5.0	4.0	1.0	0.0	3.0
	Li	29.0	32.0	84.0	65.0	22.0	49.0	58.0	95.0	49.0	92.0	40.0	57.0	32.0	28.0	48.0	38.0	25.0	118.0	105.0	38.0	24.0
	Mo	0.0	6.0	0.0	6.0	18.0	713.0	58.0	93.0	0.0	16.0	19.0	0.0	31.0	0.0	4.0	0.0	39.0	0.0	0.0	10.0	43.0
	Ni	36.0	140.0	41.0	73.0	37.0	410.0	48.0	52.0	63.0	97.0	80.0	49.0	55.0	37.0	256.0	42.0	41.0	83.0	50.0	49.0	39.0
	Pb	11.0	44.0	12.0	20.0	11.0	164.0	15.0	13.0	16.0	15.0	54.0	7.0	19.0	5.0	53.0	14.0	39.0	15.0	22.0	56.0	5.0
	Sn	0.0	0.0	0.0	0.0	0.0	0.0	4.0	20.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Sr	97.0	100.0	85.0	144.0	263.0	198.0	418.0	1375.0	104.0	187.0	158.0	146.0	440.0	133.0	119.0	107.0	220.0	157.0	157.0	96.0	341.0
	V	114.0	192.0	106.0	166.0	59.0	1627.0	58.0	76.0	123.0	236.0	148.0	109.0	115.0	93.0	167.0	102.0	181.0	168.0	109.0	112.0	95.0
	Zn	156.0	360.0	370.0	350.0	72.0	904.0	35.0	37.0	266.0	282.0	187.0	204.0	99.0	196.0	619.0	219.0	286.0	428.0	273.0	241.0	54.0
	Zr	195.0	240.0	196.0	490.0	227.0	234.0	151.0	171.0	378.0	115.0	312.0	144.0	293.0	318.0	113.0	279.0	166.0	206.0	192.0	465.0	402.0
	Heat Loss (%)	4.0	5.5	5.6	5.9	8.0	17.3	12.0	11.0	1.9	3.3	8.7	8.0	13.0	5.5	7.2	5.0	12.5	6.9	6.2	5.8	2.9

	Sample Number	194	176	180	181	184	185	186	187	197	200	205	206	208	209	261	262	212	213	264	237	235
Major Oxides (Percent)	Al_2O_3	17.1	19.6	15.1	16.3	16.4	17.5	18.3	13.6	10.9	17.1	15.4	8.5	8.4	9.1	9.0	12.1	11.6	8.8	13.2	8.3	11.8
	CaO	5.7	0.1	0.1	3.4	0.1	3.2	4.4	16.9	16.3	3.7	1.6	29.1	25.8	27.0	23.2	15.3	16.2	25.8	13.8	27.5	14.6
	Fe Oxides	4.4	6.1	5.3	4.2	4.8	4.7	5.5	6.9	5.9	4.7	5.7	3.9	4.0	3.9	3.7	3.4	3.7	2.9	4.6	1.8	5.3
	K_2O	3.0	3.7	3.0	2.2	2.2	2.7	3.1	2.9	2.4	3.0	3.5	1.6	2.3	1.8	2.5	3.0	2.8	2.8	2.6	1.6	3.6
	MgO	2.3	2.2	1.1	1.8	1.9	2.6	2.5	3.6	7.9	2.1	2.7	2.1	2.1	4.3	4.3	3.8	2.1	1.6	4.3	2.0	2.7
	SiO_2	55.2	58.0	60.3	62.6	70.2	63.9	67.0	37.2	46.0	65.2	60.3	31.6	27.6	30.7	35.9	44.0	42.6	26.5	46.5	21.3	40.0
	Mn/Fe	1.1	0.4	0.4	1.0	0.6	0.6	0.4	4.8	5.6	0.7	0.4	3.8	2.9	2.0	1.2	0.7	0.7	1.5	0.7	1.8	0.6
Minor Elements and Oxides (PPM)	MnO	470.0	237.0	212.0	410.0	276.0	300.0	229.0	3297.0	3297.0	310.0	228.0	1471.0	1172.0	785.0	453.0	224.0	245.0	444.0	320.0	320.0	326.0
	Ag	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	3.0	1.0	2.0	6.0	0.0	3.0	0.0	2.0	0.0
	Ba	502.0	475.0	446.0	299.0	405.0	352.0	230.0	457.0	240.0	351.0	350.0	168.0	143.0	180.0	216.0	254.0	261.0	227.0	316.0	174.0	295.0
	Be	7.0	7.0	5.0	5.0	2.0	7.0	5.0	7.0	7.0	3.0	5.0	5.0	8.0	7.0	7.0	3.0	4.0	7.0	3.0	3.0	4.0
	Bi	1.0	2.0	2.0	0.0	0.0	1.0	1.0	3.0	2.0	0.0	1.0	3.0	6.0	3.0	4.0	1.0	1.0	6.0	0.0	3.0	3.0
	Cd	26.0	15.0	31.0	23.0	19.0	21.0	28.0	15.0	8.0	21.0	29.0	5.0	18.0	77.0	7.0	46.0	7.0	20.0	20.0	6.0	33.0
	Co	15.0	45.0	28.0	17.0	45.0	47.0	23.0	32.0	46.0	19.0	29.0	60.0	63.0	34.0	44.0	23.0	27.0	71.0	21.0	62.0	17.0
	Cr	86.0	132.0	96.0	84.0	92.0	96.0	109.0	63.0	68.0	84.0	86.0	62.0	74.0	117.0	108.0	572.0	74.0	80.0	75.0	67.0	69.0
Minor Elements (PPM)	Cu	26.0	31.0	17.0	6.0	11.0	19.0	10.0	18.0	29.0	6.0	114.0	15.0	22.0	16.0	22.0	50.0	19.0	31.0	23.0	11.0	13.0
	Ga	22.0	30.0	25.0	20.0	20.0	20.0	25.0	17.0	12.0	21.0	22.0	10.0	13.0	10.0	11.0	17.0	14.0	13.0	16.0	10.0	18.0
	Ge	1.0	2.0	2.0	0.0	0.0	1.0	1.0	4.0	3.0	0.0	1.0	6.0	9.0	4.0	6.0	1.0	2.0	9.0	1.0	5.0	3.0
	Li	21.0	143.0	55.0	22.0	56.0	31.0	18.0	38.0	28.0	36.0	54.0	53.0	93.0	43.0	94.0	86.0	79.0	98.0	75.0	78.0	54.0
	Mo	0.0	0.0	0.0	0.0	0.0	2.0	0.0	47.0	44.0	0.0	0.0	58.0	70.0	38.0	54.0	94.0	20.0	71.0	12.0	53.0	15.0
	Ni	35.0	95.0	36.0	36.0	52.0	56.0	61.0	53.0	68.0	49.0	50.0	51.0	64.0	72.0	64.0	230.0	43.0	76.0	49.0	38.0	39.0
	Pb	11.0	25.0	33.0	10.0	8.0	10.0	12.0	18.0	84.0	7.0	9.0	9.0	8.0	11.0	7.0	23.0	18.0	23.0	19.0	2.0	10.0
	Sn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	4.0	0.0	0.0	7.0	0.0	0.0	0.0
	Sr	147.0	143.0	153.0	94.0	112.0	171.0	146.0	729.0	310.0	133.0	197.0	346.0	569.0	1844.0	212.0	267.0	148.0	496.0	469.0	479.0	543.0
	V	81.0	284.0	156.0	89.0	140.0	143.0	108.0	115.0	110.0	98.0	94.0	73.0	77.0	76.0	99.0	254.0	76.0	98.0	77.0	88.0	66.0
	Zn	155.0	291.0	216.0	172.0	229.0	213.0	132.0	139.0	73.0	213.0	192.0	0.0	46.0	72.0	49.0	229.0	97.0	119.0	102.0	27.0	123.0
	Zr	147.0	216.0	276.0	165.0	388.0	359.0	255.0	231.0	320.0	149.0	158.0	212.0	152.0	169.0	151.0	127.0	155.0	173.0	146.0	133.0	97.0
	Heat Loss (%)	8.1	6.7	3.5	5.9	3.5	4.4	8.8	10.9	8.7	7.4	5.0	1.5	7.0	9.7	10.5	4.3	8.0	8.0	5.0	4.2	14.0

	Sample Number	238	249	248	234	230	226	227	221	222	243	244	273	253	251	256	265	268	270	272	298	300
Major Oxides (Percent)	Al_2O_3	15.3	8.5	11.1	10.5	17.1	12.9	15.5	12.1	6.0	14.4	16.9	10.8	11.2	12.8	11.8	9.0	16.1	14.7	12.4	13.0	9.4
	CaO	5.9	18.0	14.7	20.9	4.2	10.6	0.2	20.6	38.0	5.5	1.0	10.5	24.3	15.2	10.7	18.5	1.7	4.6	23.3	5.2	13.2
	Fe Oxides	4.5	3.6	4.8	4.4	6.3	5.7	4.4	3.8	2.1	5.8	3.0	4.9	3.0	4.4	5.0	3.0	6.6	6.7	4.3	2.8	4.4
	K_2O	2.7	1.5	1.8	2.2	4.1	3.8	2.8	1.9	2.4	3.9	4.1	3.1	2.3	3.0	2.4	2.3	4.0	2.9	2.6	2.5	2.4
	MgO	3.6	13.1	10.4	5.7	2.6	2.7	2.8	3.5	3.2	3.6	2.9	9.1	3.8	5.2	3.6	2.3	3.3	3.8	4.4	4.0	13.3
	SiO_2	60.1	33.5	46.0	30.2	58.9	50.6	62.0	42.9	18.7	52.6	58.3	37.9	31.5	40.9	58.0	28.2	61.6	63.1	46.0	58.9	43.1
	Mn/Fe	0.6	1.3	1.2	1.1	0.9	0.5	0.6	1.7	3.1	0.6	0.3	1.3	1.4	1.2	0.9	1.2	0.5	0.5	1.0	1.1	0.9
Minor Elements and Oxides (PPM)	MnO	270.0	458.0	589.0	465.0	575.0	260.0	272.0	652.0	660.0	361.0	77.0	653.0	406.0	526.0	463.0	349.0	306.0	320.0	416.0	317.0	393.0
	Ag	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
	Ba	327.0	189.0	206.0	228.0	1594.0	284.0	287.0	165.0	149.0	468.0	397.0	211.0	224.0	281.0	328.0	234.0	470.0	1194.0	406.0	348.0	253.0
	Be	4.0	2.0	3.0	2.0	6.0	4.0	4.0	3.0	10.0	5.0	6.0	4.0	7.0	3.0	4.0	4.0	3.0	3.0	4.0	3.0	5.0
	Bi	0.0	0.0	0.0	2.0	1.0	2.0	0.0	1.0	8.0	2.0	0.0	2.0	3.0	1.0	2.0	3.0	0.0	0.0	3.0	0.0	2.0
	Cd	23.0	0.0	17.0	1.0	25.0	22.0	18.0	48.0	14.0	18.0	23.0	3.0	0.0	1.0	19.0	0.0	19.0	16.0	8.0	20.0	0.0
	Co	19.0	35.0	19.0	29.0	27.0	13.0	19.0	30.0	90.0	21.0	7.0	18.0	42.0	35.0	22.0	38.0	40.0	27.0	44.0	42.0	21.0
	Cr	76.0	51.0	55.0	61.0	94.0	66.0	65.0	82.0	59.0	92.0	107.0	68.0	66.0	103.0	66.0	82.0	108.0	90.0	110.0	77.0	87.0
Minor Elements (PPM)	Cu	24.0	10.0	11.0	14.0	40.0	6.0	16.0	13.0	14.0	46.0	34.0	23.0	16.0	13.0	8.0	14.0	17.0	8.0	12.0	14.0	11.0
	Ga	17.0	11.0	11.0	14.0	22.0	18.0	17.0	13.0	11.0	23.0	24.0	16.0	13.0	16.0	14.0	13.0	25.0	18.0	15.0	14.0	11.0
	Ge	0.0	0.0	0.0	1.0	2.0	3.0	0.0	2.0	14.0	2.0	0.0	2.0	3.0	1.0	2.0	3.0	1.0	1.0	5.0	0.0	2.0
	Li	67.0	36.0	51.0	64.0	68.0	37.0	35.0	25.0	124.0	169.0	67.0	73.0	57.0	68.0	47.0	100.0	101.0	59.0	110.0	46.0	106.0
	Mo	1.0	35.0	11.0	49.0	4.0	8.0	0.0	25.0	196.0	2.0	0.0	8.0	68.0	39.0	6.0	33.0	0.0	0.0	66.0	0.0	14.0
	Ni	49.0	35.0	32.0	54.0	56.0	29.0	34.0	46.0	63.0	77.0	14.0	36.0	49.0	64.0	33.0	38.0	49.0	46.0	65.0	36.0	40.0
	Pb	11.0	20.0	3.0	5.0	41.0	7.0	10.0	17.0	7.0	25.0	18.0	8.0	14.0	14.0	10.0	6.0	5.0	5.0	19.0	4.0	19.0
	Sn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	16.0	0.0	0.0	6.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	8.0
	Sr	261.0	406.0	485.0	493.0	100.0	267.0	53.0	1078.0	836.0	87.0	77.0	199.0	236.0	196.0	156.0	228.0	93.0	90.0	371.0	77.0	101.0
	V	60.0	48.0	55.0	89.0	105.0	51.0	54.0	62.0	124.0	104.0	165.0	73.0	120.0	122.0	64.0	68.0	136.0	109.0	158.0	67.0	88.0
	Zn	139.0	127.0	55.0	76.0	167.0	135.0	125.0	35.0	0.0	296.0	125.0	87.0	86.0	108.0	133.0	74.0	182.0	161.0	108.0	135.0	72.0
	Zr	226.0	105.0	141.0	162.0	175.0	111.0	143.0	159.0	315.0	115.0	108.0	85.0	181.0	143.0	251.0	82.0	235.0	266.0	226.0	412.0	129.0
	Heat Loss (%)	7.4	11.0	2.4	8.6	7.3	9.5	3.0	6.9	1.8	11.0	8.9	8.0	6.0	7.6	9.0	14.0	4.0	3.5	9.5	8.2	5.0

TABLE 9. Summary statistics for major oxides and minor elements.

Element	Statistic				
	Mean	Standard Deviation	Median	Minimum	Maximum
			PERCENT		
Al_2O_3	14.16	3.57	15.40	4.10	20.20
CaO	8.44	8.94	4.60	0.10	38.00
Fe Oxides	4.72	1.34	4.70	1.80	10.30
K_2O	2.73	0.82	2.80	0.10	4.90
MgO	3.13	3.14	2.30	0.30	26.80
SiO_2	55.29	15.88	58.90	14.60	114.00
Mn/Fe	1.04	0.92	0.70	0.10	5.60
			P.P.M.		
MnO	462.42	477.73	330.00	65.00	3297.00
Ag	1.25	4.76	0.00	0.00	46.00
Ba	345.69	178.86	347.00	92.00	1594.00
Be	5.15	1.94	5.00	2.00	12.00
Bi	1.46	1.58	1.00	0.00	8.00
Cd	29.87	25.74	23.00	0.00	168.00
Co	39.98	25.33	35.00	7.00	224.00
Cr	139.81	188.38	95.00	35.00	1428.00
Cu	28.70	26.04	23.00	2.00	140.00
Ga	18.94	5.97	20.00	3.00	32.00
Ge	1.94	2.25	1.00	0.00	14.00
Li	54.09	29.32	47.00	6.00	169.00
Mo	28.32	73.53	7.00	0.00	713.00
Ni	78.52	86.32	53.00	14.00	661.00
Pb	27.72	43.71	15.00	2.00	356.00
Sn	0.76	2.78	0.00	0.00	20.00
Sr	286.28	283.32	190.00	21.00	1844.00
V	197.91	402.46	114.00	19.00	3607.00
Zn	207.90	179.07	182.00	0.00	909.00
Zr	213.28	107.02	189.00	17.00	730.00
Heat loss	6.73	4.18		0.50	29.90%

same order as the means. In terms of the elements, this indicates a lognormal distribution but, as no statistical guidelines are available to determine whether the observed frequencies (Figure 22) are lognormal or not, only raw data are used in further operations. Subsequently, Link and Koch (1975) have applied lognormal theory to pseudolognormal distributions and have shown that positive or negative bias, or a combination of the two, can occur.

STRATIGRAPHIC VARIATION IN THE GEOCHEMISTRY

The variation of major oxides (Figures 23 and 24) indicates both lithological and stratigraphical control of Upper Pennsylvanian and Lower Permian shales. SiO_2, in particular, is distributed in zones that correspond to those established from mineralogical variation in the same shales. The Pleasanton, Kansas City, and Lansing Groups form a zone of highly variable SiO_2 values (from 35 to 70 percent) whereas the succeeding Douglas Group shows consistently high values (up to 90 percent). The Shawnee and Wabaunsee Groups show similarities to the Pleasanton-Kansas City-Lansing and Douglas zones respectively although the Shawnee has greater variability of values (20 to 90 percent) and the Wabaunsee does not show such intense SiO_2 development. Finally, samples from the Permian Groups all contain relatively small amounts of SiO_2.

The Al_2O_3 distribution (Figure 23) shows similarity to the SiO_2 graph with corresponding highs and lows. However, zoning the distribution is difficult as sample values only vary from six to 20 percent. The sole indication of stratigraphic control occurs in the Lower Permian where the Al_2O_3 values are approximately five percent lower than in the Pennsylvanian.

CaO is distributed with high values (zero to 40 percent) in the Pleasanton and Lower Kansas City, in the Lansing, in the Shawnee, and also in the Lower Permian, whereas few samples from the intervening zones have greater than 10 percent CaO. The increase in CaO and MgO in the Permian is comparable with increased carbonate production noted in the shale mineralogy. However, no zones are noted in the MgO distribution as the increase is only gradual throughout the Upper Pennsylvanian and Lower Permian deposits. Only one sample contained more than 15 percent, which is surprising as several dolomite-rich shales were detected by X-ray diffraction. However, an alternative site for MgO may lie within the lattice of chlorite clay minerals (Eckhardt, 1958; Van Moort, 1972).

The iron oxide content varies from 1.8 to 10.3 percent with a mean of 4.7 percent. There is some similarity to both Al_2O_3 and SiO_2 distributions as the iron oxide curve (Figure 23) has high and low values that equate with points on the Al_2O_3 and SiO_2 curves. Highs occur in the Upper Douglas, Lower Wabaunsee, and Lansing Groups, whereas lows are found in the Lower Kansas City, Lower Douglas, Shawnee, Council Grove, and Chase Groups.

The K_2O content ranges from 0.5 to 4.9 percent with a mean of 2.7 percent. Apart from a slight decrease in K_2O during the Lower Permian, corresponding mineralogically to a decrease in illite content (Weaver, 1967), little information can be gained from the stratigraphic variation in K_2O values.

MnO rarely exceeds 1000 ppm in Upper Pennsylvanian and Lower Permian shales. Allowing, therefore, for differences of scale, the MnO (Figure 25) content appears to be closely associated with the carbonate fraction of the shales. For example, the Lansing, Shawnee, Wabaunsee, and Admire Groups contain beds that are rich in MnO, CaO, and calcite. However, the association is not maintained in the Kansas City, Council Grove, and Chase Groups.

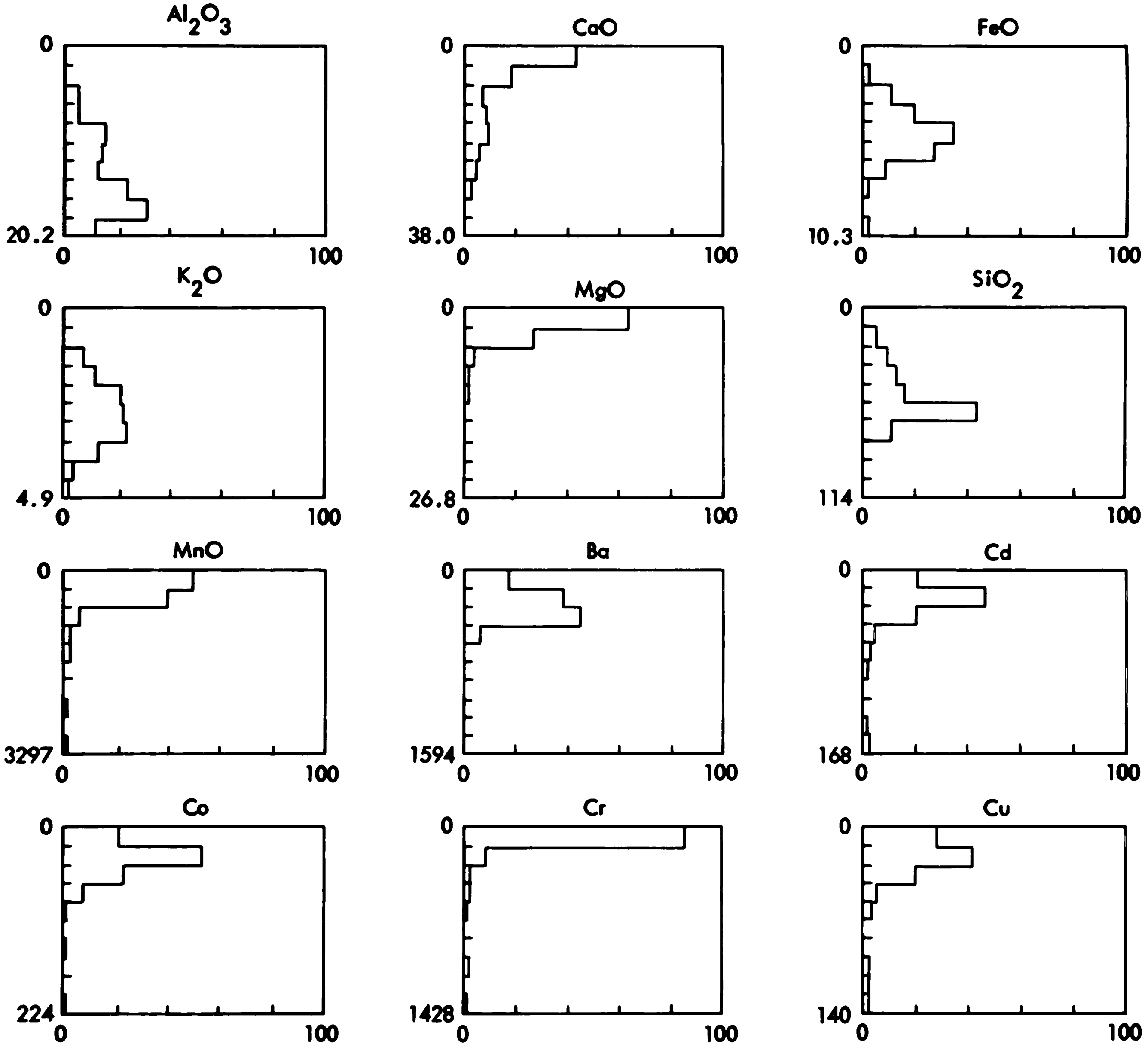

FIGURE 22. Histograms showing the variation and distribution of major oxides and minor elements in Upper Pennsylvanian and Lower Permian shales (total samples = 127). From Al_2O_3 to SiO_2, measurements are in %, and from MnO to Zr in ppm. Scales are 0 to maximum value in 10 divisions (vertical).

The concentration of Mn in shales may be related to an increase of Mn^{2+} ions (substituting for Ca^{2+} in calcite) in the reducing conditions (Bencini and Turi, 1974) developed at the end of the Pennsylvanian. Alternatively, the low MnO content of some calcareous shales may reflect differences in the original mineralogy of the sediments. Aragonite forms in shallow-water environments (Cloud, 1962) with minor Mn substitution for Ca (Thompson, 1972). Calcite, however, predominates in deep-water carbonate sediments and normally contains abundant Mn (Thompson, 1972). Therefore, the Lansing, Shawnee, Wabaunsee, and Admire Groups contain shales that may represent deposition either at times of deep-water sedimentation or highly reducing conditions. The Council Grove, Chase, and Kansas City Groups, on the other hand, contain shales that were deposited in periods of shallow-water sedimentation or less reducing conditions. Diagenetic processes, particularly dolomitization, do not appear to have seriously modified the original Mn content.

Silver (Ag) is found in low concentrations in all

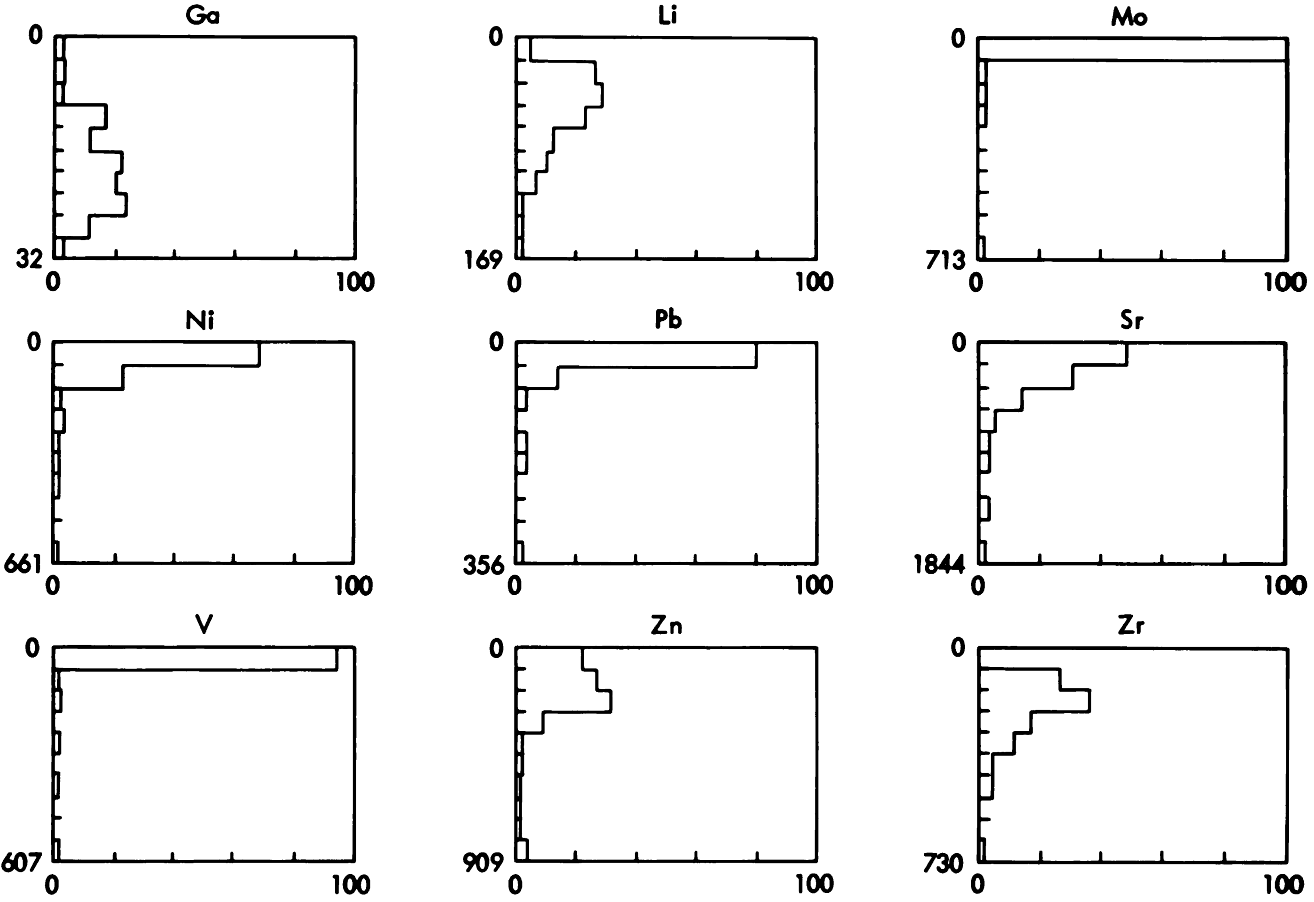

FIGURE 22. Continued.

samples (a maximum of 46 ppm) and provides negligible information for establishing the geochemical conditions prevailing during the Upper Pennsylvanian and Lower Permian. Beryllium (Be), bismuth (Bi), and germanium (Ge) are also found in minor quantities, probably as sulphides (Bi) or within clay mineral lattices (Be and Ge) (Wedepohl, 1969, 1970).

Barium (Ba) normally occurs as a substitute for Ca^{2+} in calcareous deposits. However, evidence for any such association is difficult to find in the Upper Pennsylvanian or Lower Permian shales. The distribution of barium (Figure 25) is more akin to the illite and chlorite distributions than to the carbonate fraction. Ba^{2+} substitution for K^{+} in illite (Fenner and Hagner, 1967; Krauskopf, 1967) may explain many of the minor peaks in the Ba stratigraphic distribution but two high values in the Lower Permian bear no relation to any other geochemical or mineralogical variable. In this case, the possibility of small amounts of barite occurring in the sediments cannot be ignored.

Taking into account the high Cd values recorded for the standards, cadmium's normal geochemical association with zinc in the ratio of 1:500 (Hawkes and Webb, 1962) is retained in the Kansas shales. High values are recorded in the Kansas City, Shawnee, and Council Grove Groups, whereas low values predominate in the remaining samples (Figure 26). A high Cd value recorded for the Heebner shale (Shawnee Group) indicates a possible association with black shales.

The stratigraphic variation of cobalt (Figure 26) shows only tenuous correlations with other geochemical and mineralogical variables. Two peaks occurring in the Tonganoxie Sandstone (Douglas Group) and Silver Lake Shale (Wabaunsee Group) may represent concentrations of detrital minerals containing cobalt.

The values of chromium (Cr) recorded in the Upper Pennsylvanian and Lower Permian shales divide the samples into two types. The majority of shales contain around 100 ppm Cr, comparing favorably with the "average shale" quoted in the literature (Vinogradov, 1962). The remaining eight samples (> 400 ppm Cr) are all black shales. This lithology is found in members of the Kansas City, Shawnee, Wabaunsee, and Council Grove Groups and was deposited in a highly reducing, shallow marine environ-

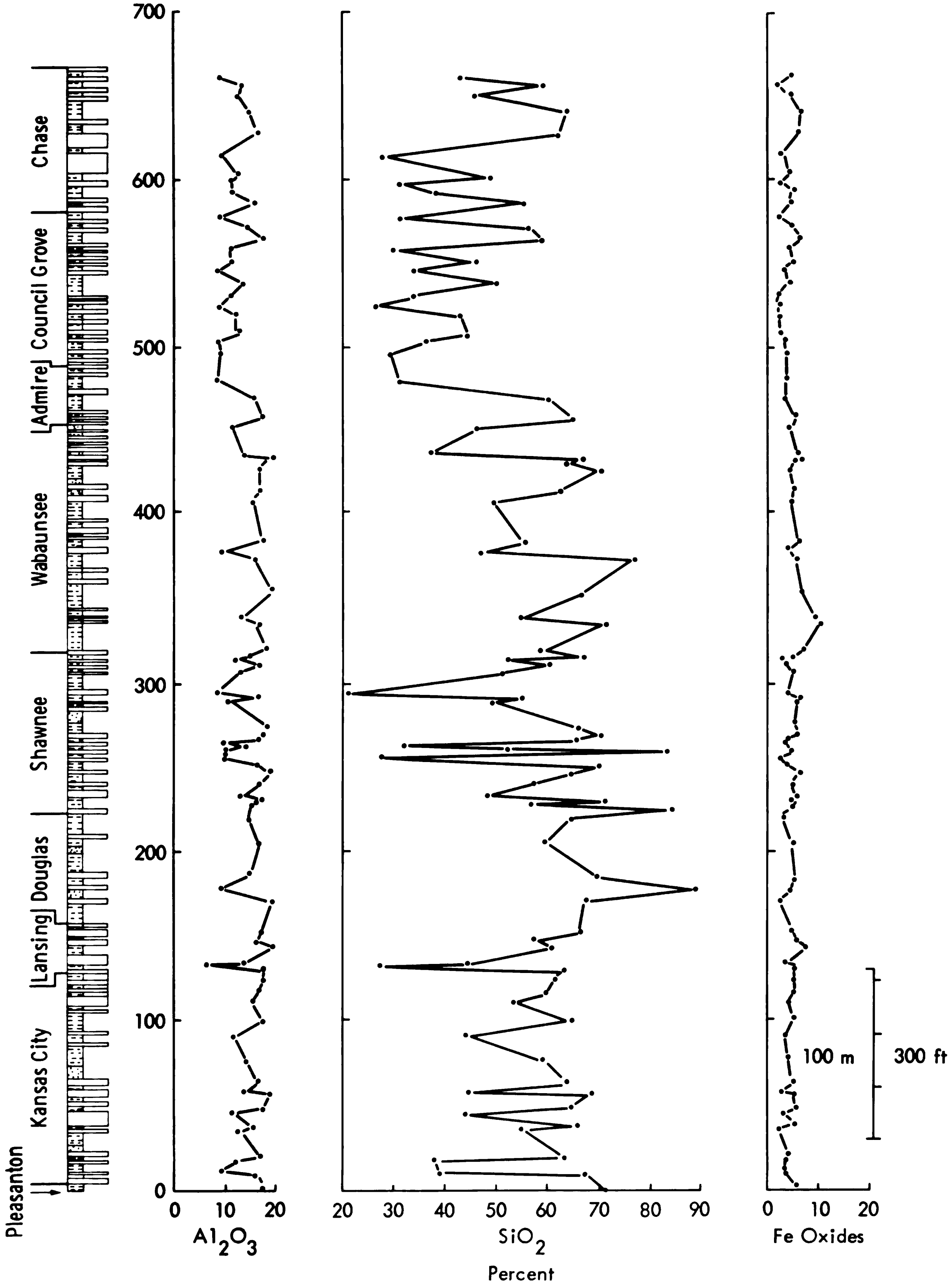

FIGURE 23. Stratigraphic variation of Al_2O_3, SiO_2, and Fe oxides.

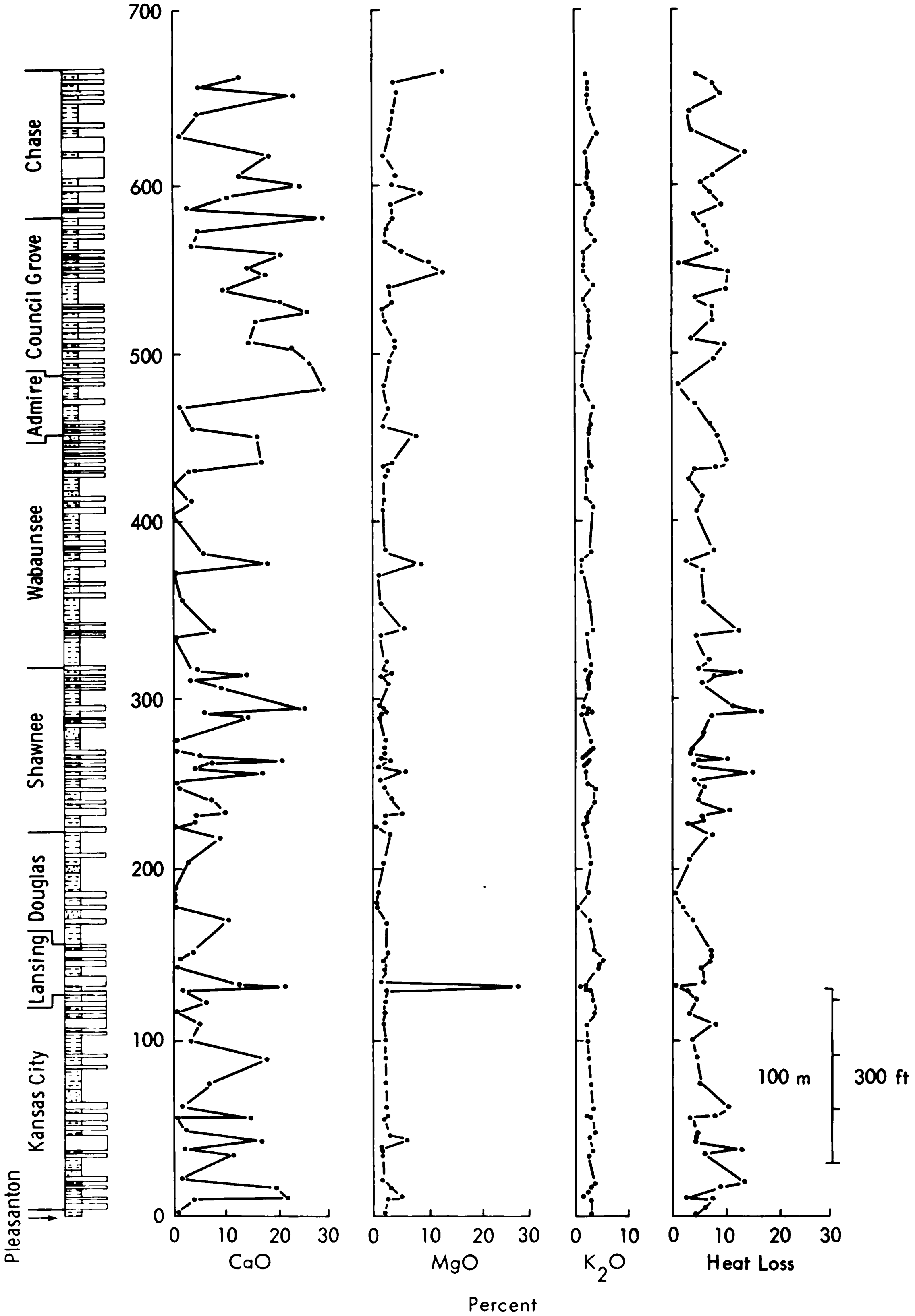

FIGURE 24. Stratigraphic variation of CaO, MgO, K_2O, and heat loss in Upper Pennsylvanian and Lower Permian shales.

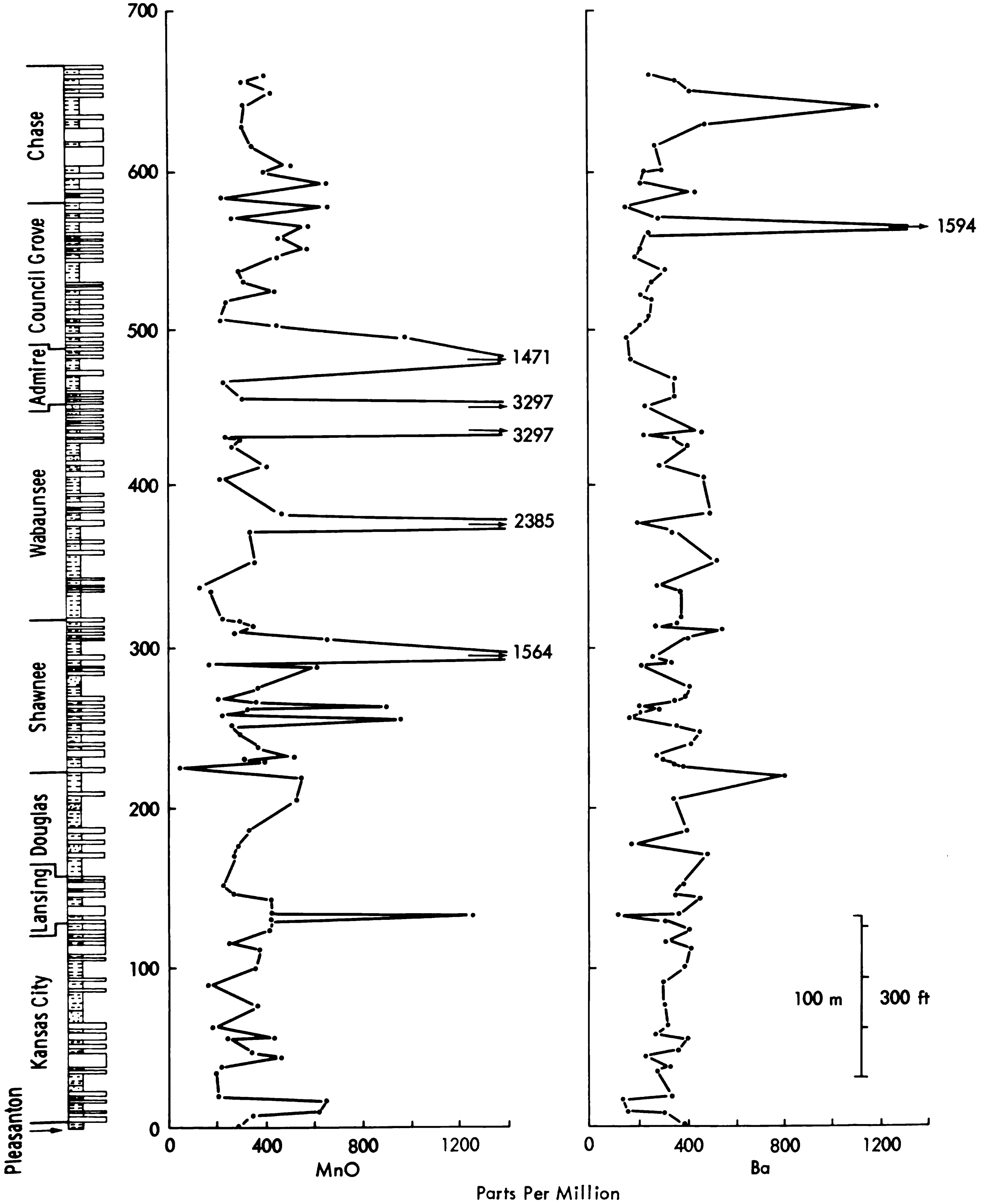

FIGURE 25. Stratigraphic variation of MnO and Ba in Upper Pennsylvanian and Lower Permian shales.

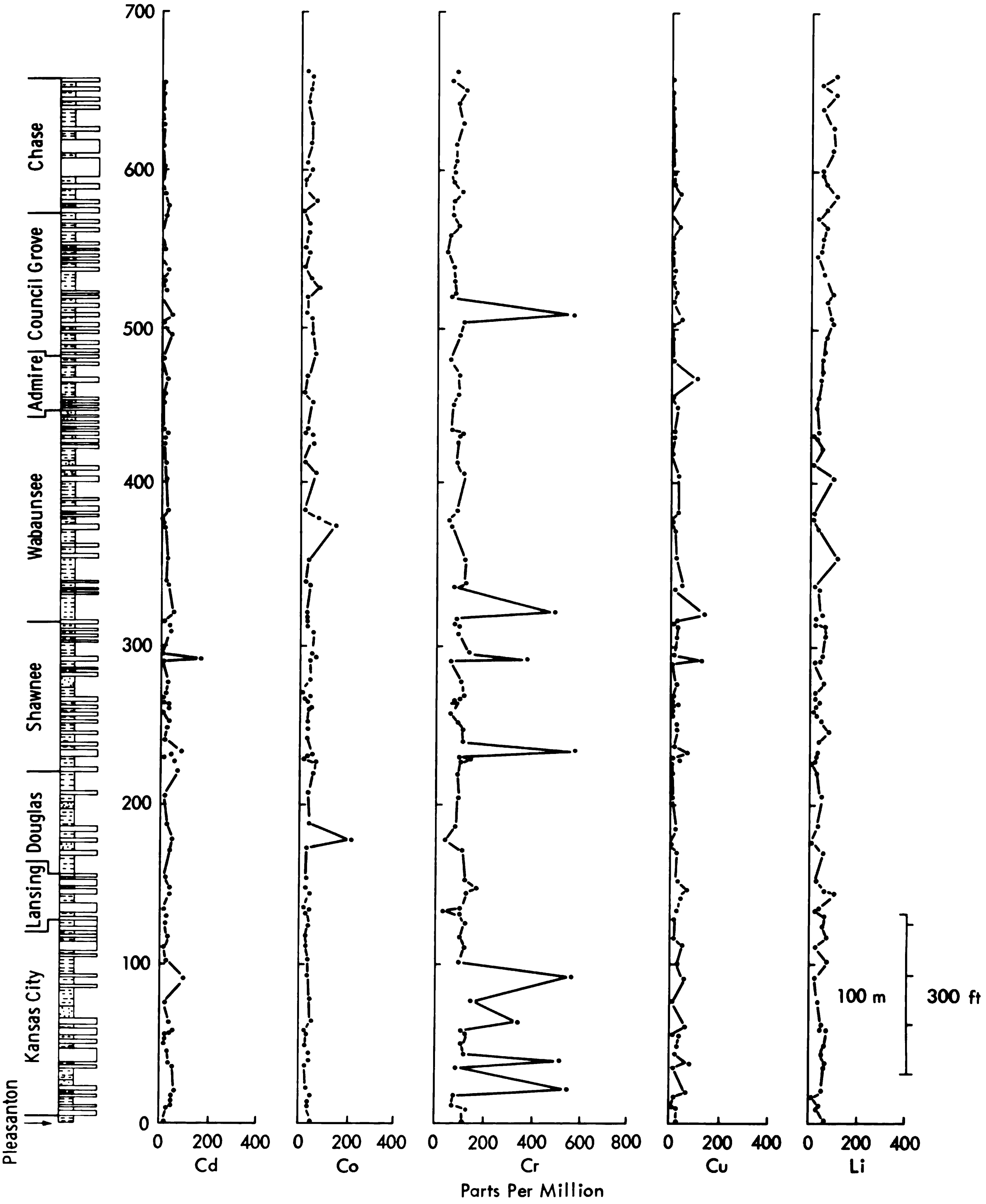

FIGURE 26. Stratigraphic variation of Cd, Co, Cr, Cu, and Li in Upper Pennsylvanian and Lower Permian shales.

ment (Heckel, 1972a), rich in organic matter. Chemical analyses of black shales are characterized not only by a considerable organic carbon content but also by sulphur present as FeS_2 (Vine and Tourtelot, 1970). Minor elements such as V, Mo, Cu, Ni, Pb, Zn, and Cr are enriched in black shales by the organic matter which acts either as a biological catalyst (Vine and Tourtelot, 1970) or as a sulphide reducing agent (Mason, 1958). This element association may be of great importance in determining the presence or absence of geochemical periodicity in the Kansas shales, for black shales have been extensively employed as marker horizons in cyclothems.

The overall stratigraphic distribution of copper matches that of Cr although the black shale values are relatively lower than Cr equivalents. Only one high Cu value—in the Hamblin Shale of the Admire Group—cannot be explained in terms of black shale enrichment.

Gallium is present in minor quantities in all shales but is geochemically of great importance. Particular interest is attached to this element as a diagnostic for the salinity of depositional environments, its concentration being generally higher in fresh water than marine argillaceous deposits (Degens *et al.*, 1958; Tourtelot, 1964). Gallium seems to be depleted in the Upper Pennsylvanian and Lower Permian shales, inferring a marine origin for the shales. For confirmatory evidence, rubidium and boron determinations would be significant.

Lithium may also be used as an indicator of freshwater or marine depositional environments (Keith and Degens, 1959). The relatively high lithium values generally indicate a marine environment for most of the Upper Pennsylvanian and Lower Permian with some non-marine deposition in the Pleasanton, Douglas, Lower Shawnee, and Wabaunsee.

Molybdenum is another element found concentrated in anoxic environments (Bertine, 1972; Bertine and Turekian, 1973), principally black shales. Within this lithology, Mo concentrations vary between 150 and 750 ppm, whereas the remaining samples have few values over 75 ppm. The Mo distribution has peaks in the Pleasanton, Shawnee (in which the Heebner Shale is prominent), Wabaunsee, and Lower Permian Groups. In the case of the Lower Permian Groups, there seems to have been a general rise in the Mo concentration from negligible amounts in the Upper Wabaunsee to between 30 and 100 ppm for most Permian sediments (Figure 27).

Nickel values are also arranged according to the development of black shales and show close correspondence to the Cr, Cu, Mo, Pb, and Zn distributions. The majority of samples have values in the range 0 to 100 ppm (Figure 27), whereas those samples associated with black shales have values ranging from 100 to 700 ppm.

Lead (Pb) shows a similar distribution (Figure 27) to Ni with only minor differences in the Wabaunsee Group samples. Here, two peaks in the Pony Creek Shale and Silver Lake Shale correspond to similar peaks in the Mo distribution (Figure 27) and may be connected with pyrite or organic residues (Wedepohl, 1974). Enriched shales have Pb values that range from 100 to 400 ppm (high for black shales; Wedepohl, 1974), whereas other samples all contain less than 100 ppm Pb.

Strontium, like most other trace elements, has a bimodal distribution (Figure 22), with many shale samples lying in the range 50 to 300 ppm and a few in the range 300 to 1900 ppm. Of the samples from the upper range, most are calcareous shales from the Kansas City, Shawnee, Upper Wabaunsee, and Council Grove Groups. The strontium distribution (Figure 27) appears to be associated with the carbonate fraction and may be controlled by salinity and basinal depth (Veizer and Demovic, 1974). The higher values, coinciding with high carbonate content may, therefore, indicate "hypersaline" or deep-water conditions. This evidence is in agreement with the MnO interpretation of the Shawnee, Upper Wabaunsee, and Admire Groups, but shows discrepancies in the Kansas City and Lower Wabaunsee Groups. The latter case may be explained in terms of low carbonate content but the Kansas City values seem contradictory. Therefore, before the implications of carbonate geochemistry can be extensively applied to calcareous shales, further experimentation and analysis are required. Meanwhile, it can be stated that there appears to be a close correlation among MnO, Sr, and the carbonate fraction and that the MnO and Sr content of the shales may be influenced by depth, original mineralogy, salinity, and basinal conditions.

Both vanadium and zinc distributions (Figure 28) show enrichment in the black shale beds of the Kansas City, Shawnee, and Council Grove Groups. Zirconium (Zr) on the other hand appears to be stratigraphically distributed (Figure 28) according to the quartz content of shales. In sedimentary rocks, Zr occurs primarily as detrital zircons and is, therefore, found concentrated in the coarse detrital beds of the Douglas and Wabaunsee Groups.

The carbonate and organic contents of shale seem to control the stratigraphic distribution of percentage weight loss on ignition (Heat Loss—Figure 24). This variable has high values recorded in the Kansas City

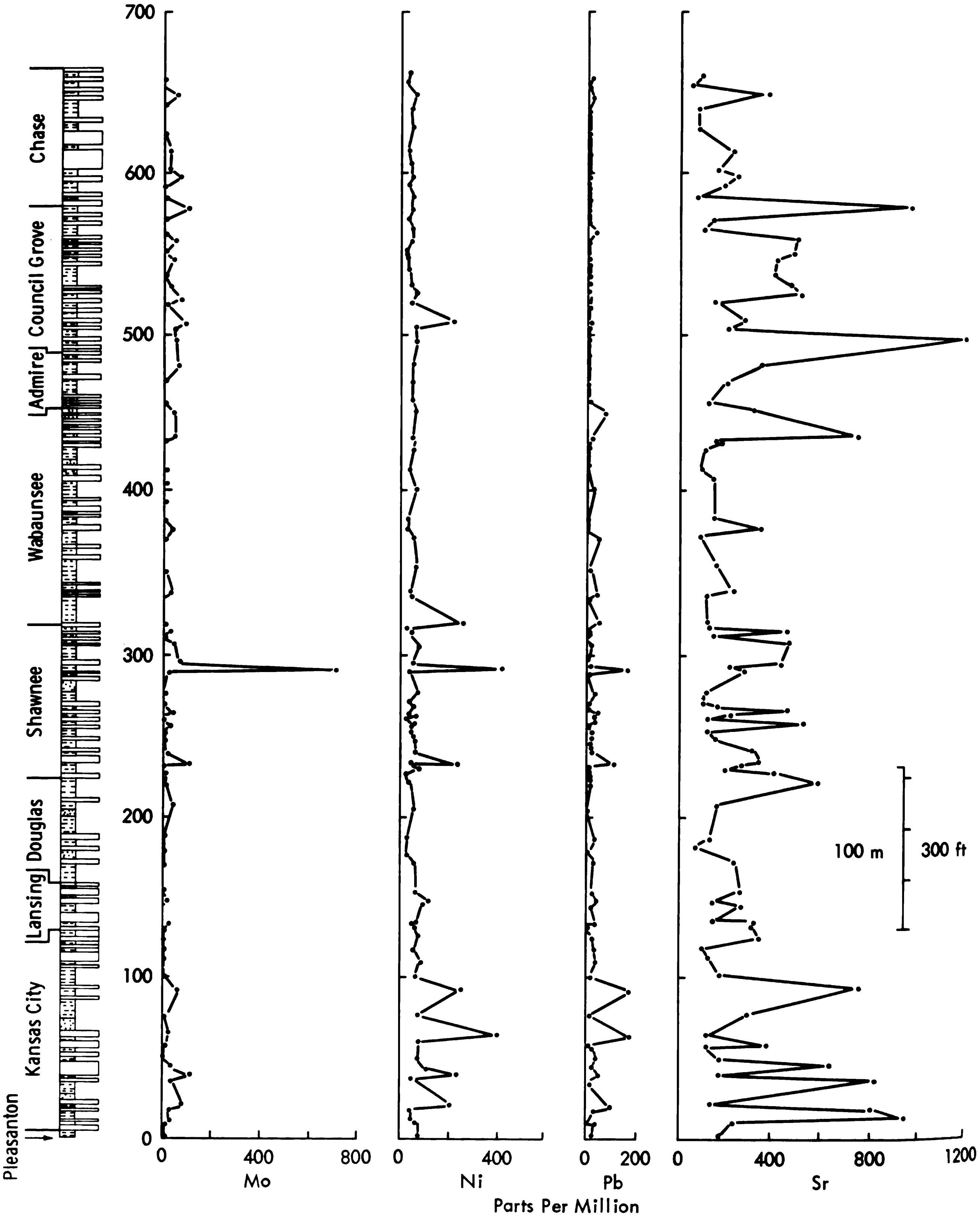

FIGURE 27. Stratigraphic variation of Mo, Ni, Pb, and Sr in Upper Pennsylvanian and Lower Permian shales.

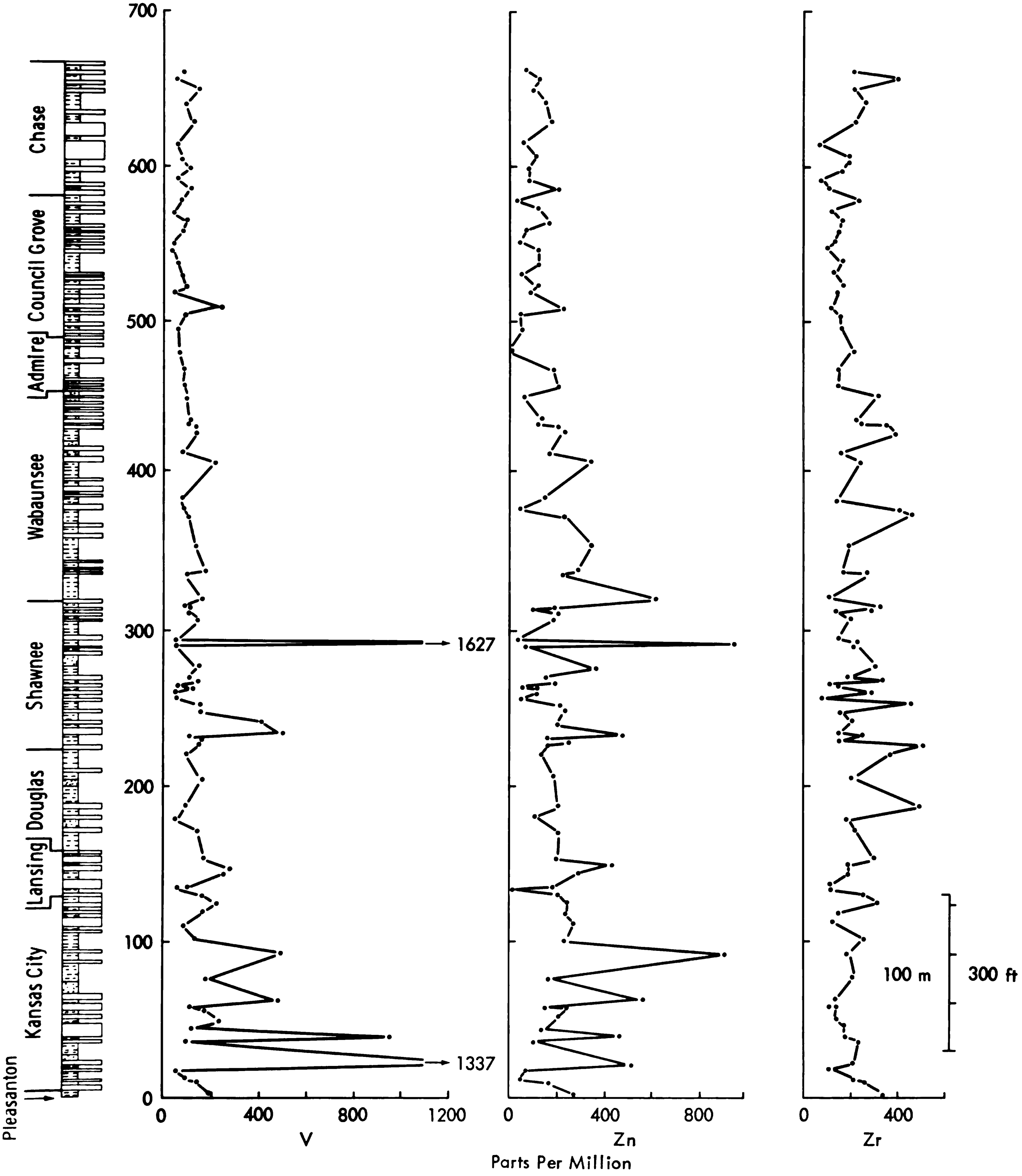

FIGURE 28. Stratigraphic variation of V, Zn, and Zr in Upper Pennsylvanian and Lower Permian shales.

(calcareous and black shales), Shawnee (calcareous and black shales), Council Grove, and Chase Groups (calcareous shales).

UNIVARIATE ANALYSIS OF GEOCHEMICAL DATA

A number of major oxide and minor element stratigraphic distributions visually examined appeared to contain geochemical oscillations. Statistical clarification and verification of the repetitions were performed by Fourier analysis. First, however, each variable was transformed using linear interpolation (Davis, 1973) from an irregularly spaced data sequence to an equal-spaced sequence having data points at 10-foot intervals. After increasing the data sequence to 218 points, the geochemical variables were analyzed by linear regression to check how equal-spacing the data may have affected the geochemical distribution. No variable, however, assumed a greatly increased goodness-of-fit or correlation coefficient. This enabled the investigator to submit the equal-spaced data points to the Fourier analysis program with the knowledge that any cycles detected would be representative of the original data. To obviate any problems associated with extraneous noise in the data, an 11-term smoothing equation was also applied to the equal-spaced data and the output submitted to the Fourier program.

The first variable studied was SiO_2 and, as expected, the raw power spectrum closely matched the quartz spectrum recorded on p. 26. Peaks are recognized at the third, seventh, 14th, 19th, 22nd, 26th, and 33rd harmonics of which the seventh and 14th harmonic peaks are retained in the power spectrum of the smoothed data. The repetitive elements with intervals of 70 and 140 feet probably represent the mineralogical cycles detected on page 26, whereas the small peaks retained in the region of the 30th harmonic possibly indicate a group-by-group cycle in the geochemistry as witnessed by the large-scale stratigraphic zones observed on page 38.

The CaO stratigraphic distribution has a raw power spectrum with peaks at the fourth, seventh, ninth, 13th, 15th, 17th, 19th, 21st, 27th, 31st, and 33rd harmonics. After smoothing the equal-spaced data, peaks at the fifth, seventh, ninth, and 13th harmonics are produced. A 70-foot interval cycle is prominent in this data, possibly indicating a cycle in carbonate deposition.

Both the K_2O and Fe oxide distribution contain a seventh harmonic peak in their raw power spectra, although in the case of Fe oxides, this shifts to the sixth harmonic after smoothing. Similarly, Al_2O_3 and MgO have sixth harmonic peaks. Another close agreement between the power spectra of SiO_2, CaO, MgO, and Al_2O_3 is the occurrence of a peak at the 12th, 13th, or 14th harmonics. However, only SiO_2 records a peak around the 30th harmonic.

It seems possible, therefore, to distinguish short-term repetitions in the major oxide geochemistry corresponding to the 70-foot cycles in the mineralogy of the Kansas shales. This is probably a reflection of the lithological cycles distinguished by Moore (1936). A 300-foot cycle distinguished in SiO_2 may represent the group-by-group stratigraphic variation noted previously.

A few minor-element distributions were also submitted to these procedures in an attempt to detect periodicity in the shales. MnO, Ba, Co, Cr, Cu, Ga, Li, Mo, and Ni distributions were considered representative of the minor-element variation detected in the Kansas shales and most likely to contain repetitive elements. In MnO, Ba, Cr, Ni, Mo, Cu, and Ga distributions, the 70-foot cycle was again dominant and in Cr, Ni, Mo, and Cu, a 130-foot cycle was also recognized. The only apparent anomaly in this study was Li which had power spectrum peaks at the fifth, ninth, and 12th harmonics. A number of elements also had peaks at harmonics between 25 and 30, but no consistency was noted. Therefore, it appears that the peaks at the seventh and 13th harmonics are the only common features among the minor elements. The heat-loss variable was also analyzed and produced peaks at the seventh and 13th harmonics.

The correspondence of results obtained from the major oxides and minor elements seems to support the hypothesis that there are geochemical cycles of 70-foot and 130-foot intervals. It also appears probable that the minor-element geochemical cycles detected in Cr, Cu, Mo, and Ni are related to the periodic occurrence of black shales. As Moore (1936) has continuously employed black shales as distinctive marker horizons in Upper Pennsylvanian cyclothems and megacyclothems, it may be inferred that the geochemical cycles (and mineralogical as these also indicate 70-foot cycles) are related to Moore's lithological cyclothems.

GEOCHEMICAL CORRELATIONS

Correlations between the geochemical variables are shown in Table 10. All variables have been included in the matrix, as parameters such as Ag, Be, Bi, and Ge that seemed at first glance unimportant (p. 39) may prove to be of significance in a multivariate analysis.

TABLE 10. Correlation coefficient matrix geochemical variables; $r_{95} = \pm .15$, $r_{99} = \pm .20$, $r_{99.9} = \pm .27$.

	Al_2O_3	CaO	Fe Oxides	K_2O	MgO	SiO_2	Mn/Fe	MnO	Ag	Ba	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Li	Mo	Ni	Pb	Sn	Sr	V	Zn	Zr	Heat Loss
Al_2O_3	1.00																											
CaO	–.81	1.00																										
Fe Oxides	.47	–.38	1.00																									
K_2O	.67	–.42	.44	1.00																								
MgO	–.42	.38	.03	–.21	1.00																							
SiO_2	.61	–.87	.18	.14	–.45	1.00																						
Mn/Fe	–.59	.68	–.19	–.41	.33	–.55	1.00																					
MnO	–.39	.47	.10	–.26	.33	–.43	.92	1.00																				
Ag	–.18	–.01	–.20	–.25	–.08	.09	.01	–.05	1.00																			
Ba	.54	–.44	.40	.42	–.22	.35	–.29	–.14	–.15	1.00																		
Be	.08	.12	.11	.25	.02	–.21	.16	.16	.13	.02	1.00																	
Bi	–.53	.69	.02	–.09	.14	–.70	.48	.37	.07	–.29	.49	1.00																
Cd	.15	–.16	–.02	.05	–.20	.22	–.24	–.23	.28	.03	.44	.04	1.00															
Co	–.25	.07	–.18	–.42	–.10	.15	.20	.11	.56	–.13	.00	.11	.12	1.00														
Cr	.19	–.18	.00	.16	–.12	.14	–.24	–.20	.37	.04	.47	.01	.67	–.02	1.00													
Cu	.30	–.26	.20	.33	–.17	.12	–.26	–.19	.19	.11	.53	.07	.60	–.05	.74	1.00												
Ga	.92	–.72	.55	.80	–.40	.44	–.57	–.37	–.18	.47	.18	–.30	.12	–.31	.18	.38	1.00											
Ge	–.54	.73	–.07	–.13	.09	–.68	.53	.38	.04	–.25	.41	.93	–.06	.15	–.12	–.08	–.33	1.00										
Li	.12	.08	.24	.37	–.05	–.24	–.09	–.09	–.14	.17	.16	.33	–.17	–.09	–.03	.07	.30	.37	1.00									
Mo	–.16	.22	–.08	–.06	.01	–.19	.10	.04	.23	–.13	.54	.36	.60	.16	.48	.53	–.10	.26	.04	1.00								
Ni	.20	–.15	.06	.21	–.11	.08	–.19	–.15	.22	.02	.46	.03	.61	.12	.75	.76	.23	–.07	.03	.53	1.00							
Pb	.14	–.14	.06	.13	–.10	.08	–.14	–.08	.21	.02	.44	.04	.59	.13	.68	.68	.15	–.08	–.09	.45	.89	1.00						
Sn	–.47	.52	–.18	–.18	.18	–.50	.37	.22	.07	–.25	.29	.71	–.08	.14	–.10	–.09	–.32	.77	.30	.19	–.08	–.08	1.00					
Sr	–.51	.71	–.27	–.26	.17	–.59	.46	.32	–.02	–.33	.13	.52	.17	.04	–.12	–.18	–.45	.57	–.01	.14	–.09	–.09	.42	1.00				
V	.17	–.19	.03	.12	–.11	.15	–.19	–.16	.39	.04	.54	.05	.62	.01	.87	.69	.18	–.08	–.01	.62	.63	.62	–.08	–.13	1.00			
Zn	.48	–.46	.27	.36	–.26	.33	–.43	–.32	.17	.20	.46	–.13	.67	.01	.76	.79	.48	–.26	.05	.44	.83	.77	–.25	–.30	.67	1.00		
Zr	.11	–.28	–.09	–.25	–.22	.53	–.02	.00	–.13	.13	–.17	–.29	.04	.33	–.14	–.21	–.07	–.22	–.26	–.07	–.16	–.11	–.18	–.18	–.09	–.04	1.00	
Heat Loss	–.04	.10	.10	.13	–.06	–.21	–.04	.02	.24	–.05	.36	.28	.34	–.16	.58	.52	.04	.12	.02	.48	.46	.48	.07	.10	.67	.38	–.36	1.00

Al_2O_3 has strong positive correlations with SiO_2, K_2O, Ba, Ga, and Zn, reflecting geochemical associations in feldspar (SiO_2) and clay mineral lattices (K_2O, Ba, Ga, Zn). Negative correlations with CaO, MgO, Mn/Fe ratio, MnO, Bi, Ge, Sn, and Sr are attributed to the lack of Al_2O_3 in carbonate environments. CaO shows a positive relationship to Mn/Fe, MnO, Bi, Ge, Sn, and Sr, all of which are commonly associated with carbonates, and negative correlations with SiO_2, Al_2O_3, K_2O, Fe oxides, Ba, Ga, and Zn. As noted above, Fe oxides have positive correlations with Al_2O_3, K_2O, Ba, and Ga and negative with CaO. K_2O shows a similar set of correlations to the Fe oxides, indicating a geochemical association in clay minerals or potash feldspar. MgO is positively correlated with CaO, reflecting an association in dolomitic shales, and negatively correlated with SiO_2 as quartz contains little MgO.

Considering the minor oxides and elements, a number of variable relationships indicated are clarified by the correlation coefficient matrix. The association of Cd, Cr, Cu, Be, Ni, Mo, Pb, V, and Zn distributions is supported by high positive correlations between all the elements. There is also a strong connection between the minor elements MnO, Bi, Ge, Sn, and Sr of the carbonate fraction. Be, Ga, Li, Cu, and Zn form a tenuous association that probably relates to substitution in clay mineral lattices. Ag, however, has no apparent affinities to any of these groups of minor elements but shows a high correlation with Co, indicating a possible connection with the detrital fraction. The heat-loss variable shows a high correlation with the Cd, Cr, Cu, Be, Ni, Mo, Pb, V, and Zn association, indicating that samples enriched in these elements also contain the most volatile materials.

The associations of geochemical variables elucidated by the correlation coefficient matrix are therefore:

1. An Al_2O_3, SiO_2, Zr, and possibly Co and Ag combination as a detrital fraction;
2. A CaO, MgO, MnO, Mn/Fe, Bi, Ge, Sn, and Sr association representing a carbonate fraction;
3. A Cd, Cr, Cu, Be, Mo, Ni, Pb, V, Zn, and heat-loss geochemical fraction common to black shales;
4. A K_2O, Fe oxides, Ga, Li, and possibly Cu and Zn association forming substitutes in clay mineral lattices.

MULTIVARIATE STATISTICAL ANALYSIS OF GEOCHEMICAL DATA

In order to further clarify the relationships among major oxides, minor elements, and inter-element associations and to establish the stratigraphic variation in geochemistry, the following standard statistical techniques—principal components analysis, Q-mode cluster analysis, and multiple discriminant analysis—were applied to the geochemical data.

R-mode principal components analysis of the data produced six significant components (eigenvalue > 1.0) which together account for 77 percent of the total variance, each component explaining more than four percent of the data variance (Table 11). Loadings of the variables on the components are shown in Figure 29 and a most complicated picture emerges. Since in geochemical investigations the components are not always independent (orthogonal), further insight into the geochemistry of the shales can be gained by performing oblique promax rotations of the six component axes. By this method, the variables influential on each axis are illuminated (Figure 30) and the geochemical controls of sediment evolution outlined. The following explanation for the components can therefore be proposed:

Component 1:—The very high loadings of CaO, MgO, MnO, and Sr suggest that this component should be designated the carbonate component. The elements Ge, Bi, Sn, and Sr all show their highest loadings on the component but evidently also play dual or triple roles by showing significant loadings on other factors. The positive loadings of these elements and oxides are opposed by high negative loadings on SiO_2 and Al_2O_3, clearly indicating a detrital phase antipathetically related to a carbonate fraction.

Component 2:—The elements Ni, Pb, Cd, Cu, V, Zn, Cr, Mo, and Be dominate this component and have low values in all samples from black shales. In contrast, Zr, Al_2O_3, and SiO_2 have moderate positive loadings on the principal components but are removed by the effect of rotation. Therefore, component 2 is referred to as the black shale component and reflects changes in the conditions under which the shales were deposited. As black shales are normally developed under reducing conditions, the component may also represent an oxidation-reduction contrast or "Eh component."

Component 3:—This component shows high negative loadings, in order of magnitude, for K_2O, Li, Fe oxides, and Ga against moderate positive loadings for

TABLE 11. Eigenvalues of the principal components extracted.

Component	Eigenvalue	% Variance	Cumulative % Variance
1	7.9	29.2	29.2
2	5.7	21.3	50.5
3	3.1	11.3	61.8
4	1.6	6.0	67.8
5	1.5	5.6	73.4
6	1.1	4.1	77.5

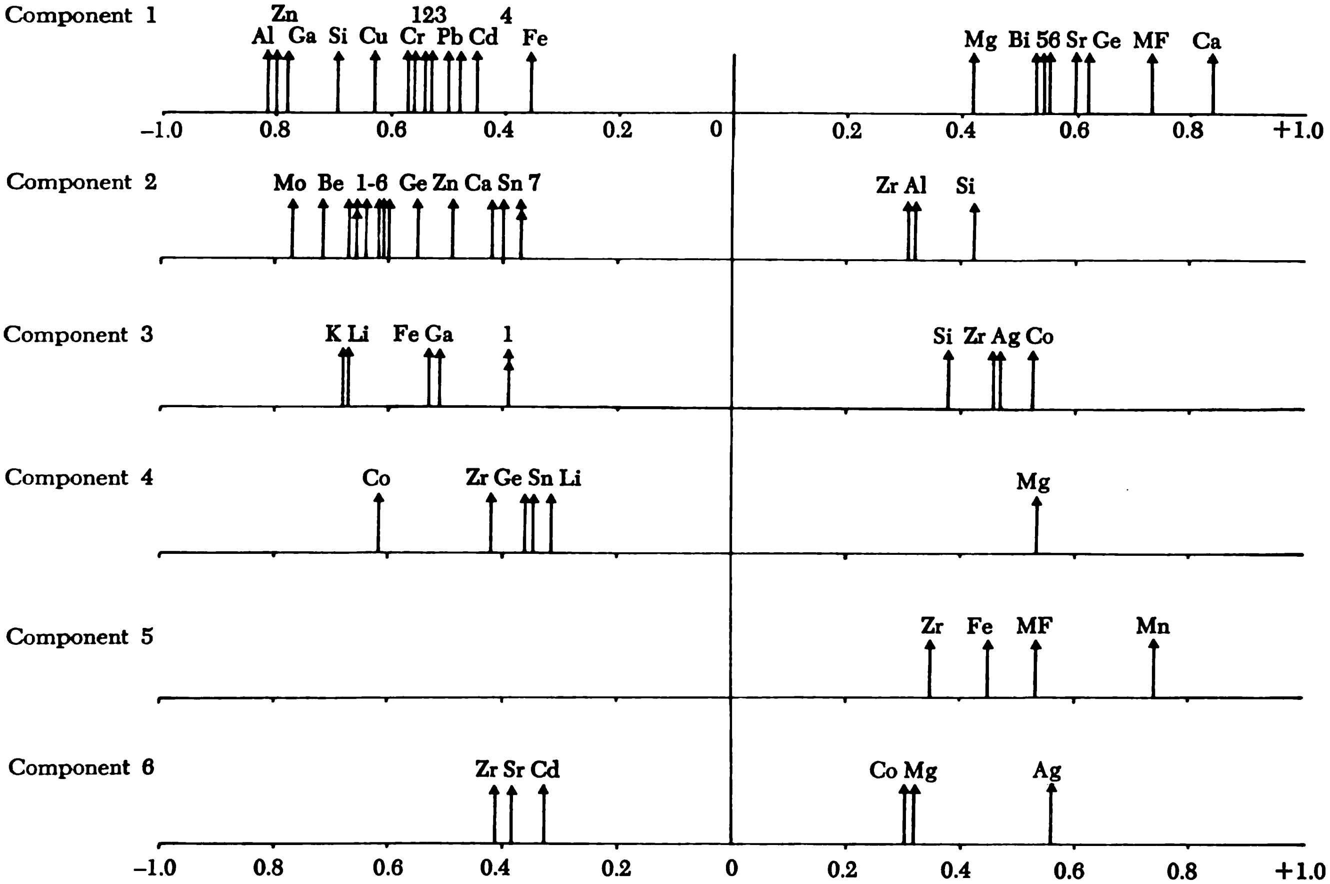

Figure 29. Principal component loadings of geochemical variables. Only loadings greater than ± 0.30 are included.

KEY

On all components:
Al = Al_2O_3
Ca = CaO
Fe = Fe oxides
K = K_2O
Mg = MgO
Si = SiO_2
MF=Mn/Fe
Mn = MnO

On component 1:
1 = Ni
2 = K
3 = V
4 = Bi
5 = Sn
6 = Mn

On component 2:
1 = Ni
2 = Cr and V
3 = Pb
4 = Bi
5 = Cu
6 = Cd
7 = Sr and Ag

On component 3:
1 = Bi and Ge

Co, Ag, Zr, and SiO_2. On rotation, negative loadings are recorded for Fe oxides, Ga, K_2O, and Al_2O_3 and positive for CaO, Mn/Fe ratio, Mo, and Sr. The close relationship of K_2O and Al_2O_3 is normally associated with potassium feldspar or clay minerals. This is to a great extent substantiated by Ga and Li which often substitute for K^+ in clay minerals. The additional high loading of Fe oxides may also be explained in terms of substitution in clay mineral lattices.

The positive loadings on the third principal component reflect the inability of detrital elements such as Ag, Co, and Zr to substitute in clay mineral lattices. On rotation this association is replaced by the carbonate component elements, CaO, Sr, and Mn/Fe ratio which again rarely combine in clay mineral lattices.

Figure 32 is a plot of the scores for component 3 against total clay mineral content, as determined by difference: 100 − (quartz + carbonate)%. Correlation is good; the line drawn is believed to represent the most realistic regression with the samples plotting well to the right of it being in error due to the relatively high feldspar content. Since feldspar is not considered in the above calculation, the total clay mineral content in the samples will be exaggerated by the amount of feldspar. It is noticeable from Figure 32 and predictable from the calculation method that the error in samples with a high clay mineral content is small (< 10%), about 10 percent at a 40 percent clay content, and can increase to about 15 percent in low clay samples.

Component 4:—High negative loadings for Co,

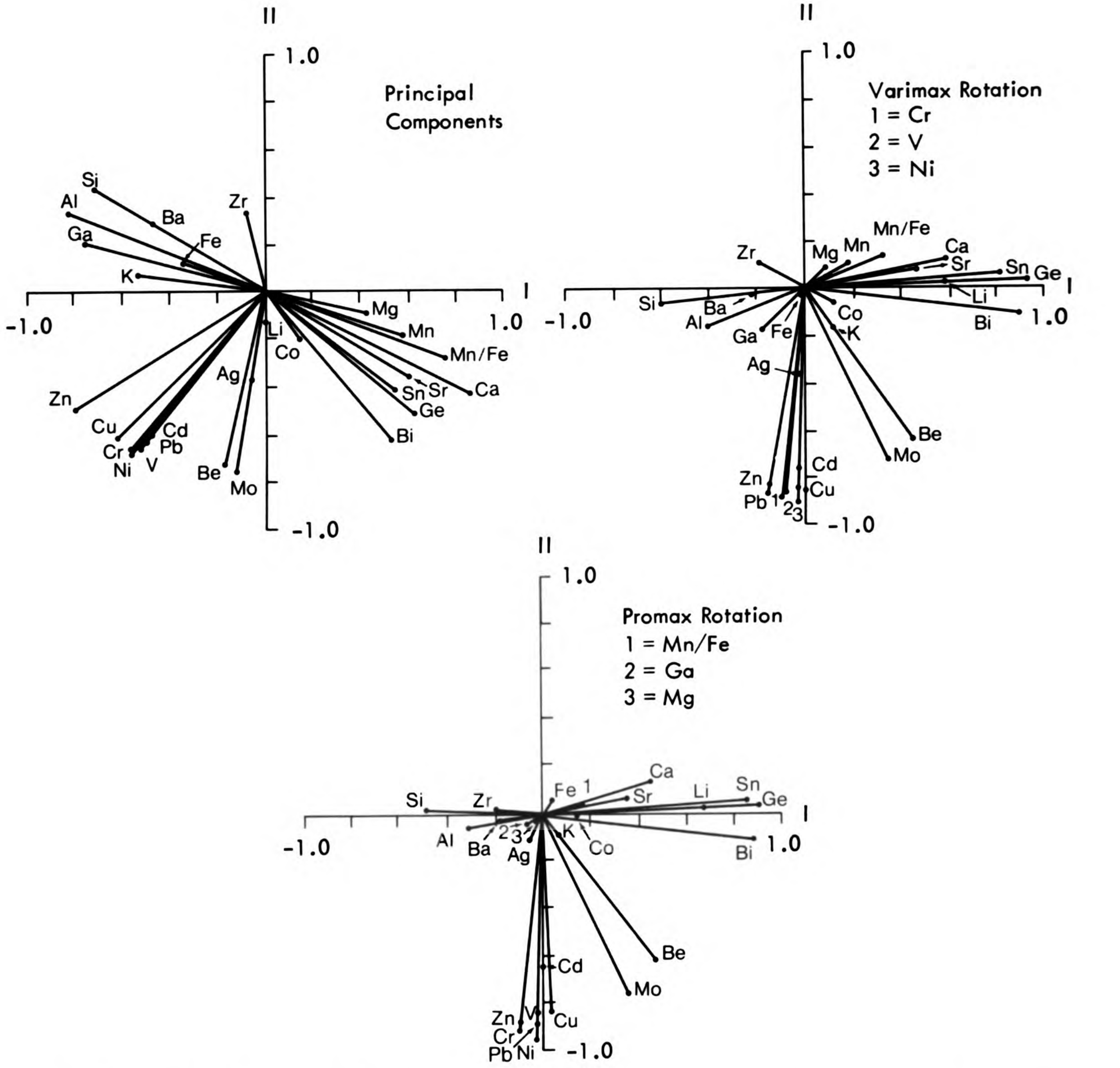

FIGURE 30. Loadings of variables on the first two axes of a principal components analysis, varimax rotation, and promax oblique rotation. In the latter case the axes are not orthogonal (correlation = 0.25) but, for simplicity, are drawn so.

Zr, and, on rotation, SiO_2 indicate that this component could represent a detrital component. High positive loadings of MgO (only principal components), Sr, CaO, Ag, and K_2O (only promax rotation) provide support for this conclusion. The positive loaded elements and oxides (except possibly Ag) are linked through the process of coprecipitation and rarely form detrital sediments. Scores for this component allow detrital or non-detrital composition for the sample to be differentiated.

Component 5:—This component is controlled by the amount of Mn occurring in the shales. MnO and Mn/Fe ratio have high positive loadings whereas Ca, Be (only promax), Zr, and Fe (only principal components) have low positive loadings. These are opposed by low negative loadings for Cd, Li, and SiO_2.

As Mn^{2+} substitutes extensively for Ca in carbonates, the correlation of 0.33 between promax factors 1 and 5 is not unexpected. Although MnO also occurs in sediments as oxides with a general pyrite structure, the negative loading for SiO_2 precludes a detrital mineral association. This component is therefore termed the manganese component and is closely related to the carbonate component (component 1).

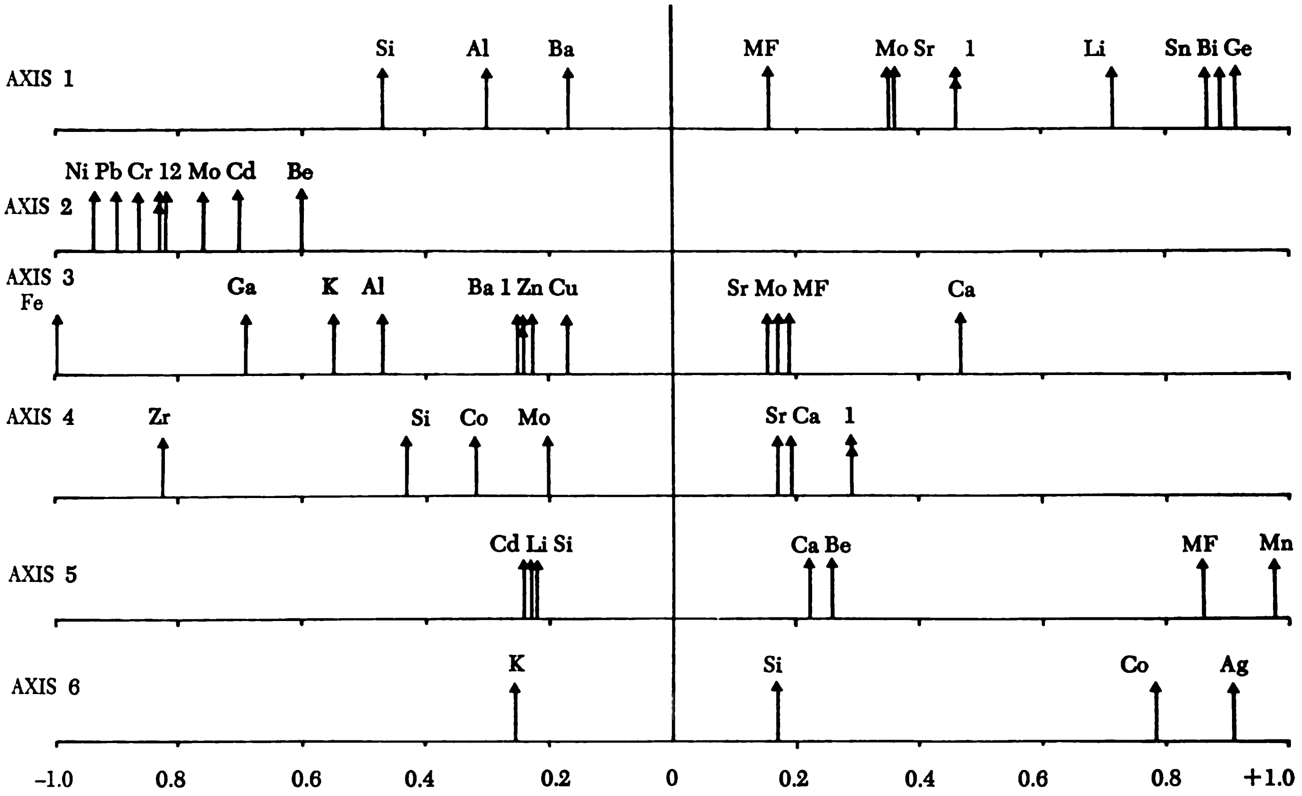

FIGURE 31. Oblique promax axis loadings. Loadings less than ± 0.15 are not illustrated.

KEY

On all axes:
Al = Al_2O_3
Ca = CaO
Fe = Fe oxides
K = K_2O
Mg = MgO
Si = SiO_2
MF = Mn/Fe
Mn = MnO

On axis 1:
1 = Be and Ca

On axis 2:
1 = Zn and V
2 = Cu

On axis 3:
1 = Si and Be

On axis 4:
1 = Ag and K

Component 6:—The elements and oxides controlling component 6 show a bipolar distribution with positive loadings recorded for Ag and Co and negative loadings for Zr, K_2O, Al_2O_3, Ga, Sr, and Cd. This component reflects the occasional high values recorded by the Ag and Co variables in sandstones and siltstones and is consequently negatively correlated with promax factor 4. However, as both these variables are generally accorded negligible values in Kansas shales, the majority of scores on component 6 occur between 0.3 and 0.5, with occasional high Co and Ag values producing high scores.

Therefore, the geochemical relationships developed in the Upper Pennsylvanian and Lower Permian shales are found to consist of six associations. First, the geochemical evolution of the shales is influenced by a carbonate component, and then, successively decreasing in significance, a black shale component, a clay mineral component, a detrital component, a manganese component, and finally what can only be termed an Ag/Co component.

Having defined the controls over the geochemical development of Kansas shales, it is possible to examine the stratigraphic effects of these controls by studying the relationships between the samples. The scores of Kansas shale samples on the six significant components were, therefore, submitted to a Q-mode cluster analysis program. The dendrogram produced is shown in Figure 33 and the samples are seen to fall into a number of natural groups. Although most of the samples appear to be closely associated, a maximum of 10 groups or clusters can be distinguished.

Before examining the stratigraphic distribution of

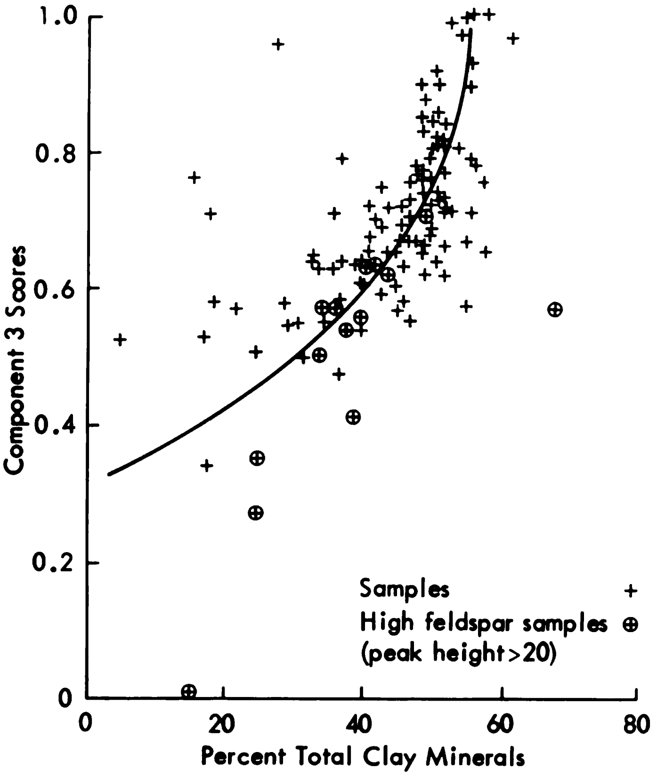

FIGURE 32. Component 3 scores against percentage total clay.

these clusters, it is necessary to confirm that the 10 groups are discrete and not simply a product of the clustering method. The procedure adopted as a test is described on page 28 and is based on the multiple discriminant analysis program of Mather (1969a, 1969b). By this method, variation between clusters is maximized to produce two discriminant axes, accounting for 70.9 percent of the sample variance (Figure 34). As the diamonds in Figure 34 represent the means of each cluster ± 1 standard deviation on each axis, it can be seen that clusters A, B, C, E, and G are indistinguishable and can be merged. Similarly, group J only consists of two samples and can be merged for convenience with group H. Group I, on the other hand, is found to be unique and represents black shales with high scores on component 2. A statistically more realistic arrangement of the dendrogram samples is therefore:

1. Clusters A, B, C, E, and G (referred to henceforth as cluster A),
2. Clusters H and J (referred to as cluster H in the succeeding discussion),
3. Cluster D,
4. Cluster F,
5. Cluster I.

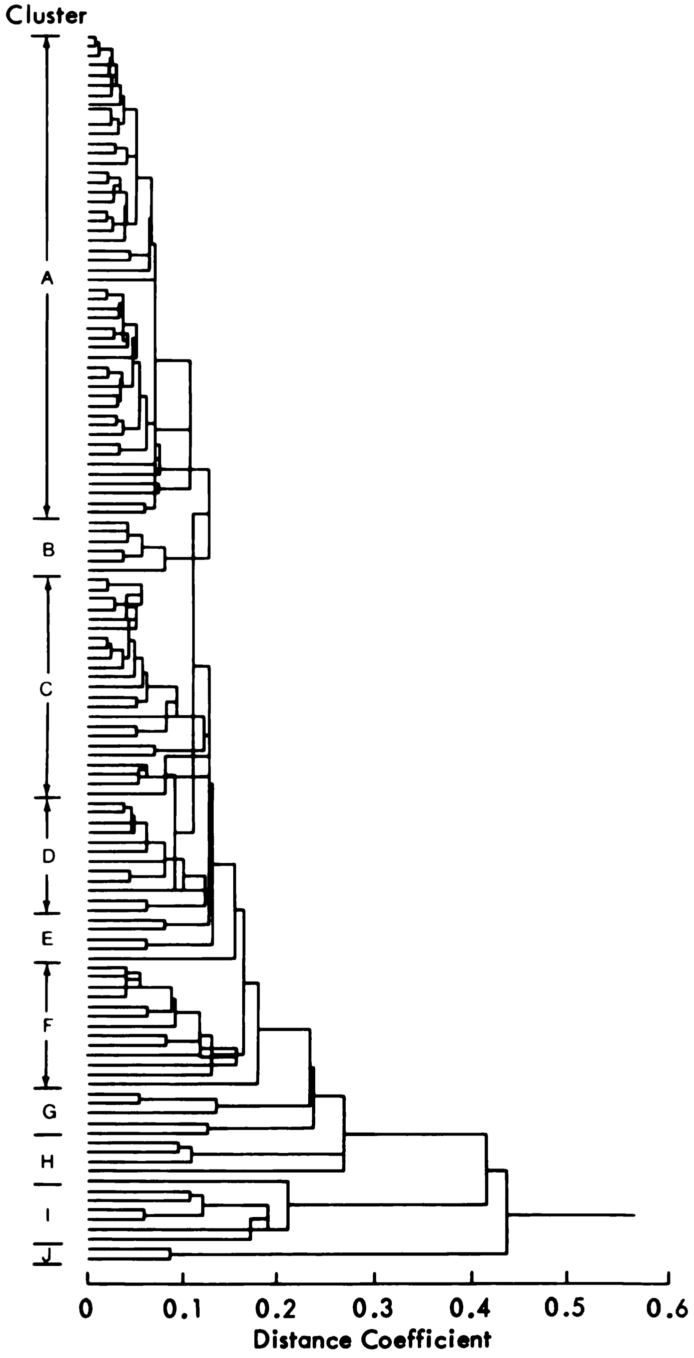

FIGURE 33. Dendrogram of Upper Pennsylvanian and Lower Permian geochemical data. Clusters produced are outlined on the left of the diagram.

When re-examined by discriminant analysis (Figure 35), the revised clusters are found to be discrete units. It can be concluded, therefore, that the geochemical controls outlined previously divide the shale samples into five groups. In Figure 34 the geochemical components are superimposed on the distribution of the groups to show that, although each cluster is unique, it is generally influenced by more than one component. For example, samples in cluster H have high scores on components 1, 4, and 5; cluster I has high scores on component 2; cluster A is characterized

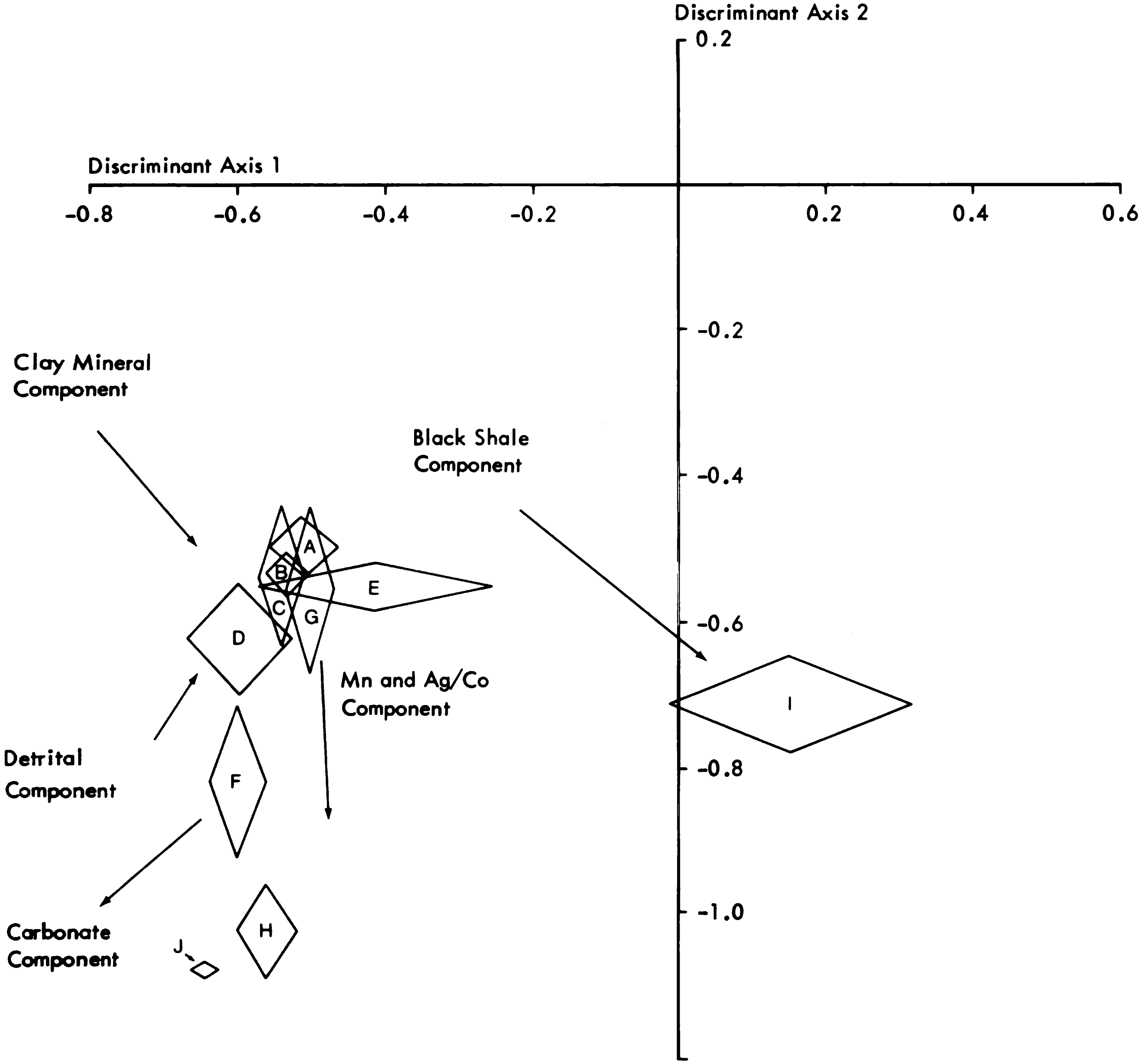

FIGURE 34. Plot of cluster groups on first two discriminant axes. Controlling components are superimposed to aid interpretation.

by high scores on component 3; and cluster F is controlled by the high scores recorded on the first component. Samples from group D, on the other hand, are characterized by low scores on components 2 and 5. The controlling components indicate that cluster I consists of black shale samples; clusters H, F, and D are dominated by calcareous and dolomitic shales; and cluster A by quartz, feldspar, and clay-rich shales, although in the latter case some overlap into the calcareous regime does occur. These findings are supported by a comparison between the distribution of shale samples in the X-ray diffraction and geochemical classifications (Table 12).

The distribution of the shale samples according to their cluster is shown in Figure 36 and reveals a five-fold division of the stratigraphic column. The lowest division consists of the Pleasanton and Lower Kansas City Group beds and contains samples that fall into all five clusters: the majority of samples belonging to cluster A, four to cluster I, and one from each of the remaining clusters. Samples from cluster I occur at approximately 70-foot intervals and reflect the

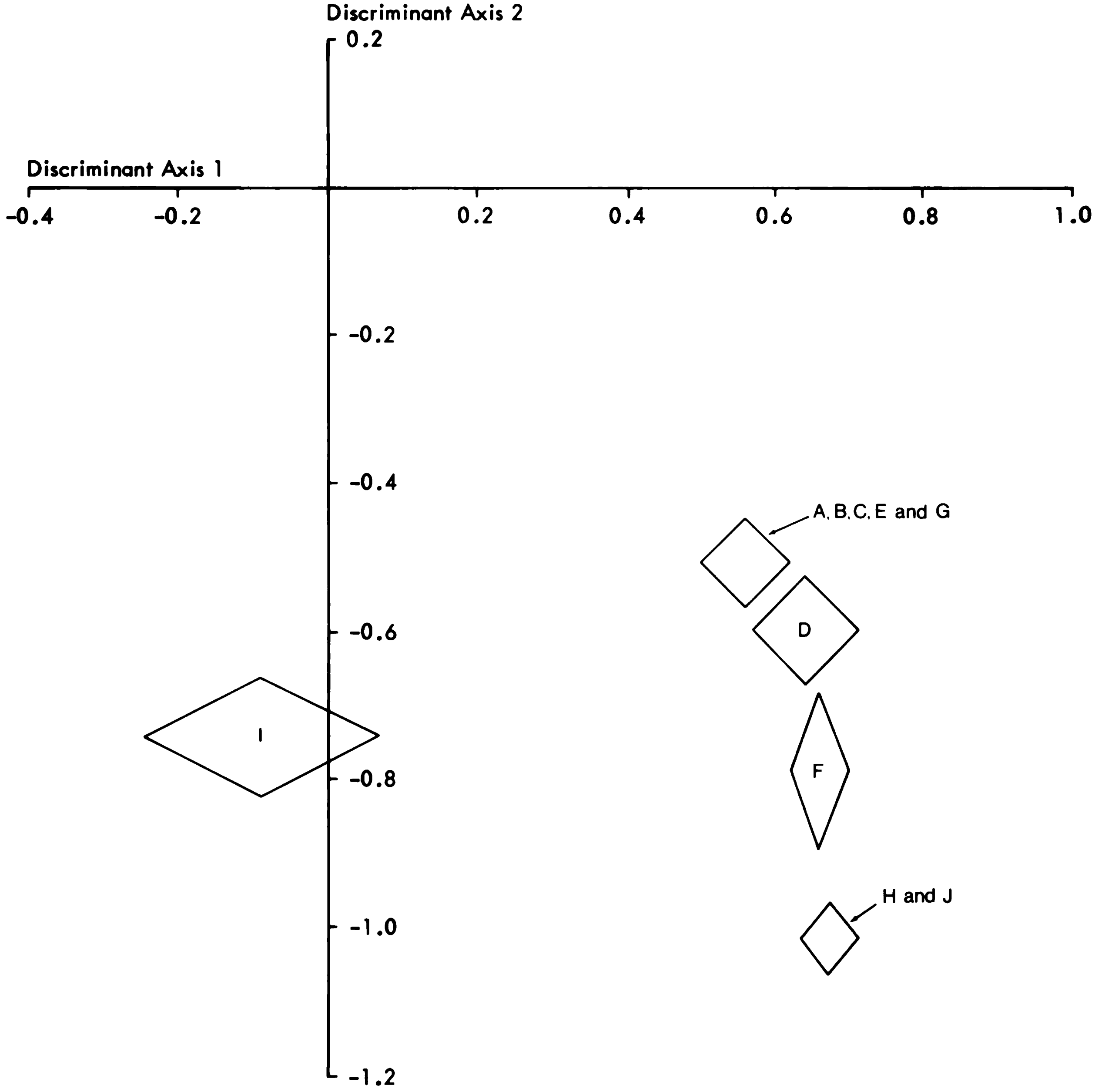

FIGURE 35. A plot of revised clusters against first two discriminant axes. Diamonds represent mean of each cluster ± 1 standard deviation on each axis.

occurrence of black shale deposits. There is, therefore, a close link between the regularity of black shales (cluster I) and the 70-foot cycles noted in the Cd, Cr, Cu, Mo, Ni, Pb, Zn, and V trace-element distributions. Carbonate-rich shales (clusters D, F, and H) are, in three of the four cases, associated with the cluster I samples, indicating a connection between the occurrence of calcareous and dolomitic shales and the geochemical cycles noted previously.

Following the Pleasanton-Lower Kansas City section is an Upper Kansas City, Lansing, and Douglas

TABLE 12. Distribution of shale samples in the X-ray diffraction and geochemical classifications, indicating, for example, that of the samples in geochemical cluster F, 4 were classified into X-ray diffraction cluster E, 1 into G, 1 into A, and 2 into H.

		Geochemical Groups				
		A	D	F	H	I
X-Ray Diffraction Groups	A	16	1	1		3
	B	48	1			3
	C	3			2	
	D	6				
	E	16	8	4	5	
	G		1	1	5	
	H		1	2		

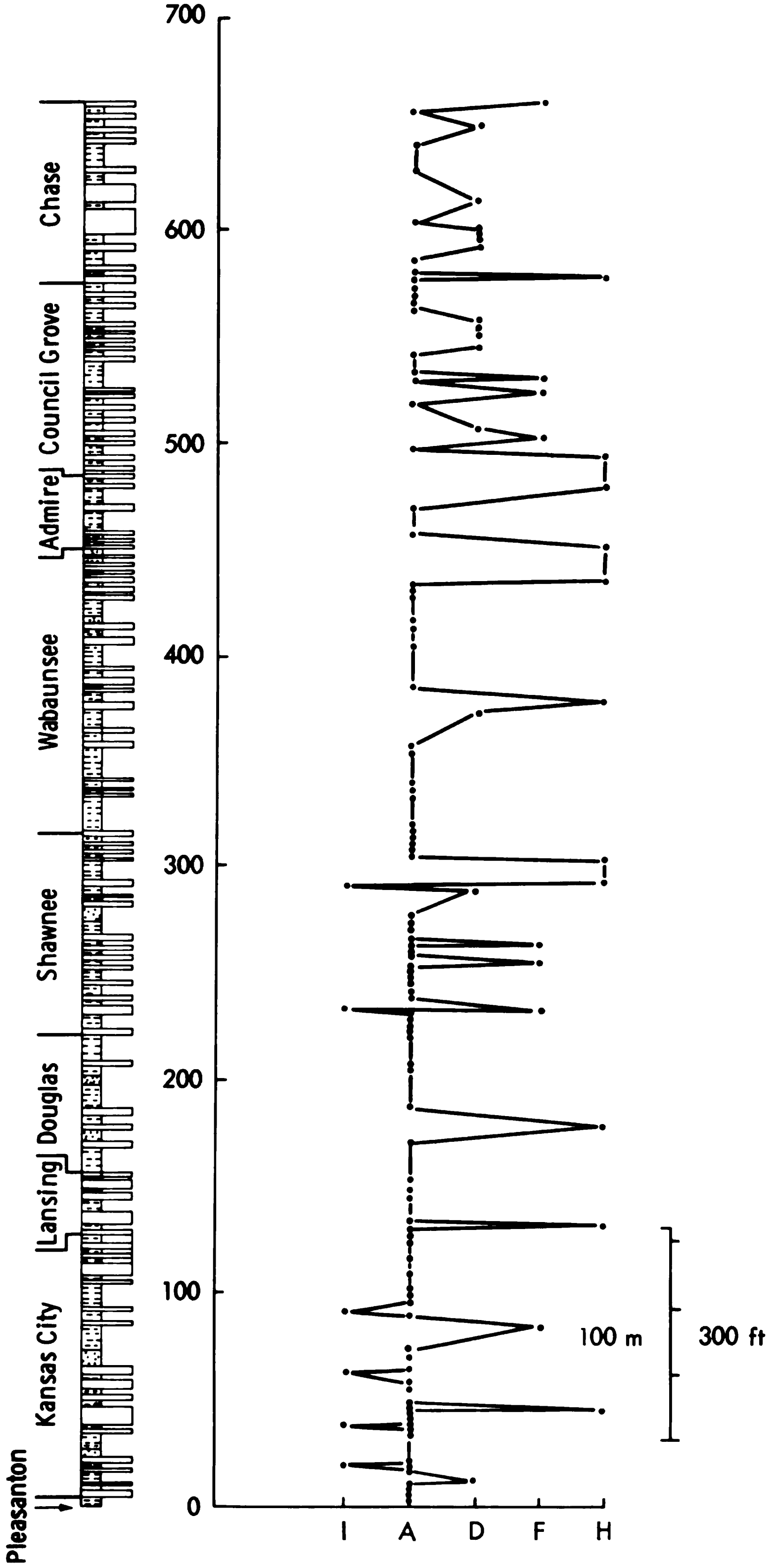

FIGURE 36. Stratigraphic distribution of shale samples arranged according to the cluster analysis groups. The horizontal scale is arbitrary.

Groups zone, which consists predominantly of cluster A samples with an occasional calcareous sample. This division reflects the large numbers of siltstones and sandstones occurring in this part of the stratigraphy.

The succeeding Shawnee Group is similar to the Pleasanton-Lower Kansas City section. Samples from all clusters are again recorded although the proportions of cluster I to D, F, and H are slightly different. Two 70-foot cycles are detected. The Wabaunsee Group constitutes the fourth section and bears a close resemblance to the Upper Kansas City-Lansing-Douglas division, i.e., cluster A samples predominate although an occasional calcareous or dolomitic shale is developed. During the Upper Wabaunsee and Lower Permian, calcareous shales dominate a section that alternates among samples of cluster A, D, F, and H.

Summarizing, the stratigraphic distribution of shales can therefore be considered in terms of five sections of which the Pleasanton-Lower Kansas City and Upper Kansas City-Lansing-Douglas sections show geochemical similarities to the Shawnee and Lower Wabaunsee sections respectively. The lower boundary of the Upper Wabaunsee and Permian zone reflects an important change in environmental conditions from the generally clastic deposition of the Upper Pennsylvanian to the carbonate-dominated sedimentation in the Permian. The Pleasanton, Lower Kansas City, and Shawnee Groups also show evidence for geochemical cycle at 70-foot intervals.

DISCUSSION

One-hundred-twenty-six samples of Upper Pennsylvanian and Lower Permian shales were analyzed for major oxides and minor elements using an ARL 2900B direct reading emission spectrometer. From the results, it has been shown that the distributions of SiO_2, Al_2O_3, CaO, MgO, MnO, Co, Cr, Cu, Mo, Ni, Pb, Sr, V, Zn, and Zr are stratigraphically controlled and that the values of Ag, Be, Bi, and Ge are so low that no stratigraphic relationships can be distinguished.

The major oxides present a similar stratigraphic zonation to that displayed by the mineralogical variables, i.e., the Pleasanton, Kansas City, and Lansing beds form one natural division of the stratigraphy and the Douglas, Shawnee, Wabaunsee, and Lower Permian Groups, further divisions. CaO and MgO have high values in the Pleasanton, Kansas City, Lansing, and Shawnee Groups, whereas the Douglas and Wabaunsee Groups are rich in SiO_2 and Al_2O_3. In the Lower Permian Groups, CaO and MgO form the major geochemical components. Fe oxide and K_2O distributions are relatively stable throughout the Lower Permian and Upper Pennsylvanian.

The minor elements, on the other hand, reveal a totally different pattern of stratigraphic control. MnO, for example, has a distribution that may reflect differences in the original carbonate mineralogy or the depositional environment of the sediments. High values are recorded in the Lansing, Shawnee, Wabaunsee, and Admire Groups. Similarly, Sr, another geochemical facies indicator, has peaks in the Council Grove, Shawnee, Chase, and Pleasanton Groups that may reflect original mineralogical differences in the carbonate content of the sediments and changes in the depth or salinity of the depositional environment. Ga and Li are enriched in marine sediments relative to fresh water and indicate that parts of the Douglas and Wabaunsee were deposited in a restricted marine or non-marine environment. However, the inference drawn from all four distributions is that a complex interrelationship among salinity, depth, and original mineralogy exists in Kansas shales that cannot be unravelled by simply examining individual geochemical variables. Further information may be gained by a multivariate statistical analysis of the geochemical data (p. 50).

Another distinguishing feature of the minor-element geochemical data is the association of Cd, Cr, Cu, Mo, Ni, Pb, V, and Zn with the occurrence of black shales. This has been extensively documented in the literature and arises from the chemical activity of organic residues in a reducing environment.

A third factor influencing the geochemical variation of the Upper Pennsylvanian and Lower Permian shales is elucidated by the distribution of zirconium. As this element is predominantly found in the detrital mineral zircon, the stratigraphic regions rich in Zr probably represent periods of detrital deposition. This conclusion is supported by the distribution of quartz, feldspar, and Co, which have peaks in the Douglas and Wabaunsee Groups.

A comparison of geochemical results obtained in this paper and by Ebens and Connor in a survey of Missouri (1972) has shown that the geochemical variation in the calcareous and black shale deposits, particularly Ca, Cr, Cu, Pb, Ni, Sr, V, and Zn, is regionally controlled. Variables that had equivalent ranges of results in both Kansas and Missouri deposits included Ba, Co, and Zr.

Published reports on the worldwide geochemical evolution of CaO, MgO, K_2O, Al_2O_3, and Fe oxides indicate that the distribution of major oxides in Kansas shales forms a geochemical association that matches worldwide trends during the Upper Pennsylvanian and Lower Permian. However, a negative correlation was noted between the evolutionary trend of Sr in shales (Reimer, 1972) and that reported here.

The factors that may affect the geochemical variation in the Upper Pennsylvanian and Lower Permian shales are, therefore, worldwide geochemical evolution, particularly in the major oxides; regional events such as the distribution of Ca, Cr, Cu, Pb, Ni, Sr, V, and Zn; and a three-fold stratigraphic control of trace elements and major oxides. In the latter case, the associations of variables noted are a carbonate fraction containing CaO, MgO, Sr, MnO, and possibly Ba, Ga, Li, and K_2O; a black shale fraction including Cd, Cr, Cu, Mo, Ni, Pb, Zn, and V; and a detrital fraction, SiO_2, Al_2O_3, Zr with possibly Co, and Fe oxides.

ELECTRON SPIN RESONANCE STUDIES

INTRODUCTION

Conventional microscopic techniques are known to be generally inappropriate for the study and classification of shales because their constituent particles are smaller than the resolving power of an optical microscope. As a result, instrumental techniques such as X-ray diffraction and emission spectroscopy were employed to determine the mineralogical and geochemical composition of the Upper Pennsylvanian and Lower Permian shales and to classify samples on the basis of such analyses. However, questions concerning the environment of deposition of some shales have been raised by geochemical variables such as Mn and Sr. This section is an attempt to clarify these inconsistencies and to verify the conclusions drawn about the geochemistry of the shales.

The geochemical distributions of Mn and Sr in Upper Pennsylvanian and Lower Permian shales indicate apparently contradictory sedimentary conditions in the Kansas City and Wabaunsee Groups. The evidence for this conclusion rests on differences in the geochemical situation of each element. Mn, for example, may occur in association with carbonates or clay minerals. However, it is possible using a spectroscopic technique known as electron spin resonance (ESR) to differentiate the structural settings of ions such as Mn^{2+} and clarify the environmental problem. The shale spectra generated for this study can serve a second function, to provide supplementary evidence on the geochemical and mineralogical classifications developed previously.

ESR is relatively unknown in the geological sciences even though it has been applied in the fields of determinative mineralogy (Marfunin, 1964), lunar mineralogy and petrology (Weeks, 1972, 1973), terrestrial silicates and carbonates (Ghose, 1968; Wildeman, 1970), crystallographic analysis (Low, 1968), and geological age dating (Morency *et al.*, 1970). A detailed list of applications is presented by Cubitt (1975b) and a brief theoretical description is expounded in Whiffen (1968), Browning (1969), and Cubitt and Wilkinson (1976).

Although primarily a chemical technique for the study of paramagnetic ions in crystals, ESR is used as an instrumental tool in geology for the detection of certain ionic species in minerals and rocks and for analyzing the structural position these ions occupy within minerals. It is particularly applicable to ions in the transition group ($3d^n$), the palladium group ($4d^n$), the platinum group ($5d^n$), the rare earth group ($4f^n$), and the actinides group ($5f^n$). In comparison with other instrumental techniques, it is inaccurate (20 percent optimum precision) as a quantitative technique but is exceptionally sensitive as a qualitative technique (10^{-5} to 10^{-12} moles). ESR also possesses three other important characteristics: less than 0.5 gm of the sample (solid, liquid, or powder) is required for analysis, the technique is non-destructive, and sample analysis can be completed within 30 minutes. Consequently, as ESR has no functional equivalent in the instrumental techniques currently employed in the analysis of shales, the simplicity and speed of analysis suggest that the technique may be a useful supplement to standard procedures.

Procedure and Results. Fifty-two finely powdered (less than 60 microns) shale samples from the Upper Pennsylvanian and Lower Permian of eastern Kansas were studied at room temperature on a Varian E-3 X-band spectrometer. Samples were placed in borate glass tubes, positioned in the sample chamber, and analyzed by the procedure described above. The samples were chosen to represent the geochemical and mineralogical range of the shales examined by X-ray diffraction and emission spectroscopy. A list of samples analyzed can be found in Table 13 and their stratigraphic positions are presented in Appendix 3.

Figures 37, 38, and 40 illustrate the types of spectra detected. The ESR signals can readily be assigned to the paramagnetic ions Mn^{2+} and Fe^{3+}, together with four discrete features in the region of free spin ($g = 2.0023$). The Mn^{2+} spectra are of two types corresponding to Mn^{2+} in a symmetric Ca-site as found in calcite (Figure 37) and to Mn^{2+} in an asymmetric Mg-site as found in dolomite (Figure 39). These two types of spectra are well documented in the literature (Ghosh *et al.*, 1970; Schindler and Ghose, 1970; Wildeman, 1970; Low and Zeire, 1972). Although the presence of Fe^{3+} ions is known to produce dipole broadening effects that obliterate weak Mn^{2+} signals (Wildeman, 1970), the majority of shale samples show strong Mn^{2+} spectra with Fe^{3+} forming the background (Figure 41). The free spin features bear some resemblance

TABLE 13. Coded values of spectral characteristics based on presence or absence of a character and the intensity of that character relative to other characters.

Sample	Variable																Remarks
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
213	1	1	0	0	0	0	1	0	1	0	1	0	1	1	1	0	
290	0	0	0	0	0	0	1	0	1	0	1	0	0	0	1	1	
94	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
36	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
500	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	—Pure calcite included as a standard
135	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
105	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
208	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
109	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
272	1	0	0	0	0	0	1	0	1	0	1	1	1	0	1	0	
69	0	0	1	0	0	0	0	0	1	0	1	1	1	0	1	0	
209	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
163	0	0	1	1	0	0	1	0	1	0	1	0	1	0	1	1	
161	0	0	0	0	0	0	1	0	1	0	1	0	0	0	1	1	
186	0	0	1	1	0	0	1	1	1	0	1	0	1	1	1	0	
81	0	0	0	0	0	0	1	0	1	0	1	0	0	0	1	1	
262	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
173	0	0	0	0	0	0	1	0	1	0	1	0	0	0	1	1	
244	0	0	0	0	0	0	1	0	1	0	1	0	0	0	1	1	
235	1	1	0	0	0	0	1	0	1	0	1	0	1	1	1	0	
243	1	1	0	0	0	0	1	0	1	0	1	0	1	1	1	0	
125	0	0	0	0	0	0	1	0	1	0	1	0	0	0	1	0	
16	0	0	0	0	0	0	1	0	1	0	1	1	1	0	1	0	
82	0	0	1	0	0	0	1	0	1	0	1	0	1	0	1	0	
110	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
46	1	0	0	0	0	0	0	0	1	0	1	0	1	0	1	0	
168	0	0	0	0	0	0	0	0	1	0	1	1	1	0	1	0	
633	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	—Pure dolomite included as a standard
122	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
300	0	0	0	0	1	1	0	0	1	0	1	0	0	0	1	0	
28	0	0	0	0	0	0	1	0	1	0	1	1	1	0	1	1	
200	0	0	0	0	1	1	1	1	1	0	1	0	1	1	1	1	
238	0	0	1	1	0	0	1	1	1	0	1	0	1	1	1	0	
298	0	0	0	0	1	1	1	0	1	0	1	0	0	0	1	1	
251	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
48	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	1	
221	0	0	1	1	0	0	1	1	1	0	1	0	1	1	1	0	
187	0	0	1	1	0	0	1	1	1	0	1	0	1	1	1	0	
137	0	0	1	1	0	0	0	0	1	0	1	0	1	1	1	0	
5	0	0	0	0	0	0	0	0	1	0	1	1	1	0	1	0	
24	0	0	0	0	0	0	1	0	1	0	1	1	1	0	1	0	
234	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
155	0	0	0	0	0	0	1	0	1	0	1	1	1	0	1	0	
184	0	0	0	0	0	0	0	0	1	0	1	0	0	0	1	0	
70	0	0	1	1	0	0	1	0	1	0	1	1	1	0	1	0	
160	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	0	
20	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	1	
194	0	0	1	1	0	0	1	0	1	0	1	0	1	0	1	1	
43	1	0	0	0	0	0	0	0	0	0	1	1	0	0	1	0	
249	0	0	0	0	1	1	0	0	1	0	1	0	1	0	1	0	
27	1	1	0	0	0	0	0	0	1	0	1	0	1	1	1	0	
281	0	0	1	1	0	0	1	0	1	0	1	0	1	1	1	1	
23	0	0	1	1	0	0	0	0	1	0	1	1	1	1	1	0	
Character Analysis:																	
Totals Present (1)	9	6	27	25	5	5	35	6	51	0	52	11	42	28	52	15	
Absent (0)	45	48	27	29	49	49	19	48	3	54	2	43	12	26	2	39	

Key on following page.

Key to Table 13

For code 1:—

Variable 1 = MnA present (MnA is the Mn^{2+} species found in calcite lattices).
2 = MnA peak much greater than the free spin feature peaks.
3 = MnB present (MnB is a Mn^{2+} species intermediate between MnA and MnC).
4 = MnB peak much greater than the free spin feature peaks.
5 = MnC present (MnC is the Mn^{2+} species found in dolomite lattices).
6 = MnC peak much greater than the free spin feature peaks.
7 = Fe^{3+} present.
8 = Fe^{3+} peak greater than the Mn^{2+} peak.
9 = Free spin species A present.
10 = Free spin species A peak relatively greater than the other free spin feature peaks.
11 = Free spin species B present.
12 = Free spin species B peak relatively greater than the other free spin feature peaks.
13 = Free spin species C present.
14 = Free spin species C peak relatively greater than the other free spin feature peaks.
15 = Free spin species D present.
16 = Free spin species D peak relatively greater than the other free spin feature peaks.

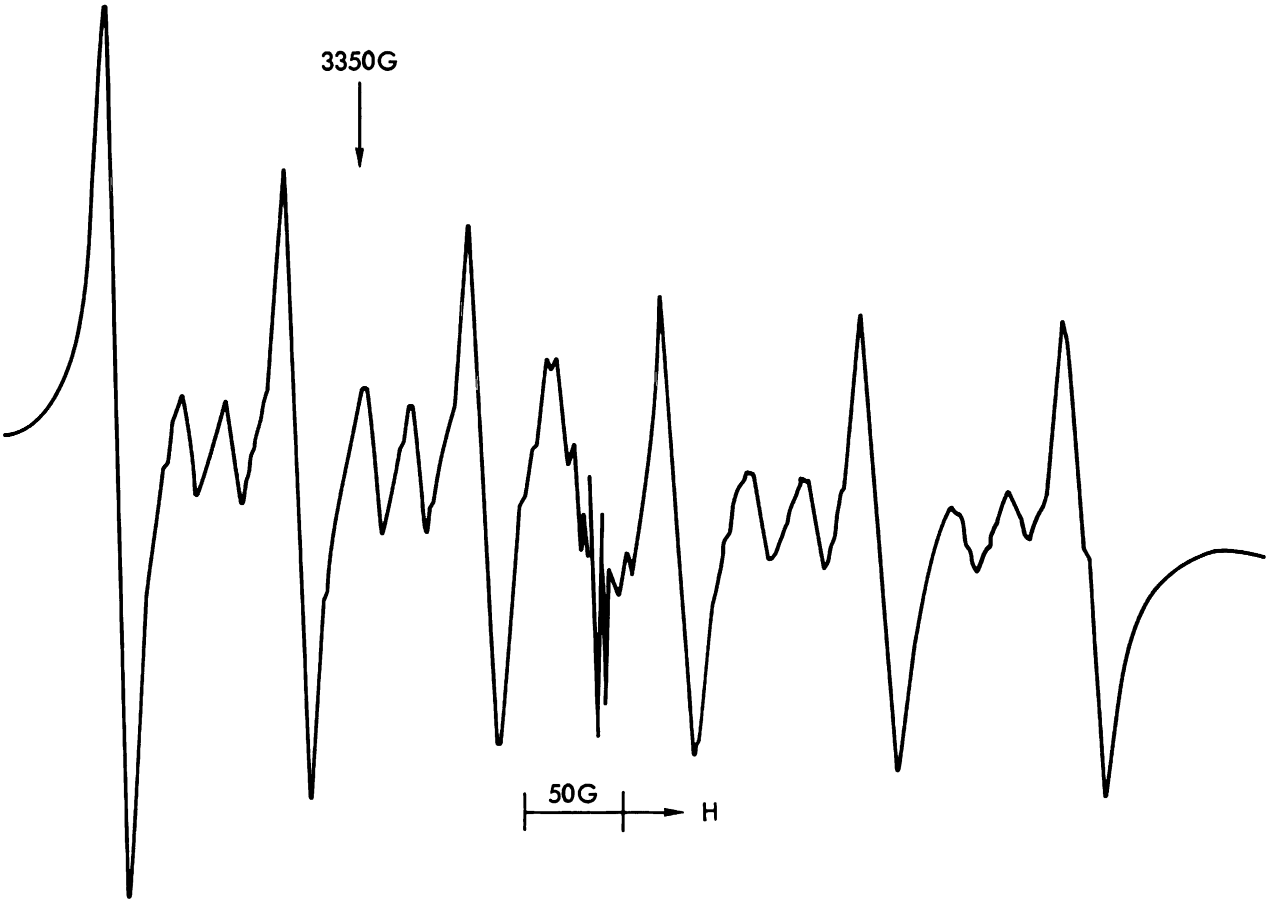

FIGURE 37. ESR spectra of sample 281 illustrating a six-peak Mn^{2+} spectrum (calcite-structure) and free spin feature.

to room temperature ESR spectra of certain clay minerals (Friedlander *et al.*, 1963; Wauchope and Hague, 1971; Boesman and Schoemaker, 1961; Angel and Hall, 1972; Hall *et al.*, 1974). These features can be seen in Figure 42 with species A, B, and D corresponding to a paramagnetic center in illite (probably Fe^{3+}), and species C to a Cr^{3+} ion. An examination of a variety of carbonates, sulphates, and clay minerals by ESR (Appendix 2) supported these conclusions. Samples of kaolinite, dickite, halloysite, vermiculite, illite, montmorillonite, strontionite, rhodochrosite, barites, celestine, and anhydrite were obtained from Dr. R. J. King of the Department of Geology, Leicester University, and run under the same experimental conditions as the

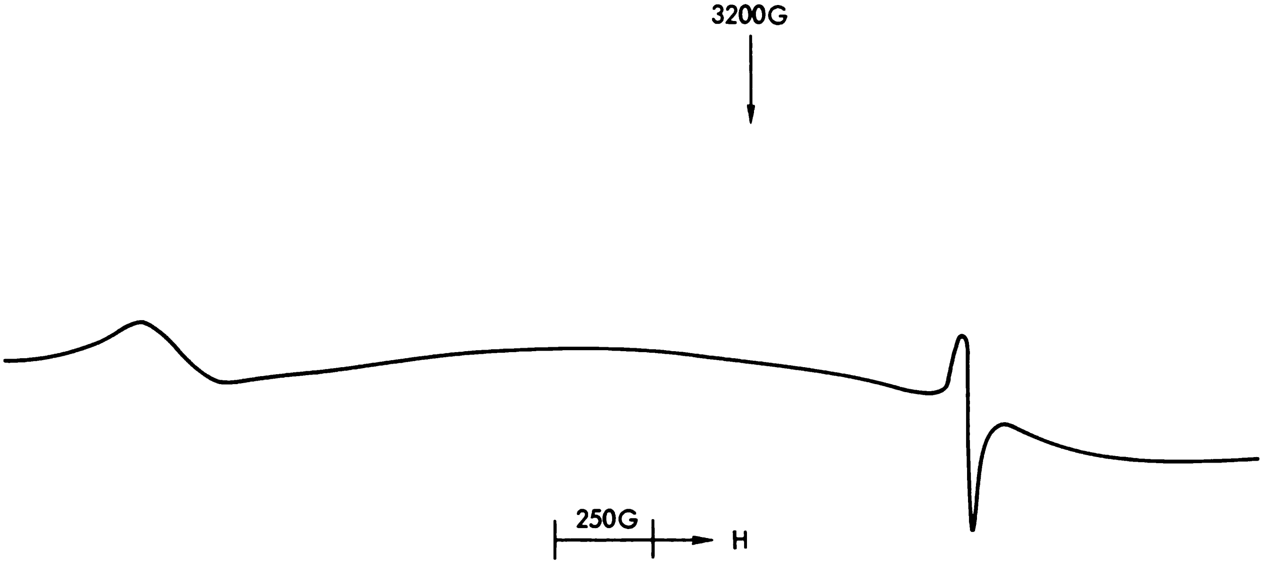

FIGURE 38. ESR spectra of sample 125 illustrating an Fe^{3+} spectrum (found in illite) at approximately 2000G and free spin features at approximately 3400G.

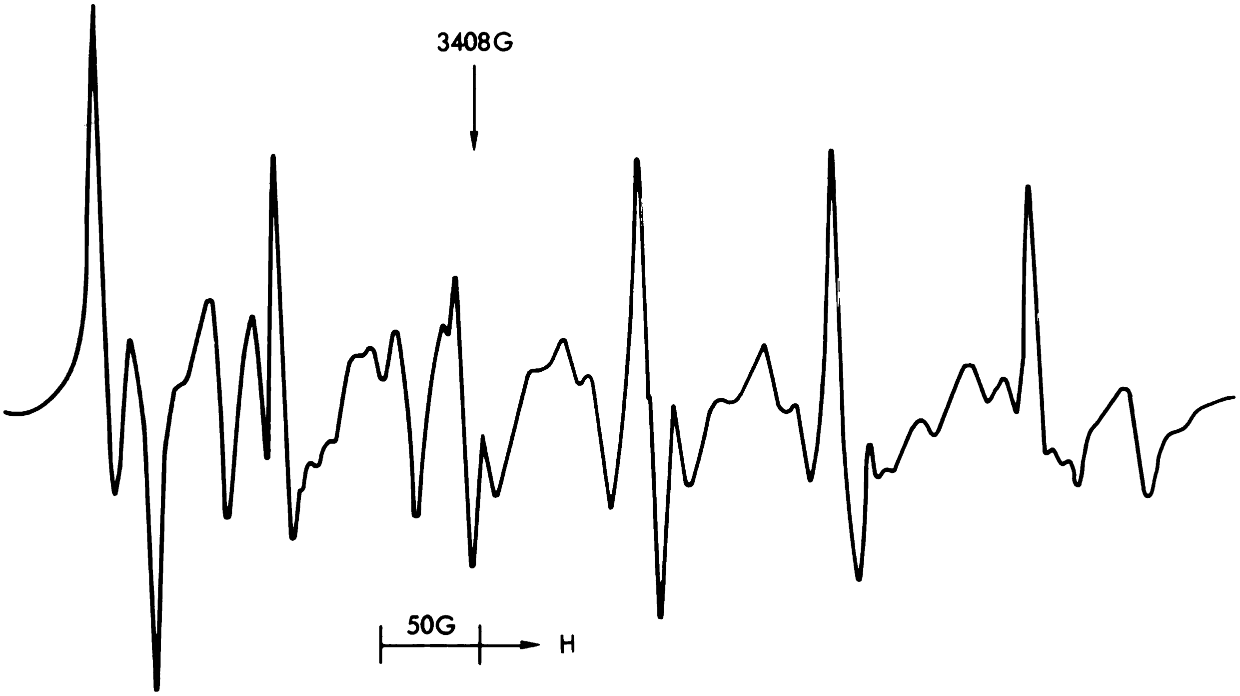

FIGURE 39. ESR spectrum of Mn^{2+} in dolomite.

shale samples. The ESR spectra showed that only the illite and montmorillonite specimens produced the free spin features described above. As montmorillonite is found in few of the shale samples, and then only in minor quantities, it was concluded that illite provided the free spin spectra detected.

The ESR spectra also indicate that the only structural site occupied by Mn^{2+} is in the lattice of carbonate minerals substituting for Ca^{2+} and is not associated with the clay minerals. This supports the conclusions drawn concerning the environment of deposition of calcareous shales inferred from the stratigraphic distribution of Mn. The conditions indicated by the Sr distribution must therefore be treated with scepticism.

The remainder of this section concentrates on a

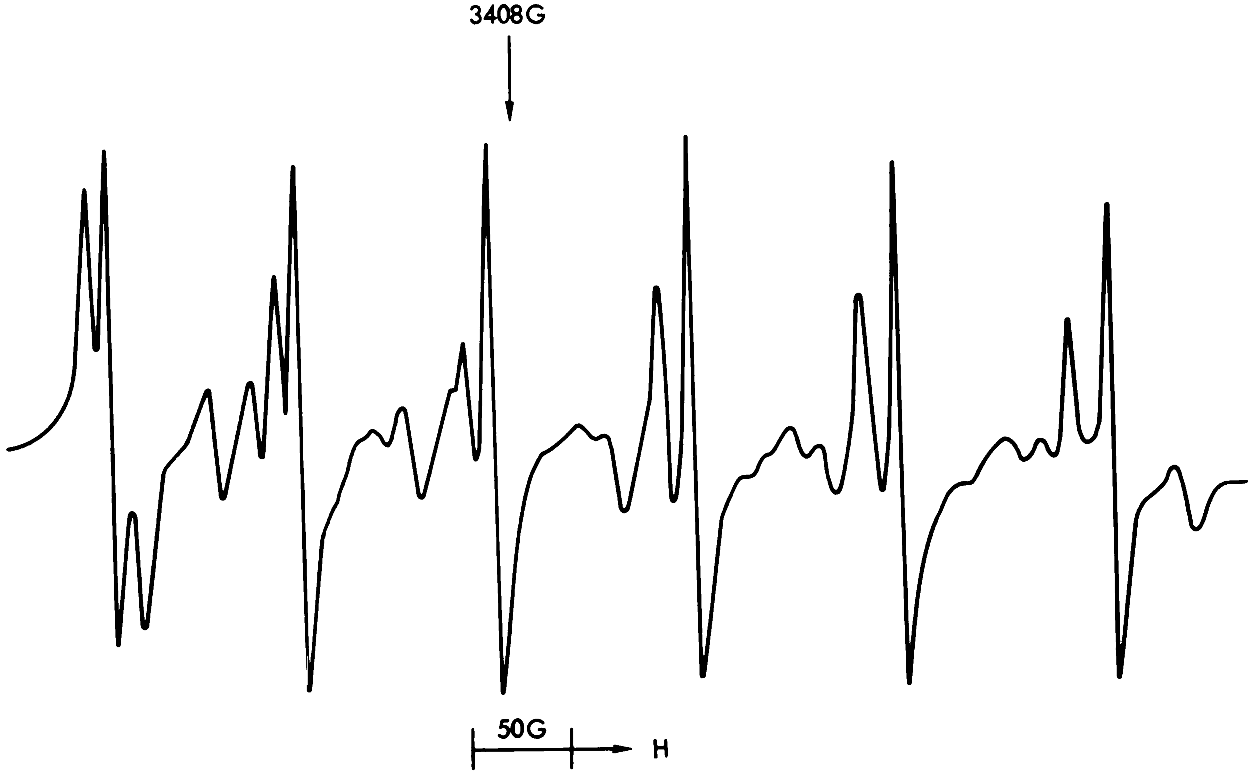

FIGURE 40. ESR spectra of sample 300 illustrating a six-peak Mn^{2+} spectrum (dolomite structure).

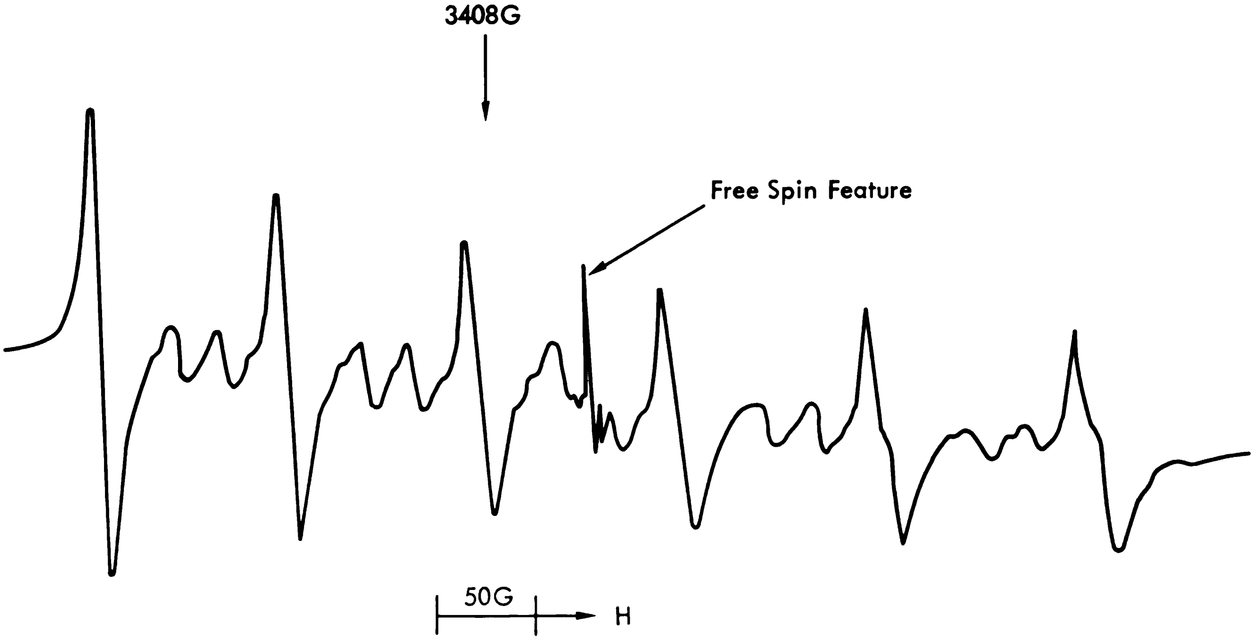

FIGURE 41. ESR spectra of sample 238 illustrating a Mn^{2+} spectrum (calcite structure) and free spin feature with a background Fe^{3+} spectrum manifested in the gradual downwards drift of the Mn^{2+} spectrum towards the higher field values.

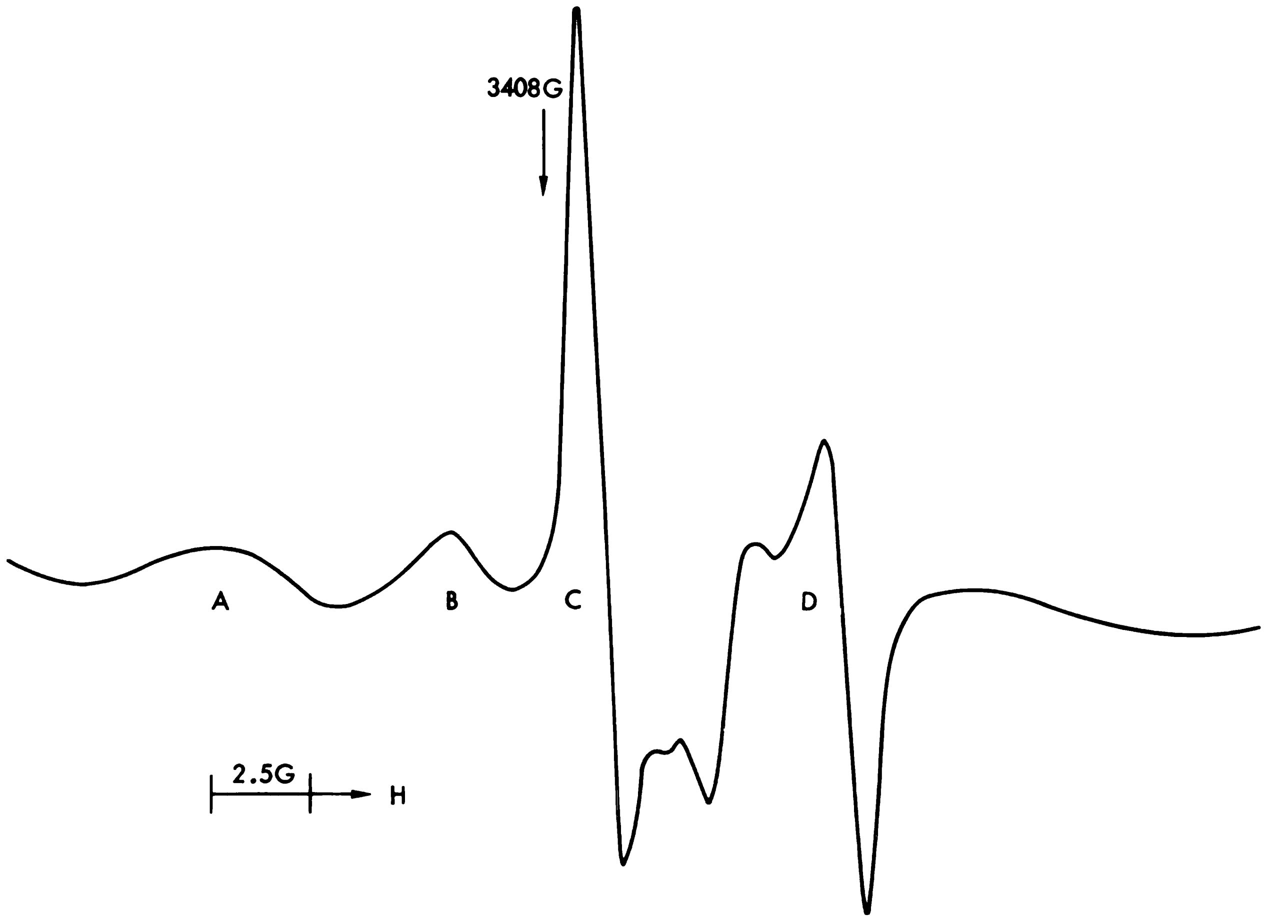

FIGURE 42. Free spin feature in the ESR spectra of sample 86. See text for explanation of diagram.

statistical analysis of the ESR spectra and a verification of the geochemical and mineralogical classifications previously developed. For such a study, the uncertain nature of the species causing ESR absorptions is not a major obstacle as precise identification of each species is unnecessary for classification purposes.

ANALYSIS OF THE ESR SPECTRAL DATA

The accumulation of a large number of ESR spectra made visual comparison of spectral characteristics difficult. Consequently, these characteristics (presence or absence of a signal and relative intensity values) were coded (Table 13) and compared using a computer method developed for taxonomic classification (Sokal and Sneath, 1963). The computer programs (ITBNTOMT and ITBNCLST) calculate similarities between the samples using the simple matching coefficient (SM) and then cluster the similarity values using an unweighted average linkage method (Sokal and Sneath, 1963). The resulting hierarchical classification (dendrogram) is illustrated in Figure 43.

The computer classification shows that the shale samples form four groups, A-D. However, this classification is still empirical as it is based solely on similarities between samples. To assess the geological significance of these groups, a direct comparison with the mineralogical classification was attempted. This classification yielded a seven-fold subdivision of the shale samples having a two-space distribution shown in Figure 18. This figure also shows the primary original variables which have been superimposed on this distribution to indicate the mineralogical nature of each group. In this classification, therefore, the geological significance of each group is known. Comparison of shale samples contained in ESR groups A-D, with their position in the mineralogical groups A-H, is summarized in Table 14. This table, combined with Figure 18, indicates the geological nature of the four ESR groups. Group C consists predominantly of shales within the mineralogical groups A, B, and C. By examining Figure 18, it is apparent that mineralogical groups A, B, and C have high quartz values. Group C samples, therefore, must be pre-

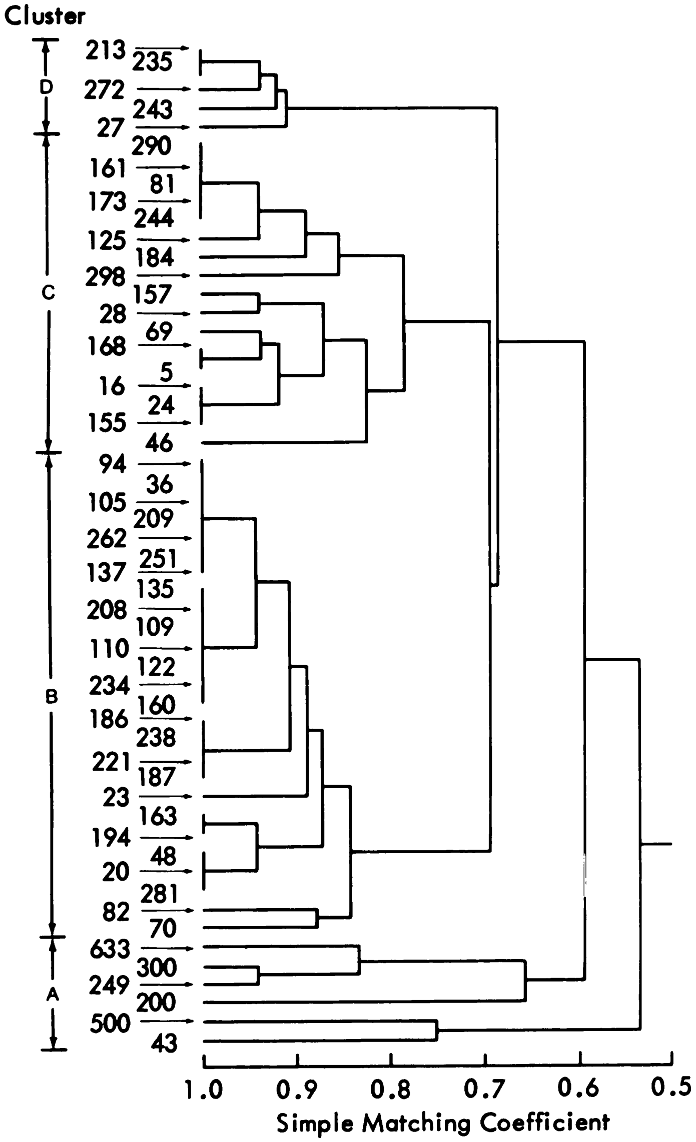

FIGURE 43. Dendrogram of ESR data calculated using an unweighted average linkage algorithm. Clusters produced are indicated on the left.

dominantly quartz rich. Similarly, ESR group A samples are predominantly dolomitic and groups B and D samples are high in calcite. The distinction between groups B and D arises from different site symmetries for Mn^{2+} in these shales.

As the mineralogical classification is, obviously, based on mineralogical data, the groups derived from this analysis must represent geologically meaningful subdivisions of the shale sample collection. As the ESR and mineralogical groups correspond, it is also probable that the parameters controlling these groups are equivalent. This assumption is supported by a plot of the samples in the four ESR groups against stratigraphical position (Figure 44), which is very similar to equivalents for the mineralogical and geochemical classifications and indicates major breaks just below the base of the Permian, at the Wabaunsee-Shawnee boundary, at the top of the Douglas, and the base of the Lansing, producing a five-fold division of the stratigraphic column. The Pleasanton and Kansas City (Lower and Middle) Groups are characterized by alternations of samples from all four clusters. The Upper Kansas City, Lansing, and Lower Douglas Groups only contain samples of group C, indicating clastic deposition throughout this period. The succeeding Upper Douglas and the Shawnee Groups consist of group B and occasionally group C samples, reflecting the general calcareous nature of the sediments. Samples in the Lower Wabaunsee Group region are also exclusively from clusters B and C. However, they are developed in different proportions to the Shawnee, indicating a higher detrital content for the beds. The Permian and Upper Wabaunsee shale samples fall into all four categories with A, D, and B predominating. Here is further support for the hypothesis that the Permian/Pennsylvanian boundary marks a change in sedimentological conditions from the clastic deposition of the Upper Pennsylvanian to the carbonate-evaporite deposits of the Permian era.

DISCUSSION

Although electron spin resonance has been employed widely in geological fields (Cubitt, 1975b), the technique has been mainly applied by physicists and chemists to geological material. Consequently, the potential of ESR as a geological tool is almost unknown. From a geological point of view the primary function of the technique is to detect certain ionic species in rocks and minerals and to define the structural sites of these ions. As a speedy, non-destructive, highly sensitive instrumental technique applicable to nearly 50 percent of all the ions in the periodic table, ESR can be used to supply supplementary information for

TABLE 14. A comparison of the position of samples in ESR groups A-D with their position within the mineralogical classification (e.g., of the five samples constituting group D in the ESR classification, four were classified in group E of the X-ray diffraction classification and one in group B).

		X-Ray Diffraction Groups							
		A	B	C	D	E	G	H	Standards
	A		2					2	2
ESR	B	7	4			13	2		
Groups	C	2	13	1		1			
	D		1			4			

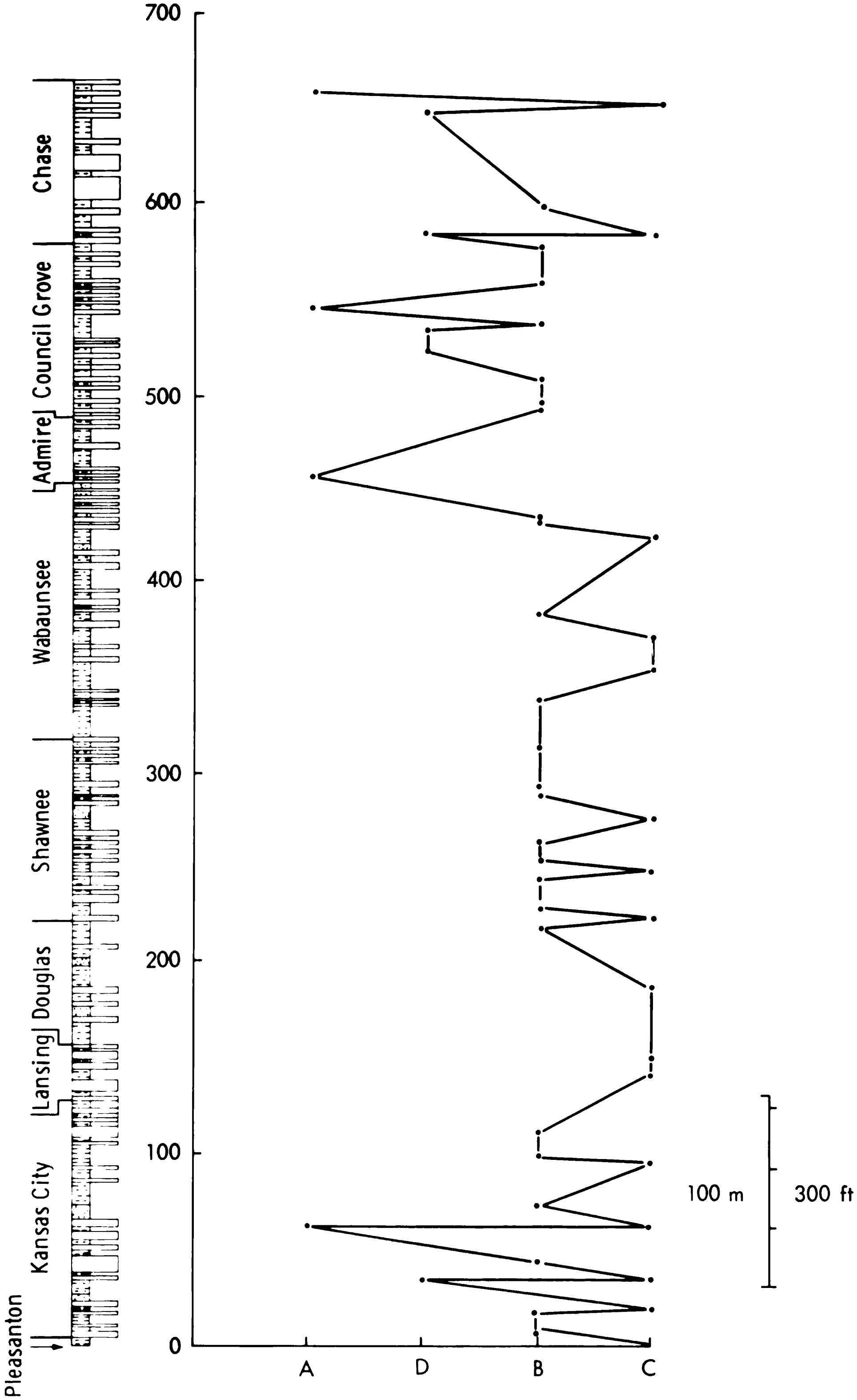

Figure 44. A plot of the stratigraphic position of shale samples against their ESR cluster. The horizontal scale is arbitrary but may give some indication of increasing carbonate content to the left.

the interpretation of shale geochemistry. A classification of the Upper Pennsylvanian and Lower Permian shale samples based on ESR detection of minor impurities in mineral constituents has been developed that shows similarity to the mineralogical and geochemical classifications. The classification produced from presence/absence spectral data has shown that the shales can be divided into four groups—a detrital shale group, a dolomitic shale group, and two calcite-rich shale groups. The distribution of these shale groups (Figure 44) revealed the following five subdivisions in the stratigraphy:

1. A Pleasanton and Kansas City Group division;
2. A Lansing and Lower Douglas division;
3. An Upper Douglas and Shawnee division;
4. A Wabaunsee division; and
5. A Permian division consisting of the Admire, Council Grove, and Chase Groups.

The differences between the sections reflect basic changes in sedimentary depositional conditions, of which the most noticeable occurs at the base of the Permian where the detrital/calcareous shale sequence of the Upper Pennsylvanian is succeeded by the carbonate-evaporite environment of the Permian.

Finally, ESR spectra of Upper Pennsylvanian and Lower Permian shales have indicated that Mn^{2+} is associated with carbonate minerals rather than clay minerals. This supports conclusions drawn previously concerning the environment of deposition of calcareous shales, namely that the Shawnee, Upper Wabaunsee, and Admire Groups probably represent periods of deep-water sedimentation and the Kansas City Group, a period of shallow-water deposition.

STATISTICAL ANALYSIS OF GEOCHEMICAL AND MINERALOGICAL DATA

INTRODUCTION

Statistical analysis of mineralogical data from the Upper Pennsylvanian and Lower Permian shales has revealed mineralogical associations that, mapped against depth, indicate a number of stratigraphic zones. Similarly, analysis of geochemical results from the same shales has produced a number of geochemical associations that also indicate stratigraphic zones. However, these mineralogical and geochemical zones do not coincide throughout the stratigraphic column. It is therefore to clarify the stratigraphic divisions and also the relationships between geochemical and mineralogical variables that a statistical analysis of the combined mineralogical and geochemical data was performed. A useful byproduct of the analysis will be an increased understanding of the relationship between mineralogical and geochemical cycles noted in Upper Pennsylvanian and Lower Permian shales.

The statistical procedures adopted were those applied in previous sections—cluster analysis, principal components analysis, and multiple discriminant analysis.

CORRELATIONS

The initial step in the multivariate analysis procedure is the calculation of a correlation matrix between all geochemical and mineralogical variables. The correlations between individual geochemical variables can be found in Table 10 and for mineralogical variables in Table 5. The correlations between mineralogical and geochemical variables are given in Table 15 and a number of inferred relationships are confirmed.

Al_2O_3 shows high correlations with quartz, feldspar, and the clay minerals, reflecting concentrations of Al_2O_3 in feldspar and the clay minerals. Similarly, SiO_2 has high correlations with the silicate minerals. CaO, on the other hand, has high correlations with the carbonate minerals, calcite, and dolomite. MgO is correlated with dolomite and feldspar as both minerals contain Mg. K_2O and Fe oxides are correlated with the clay minerals and are most likely found in the lattices either as primary constituents or as substituting ions.

MnO and Mn/Fe are correlated with calcite and dolomite, reflecting the association of Mn with carbonates. Ba on the other hand is correlated with illite and chlorite, an indication of possible substitution in the two minerals. Bi is positively associated with the carbonate minerals as are Ge, Sn, and Sr. Co and Zr form an association with quartz and feldspar as both are often deposited as detrital elements. Gallium has a high correlation with each of the clay minerals. The remaining elements, Ag, Be, Cd, Cr, Cu, Li, Mo, Ni, Pb, V, and Zn, have no significant correlations.

PRINCIPAL COMPONENTS ANALYSIS

Using the correlation table described above, an R-mode principal components analysis produced nine significant components which together account for 79.9 percent of the total variance in the data set (Table 16). Loadings of the variables on the components are shown in Figure 45 and a familiar pattern emerges.

Component 1:—The high loadings of CaO, calcite, Ge, Sr, Bi, Sn, MnO, Mn/Fe, and dolomite suggest that this component should be designated a carbonate component. The positive loadings of these elements, oxides, and minerals are opposed by high negative loadings of Al_2O_3, Ga, SiO_2, illite, chlorite, Zn, quartz, and K_2O, clearly indicating a detrital phase antipathetically related to a carbonate fraction.

This component shows a close correspondence to the first geochemical component (p. 50) and it will be apparent when the other components are discussed that the geochemical variables control most of the components.

Following the procedures established previously, a promax rotation of the principal components was performed. However, the algorithm employed in this program recreates the component axes and in doing so only eight components were developed. Components 1 to 6 matched the R-mode principal components of Figure 45 but the other two differed slightly. Consequently, only the first six promax rotated axes are illustrated in Figure 46.

The carbonate/detrital fraction antipathy is also noted in the promax rotation. Stratigraphic variation in component scores (Figure 47) indicates that the

TABLE 15. Correlations between geochemical and mineralogical variables.

	Quartz PA	Calcite PA	Feldspar PA	Dolomite PA	Kaolinite PH	Illite PH	Chlorite PH
Al_2O_3%	0.30	–0.65	0.29	–0.36	0.48	0.70	0.67
CaO%	–0.67	0.85	–0.35	0.27	–0.44	–0.67	–0.60
*Fe%	–0.02	–0.42	0.10	–0.03	0.33	0.39	0.27
K_2O%	–0.18	–0.31	0.04	–0.24	0.29	0.48	0.45
MgO%	–0.38	0.06	0.26	0.59	–0.27	–0.34	–0.29
SiO_2%	0.85	–0.73	0.30	–0.31	0.31	0.48	0.43
Mn/Fe	–0.38	0.53	–0.19	0.31	–0.32	–0.42	–0.46
MnO ppm	–0.32	0.31	–0.10	0.31	–0.22	–0.27	–0.32
Ag ppm	0.16	0.00	–0.05	–0.03	–0.16	–0.21	–0.21
Ba ppm	0.20	–0.36	0.13	–0.17	0.19	0.34	0.35
Be ppm	–0.23	0.03	0.02	0.01	0.05	0.03	0.08
Bi ppm	–0.54	0.57	–0.30	0.13	–0.23	–0.38	–0.42
Cd ppm	0.21	–0.21	0.06	–0.12	0.02	0.06	–0.01
Co ppm	0.29	0.06	0.01	–0.04	–0.03	–0.07	–0.26
Cr ppm	0.04	–0.16	0.01	–0.08	–0.04	0.02	0.04
Cu ppm	0.01	–0.23	0.03	–0.14	0.08	0.14	0.16
Ga ppm	0.13	–0.56	0.18	–0.35	0.51	0.71	0.69
Ge ppm	–0.51	0.63	–0.30	0.08	–0.22	–0.37	–0.42
Li ppm	–0.36	0.12	–0.19	–0.07	0.22	0.23	0.27
Mo ppm	–0.13	0.16	–0.13	0.01	–0.13	–0.19	–0.24
Ni ppm	–0.05	–0.15	0.03	–0.09	–0.00	0.08	0.05
Pb ppm	–0.01	–0.17	0.03	–0.04	–0.02	0.05	0.01
Sn ppm	–0.13	0.28	–0.22	0.35	–0.24	–0.31	–0.33
Sr ppm	–0.43	0.54	–0.28	0.20	–0.31	–0.41	–0.43
V ppm	0.07	–0.16	0.01	–0.07	–0.01	0.02	0.00
Zn ppm	0.17	–0.44	0.14	–0.21	0.21	0.34	0.28
Zr ppm	0.65	–0.24	0.27	–0.14	0.09	0.16	–0.07
*HL%	–0.26	0.12	–0.24	0.06	–0.19	–0.23	–0.13

PA = Peak Area.
PH = Peak Height.
$r_{95} = \pm 0.15$.
$r_{99} = \pm 0.20$.
$r_{99.9} = \pm 0.27$.
*Fe% = Total Fe oxides percent.
*HL% = Percentage weight loss on ignition, or heat loss.

TABLE 16. Eigenvalues of the components extracted. (i.e., eigenvalues > 1.0)

Component	Eigenvalue	Cumulative Variance (%)
1	9.91	28.3
2	6.09	45.7
3	3.67	56.2
4	2.03	62.0
5	1.72	66.9
6	1.26	70.5
7	1.14	73.8
8	1.12	77.0
9	1.02	79.9

Pleasanton, Lower Kansas City, Lansing, Shawnee, Chase, Council Grove, and Admire Groups have a predominance of calcareous shales, whereas the intervening beds are generally detrital in nature.

Component 2:—This component has high positive loadings for Cr, Cu, Mo, Pb, Ni, V, Cd, Zn, Be, and weight loss representing an enrichment of trace elements in the reducing conditions of organic-rich black shales. Component scores are high in the Kansas City Group and Shawnee Group black shales (Figure 47) and low for all other deposits.

Component 3:—This component has positive Li, K_2O, Ga, and Fe oxides loadings opposed by quartz, Zr, Co, Ag, and SiO_2. K_2O in the form of K^+ and Ga is normally found as ions within clay mineral lattices. Similarly, Fe oxides and Li are characteristic of clay minerals. The negative loadings of detrital components add support to the notion that this axis is essentially a clay mineral component. On rotation, the clay minerals are positively loaded with Al_2O_3 and Ga, whereas negative loadings are recorded for Co, CaO, Ag, and quartz. Component scores shown in Figure 47 indicate high positive scores on shales with high clay mineral content (Figure 12) and negative scores on shales with a high detrital quartz fraction (Figure 10). Therefore, there appears to be an antipathic relationship between clay mineral and quartz content in many shales. The negative loadings of CaO on rotation also indicate that a carbonate-clay mineral relationship replaces the quartz-clay mineral antipathy in some shales. This is most noticeable in the Permian shales where scores do not increase when the quartz fraction of shales decreases. Low scores are recorded in the Douglas Group (Tonganoxie

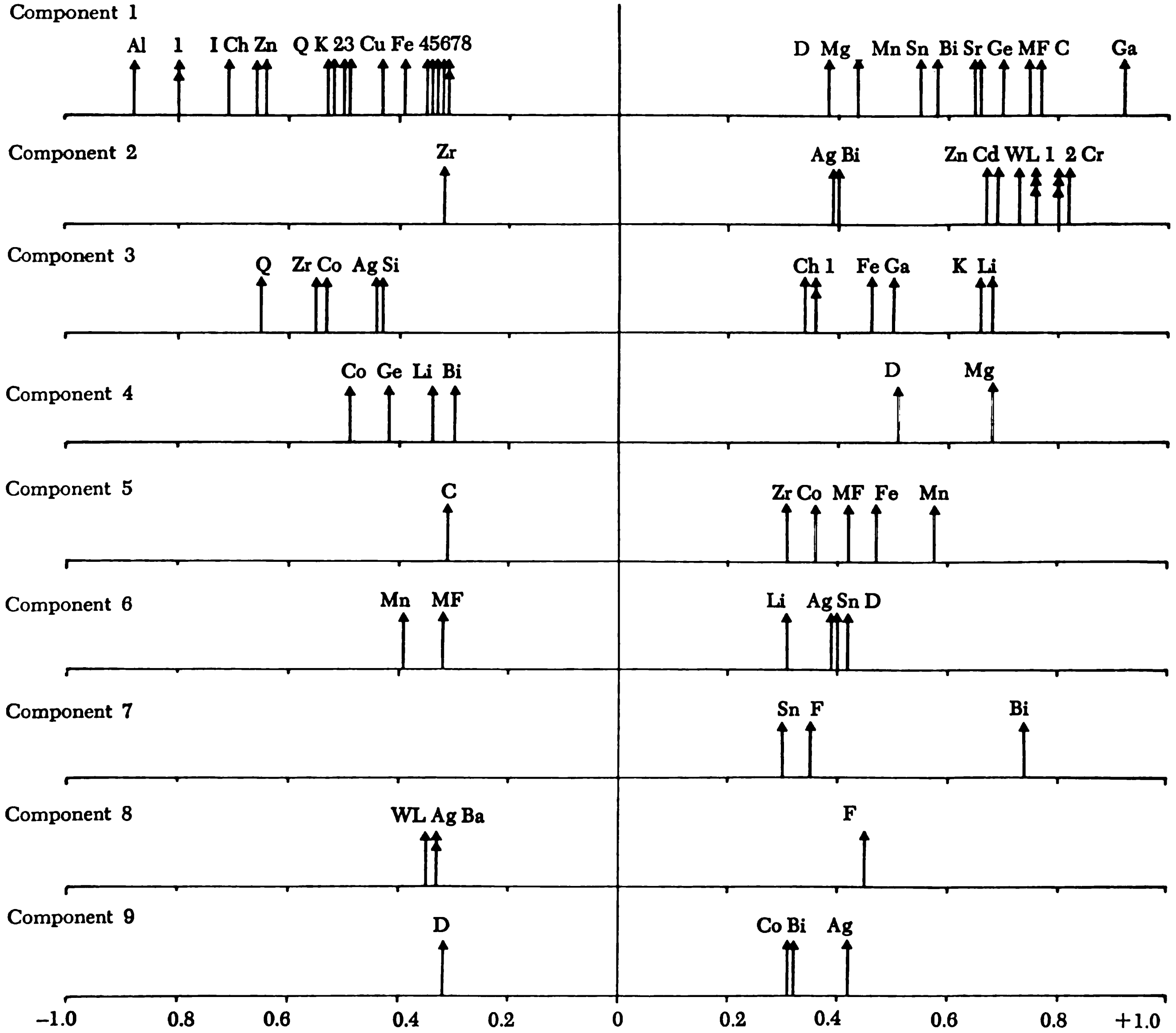

FIGURE 45. Loadings of variables on significant components. Only loadings > ± 0.30 are included.

KEY

For all components:
Same as previous figures
except K = K_2O;
Ka = Kaolinite;
WL = Weight Loss

Component 1:
1 = Ga and Si
2 = Ka
3 = Ba
4 = Cr
5 = Ni
6 = F
7 = V
8 = Cd and Pb

Component 2:
1 = Cu, Mo, and Pb
2 = Ni and V

Component 3:
1 = Ge and Bi

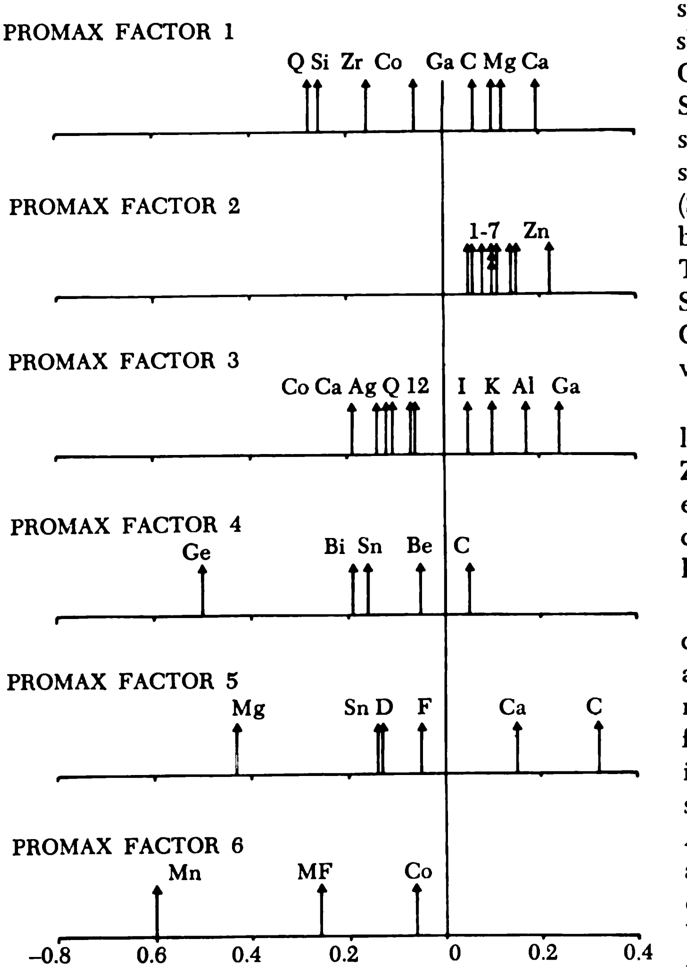

Figure 46. Loadings on promax axes. Only those loadings > ± .05 are indicated.

KEY

For all components:
The same as previous figures except K = K_2O;
Ka = Kaolinite;
WL = Weight Loss

For component 2:
1 = WL
2 = Mo
3 = Be
4 = Co, Cu, and Pb
5 = V
6 = Cr
7 = Ni

For component 3:
1 = Mg
2 = MF

Sandstone) and the Shawnee Group (Stull and Doniphan Shales), whereas high scores are noted in the Lansing (Vilas Shale), Shawnee (Calhoun Shale), Wabaunsee (White Cloud Shale), and Chase Groups (Havensville Shale).

Component 4:—High positive loadings for MgO and dolomite are opposed by negative loadings for Co, Ge, Li, and Bi. On rotation, calcite becomes positively loaded and Sn and Be become negatively loaded. This indicates that the component controls the occurrence of dolomite in the samples. Component scores (Figure 48) show high values for dolomite-rich shales (Figure 11), i.e., Heebner Shale (Shawnee Group), Havensville Shale, Stearns Shale, Paddock Shale (Chase Group), and shale partings in the Winterset Limestone (Kansas City Group), Plattsburg Limestone (Lansing Group), Spring Branch Limestone (Shawnee Group), and Grandhaven Limestone (Wabaunsee Group). Low scores are recorded for the Tonganoxie Sandstone (Douglas Group), Speiser Shale, Salem Point Shale, and Hughes Creek Shale (Council Grove Group) samples with low MgO and dolomite values.

Component 5:—This component has high positive loadings for MnO, Fe oxides, Mn/Fe ratio, Co, and Zr, indicating an association with carbonates. However, the negative loadings of calcite indicate that this component may reflect chemical rather than mineralogical control.

MnO and Fe oxides are often concentrated in deep-sea sediments where reducing conditions enable manganese nodules to develop. In normal marine waters, Mn is predominantly found substituting for Ca in the lattices of carbonates. However, Mn is not found extensively in shallow aragonite-rich sediments such as the carbonates of the Persian Gulf. As Kansas sediments during the Upper Pennsylvanian and Lower Permian were deposited in a shallow epeiric sea, it would be expected that aragonite would be deposited at the edge of the sea and calcite away from the shore. The reducing conditions commonly found in epeiric seas would aid the enrichment of Mn in the deeper sediments. Subsequent diagenetic alteration of aragonite to calcite may account for the differing amounts of MnO found in carbonates of the Upper Pennsylvanian and Lower Permian shales. The negative loadings of calcite can also be interpreted as a reflection of the aragonite to calcite diagenetic alteration.

Rotation of the component reveals a positive loading for calcite and CaO, indicating that the component was not truly bipolar. Negative loadings for MgO, Sn, dolomite, and feldspar clarify the interpretation of the component loadings. It can therefore be assumed that the component reflects relatively deep-water versus shallow-water depositional environments and also an antipathic relationship between dolomite and calcite. It may similarly reflect nearness to shoreline, as deep-water sediments are normally found furthest from the coast.

Component scores suggest that long periods of shallow-water sedimentation alternate with deeper-water sedimentation. Superimposed upon this oscil-

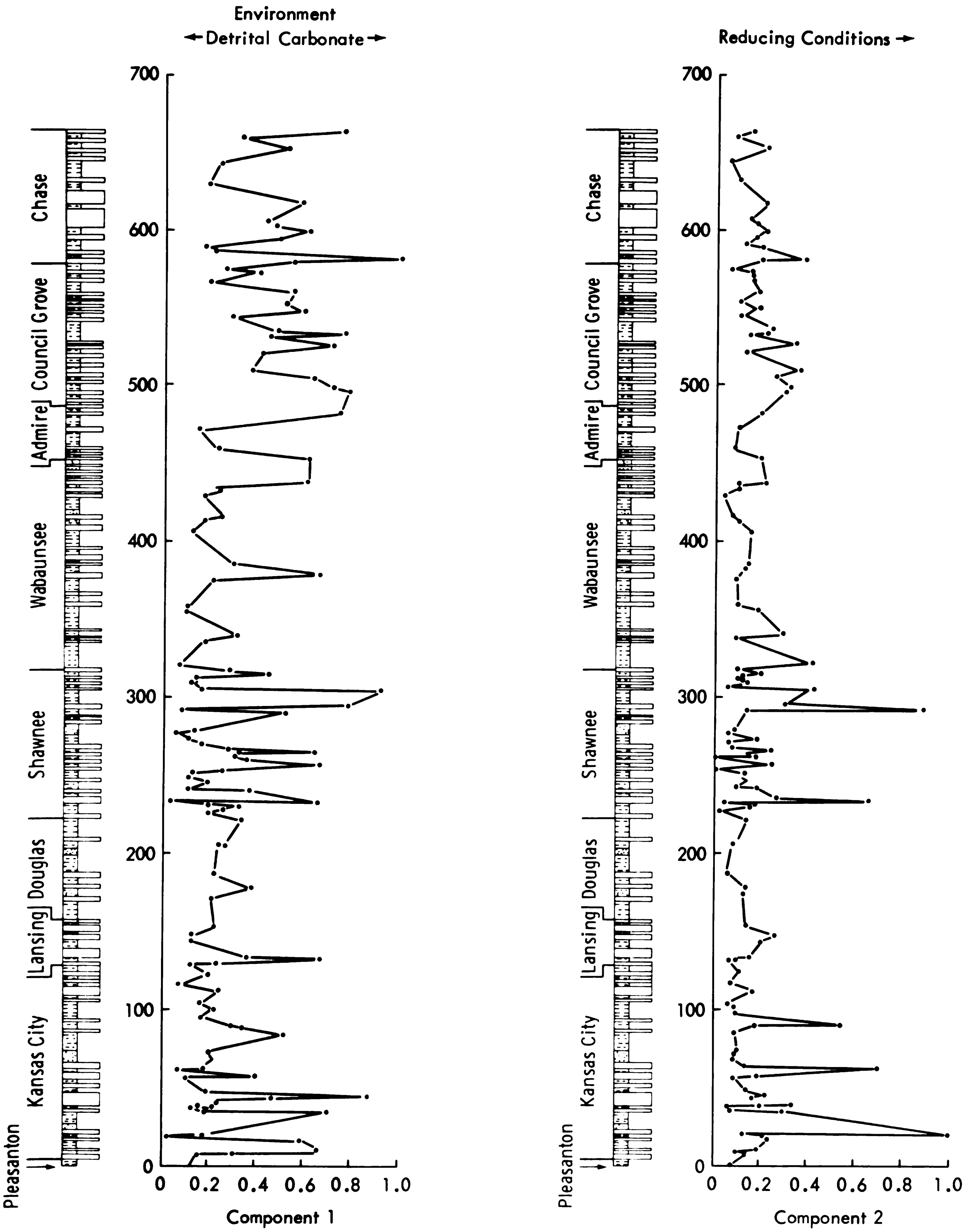

FIGURE 47. Stratigraphic variation of component scores for components 1, 2, and 3.

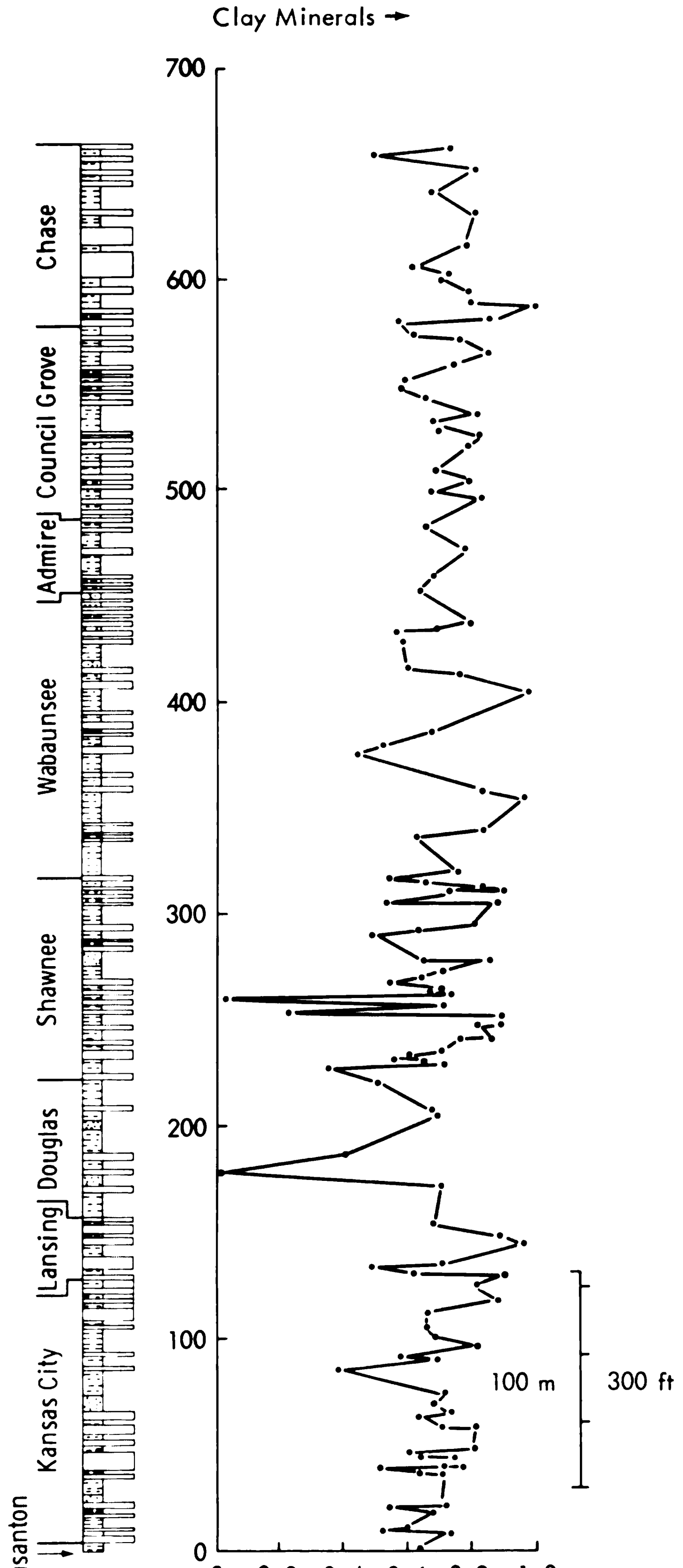

FIGURE 47. Continued.

lation are short time-scale fluctuations. The component scores generally increase from the Pleasanton to a peak in the Lansing Group, decrease through the Douglas to the center of the Shawnee, rise again to the middle of the Wabaunsee, decrease through the Council Grove Group, and finally begin to rise again through the Chase Group. Therefore, there are apparently three long-term oscillations in the depth of deposition for the Upper Pennsylvanian and Lower Permian shales. The highest scores were recorded in the Plattsburg Limestone, Calhoun Shale, Friedrich Shale, Silver Lake Shale, and Pony Creek Shale whereas the Galesburg Shale, Neva Limestone, and Oketo Shale have the lowest scores.

Component 6:—High positive loadings of dolomite, Sn, Ag, and Li are opposed by negative loadings for MnO and Mn/Fe ratio. On rotation, the high positive loadings disappear but the MnO and Mn/Fe negative loadings are accentuated. Additionally, Co develops a high negative loading. The component can, therefore, be interpreted as a manganese component.

Components 7, 8, and 9:—Component 7 is controlled by the unusual combination of Bi, feldspar, and Sn for which no explanation can be offered. Similarly, components 8 and 9 are uninterpretable. Examining Table 16, it is apparent that these components only account for 10 percent of the total data variance and are therefore relatively unimportant in controlling the mineralogical and geochemical evolution of Kansas shales. They probably account for occasional extreme conditions—both experimental and original environmental conditions.

Mineralogical and geochemical variation in Upper Pennsylvanian and Lower Permian shales can therefore be described by nine components of which only six are interpretable. Scores of individual samples on the components subdivide the stratigraphic section into a number of zones. However, these zones are not consistent across all components and may in some cases be contradictory.

CLUSTER ANALYSIS AND DISCRIMINANT ANALYSIS

Another approach to the same problem employs Q-mode cluster analysis, a technique that examines relationships between samples rather than variables. Using the scores on the nine components calculated above, similarity coefficients between samples are determined. A hierarchical classification (dendrogram) is developed from the similarity matrix (Figure 49) and produces a 10-fold division of the samples. It can be seen that almost two-thirds of the shale samples fall into one group, and only one other group contains

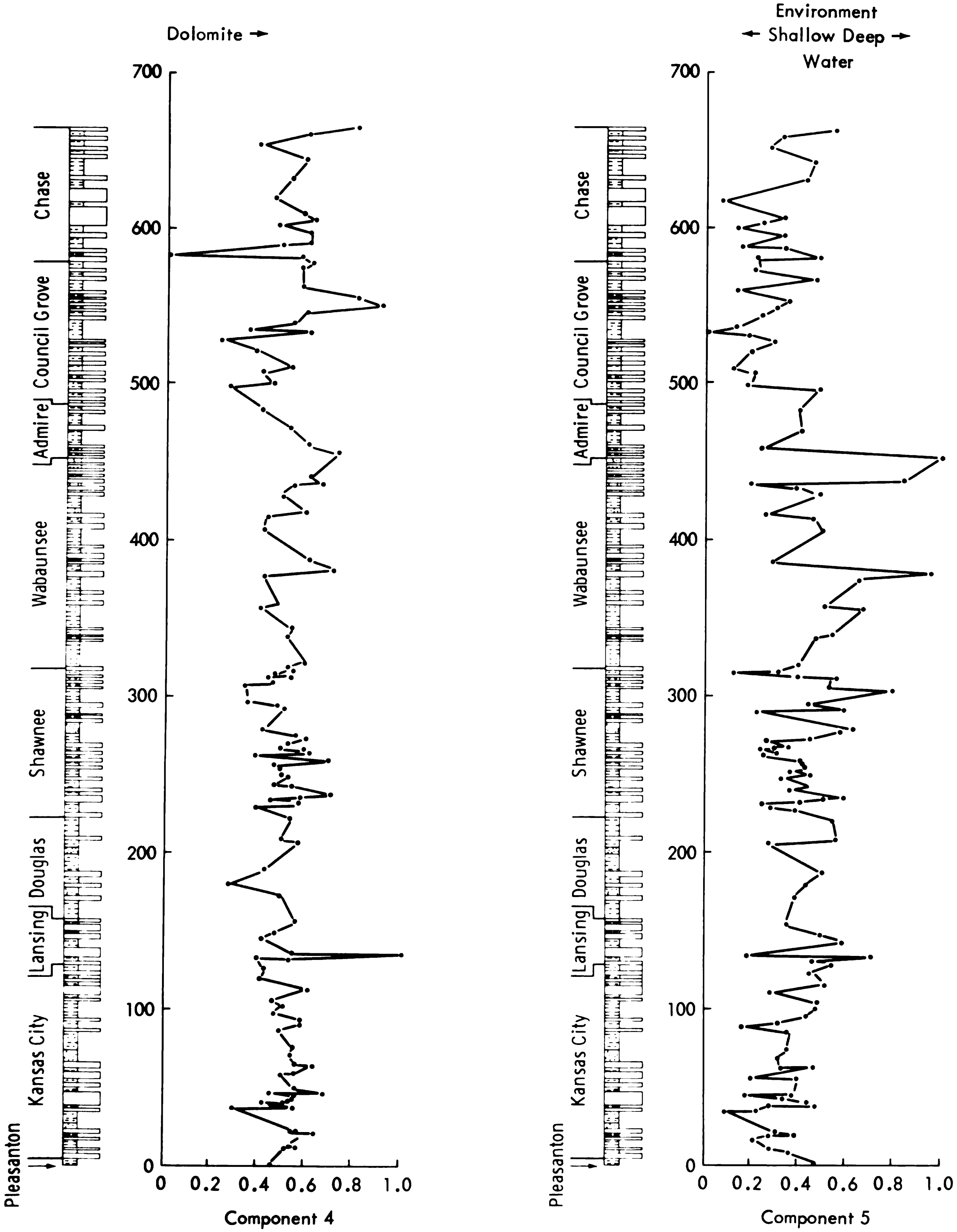

FIGURE 48. Stratigraphic variation of component scores for components 4, 5, and 6.

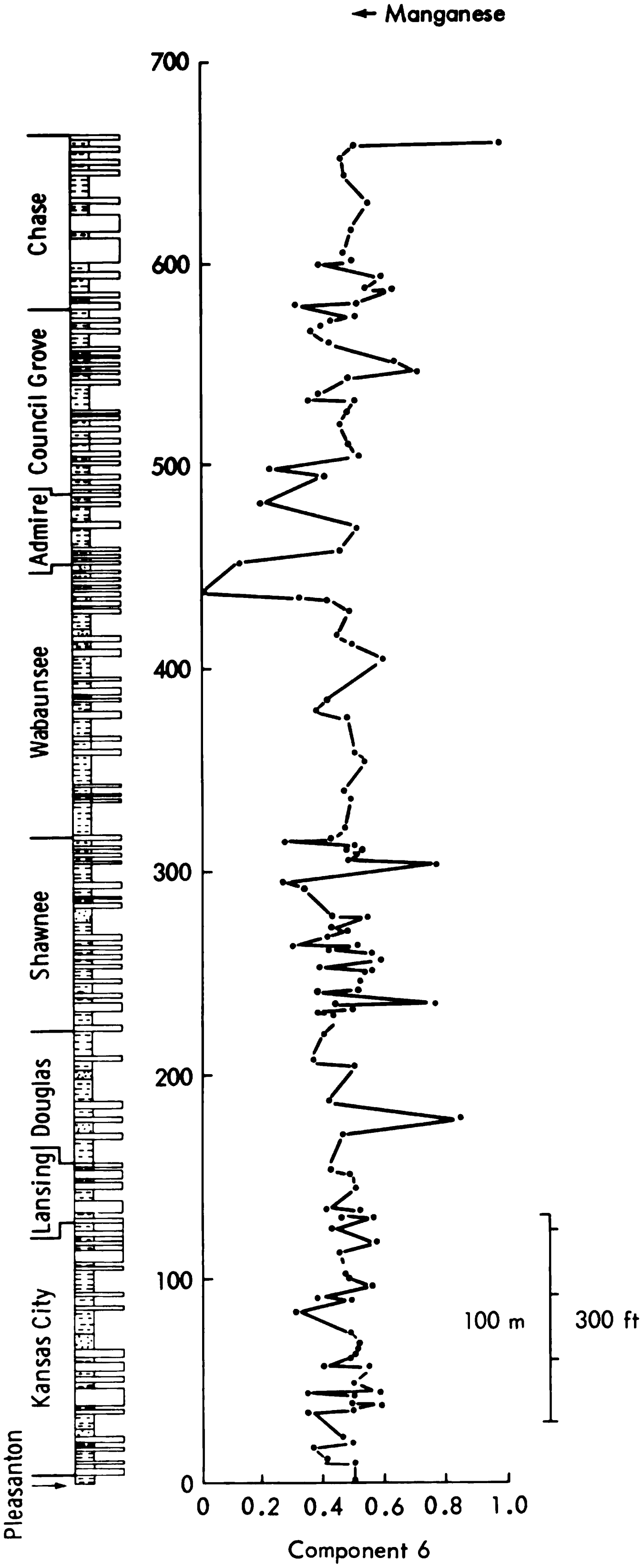

FIGURE 48. Continued.

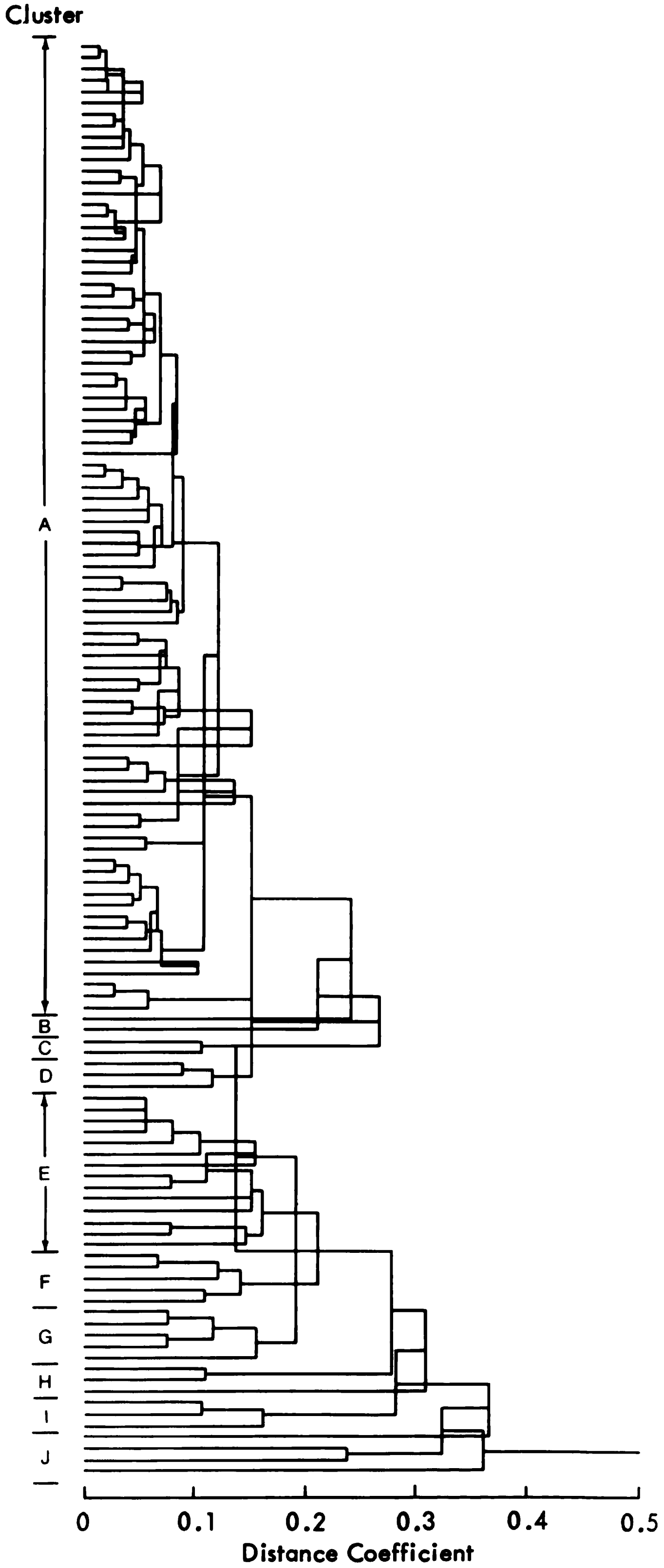

FIGURE 49. Dendrogram of Upper Pennsylvanian and Lower Permian shales based on geochemical and mineralogical data. Clusters produced are outlined on the left of the diagram.

more than five samples. It is unlikely that the remaining samples form eight natural groups, and a number are probably products of the clustering method. Therefore, following the procedure established previously, the scores of the samples on the nine significant components were analyzed by multiple discriminant analysis to check the discreteness of the groups. Four discriminant axes were found to account for 86.9 percent of the data variation (Table 17) and the resulting distributions appear in Figures 50 and 51. It can be seen that these axes successfully distinguish Groups F, J, and I, but all other groups suffer some degree of overlap. It is therefore apparent that some of the clusters are not unique and require some modification.

Along the first, second, and third axes, groups C, B, and H overlap and are only distinguishable by small differences in the manganese and dolomite content. Similarly, clusters A, G, and E are found to be inseparable on all but the fourth discriminant axis. Simplifying the sample classification, these groups can be merged together to form six distinct clusters.

In the case of group D, we can see that it overlaps clusters A, G, and E on the first and second discriminant axes, but that on the third and the fourth, it is distinct. Examining discriminant scores of individual samples, one of the samples in group D is found to have scores similar to group A samples. Simply reallocating this sample to group A distinguishes group D from A, G, and E by reducing the standard deviation of group D on the first two discriminant axes.

However, on examining the original data values, groups E, A, and G are found to be distinctly different. For example, group E samples have large calcite values, whereas those in group G have large quartz values. Within group A, some samples have a high calcite content but most have moderate calcite and quartz values. We can therefore split group A into two sections, corresponding to the emphasis (scores) on the detrital/carbonate component. Clusters H, B, and C samples show very similar data values, although the values for sample 186 are closer to cluster A samples than to other H, B, or C samples. Clusters F, I, and J values are also distinct. Consequently, there are now nine possible subdivisions of the Upper Pennsylvanian and Lower Permian shales based on mineralogical and geochemical differences:

1. Cluster A, consisting of up to one-third of the samples and dominated by shales containing primarily quartz, feldspar, and clay minerals.
2. A subdivision of cluster A (now referred to as cluster X) that consists of samples high in carbonate content.
3. Cluster B with six samples that have high scores on component two and are enriched in Be, Cd, Cr, Cu, Mo, Ni, Pb, V, and Zn trace elements. Lithologically these samples are black shales.
4. Cluster D, containing only two samples, closely associated with cluster A.
5. Cluster E consists of samples with very high concentrations of calcite.
6. Cluster F contains those shales with a high dolomite content.
7. Cluster G contains samples with high quartz content, mainly sandstones and siltstones.

8 & 9. Two clusters, I and J, with a total of seven extreme samples from all of the previous groups. The significance of these last groups is in doubt.

A stratigraphic plot of the distribution of samples from the nine groups is presented in Figure 52 and a pattern similar to both mineralogical and geochemical distributions is revealed (Table 18, Figures 21 and 36). A zonation of the stratigraphy is again in evidence and can be related to the factors controlling the mineralogy and geochemistry of the shales. The Pleasanton and Lower Kansas City Groups are characterized by a regular alternation of calcareous shales (cluster E samples), black shales (B), and shales containing primarily quartz, feldspar, and clay minerals (A). This three-component shale cycle is repeated four times at approximately 70-foot intervals from the Tacket Formation to the Iola Limestone. Between each shale cycle, a series of cluster A samples occurs. Occasionally, a carbonate shale also develops.

The succeeding Upper Kansas City, Lansing, and Douglas Groups contain samples predominantly from clusters A and G. The detrital fraction of beds in this zone is large and, noticeably in the Douglas Group, manifests itself in the development of a number of siltstones and sandstones. Shales in these beds are also very rich in quartz, feldspar, zircons, and detrital cobalt (as noted in the high negative scores on component one). One calcareous bed noted in the Hickory Creek Shale may represent a partially devel-

TABLE 17. Discriminant analysis results (only discriminant axes with eigenvalues > 1.0 are included).

Discriminant No.	Contribution of Each Variable to Discriminants									Percent of Discriminant Power	Eigenvalue
	1	2	3	4	5	6	7	8	9		
1	0.28	–0.70	0.44	0.09	0.20	–0.06	–0.54	–0.24	–0.30	37.9	5.28
2	0.88	0.31	–0.49	0.23	0.79	0.28	0.10	–0.01	0.20	22.5	3.14
3	–0.29	0.31	0.27	0.44	0.39	–0.58	–0.23	–0.46	–0.01	14.7	2.05
4	–0.09	0.05	0.32	0.52	–0.13	0.68	0.23	–0.37	0.12	11.3	1.57

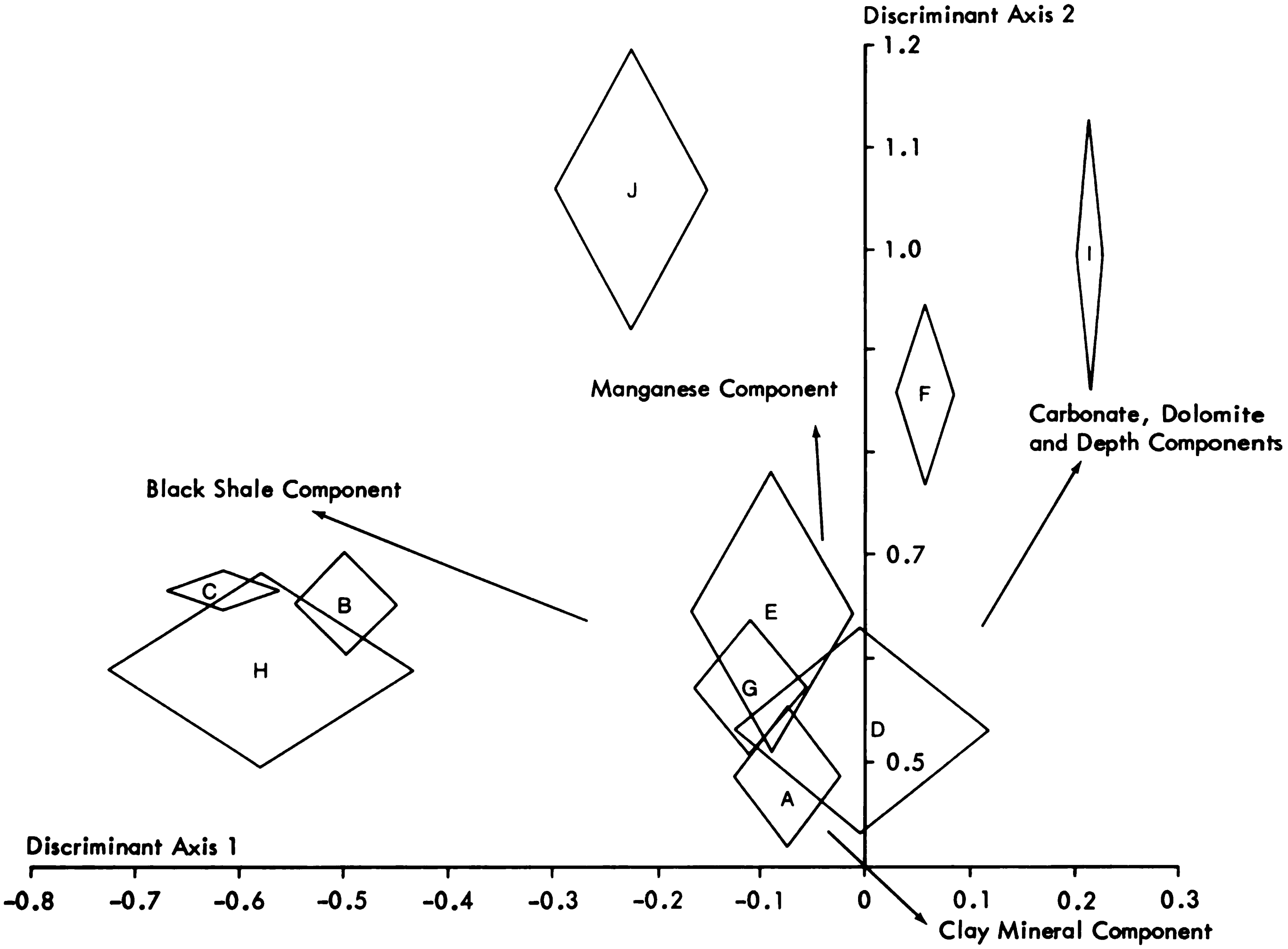

FIGURE 50. Plot of ten cluster groups on first two discriminant axes. The components controlling the distribution are superimposed to aid interpretation.

oped three-component shale cycle.

A zone defined by the boundaries of the Shawnee Group contains an irregular collection of samples. Two black shale samples are found in the Heebner and Larsh and Burroak Shales but do not form integral parts of cycles as in the Pleasanton and Lower Kansas City zone. In this section, no regular pattern appears, possibly because it contains samples from eight of the nine clusters. Nevertheless, some inferences can be made from the sample distribution. In the Shawnee, thick shale formations separate four limestone formations containing interleaved thin shales (a black shale after the second limestone bed (Moore, 1949) is the most distinctive). The majority of samples from the thick shales, known as outside shales, are classified in clusters A and G but a few occur in cluster J. The shales within the limestone formations, inside shales, vary in cluster allocation. The first shale is normally from cluster A, although one G sample was noted; the second is generally from cluster B, the black shale cluster; and the third, where developed, is usually from cluster A. However, calcareous shales replace the second and third shales on occasion. The Lower and Middle Wabaunsee Group consists almost entirely of cluster A samples and is quite similar to the Upper Kansas City, Lansing, and Douglas zone but without the thick sequences of siltstones and sandstones. Only one sample, from the Silver Lake Shale, is calcareous.

Finally, a zone of alternating calcareous and detrital shales encompasses the Upper Wabaunsee, Admire, Council Grove, and Chase Groups. Generally, these samples are much richer in both calcite and dolomite than the Pennsylvanian, indicating a distinct change in the sedimentary environment. The Pennsylvanian/Permian boundary is therefore thought to mark a change from the beds essentially dominated by the detrital fraction to those with a high carbonate

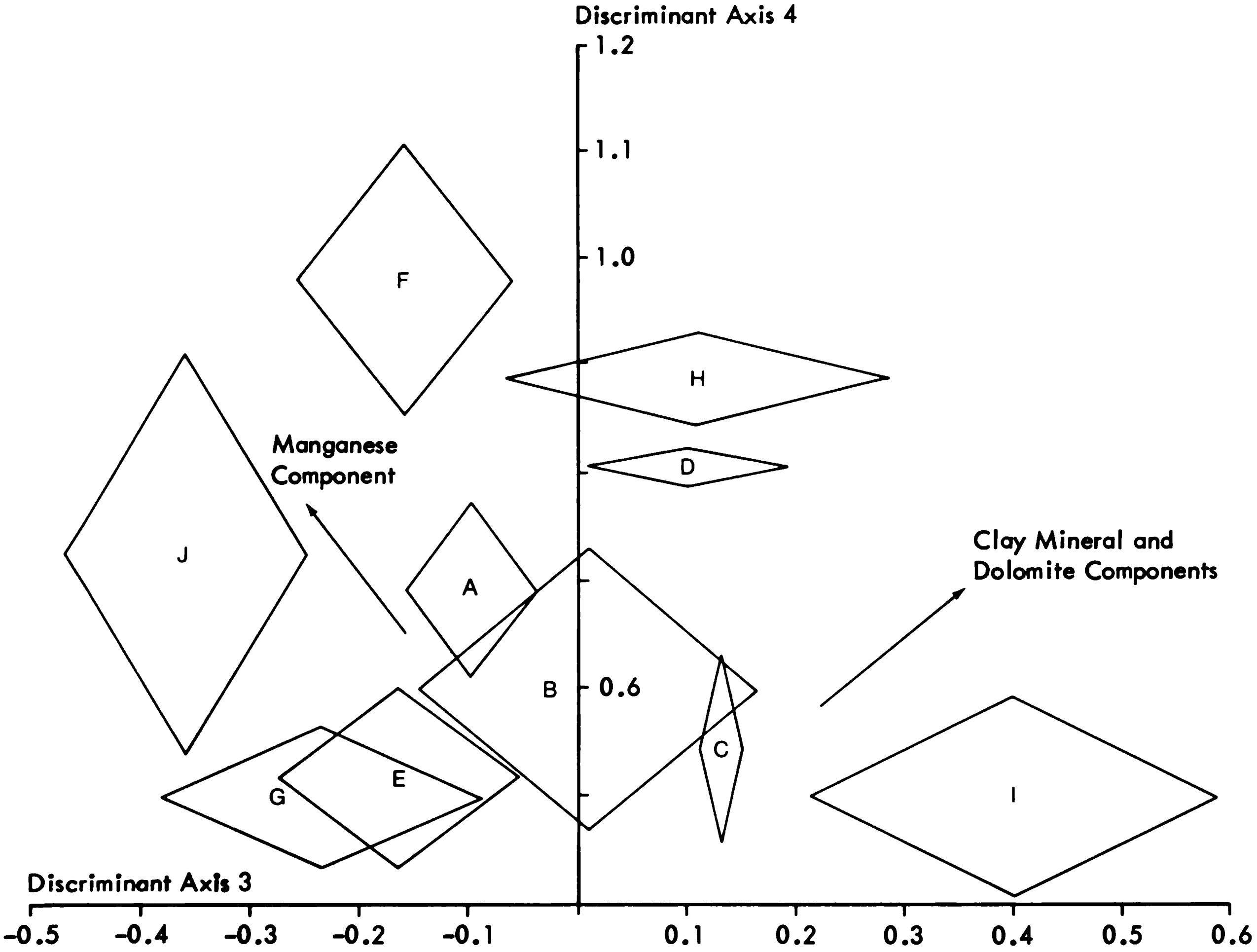

FIGURE 51. Plot of cluster groups on 3rd and 4th discriminant axes. Components affecting the distribution of groups are superimposed to aid interpretation.

content.

The subdivisions of the Pennsylvanian stratigraphy tentatively represent two periods of oscillating environments. The conditions prevalent in the Pleasanton and Kansas City zone seem to recur in the Shawnee; similarly, those developed in the Upper Kansas City, Lansing, and Douglas zone are repeated in the Wabaunsee. As these "periods" are roughly equivalent in thickness and possibly time, it is suggested that they represent a cycle of cycles.

DISCUSSION

Mineralogical and geochemical data analyzed in previous sections have been combined and studied using multivariate statistical techniques. The variation found throughout the Upper Pennsylvanian and Lower Permian shales of Kansas can be explained in terms of nine components. First, accounting for 28 percent of the data variance, is a component that describes the differences between carbonate and detrital fractions of shale samples. Subsequent components describe variations in sediment reducing conditions, clay mineral content, dolomite content, depth of deposition, and manganese content. Three components remained uninterpreted.

Scores of samples on the first six components in particular indicate that the stratigraphic section can be divided into a number of zones characterized by differing geochemical and mineralogical conditions. A statistical analysis of the zonation (using Q-mode cluster analysis and multiple discriminant analysis) was performed on the component scores. Ten natural groups of samples were revealed that were subsequently pruned down to nine. The distribution of samples from these groups indicated a five-fold division of the stratigraphical section under examination:

1. Pleasanton and Lower Kansas City Groups,
2. Upper Kansas City, Lansing, and Douglas Groups,
3. Shawnee Group,

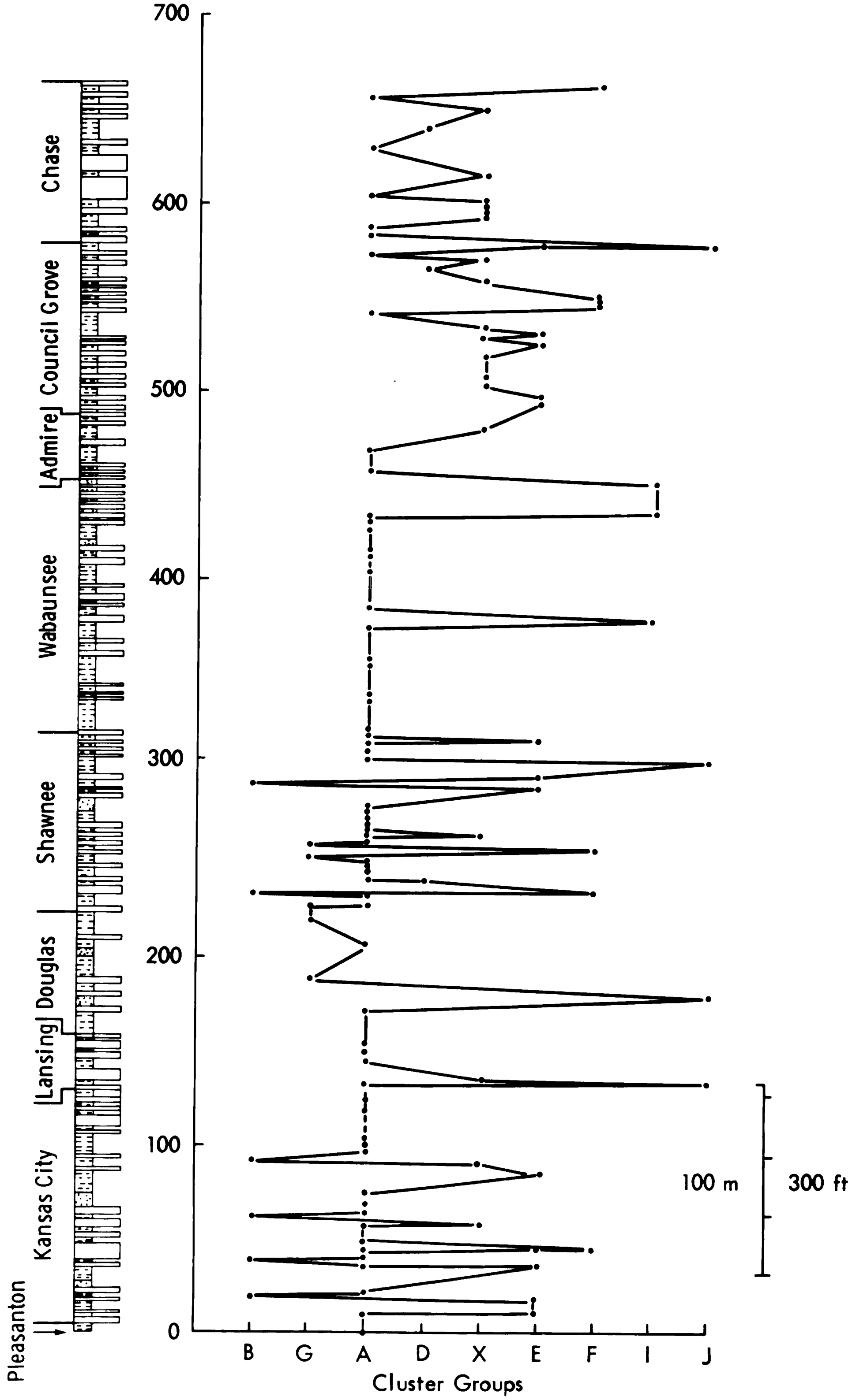

FIGURE 52. Stratigraphic distribution of samples arranged in cluster order. Horizontal scale is arbitrary but may represent a detrital to carbonate sequence from G to F.

Table 18. Distribution of shale samples within the mineralogical, geochemical, and combined mineralogical and geochemical classifications. This indicates, for example, that, of the 69 samples that fell into cluster A of the classification determined in this chapter, 12 were clustered in group A of the mineralogical classification, 48 in group B, six in group D, and three in E. In the corresponding geochemical classification 68 fell into group A and one into D.

	Mineralogical Groups						
	A	B	C	D	E	G	H
A	12	48		6	3		
B	3	3					
D	1				1		
E	2				11		
F						3	3
G		1	3		1		
I					1	2	
J			2		2		
X	3				15		

	Geochemical Groups				
	A	D	F	H	I
A	68	1			
B					6
D	2				
E	6	2	3	2	
F		2	3	1	
G	5				
I				2	
J				4	
X	8	7	2	1	

4. Lower and Middle Wabaunsee Group, and
5. Upper Wabaunsee, Admire, Council Grove, and Chase Groups.

Zones 1 and 3 consist of regular alternations of calcareous, black organic, and quartz-rich shales. Occurring at approximately 70-foot intervals, these cycles bear a close resemblance to the oscillations identified in the Kansas City Group beds by Davis and Cocke (1972). Using a method known as substitutability analysis, the stratigraphic section containing 17 distinct lithologies was found to possess a two-state oscillation, limestone—inside shale, perturbated by occasional outside shales or black shales. Inside shales are comparable to the calcareous shales (clusters X and E) of this section. Similarly, quartz-rich shales, siltstones, and sandstones (clusters A and G) roughly correspond to outside shales. The black organic shales in both cases are directly equivalent. However, the quartz shales may also develop as inside shales and therefore the cycles defined in this chapter do not directly match the oscillatory patterns recognized by Davis and Cocke (1972), and Schwarzacher (1969). There also seem to be dissimilarities between the cycles recognized in this section and those identified by Moore (1936, 1949) and Merriam (1963). Nevertheless, simple three-component shale cycles have been recognized in both zones 1 and 3.

Zones 2 and 4 are characterized by quartz-rich shales, siltstones, and sandstones with occasional calcareous shale. No evidence for cyclic variation in the geochemistry or mineralogy of these beds is apparent. These zones do, however, oscillate with zones 1 and 3 and form the only manifestation of large-scale cycles found in Kansas deposits.

The last recognizable zone, 5, consists of a two-state oscillation from calcite or dolomite-rich shales to quartz-rich shales. This zone is dominated by calcareous beds and reflects a basic change in environmental conditions from a detrital-dominated shale regime in the Pennsylvanian to carbonate deposition in the Lower Permian.

PETROLOGY

INTRODUCTION

A classification of Upper Pennsylvanian and Lower Permian shales has produced nine groups of samples that can be distinguished on mineralogy and geochemistry. As a laboratory exercise this has its merits, but to be of practical benefit it is also necessary to relate this classification to the sedimentary deposits observed in the field. It was with this aim in mind that a number of samples, analyzed by X-ray diffraction, emission spectroscopy, and electron spin resonance, were thin-sectioned and petrologically examined. This section presents a brief description of the facies distinguished and the implications for environments of deposition.

Following the recent work of Gipson (1965), Odom (1967), Gillott (1969, 1970), and O'Brien (1968, 1970) on the environmental significance of shale fabrics, select samples were examined using a scanning electron microscope to aid the interpretation of fine-grained sedimentary rock fabrics and to determine the depositional conditions under which the rocks were developed. A microscopic fabric analysis technique, developed by Brewer (1964, 1972) for the study of soils, was also applied with the general view of elucidating depositional environments.

LABORATORY PREPARATION

Two-hundred-fifty thin sections of selected shales were prepared at the Central Petrographic Section Services of Dallas, Texas by a process of vacuum-impregnation in epoxy and cutting in kerosene. Some wedge-shaped sections were prepared for examination of shale fabrics. Photomicrographs of representative slides are included with discussions of specific rock types.

Several scanning electron microscope sample mounts were prepared by breaking roughly square chips off the original shales. Samples (three cubic mm approximately) were cemented onto aluminum stubs leaving a freshly fractured surface face up. A fine platinum coating was then vacuum sprayed over each sample to alleviate conductivity problems. The samples were then examined using a Cambridge scanning electron microscope belonging to the Geology Department at Leicester University. Electron photomicrographs of shale samples are included in the following sections

SHALE PETROLOGY

Four principal facies were recognized in Upper Pennsylvanian and Lower Permian clastic deposits. These include a black shale that is considered the most distinctive of all Kansas deposits; a calcareous, grey shale facies that with the black shale facies constitutes a group of sediments known as inside shales (Davis and Cocke, 1972); and a sandstone and siltstone facies that together with a thick, brown clay-shale facies forms outside shales. Minor facies, such as a red and purple shale and shale partings in limestone beds, are also recognized. Aspects of each facies apparent in hand specimens or thin sections are discussed in the following sections.

Black Shale Facies. Shales belonging to this facies are typically black, carbonaceous, fissile, and thin-bedded, containing numerous phosphorite laminae and scattered elliptic phosphorite nodules (Plate 2A, B). Fossils commonly recognized in black shales include fish spines, conodonts, orbiculoid brachiopods, and thin-shelled pectinid clams, although radiolaria, sponge spines, cephalopods, and sharks' teeth have been found (Plate 2C, D). Macerated plant fragments are also common.

This facies, although normally represented only by a few meters of sediments, is laterally persistent from Iowa to southern Kansas (Moore, 1964). Further south, the black shales grade into thicker sections of light-colored shales that contain normal marine fossils such as brachiopods, gastropods, echinoderms, corals, and bryozoans (Evans, 1967, 1968; Heckel, 1972a). This, in turn, grades into the nonmarine deltaic clastics of Oklahoma (Wanless *et al.*, 1970). In Iowa and Nebraska, a facies change to a fully marine section is often suggested by the reappearance of light-colored marine shales below the black shale facies.

Evans (1967) and Heckel (1972a) have established that the undisturbed nature of even stratification manifest in the primary phosphorite laminae precludes the former existence of either a root system of attached vegetation or an unpreserved burrowing or bottom-feeding fauna. The presence of detrital material of only the finest sizes (primarily quartz grains scattered throughout the black shales), combined with the abundance of thin phosphorite laminae indicating

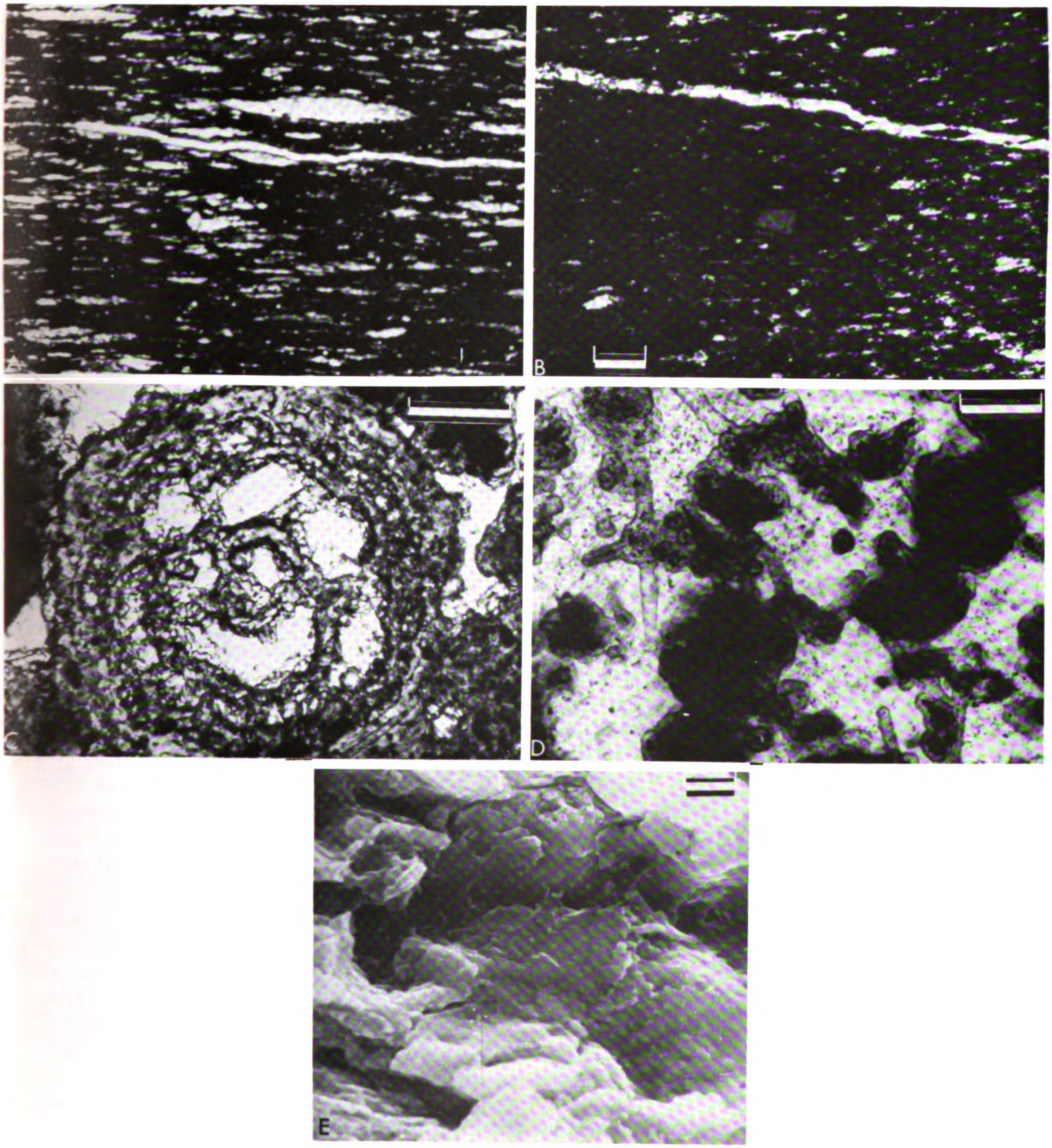

Plate 2. A. Hushpuckney Shale (sample 24) showing small elliptic phosphorite nodules and thin phosphorite laminae in a black, clay mineral matrix. The nodules lie parallel to the laminations of the shale. Scale matches that of the following photomicrograph. **B. Stark Shale (sample 31)** showing occasional phosphorite nodules in a dense clay matrix. A few quartz grains can be detected on the thinner edge of the slide. Scale = 2 mm. **C.** Muncie Creek Shale (sample 55) contains large elliptic phosphorite nodules (up to 4 cms in length). Within the nodules a number of radiolaria are preserved. Scale = 0.5 mm. **D.** Within the same nodules, spicules are concentrated in large numbers. The irregular black patches are thought to be organic material. Scale = 0.5 mm. **E.** An electron photomicrograph of a Stark Shale (sample 7) fabric, showing flat plate-like clay minerals lying parallel to the planes of fissility. The clay mineral plates occur in groups or domains. Scale = 0.14 mm.

long-term cessation of detrital sedimentation (Bromley, 1967; Heckel, 1972), suggests that the areas of black shale development represent nearly currentless, sediment-starved regions where slow deposition occurs. The fully marine extensions of black shales in Iowa and southern Kansas indicate that black shales are probably marine deposits resulting from slow sedimentation.

The conditions responsible for the formation of black shales have been reviewed by Heckel (1972a, 1978), who concluded that in respect to the Heebner black Shale (Shawnee Group) stagnation of the sea was the most likely cause. Evans (1967) has suggested that stagnation could have been caused by a submarine barrier, resulting from sedimentation across the mouth of the Midcontinent sea. Alternatively, the barrier may have developed as a topographical high associated with the continuation of the Ouachita foldbelt.

One view of the Kansas epeiric sea during the deposition of black shales consists of a broad saucer-shaped basin in which circulation ceased over most of the bottom and into which only the finest suspended detritus was spread by currents. The aerated surface waters contained a fauna of nektonic fish and conodont organisms along with epiplanktonic brachiopods and pectinids (Heckel, 1972a). On the edges of the basin, deltaic detrital sediments built the sea bottom up above the level of stagnation into aerated waters where benthonic life could be supported (Wanless *et al.*, 1970).

However, studies by Heckel (1977) now suggest that black shales may be developed below an established thermocline "that was strong enough to prevent local wind-driven cells of vertical circulation from replenishing oxygen to the sea bottom" (Heckel, 1977, p. 1054). In high sea-level stands, a quasiestuarine cell may have existed in which upwelling cold phosphate-rich water depleted the epicontinental sea of oxygen, resulting in anoxic water conditions and deposition of black, organic-rich muds.

Berendsen and Zeller (1978) have alternately suggested that some black shales (in the Cherokee) exhibiting a radiolarian-sponge fauna (Plate 2C, D) indicate relatively shallow water conditions of deposition, possibly in anoxic shoreline embayments and lagoons. Similarly, Merrill and Von Bitter (1976) have accepted the presence of two types of black shale in the Midcontinent, reflecting the earlier conclusions of Moore (1964) and Schenk (1967).

Geochemically, the presence of organic matter in black shale environments encourages the development of reducing conditions in which the trace elements Cd, Cr, Mo, Ni, Pb, V, and Zn are enriched. The organic matter also causes the dispersion of clay mineral particles by neutralization of surface changes (Moon, 1972) and gives rise, on compaction, to the fissility of black shales. Scanning electron micrographs of black shales (O'Brien, 1968; Plate 2E) indicate that clay particles occur in parallel "domains" and that planes of fissility correspond to zones of organic material (Odom, 1967). High fissility also indicates an abiotic environment of deposition (Byers, 1974).

In thin section, black shales contain abundant phosphorite bands and nodules in a black, organic-rich matrix. The phosphorite laminae rarely exceed one mm in thickness but may extend up to several centimeters in length. Phosphorite nodules also vary considerably in size and often contain fossils such as radiolaria and spicules (Plate 2C). Both laminae and nodules lie along planes of fissility. In the intervening black matrix, little detail can be distinguished except a few small quartz grains. In Brewer's micromorphological classification of sedimentary facies (Brewer, 1964, 1972; Bullock and Mackney, 1970; Burnham, 1970), the fabric of black shales is generally argillasepic unistrial, i.e., they consist primarily of clay minerals that exhibit preferred parallel orientation, giving specimens as a whole a unidirectional striated extinction pattern.

Although samples of this facies are mineralogically indistinguishable from other fine-grained shale groups, they are geochemically distinct, i.e., they all fall into one cluster. This facies is, therefore, a unique constituent of Kansas sediments supporting the level of importance as marker units currently placed on these shales by the Kansas Geological Survey.

Summarizing: the black shale facies is inferred as a marine deposit resulting from slow deposition in an oxygen-depleted sea. Parts of the Heebner Shale, Muncie Creek Shale, Eudora Shale, Larsh and Burroak Shale, Hushpuckney Shale, and Stark Shale are typical of this facies.

Sandstone and Siltstone Facies. The sandstone and siltstone facies is found irregularly throughout the Upper Pennsylvanian clastic deposits but is almost unknown in the Lower Permian. It consists primarily of yellow to brown, arkosic greywackes and yellow/brown to grey, laminated siltstones that possess all the features of deltaic clastics. In outcrops, the sandstones are generally massively bedded with occasional irregular laminations (outlining particles or organic matter) and cross-bedding (Plate 3A). The physical extent of these sandstone bodies, documented by Sanders (1959) and Wanless *et al.* (1963, 1970), in-

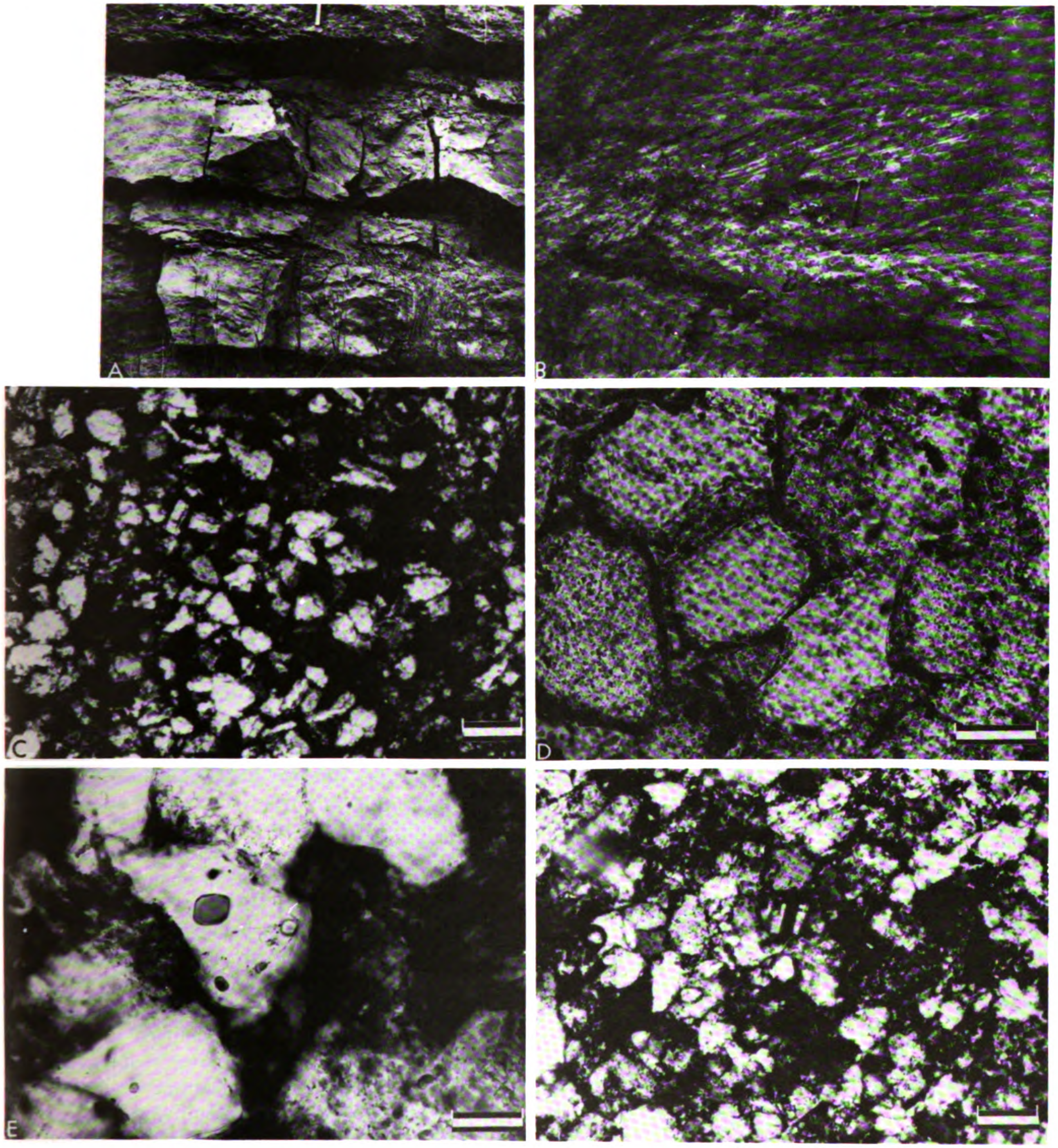

Plate 3. A. **A section of the Tonganoxie** Sandstone (samples 294, 295) showing several beds of massive sandstone with occasional irregular laminations. Beds are approximately 2-3 ft. thick. **B.** In the same outcrop as **A**, cross-bedded sandstones are also in evidence. **C.** In thin section, sample 294 consists of moderately sorted, subangular to angular quartz grains, plagioclase feldspar and zircon grains in a matrix of clay minerals. Scale = 0.1 mm. **D.** A Doniphan Shale sample (121) typifies many sandstones in the Upper Pennsylvanian, with hematite coating on the subangular quartz grains. Scale = 0.05 mm. **E.** Frequently, quartz grains in the sandstones (sample 85) contain fluid and solid inclusions. One of the fluid inclusions in the central quartz grain also appears to contain a gas bubble. Scale = 0.05 mm. **F.** A photomicrograph of a Stull Shale sample (85) showing numerous angular to subangular quartz grains in a matrix of mica and clay minerals. In the center, one relatively fresh albite-twinned plagioclase grain is preserved. Scale = 0.1 mm.

dicate that they represent basal deltaic channel deposits. The laminated siltstones, on the other hand, show graded bedding and flow structures such as load casts and microslumps, and probably represent delta-front deposits.

Massive channel sandstones are found in the Noxie Sandstone Member (Horne, 1965) of the Kansas City Group, in the Tonganoxie Sandstone (Plate 3B) and Ireland Sandstone Members of the Douglas Group (Bower, 1961), in the Pillsbury Shale, Root Shale, and Wood Siding Formation of the Wabaunsee Group, and finally in the Towle Shale Member of the Admire Group. Most are sinuous bodies that extend over northeast Kansas, southeast Kansas, or northern Oklahoma and contain sediments derived from the Ozark Dome of Missouri and the Ouachita tectonic belt of Oklahoma and Arkansas respectively. Channel deposits pass laterally into deltaic fine sands and siltstones (Wanless *et al.,* 1970) characterized by uneven cross-lamination and reworking.

In thin section, the sandstones appear to be poorly to moderately sorted with numerous angular and subangular rock fragments, hematite, and clay mineral coated quartz grains (Plate 3D, E, F), and occasional fresh to slightly weathered, albite-twinned plagioclase (Plate 3E), microcline, orthoclase, and zircon grains in a clay mineral matrix (Plate 3C). Samples vary in texture from immature sandstone to arkosic greywackes. Fragments of shale, igneous rocks, quartzite, undulous quartz, chert, and organic material may be seen.

Laminated siltstones are found primarily in the beds separating the limestone formations, designated by Schwarzacher (1967, 1969) as outside shales, e.g., Kanwaka, Tecumseh, and Calhoun Shales of the Wabaunsee Group. In hand specimen and thin section, samples consist of alternating yellow-brown siltstones or silty shales and darker, fine-grained, slightly more carbonaceous shales (Plate 4C). Graded beds and fining upwards cycles are common. Although contacts at the base of each siltstone band are sharp, indicating a brief diastem, boundaries are often quite wavy, load casts are frequently present (Plate 4A, B), and some small slumps are visible. The siltstone bands contain moderately sorted subangular quartz grains with occasional mica flakes, plagioclase feldspars, rock fragments, and carbonaceous material. In contrast, the finer bands are made primarily of mica and clay minerals with irregular amounts of fine silt-size quartz grains. In both layers, however, it is apparent that the mica flakes lie parallel to the laminae (Plate 3C), giving the siltstones an argillasepic, insepic, or silasepic unistrial fabric (Plate 4D, E; Brewer, 1964).

The zones of laminated siltstones closely resemble the regular layered structures recognized by Moore and Scrutton (1957) in modern prodelta deposits in bays and along the coast of the Gulf of Mexico. Formation of these deposits apparently results from rapid deposition with little reworking of sediments. Fossil criteria (Heckel, 1972a) also indicate a restricted marine environment undergoing rapid sedimentation and subject to high turbidity and fluctuating salinity for many of these thick, poorly fossiliferous Pennsylvanian shales. A few siltstones and silt shales characterized by uneven lamination, ripple cross-lamination, and extensive reworking are identified by Wanless *et al.* (1970) as also belonging to a deltaic facies.

This facies, therefore, represents a deltaic sequence consisting of channel sandstones, delta sands and siltstones, and delta-front silts and shales which correspond to the deltaic units described by Wanless *et al.* (1970) for the Midcontinent.

Calcareous, Grey Shale Facies. Thin beds separating limestones in limestone formations are known as inside shales (Schwarzacher, 1969) and consist primarily of fossiliferous, grey, green, and brown, blocky, calcareous shales. Most samples from this facies are massive or rubbly, but a few are laminated and fine-grained in texture.

This facies is thought to be a fully marine phase of deposition as it contains a characteristic marine fauna. Moore (1964) identified a number of ecosystems in these sediments of which the Derbyia, Rhombopora, Neochonetes, and Derbyia-Neochonetes assemblages are most distinctive. Derbyia and other salinity-tolerant brachiopods and clams characterize the ecosystem found, for example, in the Speiser Shale of the Council Grove Group. Hattin (1957) interpreted the environment of deposition as belonging to an offshore zone of near normal salinity in which weak turbulence resulted from wave activity. Disseminated calcium carbonate was judged to be derived from shell disintegration. The Rhombopora assemblage is identified in the initial parts of several marine sequences, e.g., the Doniphan Shale of the Wabaunsee Group, and is characterized by abundant ramose bryozoans such as Rhombopora and Batostomella. The lowest marine shaley deposits of some limestone formations contain abundant chonetoid brachiopods, particularly Neochonetes. This ecosystem, exemplified by a Neochonetes assemblage in the Snyderville Shale of the Shawnee Group, has a shallow-water habitat where a mud bottom bordered the shore (Moore, 1964). Finally, Moore (1964) and Imbrie, Laporte, and Merriam (1964) distinguished an ecological community, typified in the Florena Shale (Council Grove Group),

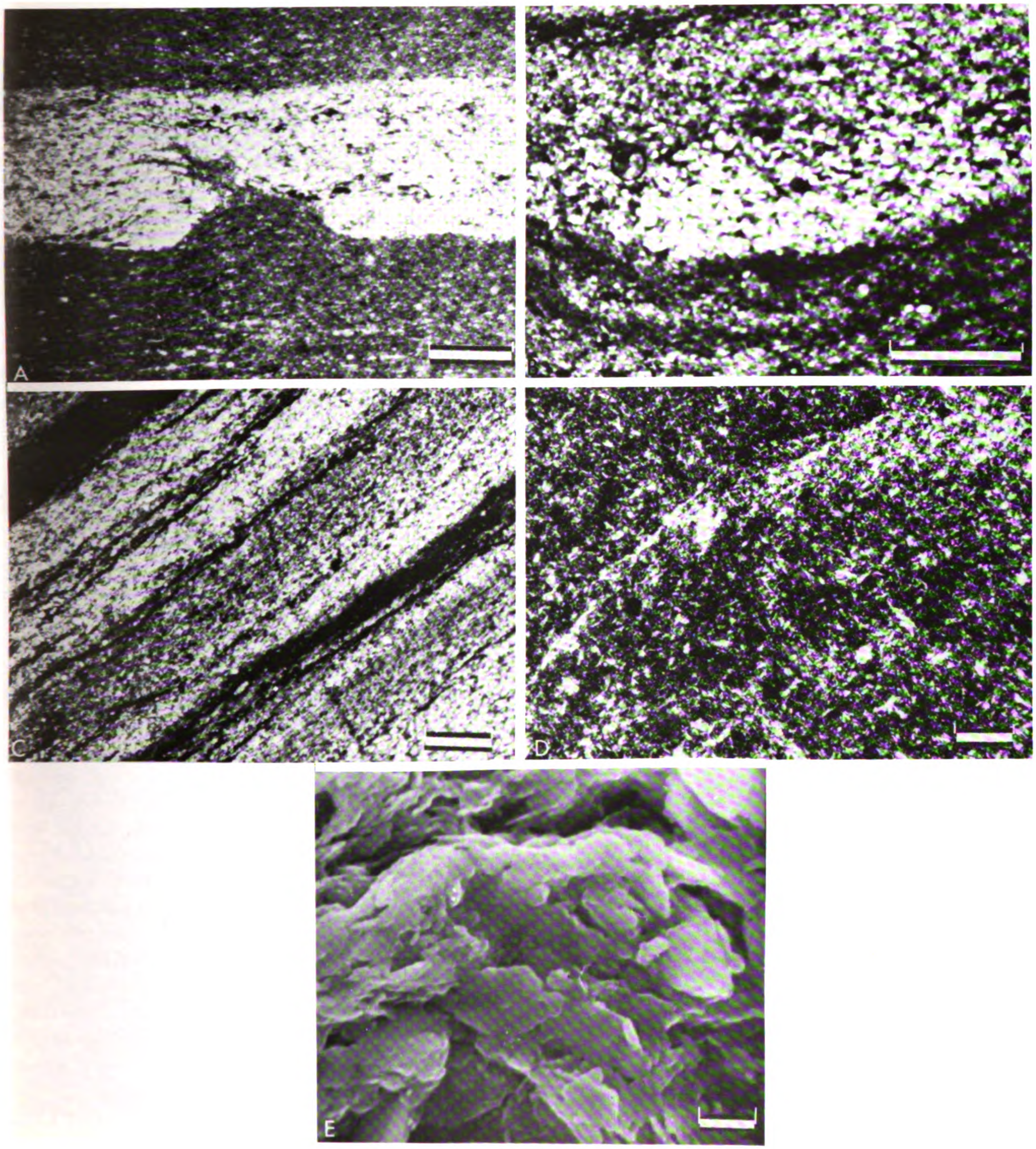

Plate 4. **A.** A siltstone band in the Heumader Shale (sample 75) shows regular alternations of silty shales (light area) and fine-grained, slightly carbonaceous shales (darker zones). In many cases, load casts are developed, particularly where concentrations of silt grains develop. In this example, the pressure of the overlying silt has forced the softer darker shale up into the silt band. Scale = 0.5 mm. **B.** A load cast, developed in the Severy Shale (sample 162), shows how silt grains are concentrated at the base of the structure. Note also how the organic matter forms a layer around the base of the cast. Scale = 0.5 mm. **C.** Alternating carbonaceous and silty shale bands predominate in most siltstone, including the White Cloud Shale (sample 173). Note the wavy nature of the banding. Scale = 1 mm. **D.** The fabric of siltstones is typically argillasepic unistrial, i.e., all the clay minerals and mica flakes are aligned, producing a undirection extinction pattern. Sample 16. Scale = 0.2 mm. **E.** An electron photomicrograph of sample 16 shows the regular plate-like distribution of clay minerals. Occasional quartz grains interrupt this pattern. Scale = 0.015 mm.

that corresponds to the Snyderville assemblage in Neochonetes and Derbyia content but also contains abundant fusulinids such as Schwagerina. The assemblage is, therefore, thought to have developed in the middle or regressive part of a cyclothem.

Although four fossil assemblages can be distinguished in this facies, it is most difficult to subdivide the facies on lithological evidence. However, from Moore's ecological survey, we can conclude that this facies generally represents open-marine and shallow-water conditions.

In thin section, samples vary from slightly silty, laminated, brown shales to highly calcareous, fossiliferous, marine, grey shales although the majority are calcareous, fine-grained, light grey or brown, coarsely laminated shales. The presence of laminae in shales reflects the absence of burrowing organisms in the substrate and indicates deposition in an environment free from tidal or current movements. Off-shore marine deposition is inferred by the occurrence of brachiopods such as Derbyia and thin-shelled bivalves. However, in the calcareous shales there is evidence for both near-shore and off-shore environments. In samples that are listed as dolomitic shales in the mineralogical classification, dolomite crystals are developed extensively, suggesting a diagenetic alteration of some sediments. Plate 5A-D illustrates the variety of sediments and textures associated with this facies.

Red and Purple Shale Facies. This facies is characterized by red, green, and purple mottled, calcareous shales and is only found in Lower Permian beds. Although only a few samples belonged to this facies, their characteristic colors make it a distinctive facies in the field, and a brief description is therefore included here.

In hand specimen, samples are mottled red, green, or purple, hard, blocky, calcareous shales containing no fossils. The facies is found within outside shales (thick grey shales separating limestone formations) and rarely thickens to more than 3 m in any one bed. Furthermore, this facies shows rapid lateral variations.

Thin sections (Plate 5E, F) reveal the presence of many fine, silt-size quartz particles within a matrix of stained, fine-grained calcite and clay minerals. Some samples appear to contain reworked pellets and sediments. Color variation recorded in the shales is a reflection of the iron and/or organic content. Red colors arise from the presence of ferric oxide in the essential absence of organic material whereas green shales are probably deposited with some organic material that reduces the red ferric ion to the ferrous state (Elias, 1937). The stratigraphic association of green shales immediately above and below red shales indicates this to be true. Wells (1950) found small amounts of organic material in Eskridge red shales which he interpreted as an indication of deposition on land or in the tidal zone. Green shales were thought to be of shallow-marine origin. However, red deposits are now known to form in a variety of climates and depositional environments (Broecker, 1974; Walker, 1974) from deep sea clays to moist tropical soils. It can therefore be inferred that, as red beds are not good paleoenvironmental indicators (Berner, 1971), Wells' interpretation is open to doubt. Unfortunately, until some viable alternative is proposed, this hypothesis has to be retained.

Mineralogically, samples from this facies are all carbonates and consequently fall into group E of the mineralogical classification. However, their trace-element geochemistries vary so considerably that samples fall into clusters X, A, and D of the combined mineralogical and geochemical classification. Nevertheless, there is some uniformity in the major oxide content of the shales, for example consistently high Fe oxide and CaO content.

This facies represents, therefore, a locally important field unit, but at the same time is indistinguishable from other calcareous shales in terms of mineralogy and geochemistry. It would seem appropriate to consider this facies as a minor variation of the calcareous shale facies described previously.

Shale Partings in Limestone. A number of limestone units exhibit distinct layering in which the limestone beds are separated by thin shale partings. Although the thin shale studied by Troell (1969) was used as an internal stratigraphic datum, normally on exposure the partings weather back into the outcrop face and thus receive little attention. They frequently contain corals and encrusting bryozoans that require clear water, relatively slow deposition, and a firm substrate (Heckel, 1972a). These ecological considerations and the areal extent of each thin parting indicate that the shales result not from a rapid influx of clastics but rather from a long-term cessation of carbonate deposition with very slow accumulation of suspended detritus.

In thin section, partings from the Winterset Limestone (Kansas City Group) and Beil Limestone are laminated calcareous brown to grey shales with abundant fragments of brachiopods, fusulinids, corals, and organic matter (Plate 6A, B).

Brown, Soft, Clayey Shale Facies. Thick, fine-grained, soft shale bands occur in many outside shales constituting a poorly fossiliferous, near-shore, marine sedimentary deposit. This facies generally displays a monotonous sequence of olive-grey to

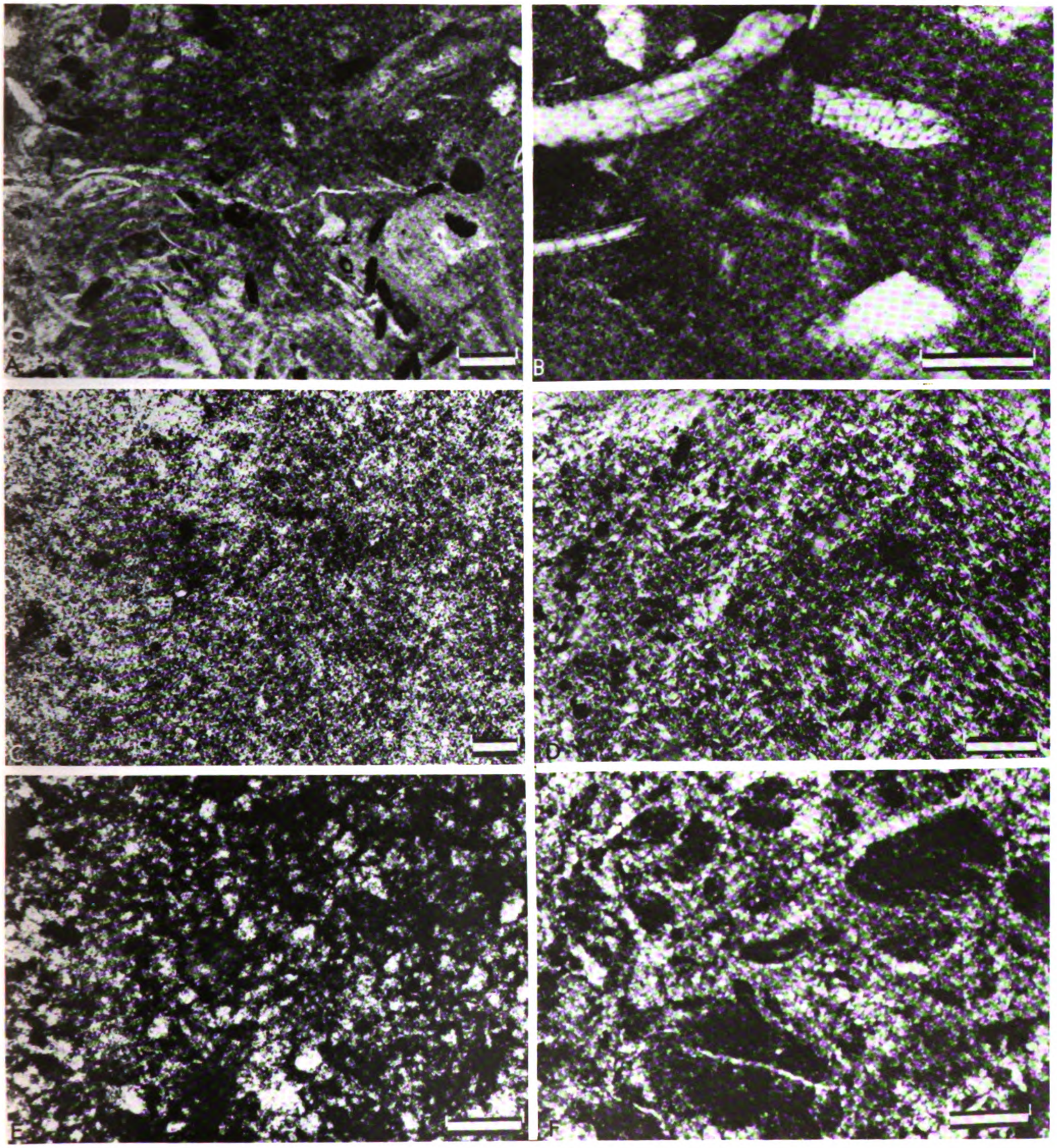

Plate 5. A. A sample of the Oketo Shale (265) contains numerous fossils such as fusulinids (outlined by organic matter), bryozoans, and clam fragments, in a fine-grained calcite matrix. Scale = 0.25 mm. **B.** A fossiliferous sample of the Queen Hill Shale (136). Punctate brachiopods, lamellibranch fragments, and the fusulinids are found in abundance. Apart from an occasional quartz grain, the matrix is a grey micrite. Scale = 0.5 mm. **C.** A Grant Shale sample (272) illustrates the type of fabric developed in a shale containing few fossils. Numerous small calcite crystals can be seen within matrix of organic matter, clay minerals, and the occasional quartz grain. Scale = 0.1 mm. **D.** Another fabric developed in a calcareous shale —Galesburg Shale (27)—contains far more organic matter and clay minerals. The beginning of mica alignment can be seen on the right of the sample. Scale = 0.1 mm. **E.** Red shales have many types of fabrics but the two most commonly recognized are illustrated in this and the following photomicrograph. Numerous well-sorted quartz grains are surrounded by a stained, fine-grained matrix of clay minerals and calcite. Sample 270. Scale = 0.1 mm. **F.** This fabric contains reworked stained pellets surrounded by a fine-grained calcite matrix. Calcite overgrowths on the pellets are developed. Sample 256. Scale = 0.5. mm.

brown, slightly silty shales with thin zones of laminated siltstones occasionally carrying plant fragments.

Early work recognized both non-marine and marine environments in the outside shales (Moore, 1929). Later, however, identification of the consistent position of outside shale formations between definitely marine limestone sequences, the general barrenness of the shales, and the occurrence (even though local) of non-marine lithologies caused them to be considered as wholly or predominantly non-marine deposits (Moore, 1936), a concept that persists today.

However, recent investigations by Heckel (1972a), and Heckel and Baesemann (1975) have revealed the presence of fossils scattered throughout a number of outside shales, particularly in the Kansas City and Lansing Groups. Most of the fossils recovered are conodonts and small, thin-shelled pelecypods and gastropods, suggesting shallow-water or relatively rapid deposition or both. Shales of this facies are often found in association with deltaic sandstones and siltstones which necessarily place much of the facies in the near-shore shallow marine regime. Wanless *et al.* (1970) have therefore equated these deposits with prodeltaic marine muds and bottomset deltaic beds.

In thin section, samples from this facies are revealed as fine-grained brown to grey, occasionally silty shales containing a few isolated fossils and organic material (Plate 6C, D, E). Texturally, these shales are generally argillasepic and moderately to weakly unistrial (Brewer, 1964) although an occasional inundulic or insepic fabric was noted, indicating a lack of disruptive influences such as burrowing animals, tides or currents, and confirming the environmental interpretations placed on this facies.

DISCUSSION

Clastic sedimentary deposits from the Upper Pennsylvanian and Lower Permian of Kansas can be grouped into six facies representing differing environmental conditions.

The most distinctive of these facies is a black, laminated shale that is used as a marker horizon in cyclothems (Moore, 1950). Developed in a shallow-water epeiric sea, it contains a sparse epiplanktonic fauna indicating anoxic bottom waters. Closely associated with this facies (as inside shales) are sediments that fall into the calcareous grey shale facies. These shales are deposited primarily in open-marine, shallow-water conditions and are characterized by abundant brachiopods, bivalves, fusulinids, and bryozoans.

Inside shales separate limestone units within limestone formations whereas outside shales are intercalated between the formations. Two facies can be differentiated in the outside shales, a sandstone and siltstone facies and a brown, soft, clay-shale facies. Both represent environments of deposition characteristic of deltaic sedimentation. First, the sandstone and siltstone facies consists of channel sandstones, laminated prodelta siltstones, and deltaic sands and siltstones (terminology of Wanless *et al.*, 1970). The source of the detrital material is primarily from the Ouachita foldbelt although subsiding deltas are developed on the low-lying land area to the north of the Forest City Basin. A minor source may originate in the Ozark dome of Missouri (Wanless *et al.*, 1970). The brown, clay-shale facies can be equated to delta bottomsets and prodelta marine clays (Wanless *et al.*, 1970).

A number of shale partings occurring in limestones constitute the fifth facies. Although geochemically and mineralogically indistinguishable from other calcareous shales, they form a unique sedimentological facies. From ecological and lithological considerations, it is inferred that each thin parting developed in near-diastemic conditions.

A minor facies recognized in Lower Permian deposits is a red and purple shale lithology. It is interpreted as a product of near-shore or even tidal environments.

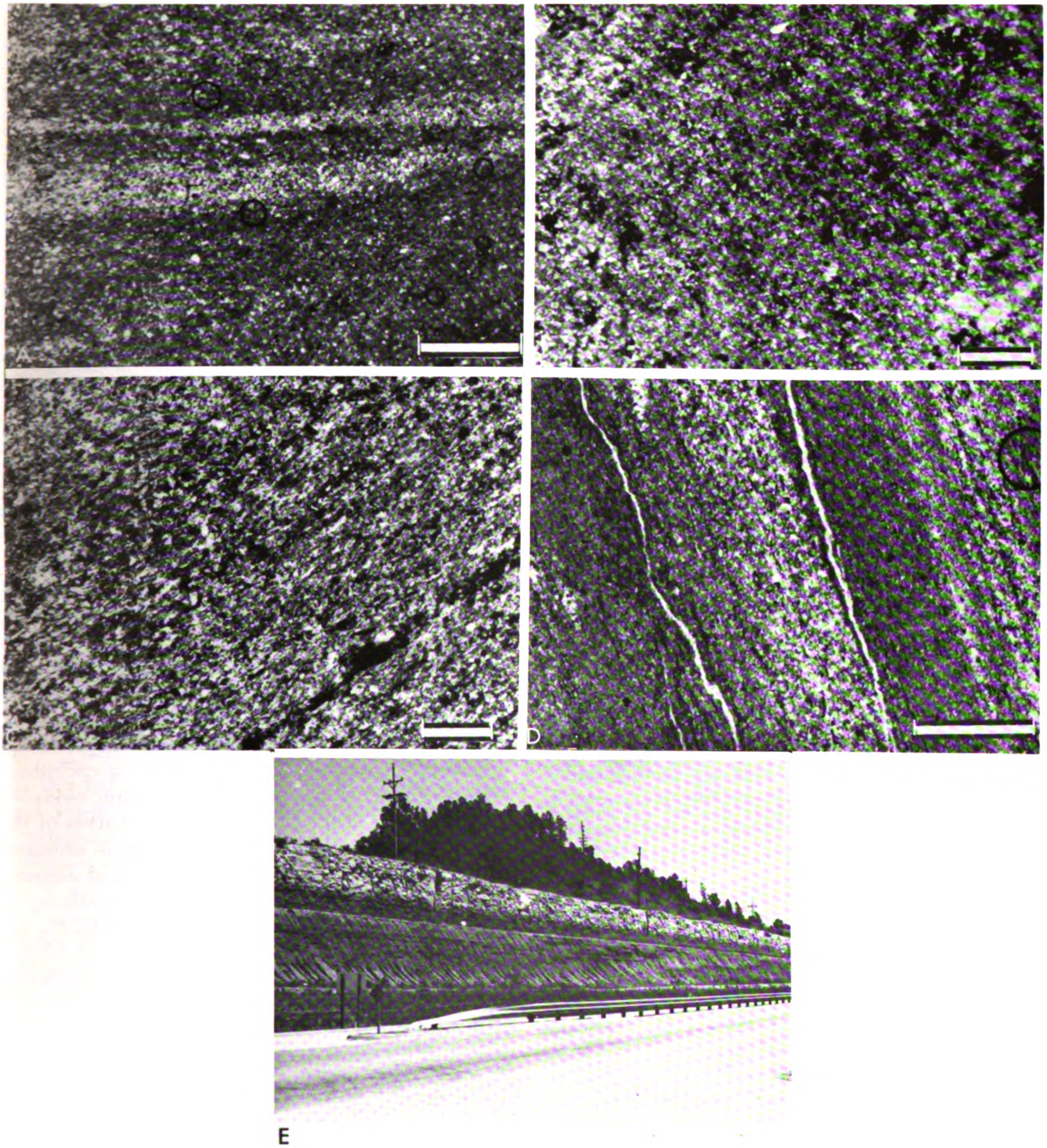

Plate 6. **A.** A shale parting in the Winterset Limestone (sample 35) is calcareous, fine-grained, and laminated with a few fossils. Scale = 0.4 mm. **B.** A Beil Limestone sample (137) illustrates the fabric of shale partings. They are typically fine-grained, calcareous, grey or brown with occasional quartz grains. Scale = 0.1 mm. **C.** A sample from the Chanute Shale (48) is representative of the clayey-shale facies. In this thin-section, most are fine-grained, brown to grey, rather silty shales with scattered fossils. Scale = 0.1 mm. **D.** Another laminated silty shale showing gravitational bands. Scale = 0.05 mm. **E.** A typical exposure of the clayey-shale facies in a road-cut near Kansas City. Samples (69 to 71) of the Lane Shale were obtained from this site.

CONCLUSIONS

In this study, Kansas shales were found to consist of six major facies (based on the combined mineralogical, geochemical, and petrological data), each corresponding to a separate depositional environment.

1. A sandstone and siltstone facies corresponding to deltaic sands and siltstones with a source in the Ouachita Mountains of Oklahoma and Arkansas and, occasionally, the lowlands of Iowa, Nebraska, and Missouri. This facies contains abundant quartz, feldspar, and detrital zircons and is, therefore, enriched in SiO_2, Al_2O_3, and Zr.
2. A clayey shale facies corresponding to prodeltaic marine muds, the seaward extension of the previous facies. The shales are rich in quartz and feldspar and have an increased clay mineral content. Ga, Li, and K_2O may also be enriched in these shales.
3. A black shale facies that is a product of a restricted marine environment (Heckel, 1972a, 1977, 1978). The regular stagnation of bottom waters, leading to development of reducing conditions in the sediments, may be caused by tectonic uplifts of a barrier at the mouth of the epeiric sea, a thermocline developed in a quasiestuarine cell, or a shallow-water lagoonal formation. These shales are enriched in the trace elements Cd, Cr, Cu, Be, Mo, Ni, Pb, V, and Zn by the chemical action of organic matter.
4. A calcareous grey shale facies that represents open-marine, shallow-water deposits that are characterized by abundant brachiopods, bivalves, fusulinids, and bryozoans. These shales have high calcite, CaO, MnO, Sr, Sn, Ge, and Bi content.
5. A shale partings in limestone facies equated to diastemic conditions but mineralogically and geochemically similar to the calcareous facies.
6. A facies of minor importance is a red and purple shale facies that occurs in certain sections of Lower Permian shales and possibly represents a calcareous equivalent of facies 2.

These facies equate to the lithologic divisions noted by Schwarzacher (1969), Davis and Cocke (1972), and Heckel and Baesemann (1975). By combining facies 1 and 2, a group of deltaic shales is obtained that occurs primarily in the thick shale formations separating limestone formations (outside shales). Discussing the stratigraphy and tectonic framework of Kansas, it was conjectured that the appearance of these deposits may be related to tectonic uplifts of the Ouachita foldbelt resulting from cyclic movement along subduction zones (Bott and Dean, 1973). Facies 3 and 4 generally occur as shale members separating individual limestone beds in a limestone formation (inside shales). The black shales are normally located above the second limestone bed. Facies 5 (equivalent to inside shales) and 6 (equivalent to outside shales), however, are only of minor importance as they represent a small number of shale samples.

Stratigraphically, these facies were found to be distributed in a number of zones:

1. In the Pleasanton, Kansas City, and Lansing Groups, there are regular alternations of limestones and inside shales separated into formations by thick beds of deltaic outside shales;
2. The succeeding Douglas Group, however, appears to contain only outside shales;
3. The Shawnee Group reverts to the limestone-inside shale alternation with outside shales separating limestone formations;
4. The Upper Pennsylvanian culminates in the Wabaunsee Group with outside shales and occasional limestones; and
5. In the Admire, Council Grove, and Chase Groups of the Lower Permian, a general increase in the carbonate content of all rocks is manifest in the development of calcareous outside shales (red and purple shale facies) separating the alternations of inside shales and limestones. Towards the top of this division evaporites are developed, although the geochemical data show no evidence for increasing salinity.

A number of different oscillatory patterns can be detected in these deposits. First, in the Pleasanton, Kansas City, Lansing, Shawnee, and Lower Permian Groups, a succession of alternating inside shales and limestones constitutes a limestone formation. The limestone formations are separated by outside shales, thereby outlining a set of sedimentary deposits approximately equivalent, in thickness, to a cyclothem (Moore, 1950). However, there is no firm evidence for such cycles in the stratigraphic distribution of the facies. The only corroborative support is obtained from the statistical analysis of mineral and element distributions. Fourier analyses of the stratigraphic distribution of quartz, SiO_2, Al_2O_3, CaO, MnO, Ba, Cr, Ni, Mo, Cu, and Ga indicate the presence of 70-foot cycles in the shales. This agrees with the thickness attributed to cyclothems by Moore (1950), although no evidence for the lithological complexity of cycles presented by Moore (1950) can be found. It is, therefore, suggested that the 70-foot cycles recognized in this study match the mathematically derived oscillations noted by Schwarzacher (1969) and Davis and Cocke (1972) and are possibly manifestations of a simplified "ideal" cyclothem. It can also be inferred that, in terms of detecting cyclicity, Fourier analysis is a more appropriate and sensitive tool than multivariate analysis. Dunn (1974) also recognized this potential.

In the intervening Douglas and Wabaunsee Groups no evidence for cycles was noted. The beds are primarily deltaic clastics and may represent the products of important tectonic events in the orogenic belts to the South. The Douglas and Wabaunsee Groups are also recognized by Moore (1964) and Schwarzacher (1969) as distinct zones although they distinguish poorly developed or incomplete cyclothems in the formations.

The stratigraphic zones 1 to 4, therefore, form an alternation of cyclothem-bearing and non-cyclothem-bearing deposits, i.e., the Pleasanton, Kansas City, and Lansing Groups contain cyclothems whereas the succeeding Douglas Group does not contain cycles and similarly the Shawnee Group contains cycles and the Wabaunsee does not. The oscillation of stratigraphic zones may represent a large-scale cyclic development, possibly related to tectonism. These cycles roughly correspond to hypercyclothems (Merriam, 1963), but have been described in detail only in this project.

The cyclic development of outside shales and black shales has been accounted for by orogenic events in the Ouachita foldbelt. Major tectonic periods may also account for the differences between zones containing cyclothems and those without. Although the basic cause of the oscillation remains unknown, several tectonic controls have been proposed:

a) Varying rates of subsidence allowing transgressions and regressions (Matthews, 1974);
b) Repeated eustatic changes in sea level and variation in clastic influx, controlled by climatic changes (Wanless and Shepard, 1936); and
c) Diastropic uplift and subsidence of source area (Weller, 1956).

In the light of modern theories of global tectonics and sea-floor spreading, it would seem likely that a combination of controls such as (a) and (c) may provide the answer.

A multivariate statistical analysis has elucidated the geochemical and mineralogical evolution of the Upper Pennsylvanian and Lower Permian shales and has indicated that the stratigraphic variation in the mineralogical and geochemical data is controlled by nine components—a carbonate component, a black shale component, a clay mineral component, a dolomite component, a shallow- versus deep-water environment component, a manganese component, and three uninterpretable components. These carbonate and black shale factors may be related to the orogenic controls of outside and inside shales and, similarly, the manganese component is related to marine conditions of the inside shales. The dolomite component indicates that diagenetic activity has affected the shales, particularly in the Lower Permian.

In conclusion, therefore, the concept of a 10-component "ideal" cycle envisaged by Moore (1936) is not supported in detail by mineralogical, geochemical, or petrological data from the Upper Pennsylvanian and Lower Permian shales of Kansas. However, a simplification of the clastic classification to three components—calcareous marine shales, restricted-marine black shales, and finally deltaic and prodeltaic shales, sandstones and siltstones—suggests cycles at approximately 70-foot intervals in the Pleasanton, Kansas City, Lansing, and Shawnee Groups. This classification matches the mathematically derived lithological divisions observed in the Kansas City Group by Davis and Cocke (1972). The calcareous shales equate to inside shales and similarly deltaic shales to outside shales. Black shales are in both cases equivalent.

However, a major limitation of this research project is the extensive number of interpretations and conclusions made from such a small data set. In retrospect, a more satisfactory data set could have been obtained by sampling at a fixed interval within the clastic deposits. It would also have been more appropriate to have chosen a smaller section, for example the Shawnee and Wabaunsee Groups, and to have analyzed both the limestones and shales. The sampling interval should be related to the oscillatory patterns noted in this study, i.e., less than 70 feet.

A further constraint on generalizing the results obtained was the relatively subjective decision to sample on a bed-by-bed basis. In retrospect, it would have been more desirable to have sampled extensively within beds (on a fixed-interval scale) and also along the strike of the beds, producing another level of replication and information for the project. Despite the inherent limitations due to these problems, it can be inferred that Moore's "ideal" cyclothem is not developed in the stratigraphic section examined but that a simplified cycle may be.

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APPENDIX ONE

THE PREPARATION OF SHALE SPECIMENS FOR X-RAY DIFFRACTION ANALYSIS BY A SUCTION-ONTO-MEMBRANE FILTER METHOD

One major requirement of quantitative X-ray diffraction analysis of shale mineralogy is a simple, accurate and reproducible method of sample preparation (Gibbs, 1965, 1967, 1968, 1969; Gipson, 1966; Shaw, 1972). However, problems arise first with the tendency of the clay minerals to assume preferred orientations which cannot be accurately reproduced from sample to sample, and second with the segregation of mineral phases during the settling stage. Quantitative determination of mineral percentages in shales by X-ray diffraction must avoid both these problems, and a number of techniques for producing randomly orientated samples have been proposed, e.g., Hughes and Bohor's (1971) spray drying technique, a method employing polyester foam sheeting (Thomson, Duthie and Wilson, 1972) and others by Brindley and Kurtossy (1961), Jonas and Kuykendall (1966), Martin (1966) and Niskanen (1964). However, all these techniques were developed specifically for clay mineral studies and few are suitable for the analysis of shale samples.

A method has been developed for the quantitative mineralogical analysis of shales by X-ray diffraction using Millipore filter equipment and membrane filters (Millipore equipment is manufactured by Millipore Filter Corporation, Bedford, Massachusetts). The method has proved simple and quick to operate and the accuracy and reproducibility are very high in comparison with alternative techniques (Cubitt, 1975a). This technique has been successfully applied in the study of Upper Pennsylvanian and Lower Permian shales of Kansas.

Sample Preparation

Approximately 0.05 gm of ground shale sample (less than 60 microns) is placed in a small beaker and 20 ml of distilled water added by pipette. The materials are then agitated by sonic probe and the disaggregated shale/water mixture is placed in a Millipore filter funnel. Vacuum pressure applied to the membrane filter sucks all the liquid through the filter in 20-30 seconds, preventing orientation and segregation of minerals. The filter paper is removed from the apparatus, and taped onto a microscope slide. After drying for a few minutes, the slide-mounted filter paper can be examined by X-ray diffraction.

The Millipore filter apparatus consists of four parts—a vacuum flask, a fretted glass funnel base and filter support, a clamp, and a funnel top. A 1.2 micron opening membrane filter is placed on the filter support and a glass funnel is clamped to it. The base is then placed in the vacuum flask and secured with a rubber bung. A water pump attached to the vacuum flask provides the pressure.

Discussion

This method of preparing mounts for the X-ray diffraction analysis of shales has several advantages over alternative techniques.

1. *Simplicity:* The system is very simple to operate and prevents the majority of human errors creeping into the mounting preparation, a failure that has dogged many sample preparation techniques.
2. *Speed:* The simplicity of the system also ensures that the preparation time is reduced to a minimum. Ten minutes per sample seems to be an optimum operating figure.
3. *Accuracy and reproducibility:* In comparison with standard techniques, the accuracy and reproducibility are appreciably higher. This is due to the method of particle collection on the surface of the filter paper. The rapid suction of particles onto the membrane filter obviates preferential settling and orientation. Any preponderance of non-flaky minerals in the shales will also aid the random orientation of mineral grains.

The technique was found to be suitable for large numbers of shale samples and has been successfully applied to the mineralogical analysis of the Upper Pennsylvanian and Lower Permian shales of Kansas. This technique has only one disadvantage when applied to these shales—no detailed high temperature analysis of clay minerals may be undertaken due to the nature of the mount. In this case, an alternative technique, i.e., ground dry sample molded into a pellet using a high pressure press (Hildago and Renton, 1971), may prove to be a suitable substitute. However, the value of the method lies in its speed, accuracy, simplicity, and reproducibility and as such provides a "quick look" technique for the mineralogical analysis of shales.

APPENDIX TWO

ELECTRON SPIN RESONANCE SPECTRA OF SELECTED CARBONATES, SULPHATES, AND CLAY MINERALS

This study was conducted to establish the nature of free spin features detected in shale ESR spectra.

A number of common carbonate, sulphate, and clay minerals were chosen to represent possible constituent minerals of the Upper Pennsylvanian and Lower Permian shales of Kansas. Table 19 contains a list of these minerals, provided by Dr. R. J. King of the Geology Department, University of Leicester, with their standard chemical formulae and localities.

Small pieces of mineral were ground with a pestle and mortar and analyzed on a Varian E-3 X-band Spectrometer using the procedure described on page 60. The majority of these minerals have never been examined by ESR previously, and it is hoped that the spectra recorded in this appendix (Figures 53 to 64) will serve as reference spectra for future experimental studies on individual minerals in a similar manner to the service provided to organic chemists by the ESR spectra recorded in Bielski and Gebicki (1967).

The spectra have brief descriptions as figure captions but it was beyond the scope of this study to perform experimental work to confirm these assertions. The descriptions must therefore be considered to be suggestions rather than fact. The figures include, where necessary, references to other experimental ESR spectra on minerals.

TABLE 19. Common minerals representing possible constituents of Upper Pennsylvanian and Lower Permian shales of Kansas.

Mineral Name	Chemical Formula	Mineral Locality
1. Strontianite	$SrCO_3$	Whitesmith Mine, Strontian, Argyllshire, U.K.
2. Rhodochrosite	$MnCO_3$	Emma Mine, Butte, Montana, U.S.A.
3. Chalybite	$2(FeCO_3)$	Ivigtut, Greenland
4. Barytes	$BaSO_4$	Silverband Mine, Knock, Westmoorland, U.K.
5. Celestine	$SrSO_4$	Yate, Gloucestershire, U.K.
6. Anhydrite	$CaSO_4$	Billingham, Durham, U.K.
7. Kaolinite	$Al_4Si_4O_{10}(OH)_8$	St. Austell, Cornwall, U.K.
8. Dickite	$Al_4Si_4O_{10}(OH)_8$	San Juanito, Chihuahua, Mexico
9. Halloysite	$Al_4Si_4O_{10}(OH)_8$	Wagon Wheel Gap, Colorado, U.S.A.
10. Vermiculite	$Mg_3Si_4O_{10}(OH)_2 \cdot xH_2O$	Ampandrandar, Madagascar
11. Chlorite (Pennine)	$Mg_5Al(AlSi_3O_{10})(OH)_8$	Traversella, Piedmont, Italy
12. Illite	$KAl_2(AlSi_3O_{10})(OH)_2$	Morris, Illinois, U.S.A.
13. Montmorillonite	$Al_2Si_4O_{10}(OH)_2 \cdot xH_2O$	Clay Spur, Wyoming, U.S.A.

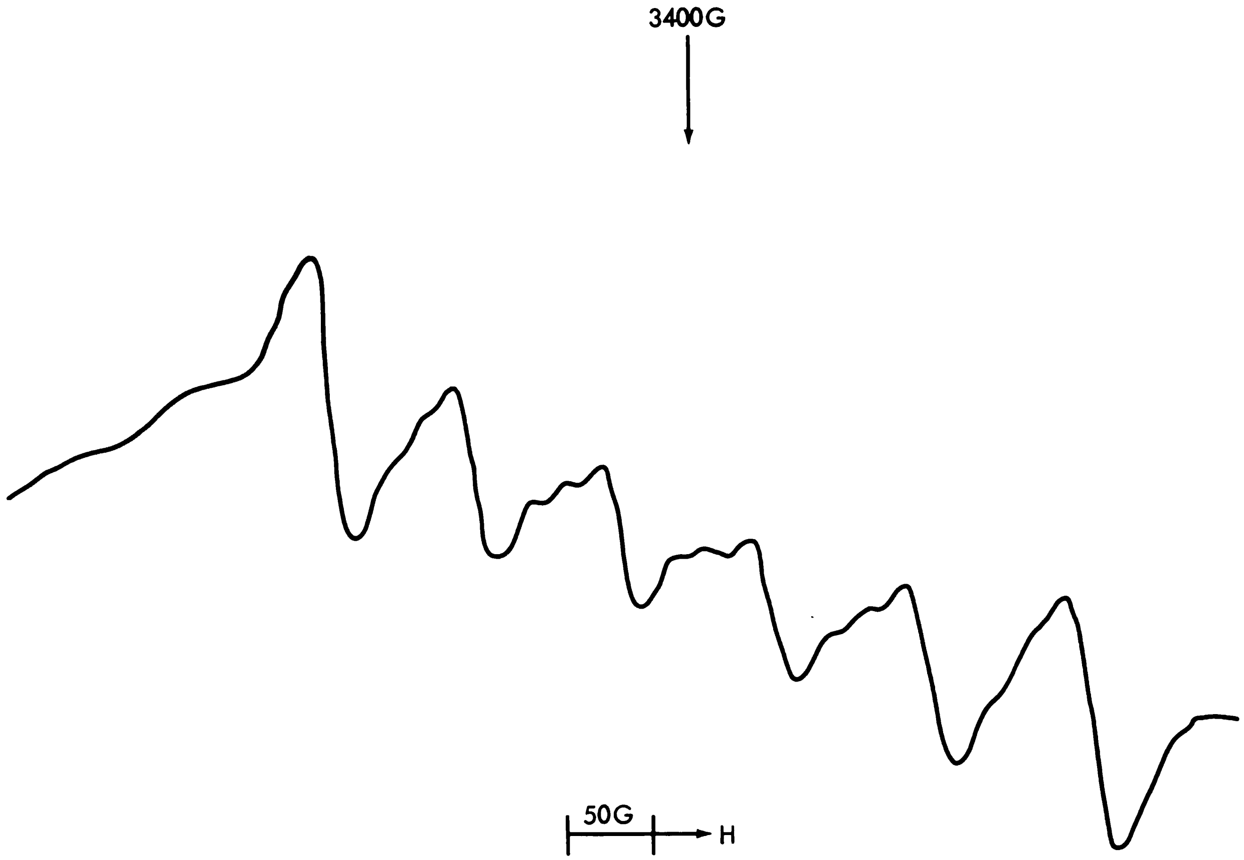

FIGURE 53. A room-temperature ESR spectra of strontianite showing typical Mn^{2+} features. The Mn^{2+} is substituting for Sr^{2+} in the $Sr^{2+}CO_3^{2-}$ lattice. The hyperfine splitting is 100G approximately.

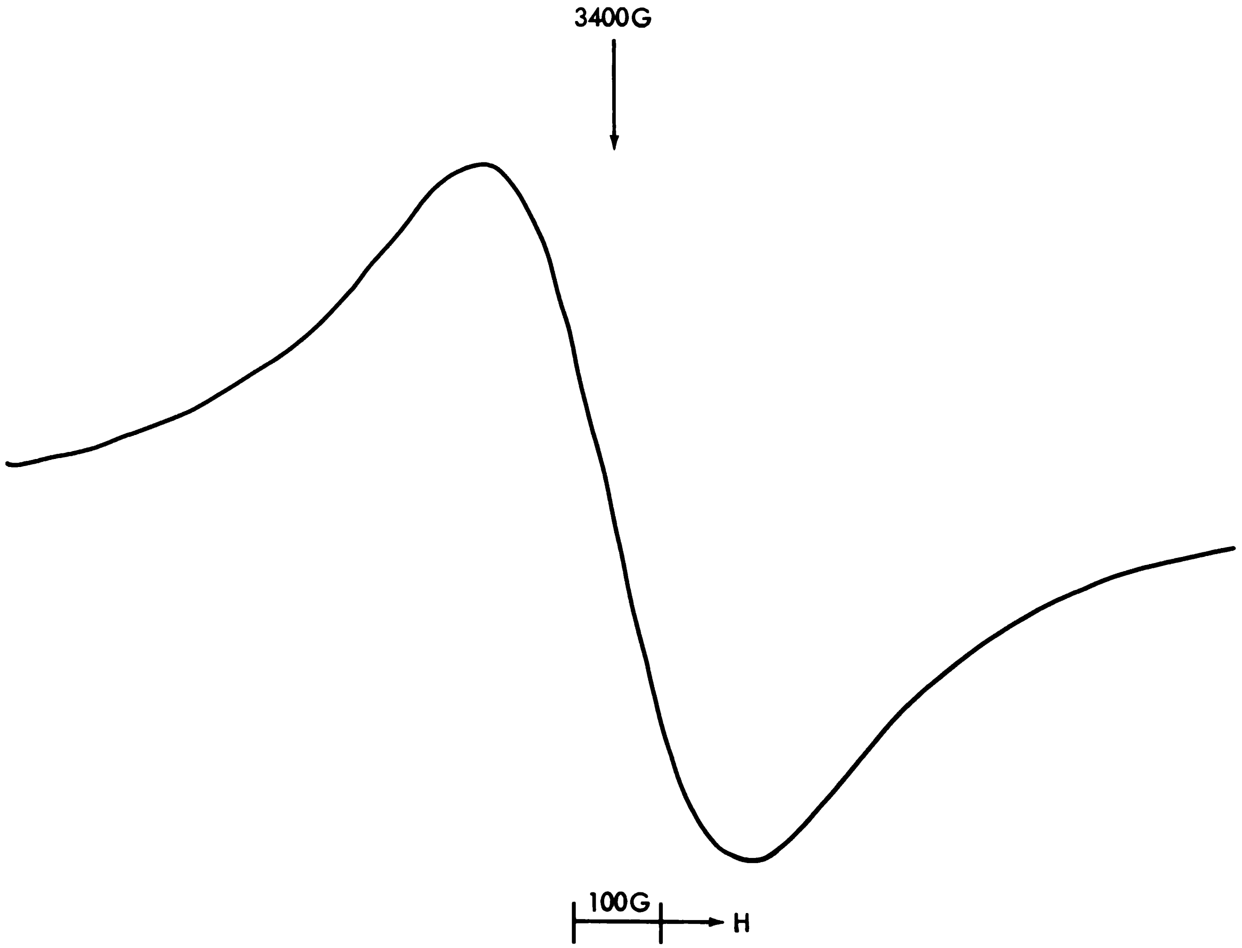

FIGURE 54. A room-temperature spectra of rhodochrosite.

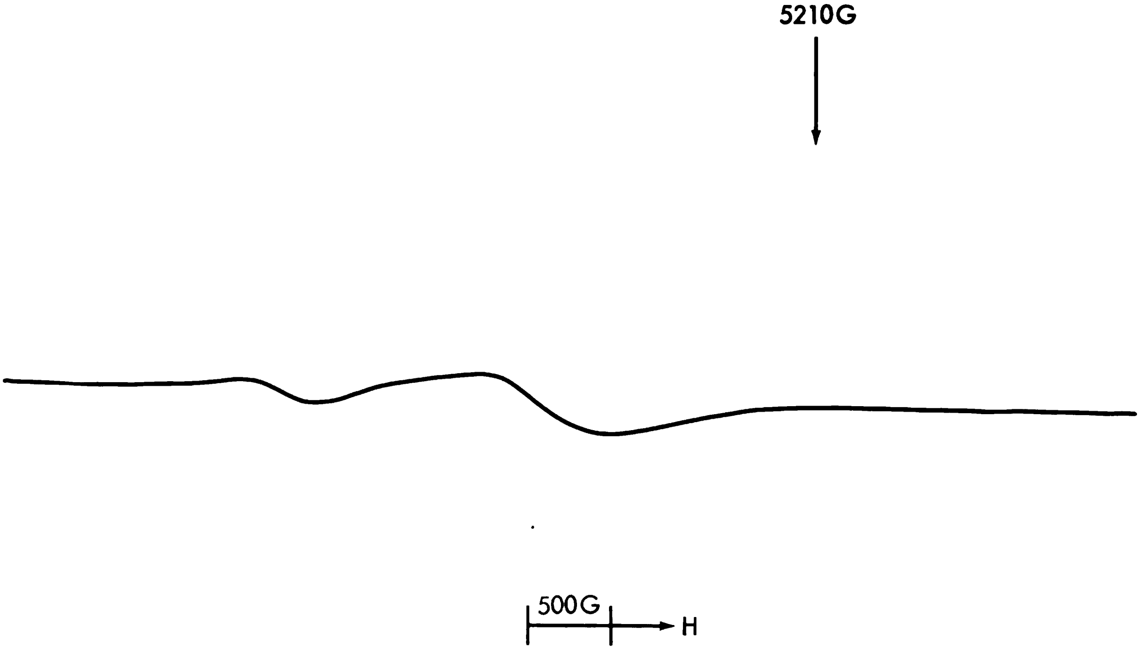

FIGURE 55. This spectrum is caused by Fe^{3+} in chalybite ($2(FeCO_3)$). The low intensity of the Fe spectrum indicates that $Fe^{2+} \gg Fe^{3+}$ (Fe^{2+} is not detectable by ESR).

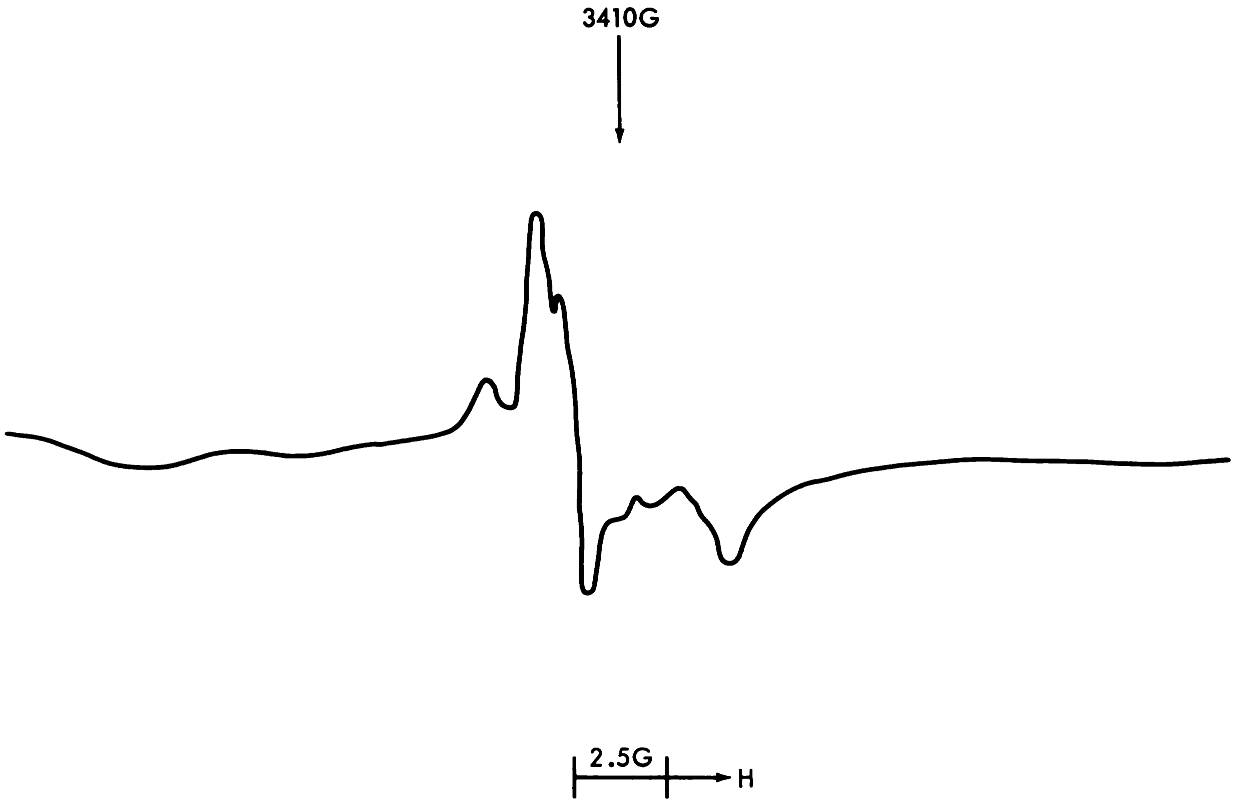

FIGURE 56. The spectra of barytes ($BaSO_4$) shows little except for a free spin feature which seems to be Fe^{3+} replacing Ba^{2+} in the $BaSO_4$ lattice. The hyperfine splitting is 1.25G approximately.

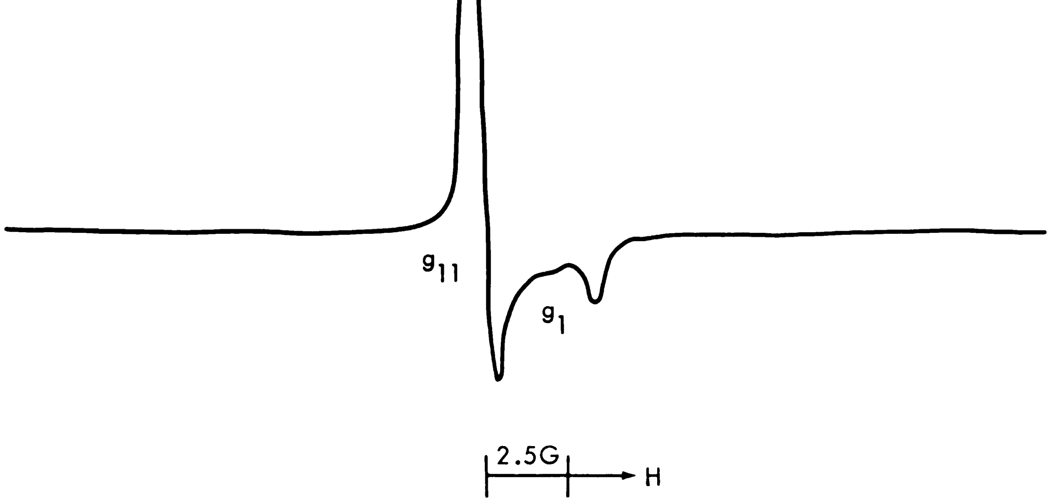

FIGURE 57. Celestine ($SrSO_4$) unlike strontianite ($SrCO_3$) shows no Mn^{2+} but does exhibit free spin features, the origin of which are unknown. Fe^{3+} may be a contributor to this spectrum. The hyperfine splitting of this feature is 3.75G.

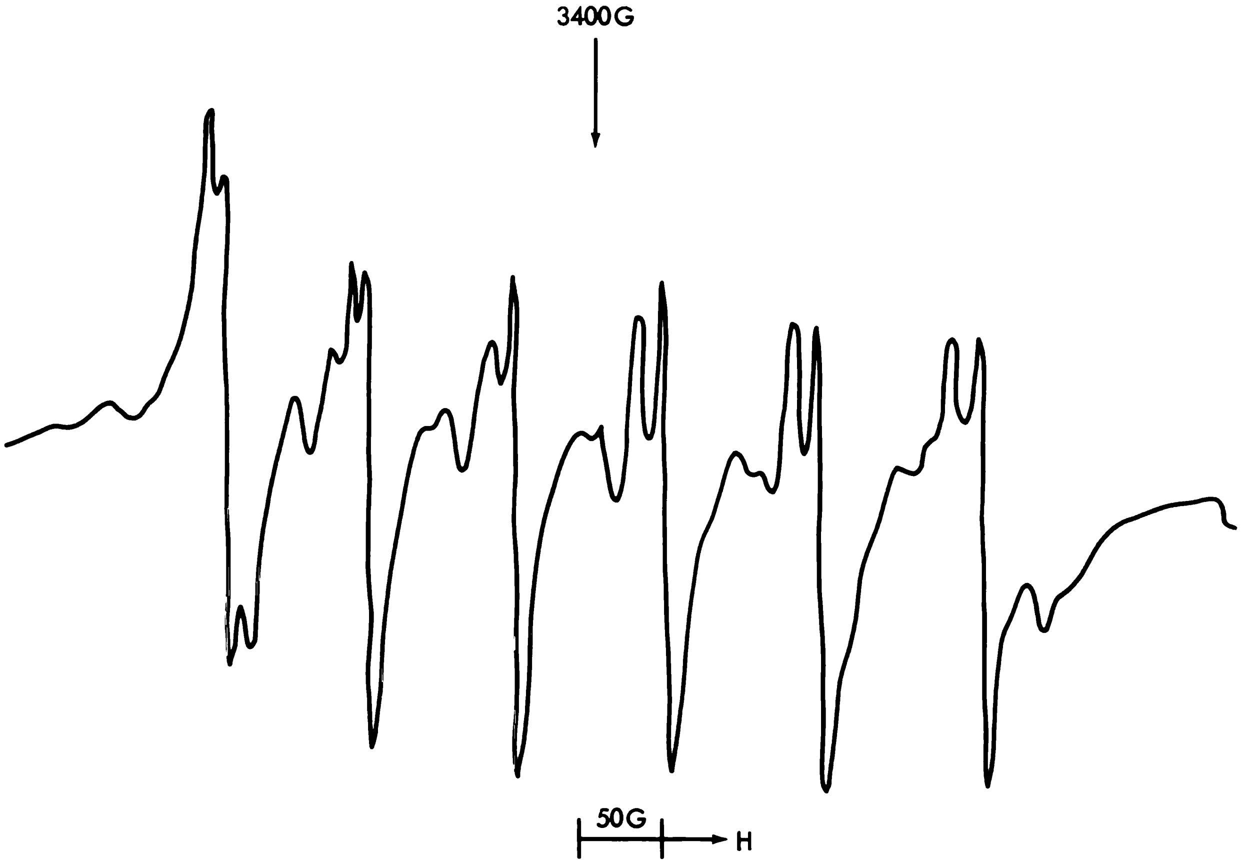

Figure 58. Mn^{2+} is found in anhydrite ($4(CaSO_4)$) substituting for Ca^{2+} in the $CaSO_4$ tetrahedron. A free spin feature was detected but the low peak intensity prevented accurate determination of its origin.

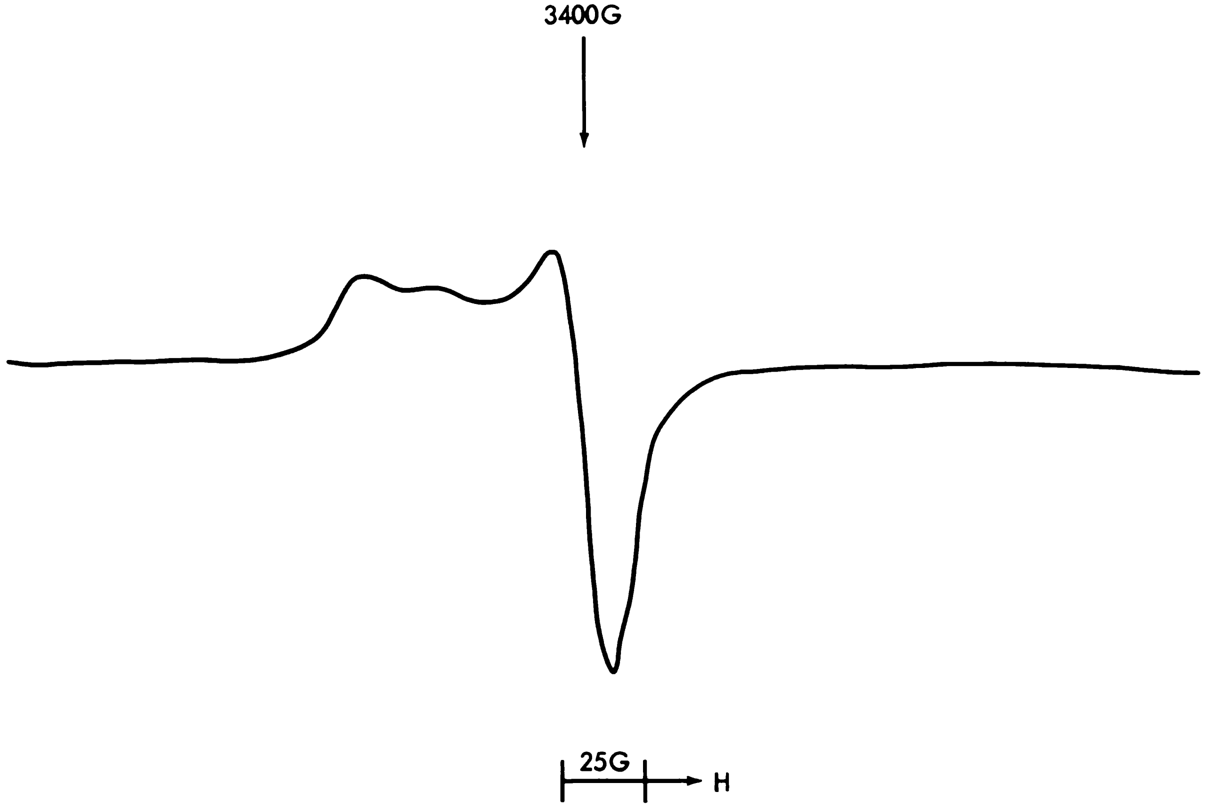

FIGURE 59. The asymmetric double peak of kaolinite is identical to that reported by Friedlander *et al.* (1963), Wauchope and Hague (1971), and Angel and Hall (1972). Angel and Hall have suggested that this may be caused by a tetrahedrally coordinated Fe^{3+} ion whereas Wauchope and Hague have identified it as an oxygen species.

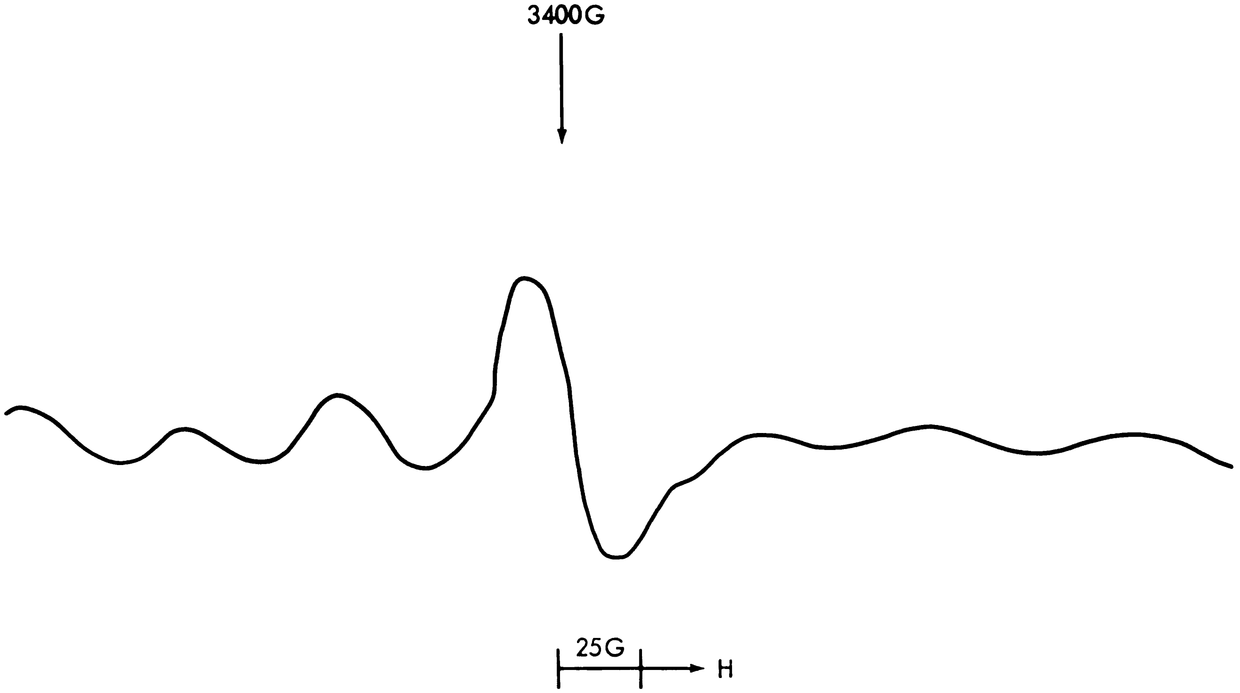

FIGURE 60. The dickite spectrum shows an asymmetrical peak distribution with a central peak surrounded by six less intense peaks. Its origins are entirely unknown at present.

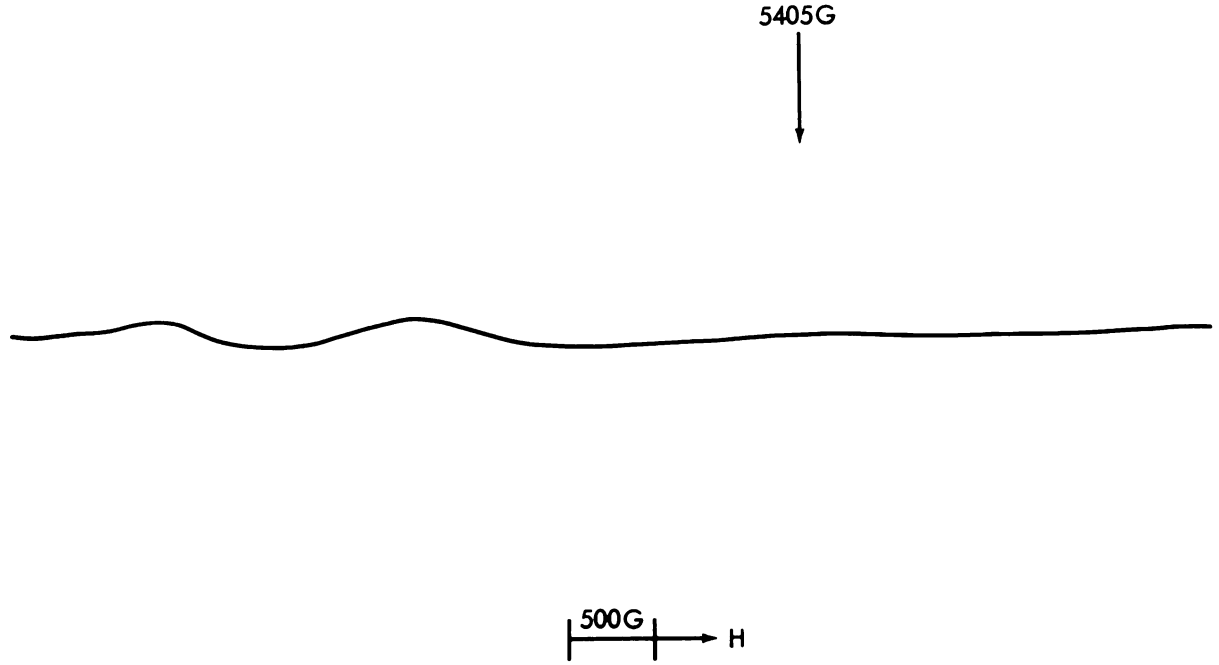

FIGURE 61. Halloysite produced a low field peak that is accounted for by an Fe^{3+} ion. Peaks in this region are found in most of the clays studied and are particularly prominent in illite and montmorillonite. The lack of a low field peak in kaolinite can be attributed to a differing site position for the Fe^{3+}.

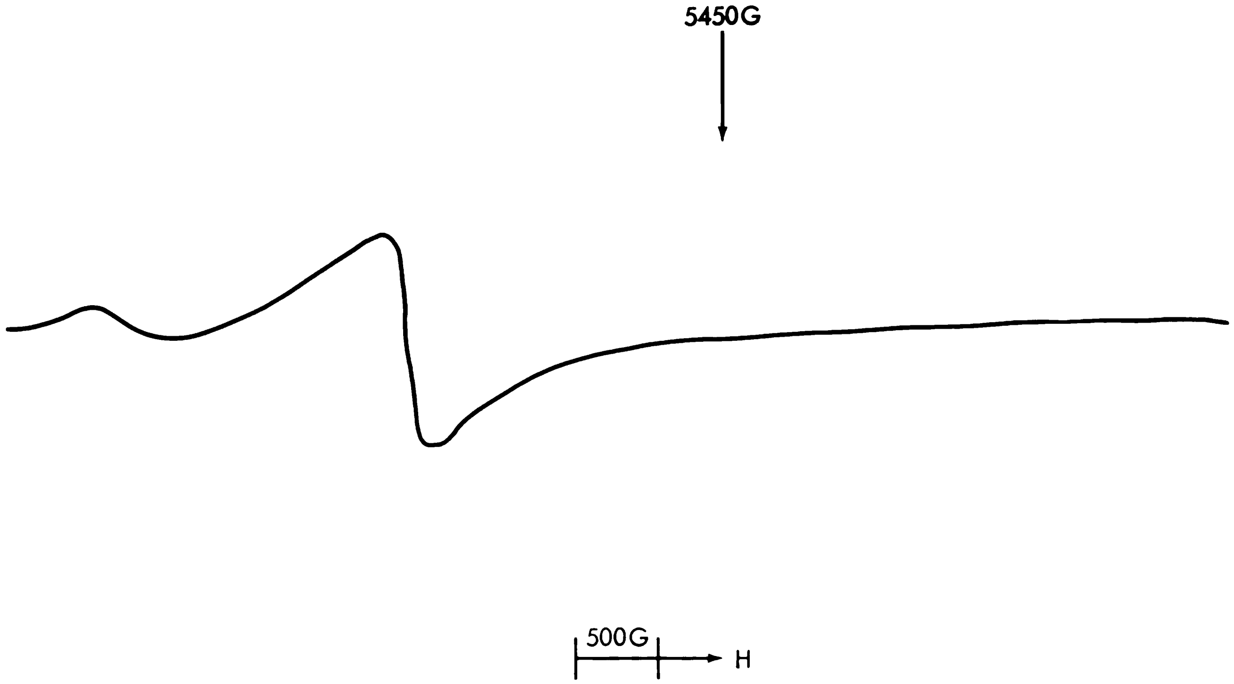

FIGURE 62. Vermiculite shows peaks at both 3400G and 1600G approximately. Again Fe^{3+}, possibly in two differing sites, accounts for the peak positions.

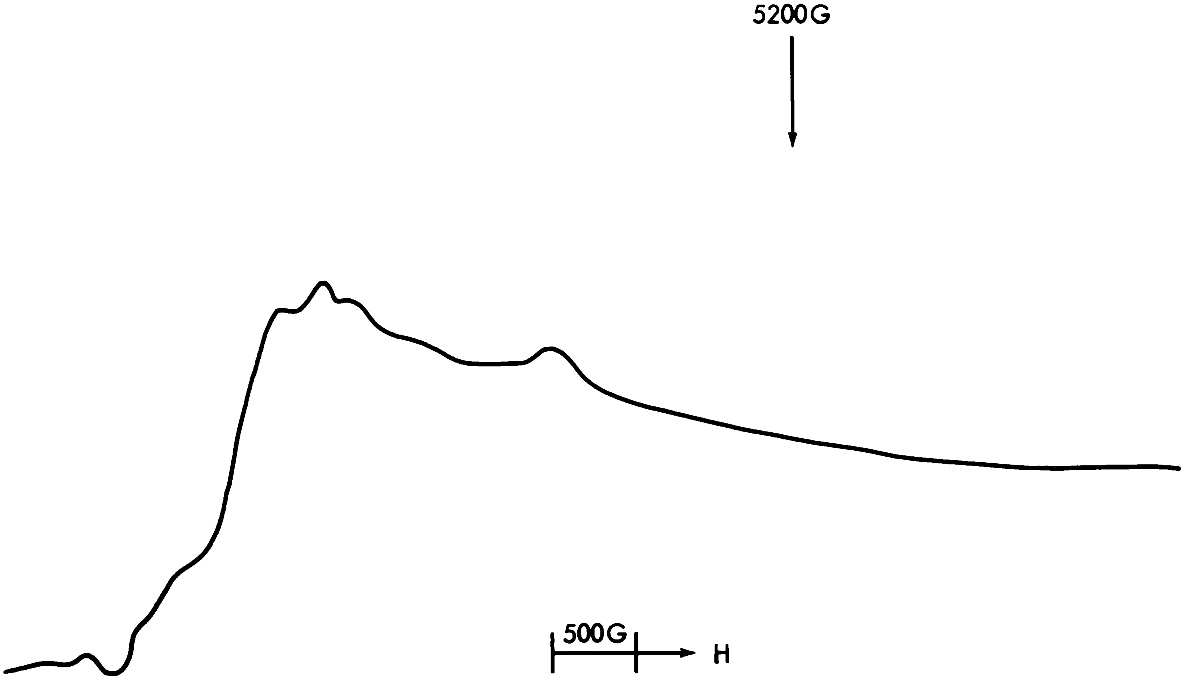

Figure 63. A most complex and unusual spectrum was produced by chlorite. This spectrum will require further study to determine the exact nature of the paramagnetic species.

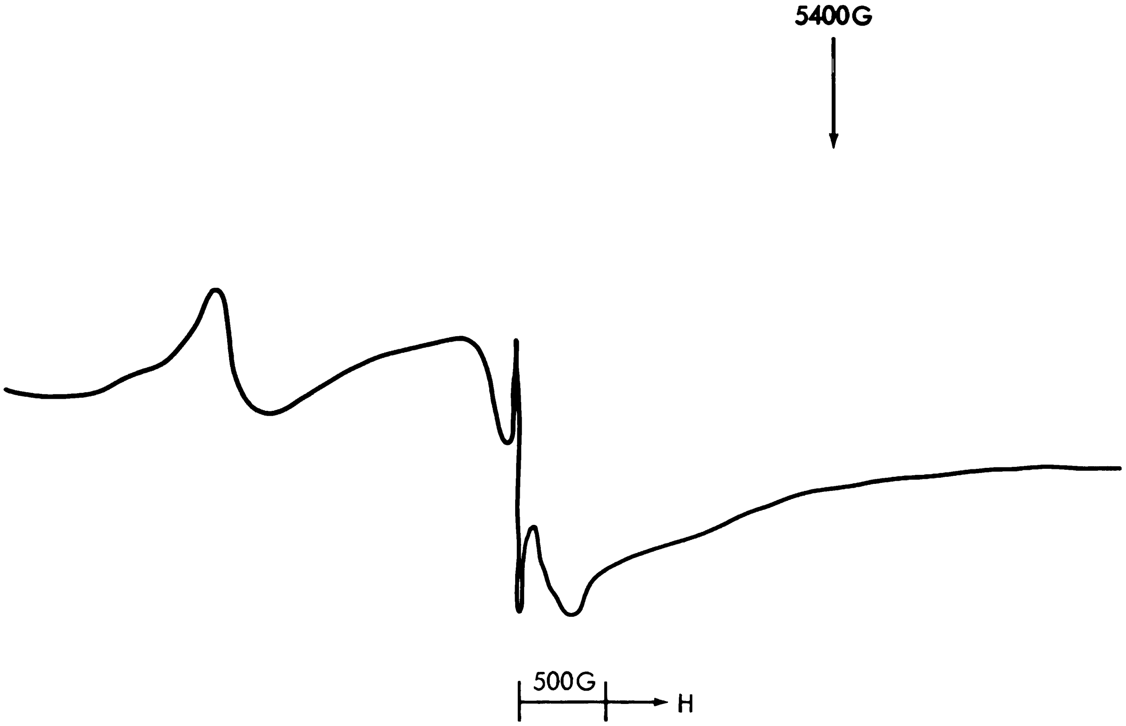

Figure 64. This spectrum of illite shows two Fe^{3+} peaks previously identified and a set of free spin features. The Fe^{3+} peaks are seen at 3400G and 1600G with the free spin features at 3100G.

APPENDIX THREE
SAMPLE-COLLECTING STATIONS

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
1	K96 Route out of Neodesha, Wilson County	Spring Hill Limestone	T30S R15E				
2	Highway 75, Near Altoona, Wilson County	Vilas Shale	T29S R16E				
3	"	"	"		1	1	
4	"	"	"				
5	"	"	"		1	1	1
7	Highway 59, 3 Miles west of Stark, Neosho County	Stark Shale	SE corner SE SE Sect. 15 T27S R20E		1	1	
10	Intersection Highways, 52/31/59 W of Kincaid, Anderson County	Lane Bonner Springs Shale	T22S R20E, S line, SE SE Sect. 35	1			
11	"	"	"	1			
12	"	"	"		1	1	
13	¼ mi. S. of Intersection 52/31/59 on Highway 52/59, Anderson County	Lane Bonner Springs Shale	W line NE NE Sect. 2 T23S R20E				
14	"	"	"				
15	"	Hickory Creek Shale	"		1	1	
16	Route 52, 2-3 miles SW of Mound City, Linn County	Tacket Formation	SW Corner NESE Sect. 23 T22S R23E	2	1	1	1
17	"	"	"	2			
18	"	"	"	2			
19	"	Mound City Shale	"	2	1	1	
20	"	"	"		1	1	1
21	"	Sniabar Limestone	"		1	1	
22	"	Ladore Shale	T22S R23E SW Corner NESE Sect. 23	2			
23	"	"	"	1	1	1	1
24	"	Hushpuckney Shale	"	2	1	1	1
25	"	"	"		1	1	
26	"	"	"		1	1	
27	Cold Storage plant on Inland Drive, Nr. Kansas City, Johnson County	Galesburg Shale	T12S R23-24E	2	1	1	1
28	"	"	"		1	1	1
29	"	Stark Shale	"				
30	"	"	"	2			
31	"	"	"	2	1	1	
32	"	"	"	2	1	1	
33	"	Winterset Limestone	"				
34	"	"	"		1	1	
35	"	"	"	2	1	1	
36	"	"	"	2	1	1	1
37	"	"	"	2			
38	"	Fontana Shale	"		1	1	
39	"	Wea Shale	"	2			
40	"	"	"		1	1	
41	"	Westerville Limestone	"		1	1	

Sample	Sample Site Sample Collection Station	 Stratigraphical Position	 Township/ Range	Analysis Thin Section	 X.R.D.	 Emiss. Spec.	 E.S.R.
42	¼ mile from Cold Storage Plant on Inland Drive, towards Kansas City, Johnson County	Quivira Shale	T12S R23-24E	2			
43	″	″	″	2	1	1	1
44	″	″	″	2			
45	″	″	″	2			
46	″	″	″		1	1	1
47	″	Chanute Shale	″	2	1	1	
48	″	″	″	2	1	1	1
49	″	″	″				
50	″	″	″		1	1	
51	″	Muncie Creek Shale	″				
51C	″	″	″	2			
52	″	″	″				
53	″	″	″		1	1	
54	Highway 10, 2½ mls. E of Zarah, Johnson County	Chanute Shale	N side SE NE Sect. 14 T12S R23E	2	1	1	
55	″	Muncie Creek Shale	″	2			
56	″	″	″	2			
57	Highway 10, 3 mls. E of Zarah, Johnson County	Island Creek Shale	N side SE NE Sect. 14 T12S R23E				
58	″	″	″	2			
59	″	Farley Limestone	″				
60	″	″	″	2			
61A	″	″	″		1	1	
61B	″	Bonner Springs Shale	S side NE NE Sect. 13 T12S R23E				
62	″	″	″				
63	″	″	″		1	1	
64	″	″	″				
65	″	Plattsburg Limestone	″				
66	″	″	″	2	1	1	
67	″	″	″		1	1	
69	K32, E of intersection with K7, Wyandotte County	Lane Shale	W side SE SE Sect. 28 T11S R23E	1	1	1	1
70	″	″	″	2	1	1	1
71	″	″	″		1	1	
72	Highway 10, 3 mls. E of Zarah, Johnson County	Bonner Springs Shale	E side NE NE Sect. 13 T12S R23E	2			
73	Kerford Quarry, 1 ml. S of Atchison on Highway 7, Atchison County	Heumader Shale	Center SW SE Sect. 7 T6S R21E	1			
74	″	″	″	2			
75	″	″	″	3			
76	″	″	″				
77	″	″	″	2			
78	″	″	″				
79	″	″	″		1	1	

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
80	″	Jackson Park Shale	″		1	1	
81	5½ mls. E of Doniphan, Atchison County	Stull Shale	Center SW SE Sect. 7 T6S R21E		1	1	1
82	″	Jackson Park Shale	″		1	1	1
83	″	Stull Shale	″	1			
84	″	″	″	2			
85	″	″	″	1	1	1	
86	5½ mls. E of Doniphan, Atchison County	″	T5S R20E				
87	″	Spring Branch Limestone	″				
88	″	″	″				
89	″	Doniphan Shale	″				
90	″	″	″				
91	″	″	″	2			
92	″	Queen Hill Shale	″	1			
93	″	″	″				
94	Quarry, 4 mls. NE of Lancaster, Atchison County	Calhoun Shale	NW SW Sect. 11 T5S R19E	1	1	1	1
95	″	″	″	2			
96	″	″	″	2	1	1	
97	″	″	″	2	1	1	
97B	Road alongside quarry, 4 mls. NE of Lancaster, Atchison County	Turner Creek Shale	NW SW Sect. 11 T5S R19E		1	1	
98	″	Jones Point Shale	″				
99	″	″	″				
100	″	Iowa Point Shale	″				
101	″	″	″		1	1	
102	″	Tecumseh Shale	″	2			
103	″	″	″	2			
104	″	″	″	1			
105	Roadside 4 mls. NE of Lancaster, Atchison County	Oskaloosa Shale	Center of S side SW Sect. 10 T5S R19E	2	1	1	1
106	″	″	″	1			
107	″	Larsh & Burroak Shale	″		1	1	
108	″	″	″				
109	Roadside 4½ mls. NE of Lancaster, Atchison County	Ervine Creek Limestone	Center of E half NE Sect. 11 T5S R19E		1	1	1
110	Quarry SE of Burlington, Coffey County	Snyderville Shale	Center NW NW Sect. 31 T21S R16E		1	1	1
111	Intersection of Highways 75/57, Coffey County	″	SW Corner SW SW Sect. 35 T22S R15E	2			
112	″	″	″		1	1	
113	Intersection of Highways 75/57, Coffey County	Snyderville Shale	SW Corner SW SW Sect. 35 T22S R15E	2			
114	″	″	″	2			
115	″	″	″				

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
116	100 yds. N of intersection of 75/57, Coffey County	Toronto Limestone	W side SW SW Sect. 35 T22S R15E		1	1	
117	Intersection of Highways 75/57, Coffey County	Snyderville Shale	SW Corner SW SW Sect. 35 T22S R19E				
118	″	″	″				
119	2½ mls. NE of Gridley, Coffey County	King Hill Shale	West Line SW NW Sect. 14 T22S R14E				
120	″	Beil Limestone	″				
121	3 mls. NE of Gridley, Coffey County	Doniphan Shale	E line NE Sect. 24, T22S R14E	2	1	1	
122	Quarry 9½ mls. W of Burlington, Coffey County	Jones Point Shale	Center NE NW Sect. 30 T21S R14E		1	1	1
124	Highway 70, 3½ mls. E of Big Springs, Douglas County	Snyderville Shale	NW Corner Sect. 21 T12S R18E				
125	″	Lawrence Shale	″		1	1	1
126	″	Snyderville Shale	″				
127	″	″	″	1			
128	″	Heebner Shale	″	3	1	1	
129	″	″	″				
130	″	″	″		1	1	
131	″	″	″				
132	″	Heumader Shale	″	1			
133	Highway 70, 5 mls. W of Lawrence, Douglas County	Spring Branch Limestone	NW NW Sect. 19 T12S R19E	1			
134	″	″	″	1			
135	″	″	″	1	1	1	1
136	Highway 70, 5½ mls. W of Lawrence, Douglas County	Queen Hill Shale	NE NE Sect. 24 T12S R18E	1	1	1	
137	″	Beil Limestone	″	1	1	1	1
138	Highway 70, 5 mls. W of Lawrence, Douglas County	Doniphan Shale	NW NW Sect. 19 T12S R19E		1	1	
139	Highway 70, 7½ mls. W of Lawrence, Douglas County	Oskaloosa Shale	NE NW Sect. 22 T12S R18E	1			
140	″	″	″	2			
141	″	″	″	1			
142	″	Larsh and Burroak Shale	″				
143A	Highway 70, 4 mls. E of Topeka, Shawnee County	Larsh and Burroak Shale	SE NE Sect. 8 T12S R17E				
143B	Highway 70/40 intersection in Topeka, Shawnee County	Iowa Point Shale	Center NW SE Sect. 4 T12S R16E				
144	″	Calhoun Shale	″	3	1	1	
145	″	″	″	2			
146	″	Jones Point Shale	″	2			
148	Highway 24, ½ ml. W of intersection with Highway 4, Shawnee County	Holt Shale	S of Center Sect. 14 T11S R16E		1	1	
149	Roadside 7 mls. W of Lawrence, Douglas County	King Hill Shale	S line SW SW Sect. 13 T12S R18E	2	1	1	

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
150	″	Avoca Limestone	″	1	1	1	
151	Lecompton Quarry, Douglas County	Heumader Shale	Center SW SW Sect. 35 T11S R18E	2	1	1	
152	Highway 7, 3½ mls. N of Atchison, Atchison County	Tecumseh Shale	W side SW SW Sect. 12 T5S R20E		1	1	
153	″	″	″	2	1	1	
154	″	″	″				
155	″	″	″		1	1	1
156	Highway 70, 1 ml. W of Bonner Springs, Wyandotte County	Eudora Shale	Center Sect. 18 T11S R23E				
157	″	″	″	1	1	1	1
158	″	Rock Lake Shale	″				
159	Highway 70, 7/10 ml. E of Kansas City Toll Booth, Wyandotte County	Quindaro Shale	E line NE SE Sect. 9 T11S R24E	1			
160	″	″	″		1	1	1
161	Highway 70, 1 ml. W of Bonner Springs, Wyandotte County	Rock Lake Shale	Center Sect. 18 T11S R23E		1	1	1
162	Highway 470, S. Topeka, Shawnee County	Severy Shale	Center S side NW Sect. 19 T12S R16E	2	1	1	
163	″	Aarde Shale	″	1			
164	″	″	″				
165	″	″	″	2			
166	″	″	″	2			
167	Highway 470, 4½ mls. SW of Topeka, Shawnee County	Silver Lake Shale	SE NE SE Sect. 4 T13S R15E	1			
168	″	″	″	1	1	1	1
169	″	Cedar Vale Shale	″				
170	″	″	″	1	1		
171	Highway 470, 5½ mls. SW of Topeka, Shawnee County	White Cloud Shale	SE NE SW Sect. 9 T13S R15E	1	1	1	
172	″	″	″	2			
173	″	″	″	2	1	1	1
174	Highway 470, 2 mls. SW of Auburn, Shawnee County	Harveyville Shale	NE SW SW Sect. 35 T13S R14E	1			
176	Highway 470, 2½ mls. SW of Auburn, Shawnee County	Willard Shale	NE SW NE Sect. 3 T14S R14E				
177	″	″	″	2			
178	″	″	″	2			
179	″	″	″	2			
180	Highway 470, 3 mls. SW of Auburn, Shawnee County	″	SW SW NE Sect. 3 T14S R14E	2	1	1	
181	″	Wamego Shale	″		1	1	
182	Highway 470, 4 mls. NE of Admire, Lyon County	Pillsbury Shale	SW SW NW Sect. 12 T16S R13E				
183	″	″	″	2			
184A	″	″	″	2	1	1	1
184B	″	″	″				
185	″	Dry Shale	″		1	1	
186	″	Grandhaven Limestone	″		1	1	1

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
187	〃	Friedrich Shale	〃	2	1	1	1
188	〃	〃	〃	2			
190	〃	Dry Shale	〃				
191	Highway 70, 2 mls. W of Topeka, Shawnee County	Silver Lake Shale	SW NE NW Sect. 31 T11S R15E				
192	〃	〃	〃		1	1	
193	〃	Soldier Creek Shale	〃				
194	〃	〃	〃		1	1	1
195	Highway 70, 2 mls. W of Topeka, Shawnee County	Soldier Creek Shale	SW NE NW Sect. 31 T11S R15E				
196	Highway 70, 2 mls. S of Maple Hill, Wabaunsee County	Pony Creek Shale	Center S line SW Sect. 26 T11S R12E	1			
197	〃	〃	〃		1	1	
198	〃	〃	〃				
199	〃	Towle Shale	〃				
200	〃	〃	〃		1	1	1
201	Highway 70, 2½ mls. SW of Maple Hill, Wabaunsee County	Hawxby Shale	SW SW SW Sect. 27 T11S R12E				
202	〃	〃	〃				
203	〃	〃	〃				
204	〃	West Branch Shale	〃				
205	〃	〃	〃		1	1	
206	Highway 70, ½ ml. S of Paxico, Wabaunsee County	Hamlin Shale	SW SW SW Sect. 27 T11S R12E		1	1	
207	〃	Hughes Creek Shale	SE SW SE Sect. 27, T11S R11E				
208	〃	〃	〃		1	1	1
209	〃	〃	〃		1	1	1
211	Highway 70, 3 mls. N of Alma, Wabaunsee County	Roca Shale	Center W side Sect. 26 T11S R10E				
212	〃	Legion Shale	〃		1	1	
213	〃	Salem Point Shale	〃		1	1	1
214	Highway 70, ½ ml. S of Paxico, Wabaunsee County	Hamlin Shale	SE SW SE Sect. 27 T11S R11E				
220	Highway 70, 3 mls. NW of Alma, Wabaunsee County	Speiser Shale	S line SE NW Sect. 29 T11S R10E		1	1	1
221	Highway 70, 3 mls. NW of Alma, Wabaunsee County	Speiser Shale	S line SE NW Sect. 29 T11S R10E	1	1	1	1
222	〃	〃	〃	2	1	1	
223	〃	〃	〃				
225	Highway 70, 3½ mls. NW of Alma, Wabaunsee County	Blue Rapids Shale	SE SE NE Sect. 30 T11S R10E				
226	〃	〃	〃		1	1	
227	〃	〃	〃		1	1	
228	〃	〃	〃	2			
229	〃	〃	〃	1			

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
230	Highway 70, 4 mls. NW of Alma, Wabaunsee County	Easly Creek Shale	S line SW NE Sect. 30 T11S R10E	1	1	1	
231	"	"	"				
232	"	"	"				
233	"	"	"	2			
234	"	Hooser Shale	"		1	1	1
235	Highway 70, 4½ mls. NW of Alma, Wabaunsee County	Eskridge Shale	W line NE SW Sect. 30 T11S R10E	1	1	1	1
236	"	"	"	2			
237	"	Neva Limestone	"	2	1	1	
238	"	Eskridge Shale	"		1	1	1
239	"	"	"				
240	"	"	"				
241	"	Neva Limestone	"				
242	"	Salem Point Shale	"				
243	Highway 70, 6½ mls. S of Zeandale, Riley County	Havensville Shale	W line NW SW Sect. 28 T11S R9E		1	1	1
244	"	"	"		1	1	1
247	Highway 70, 6 mls. SE of Manhattan, Riley County	Stearns Shale	W line SW NW Sect. 25 T11S R8E				
248	"	"	"	1	1	1	
249	"	Florena Shale	"		1	1	1
250	Highway 70, 1 ml. E of Manhattan Exit, Geary County	Blue Springs Shale	W line NW SW Sect. 27 T11S R8E				
251	"	"	"		1	1	1
252	"	"	"				
253	"	Kinney Limestone	"	1	1	1	
254	"	Blue Springs Shale	"				
255	"	"	"				
256	"	"	"	2	1	1	
258	Highway 177, ½ ml. SE of Manhattan, Riley County	Johnson Shale	SW SW NE Sect. 20 T10S R8E				
259	"	"	"				
260	"	Bennett Shale	"	1			
261	"	Johnson Shale	"		1	1	
262	Highway 113, ½ ml. W of Manhattan, Riley County	Bennett Shale	NW SE NE Sect. 14 T10S R7E		1	1	1
263	Highway 113, 1 ml. N of Manhattan, Riley County	Neva Limestone	N line NE NW Sect. 2 T10S R 7E	2			
264	"	"	"	2	1	1	
265	Highway 77, 2 mls. N of Junction City, Geary County	Oketo Shale	Center SW NW Sect. 27 T11S R5E	2	1	1	
266	"	"	"	2			
267	"	Holmesville Shale	"				
268	Highway 77, 2½ mls. N of Junction City, Geary County	"	Center NW NW Sect. 27 T11S R5E	2	1	1	
269	"	"	"	1			
270	3/10ths ml. S of Intersection of Highways 57/77, Geary County	Gage Shale	N line NW NW Sect. 34 T11S R5E	2	1	1	
271	"	"	"				

	Sample Site			Analysis			
Sample	Sample Collection Station	Stratigraphical Position	Township/ Range	Thin Section	X.R.D.	Emiss. Spec.	E.S.R.
272	Junction of Highway 57/77, Geary County	Grant Shale	Center NW SW Sect. 27 T11S R5E	1	1	1	1
273	Highway 70, 2 mls. E of Junction City, Geary County	Wymore Shale	Center SE SE Sect. 5 T11S R5E		1	1	
274	″	″	″	1			
280	1½ mls. N of Baldwin, Douglas County	Wathena Shale	W line SW NW Sect. 27 T14S R20E				
281	″	″	″	2	1	1	1
282	″	″	″				
283	″	Ireland Sandstone	″				
284	″	″	″		1	1	
286	2 mls. N of Baldwin, Douglas County	″	NW NW NW Sect. 27 T14S R20E	2			
287	2½ mls. N of Baldwin, Douglas County	″	W line NE SW Sect. 22 T14S R20E		1	1	
288	Highway 10, 2 mls. E of Lawrence, Douglas County	Ireland Sandstone	N line NE NE Sect. 10 T13S R20E				
289	″	″	″	2			
290	15th Street, Lawrence, Douglas County	Vinland Shale	N line NW NE Sect. 5 T13S R20E		1	1	1
291	″	″	″	1			
292	″	″	″				
294	Highway 7, 3 mls. N of Bonner Springs, Wyandotte County	Tonganoxie Sandstone	NE SW NW Sect. 8 T11S R23E	1	1	1	
295	″	″	″	3			
296	″	Weston Shale	″	1	1	1	
297	1 ml. N of Chapman, Dickinson County	Odell Shale	SE SW Sect. 17 T12S R4E				
298	″	″	″		1	1	1
299	″	″	″				
300	Intersection of Highways 206/70, Dickinson County	Paddock Shale	N, NE Sect. 30 T12S R4E		1	1	1