Composition and Depositional Environment of Concretionary Strata of Early Cenomanian (early Late Cretaceous) age, Johnson County, Wyoming

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By E.A. Merewether *and* D.L. Gautier

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Evolution of Sedimentary Basins—Powder River Basin

A multidisciplinary approach to research studies of sedimentary rocks and their constituents and the evolution of sedimentary basins, both ancient and modern

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Abstract

Unusual, concretion-bearing mudrocks of early Late Cretaceous age, which were deposited in an early Cenomanian epeiric sea, have been recognized at outcrops in eastern Wyoming and in adjoining areas of Montana, South Dakota, Nebraska, and Colorado. In Johnson County, Wyo., on the western flank of the Powder River Basin, these strata are in the lower part of the Belle Fourche Member of the Frontier Formation. At a core hole in south-central Johnson County, they are informally named Unit 2. These strata are about 34 m (110 ft) thick and consist mainly of medium- to dark-gray, noncalcareous, silty shale and clayey or sandy siltstone; and light-gray to grayish-red bentonite. The shale and siltstone are either bioturbated or interlaminated; the laminae are discontinuous, parallel, and even or wavy. Several ichnogenera of deposit feeders are common in the unit but filter feeders are sparse. The unit also contains marine and continental palynomorphs and, near the top, a few arenaceous foraminifers. No invertebrate macrofossils have been found in these rocks. Unit 2 conformably overlies lower Cenomanian shale in the lowermost Belle Fourche Member, informally named Unit 3, and is conformably overlain by lower and middle Cenomanian shale, siltstone, and sandstone within the member, which are informally named Unit 1.

The mineral and chemical composition of the three Cenomanian units is comparable and similar to that of shale and siltstone in the Upper Cretaceous Pierre Shale, except that these units contain more SiO_2 and less CaO, carbonate carbon, and manganese. Silica is generally more abundant and CaO is generally less abundant in river water than in seawater. The composition of Unit 2 contrasts significantly with that of the underlying and overlying units. Unit 2 contains no pyrite and dolomite and much less sulfur than Units 1 and 3. Sulfate is generally less abundant in river water than in seawater. Unit 2 also includes sideritic and calcitic concretions, whereas Units 1 and 3 contain neither concretions nor siderite and only sparse calcite. Carbon-sulfur-iron chemistry for the concretions suggests that sulfate availability was the limiting factor in pyrite formation and sulfide incorporation in Unit 2. Isotopic compositions of the carbon and oxygen in siderite and calcite from several concretions are variable and suggest cementation during early diagenesis in a variety of microenvironments. The isotopic composition of these carbonate minerals differs from that of Upper Cretaceous marine limestones. When considered in conjunction with the proportions of sulfur, organic carbon, and iron in Unit 2, major-element and micropaleontological data suggest that the composition of the original pore waters and of overlying waters in the late early Cenomanian sea was brackish to fresh.

The mudrocks of Units 3 and 2, and a lower part of Unit 1, accumulated on a shelf at low to moderate rates of sedimentation in association with variable but generally weak current action. In Unit 2 and laterally equivalent rocks of the region, the sideritic and calcitic concretions probably indicate the extent of a body of brackish to fresh and oxygen-deficient water. Rates of precipitation in this region during the mid-Cretaceous could have been unusually high and the precipitation probably was seasonal. The organic matter in Unit 2 is humic-rich and would have been derived from continental environments. If the epeiric sea was brackish to fresh in the region of eastern Wyoming and contiguous areas, meteoric runoff from the adjoining lowlands must have been periodically large and the seaway north of the region probably was constricted. Seasonal changes in salinity might have been accompanied by changes in water temperature and oxygen content.

The lower part of the Frontier Formation (Units 3, 2, and 1) in Wyoming records an intermittently and easterly prograding shoreline during late early and early middle Cenomanian time. Laterally equivalent strata in Nebraska and adjoining areas seemingly reflect a westerly prograding shoreline during late early Cenomanian time and a retrograding shoreline during the latest early Cenomanian and the early middle Cenomanian. Presumably, in that region a marine regression was followed by a marine transgression. Tectonism in western Wyoming and adjoining areas during the late Albian and early Cenomanian, as well as a eustatic fall in the late early Cenomanian, could have caused marine regressions, whereas regional subsidence and a eustatic rise in the latest early Cenomanian and the early middle Cenomanian probably caused the transgression. The boreal epeiric sea of early Cenomanian time in eastern Wyoming and contiguous areas contracted during the late early Cenomanian; thereafter, in the early and middle Cenomanian, it expanded to join the Tethyan sea and became the Late Cretaceous epicontinental seaway.

Introduction

Distinctive sedimentary rocks of early Cenomanian (early Late Cretaceous) age, characterized by dark-gray mudstone, abundant reddish and bluish concretions as thick as 0.6 m (2 ft), and the absence of molluscan fossils, have been long recognized at outcrops along the edges of intermontane basins in eastern Wyoming and adjoining areas (fig. 1). In this report, we discuss the lithological and paleobiological contrast between these mudstones and other Cretaceous rocks in the region, and we suggest depositional environments for these contrasting rock types.

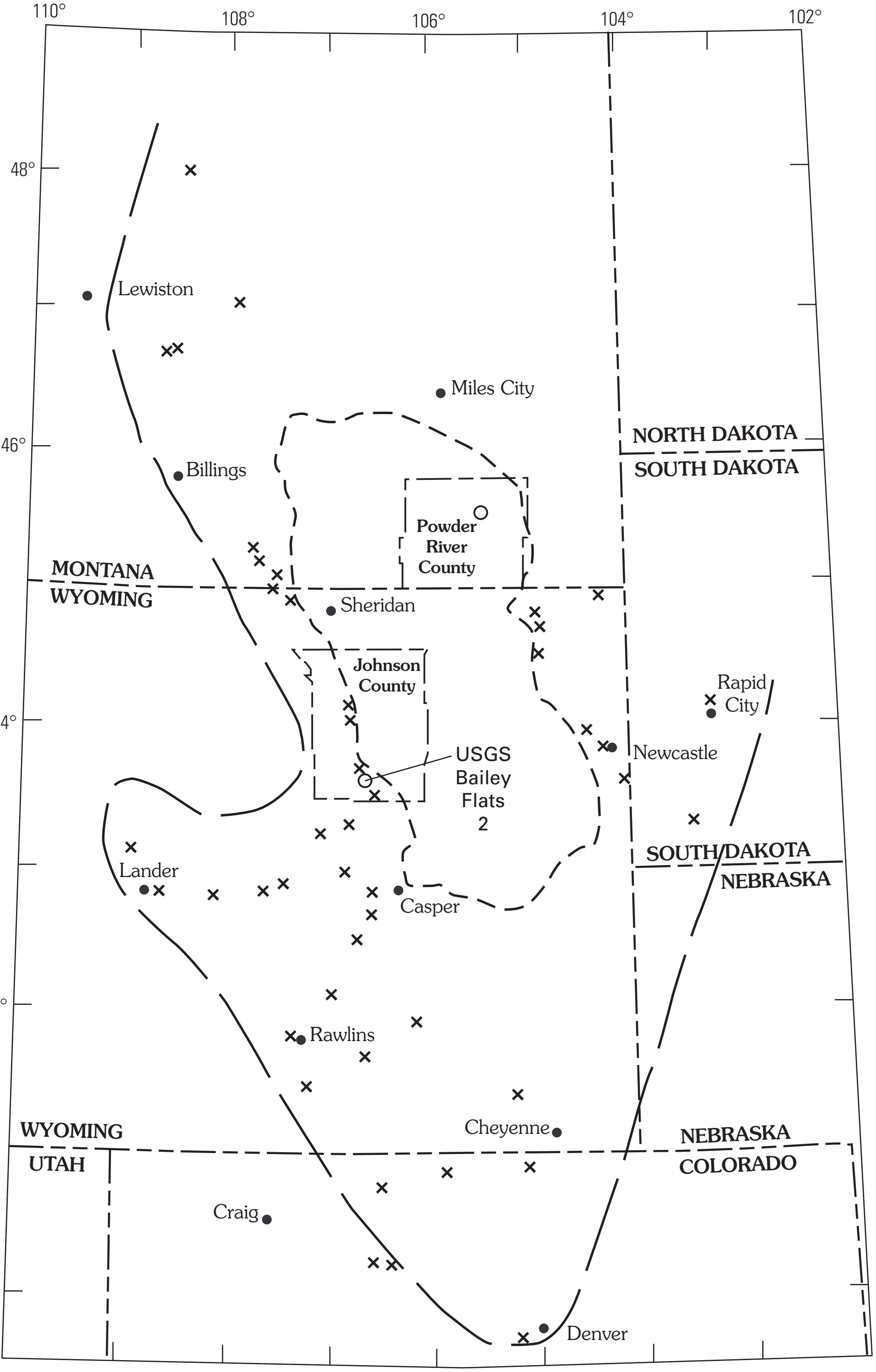


Figure 1. Map of eastern Wyoming, eastern Montana, and adjoining areas, showing the Powder River basin (short dashed line) and selected counties, as well as outcrops (x), boreholes (o), and the approximate geographic extent (long dashed line) of concretionary strata of early Cenomanian age.

Ferruginous concretionary mudrocks comprise a lower part of the Frontier Formation and laterally equivalent lower parts of the Belle Fourche Shale, Benton Shale, and Graneros Shale in eastern Wyoming and in adjoining areas of Montana, South Dakota, Nebraska, and Colorado (fig. 1). Within that region, these concretionary rocks are a lithostratigraphic unit that overlies, with apparent conformity, lower Cenomanian beds, either the uppermost Mowry Shale or nonconcretionary mudrocks that overlie the Mowry. The unit is overlain, seemingly conformably, by nonconcretionary siliciclastic beds of early and middle Cenomanian age in the Frontier, Belle Fourche, Benton, and Graneros formations.

The concretionary unit generally consists of noncalcareous, silty shale and clayey or sandy siltstone, minor sandstone, and bentonite as well as ferruginous concretions and concretionary beds (fig. 2). It was first investigated in northeastern Wyoming in 1923 by W.W. Ruby who sampled a concretion from a lower part of the Belle Fourche Shale, and subsequently determined that the concretion was composed of manganiferous siderite (Robinson and others, 1964, p. 54).

At outcrops in the region (fig. 1), the concretion-bearing unit ranges in thickness from a featheredge to as much as 104 m (340 ft). At outcrops and a core hole in Johnson County, Wyo. (Merewether and others, 1976), the unit is about 34 m (110 ft) thick (fig. 3). The rocks in Johnson County are herein assigned to the late early Cenomanian, although they could possibly be early middle Cenomanian. The Mowry Shale, which underlies the Frontier and laterally equivalent formations, contains molluscan fossils of early Cenomanian age (Cobban and Kennedy, 1989). Nonconcretionary beds, which overlie the concretion-bearing unit in lower parts of the Frontier and laterally equivalent formations, contain molluscan fossils of earliest middle Cenomanian age. In Johnson County, early middle Cenomanian mollusks were collected from beds about 50 m (165 ft) above the concretionary unit. Throughout the region (fig. 1), the concretionary strata contain few macrofossils but they contain scattered foraminifers, which indicate deposition in marine environments of less than normal salinity (Eicher, 1965, 1967; Eicher and Diner, 1985). Palynomorphs of marine and continental origins were identified by Okumura (1994) in core of the lower part of the Frontier from Johnson County. Dinocysts of the *Litosphaeridium siphonophorum* biozone were recognized in samples of core from the concretionary unit. In Wyoming and adjoining areas (McGookey and others, 1972, figs. 17, 26), the locations of shorelines for an upper part of the Mowry Shale and for the concretion-bearing strata in the overlying formations seemingly indicate a reduction in the areal extent of the mid-Cretaceous epeiric sea (fig. 4).

Stratigraphy

Concretionary strata of late early Cenomanian age, in the lower part of the Belle Fourche Member of the Frontier Formation, crop out along the western margin of the Powder River Basin (fig. 1). They were cored near the western margin of the basin at a borehole, USGS Bailey Flats 2, in south-central Johnson County, Wyo. (NE$^1/_4$SW$^1/_4$ sec. 6, T. 42 N., R. 81 W.). The core is stored by the U.S. Geological Survey in Lakewood, Colo. At outcrops in Johnson County (NW$^1/_4$NE$^1/_4$ sec. 3, T. 41 N., R. 81 W.), these strata are about 34 m (110 ft) thick and are

Figure 2. Outcropping concretionary strata of the lowermost Frontier Formation in NE$^1/_4$ sec. 5, T. 38 N., R. 85 W., Natrona County, Wyo. Arrows indicate conspicuous, ledge-forming, concretionary beds. Strata between underlying light-gray bentonite (uppermost Mowry Shale) at far-right center and overlying sandstone (Frontier Formation) at center skyline are about 54 m (177 ft) thick. View is west-northwest.

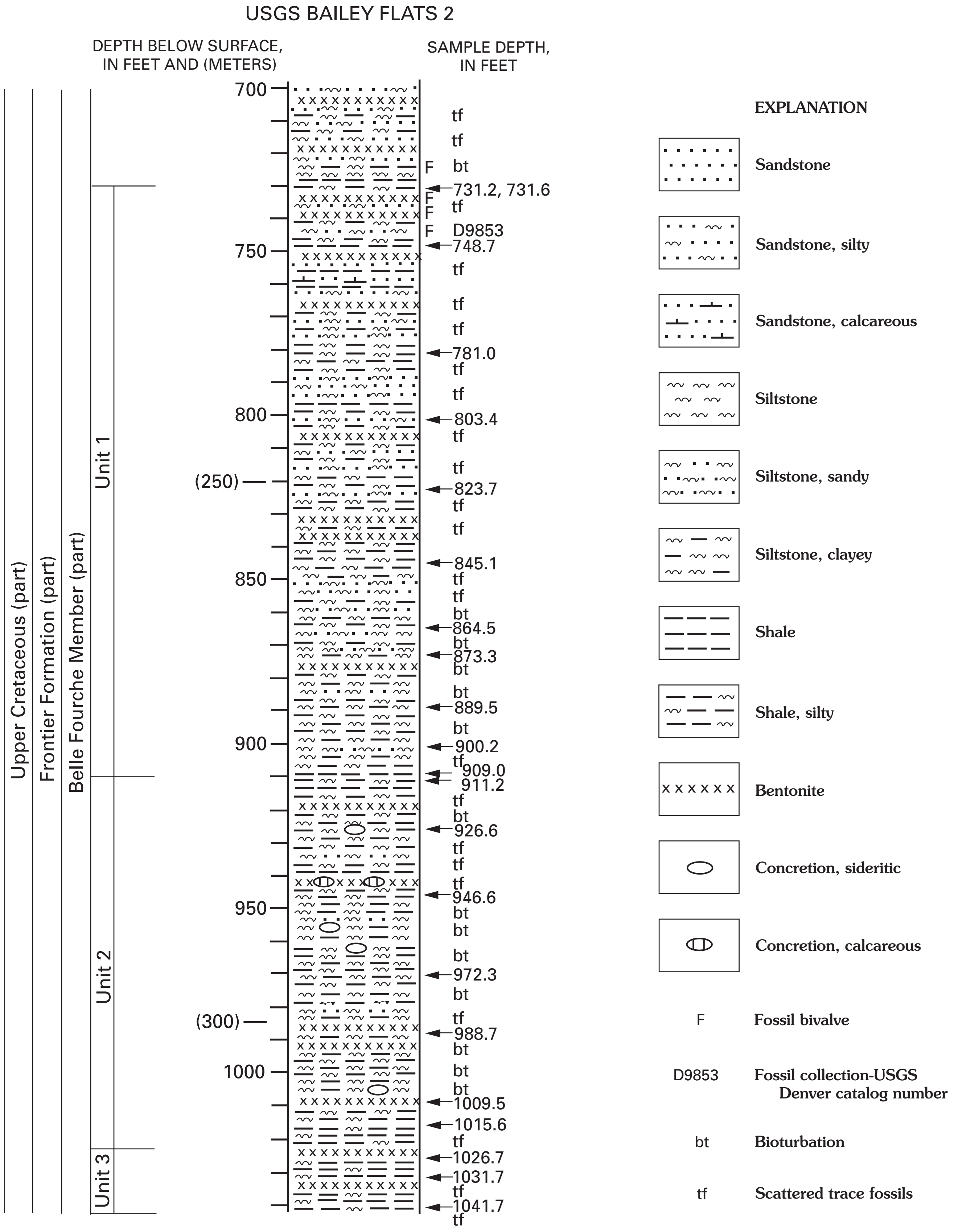


Figure 3. Lithologic log of a lower part of the Frontier Formation, from USGS, Bailey Flats 2. NE$^{1}/_{4}$ SW$^{1}/_{4}$ sec. 6, T. 42 N., R. 81 W., Johnson County, Wyo. Location of core hole shown in figure 1.

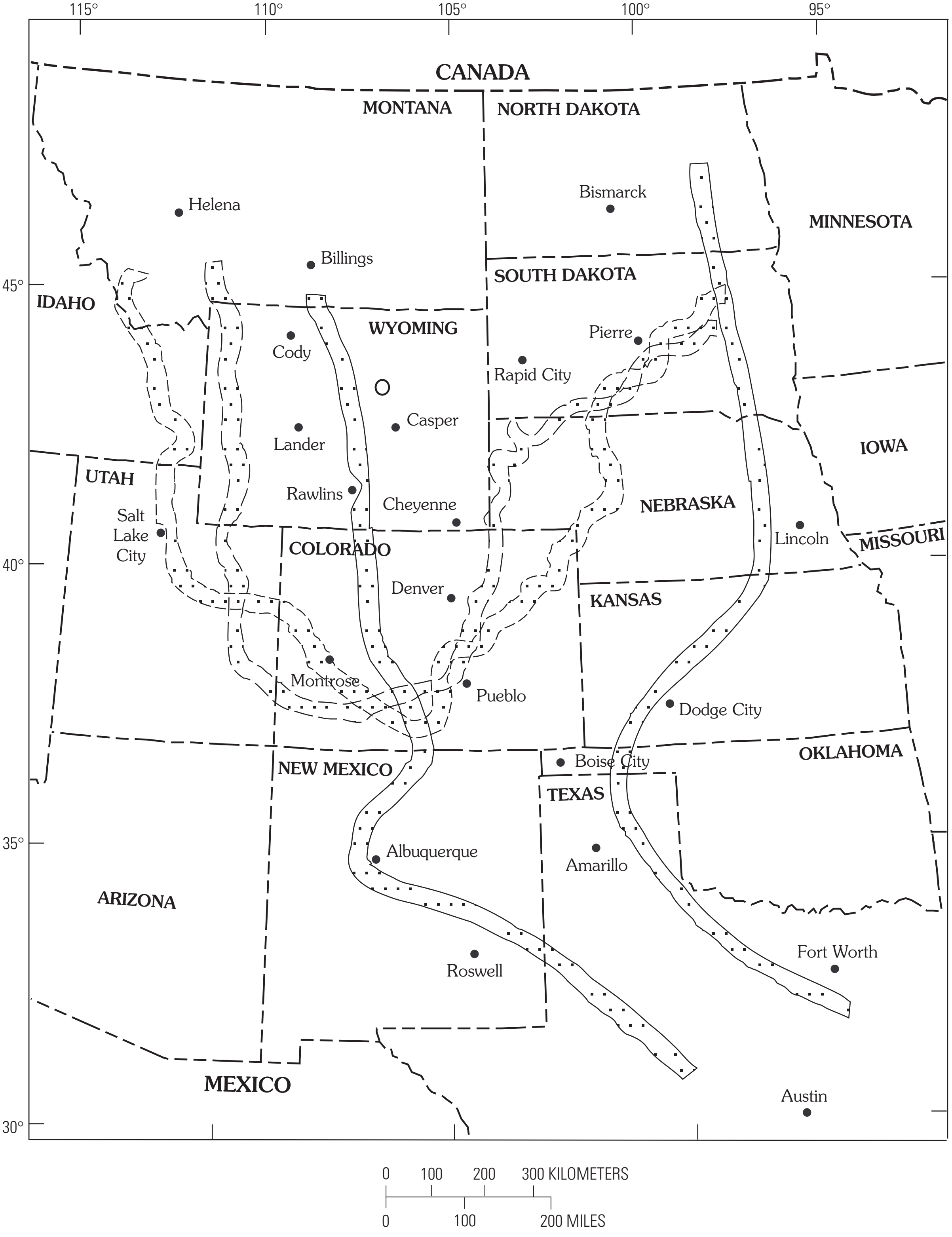


Figure 4. Approximate location of coastal sand during the early early Cenomanian (short-dashed lines derived from lithofacies in the upper part of the Mowry Shale), late early Cenomanian (long-dashed lines derived from lithofacies laterally equivalent to the concretionary, lower part of the Belle Fourche Member of the Frontier Formation), and early middle Cenomanian (solid lines derived from lithofacies in the middle part of the Belle Fourche Member) in the Western Interior of the United States. Modified after McGookey and others (1972) and Cobban (1993). Location of corehole in northeastern Wyoming shown by open circle.

composed of moderately indurated, medium- to dark-gray, silty shale and clayey or sandy siltstone, and soft, light-gray to grayish-red bentonite. The shale and siltstone are noncalcareous and enclose scattered, lenticular, dusky-red and dusky-blue ferruginous concretions and concretionary beds which are as thick as 20 cm (7.9 in.).

Description of Core

Core of most of the lowest part of the Belle Fourche Member (Unit 3 in this report) from depths of 312-318 m (1024-1042 ft), which underlies the concretionary strata, consists of interlaminated, medium- to dark-gray silty shale and siltstone and laminae and beds of light-gray bentonite (fig. 3). Some of these mudrocks are slightly pyritic. The laminae of shale and siltstone are discontinuous, wavy, and nonparallel and enclose small, mainly horizontal burrows, mostly *Planolites,* and a few *Teichichnus*, and *Asterosoma*. Samples of the core also contain the following arenaceous foraminifers, in low diversity assemblages (as many as 3 species per sample): *Verneuilinoides perplexus* (Loeblich) is moderately abundant; *Haplophragmoides* sp., *Trochammina* sp., *Psamminopelta* sp., and *Ammobaculoides* sp. are sparse (B.R. North and W.G.E. Caldwell, retired, written commun., 1977).

Where cored, the concretionary strata (Unit 2 in this report) are at depths between 277 and 312 m (910–1,024 ft; fig. 3). The strata consist mainly of bioturbated mudrock and interlaminated, medium- to dark-gray, silty shale; clayey siltstone; minor sandy siltstone; and very light to light gray, bentonitic shale and bentonite (fig. 3). The rocks are generally noncalcareous and, where not bioturbated, are thinly laminated to very thinly bedded. The laminae and beds, which differ in grain size and composition, are discontinuous, even parallel and discontinuous, wavy nonparallel. Trace fossils are common in the shale and siltstone, and consist mainly of *Planolites.* A few specimens of *Chondrites, Teichichnus* (fig. 5), *Zoophycos* (fig. 6), *Asterosoma*, *Terebellina,* and *Skolithos* were recognized. Most of the trace fossils are small (less than 5 mm in diameter) and filled with mud, silt, or sand; and nearly all represent deposit feeders. No foraminifers were found in the core of Unit 2 from depths of 282 to 312 m (925–1024 ft); one foraminifer (*?Gavelinella* sp. A) was found in Unit 2 from depths of 277 to 282 m (910–925 ft) (B.R. North and W.G.E. Caldwell, written commun., 1977). Palynomorphs in the unit include the species *Ovoidinium verrucosum* of the dinocyst biozone *Litosphaeridium siphonophorum* (Okumura, 1994). Scattered intervals of sideritic to calcareous cement in the core are grayish red to light brown, grade into the surrounding strata, and are as thick as 0.6 m (2 ft). In outcrops, these cemented intervals are concretions.

Unit 2 of the core can be divided into three parts. The basal part is 4.9 m (16 ft) thick and composed mainly of discontinuous, even, parallel laminae of silty shale that encloses a few small burrows. The middle part is 18.3 m (60 ft) thick and consists mostly of bioturbated clayey siltstone. The upper part of Unit 2 is 11.6 m (38 ft) thick and composed dominantly of discontinuous, even, parallel laminae of silty shale and clayey siltstone that contain many small burrows.

The rocks overlying the concretionary strata, at depths from 222.5 m (730 ft) to 277 m (910 ft) in the core hole (Unit 1 in this report), consist of bioturbated mudrock and interlaminated,

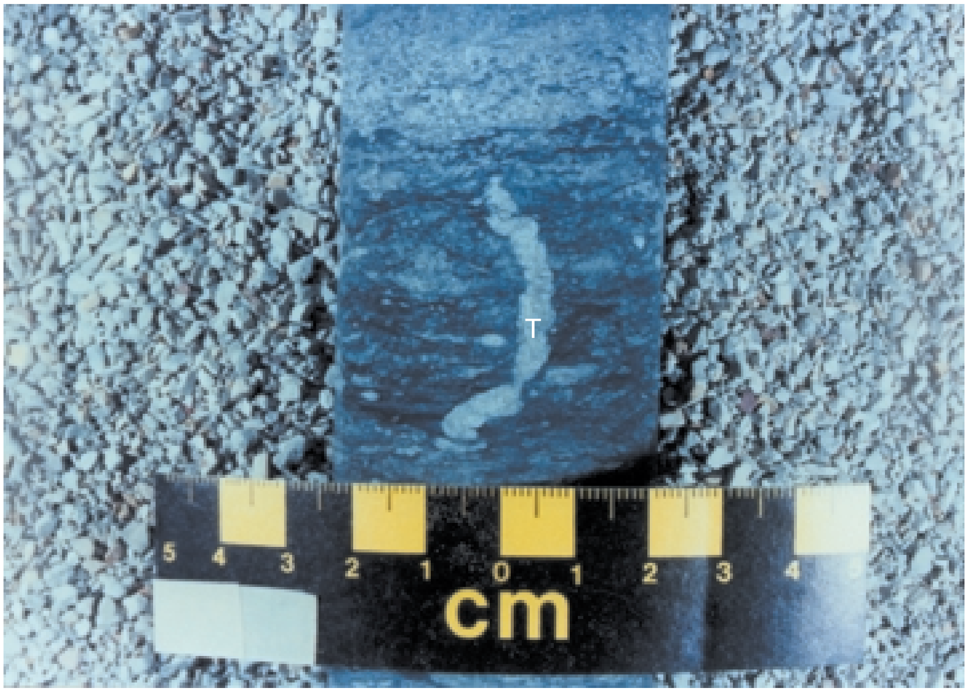


Figure 5. *Teichichnus* (T) in a core of Unit 2 at a depth of 291.2 m (955.5 ft) in USGS Bailey Flats 2, south-central Johnson County, Wyo. Location of corehole shown in figs. 1 and 4; stratigraphy of core shown in fig. 3. Scale in millimeters and centimeters.

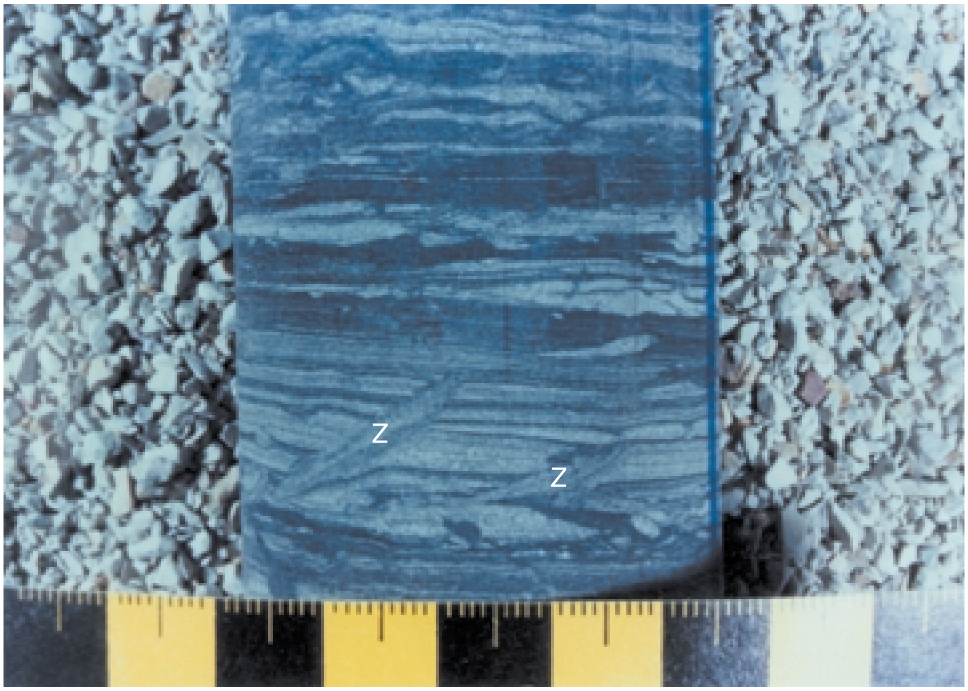


Figure 6. *Zoophycos* (Z) in a core of Unit 2 at a depth of 300.2 m (984.8 ft) in USGS Bailey Flats 2, south-central Johnson County, Wyo. Location of corehole shown in figs. 1 and 4; stratigraphy of core shown in fig. 3. Scale in millimeters and centimeters.

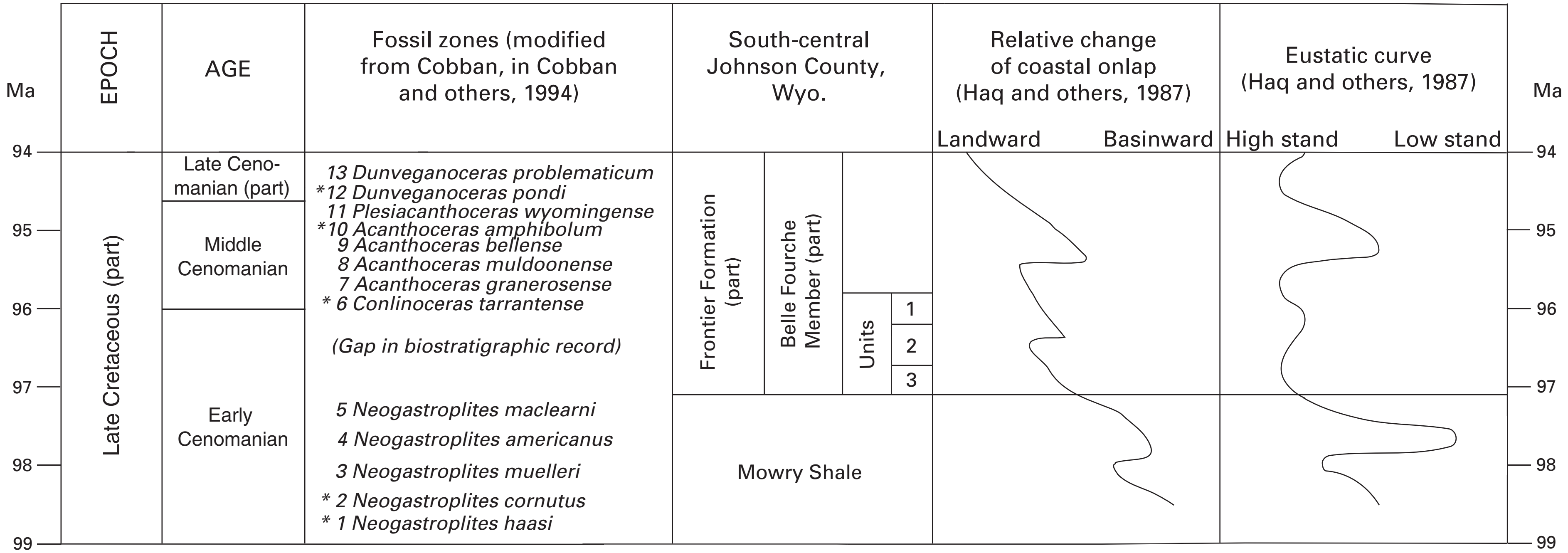
medium-gray to dark-gray shale, siltstone, and very fine to medium grained sandstone, and light-gray bentonite (fig. 3). Some of these rocks are slightly calcareous, and some contain pyrite. The laminae of Unit 1 generally contain trace fossils, mostly *Planolites* but a few *Teichichnus, Terebellina*, and *Zoophycos.* Low diversity assemblages of mainly arenaceous foraminifers (as many as 4 species per sample) in Unit 1 include *Trochammina* sp. A, *Trochammina* sp., *Trochammina rainwateri*, *Miliammina ischnia*, *Ammobaculites impexus*, "polymorphinid", *Rhizammina* sp., *Hormosina* sp., *Psamminopelta* sp., *Haplophragmoides impensus*, *Haplophragmoides* sp. A, and *Verneuilinoides perplexus* (B.R. North and W.G.E. Caldwell, written commun., 1977). Molluscan fossils of earliest middle Cenomanian age, including the ammonite *Borissiakoceras compressum* Cobban (USGS Mesozoic locality D9853, identified by W. A. Cobban in 1976), were found in the core of this sequence at a depth of about 227 m (745 ft). These species belong to a Tethyan fauna (fig. 7; fossil zone 6) that characterizes deposits of the warm, southern part of the Late Cretaceous epeiric sea, near the present-day Gulf of Mexico (Cobban, 1993).

Unit 1 of the core is also divisible into three parts. The basal part is 16.5 m (54 ft) thick and consists mainly of bioturbated, clayey to sandy siltstone that is very slightly pyritic. The middle part of Unit 1 is 31.4 m (103 ft) thick and composed mostly of interlaminated shale, siltstone, and very fine to medium-grained sandstone. These laminae are discontinuous, wavy, and nonparallel; flaser and contorted bedding and small burrows are also present. In the upper part of Unit 1, the rocks are mainly interlaminated shale and siltstone and 7.0 m (23 ft) thick. The laminations in the upper part are discontinuous, wavy, and nonparallel; minor flaser bedding is present. Small burrows are abundant in these rocks and marine molluscan fossils of middle Cenomanian age (fig. 7; fossil zone 6) were found in the uppermost 4.9 m (16 ft) of the unit.

Depositional Environments of Some Cenomanian Rocks

According to Byers and Larson (1979), the uppermost Mowry, which underlies Unit 3 of the Frontier in Johnson County, was deposited in quiet water in a marginally aerobic marine environment, at water depths between 15 and 150 m (49-492 ft). The locations of two early Cenomanian strandlines, a middle Cenomanian strandline, and the core hole in south-central Johnson County (fig. 4) indicate that Units 3 and 2 in the core were deposited in offshore environments, probably during a marine regression, and that Unit 1 was deposited in nearshore environments. Okumura (1994) found that the relative abundance of nonmarine palynomorphs in the core increases gradually upward through the three units, which reflects the increasing proximity of the western shoreline of the seaway to the site of the core hole. Unit 1 was interpreted by Tillman (Tillman and Merewether, 1994) as distal valley fill as well as tidal and storm deposits in bays and estuaries. At outcrops about 10 km (6 mi) south of the core hole, Unit 1 is represented mainly by the sandstone of Frewens Castle which accumulated, according to Willis and others (1999), on the shoreface of a tide-influenced river delta.

The grain sizes of Units 3, 2, and 1 generally increase upward. Unit 2 and most of Unit 1 comprise a sequence much



* Radiometrically dated by Obradovich (1993)

Figure 7. Age and molluscan-fossil sequence for some mid-Cretaceous strata in Johnson County, Wyo., and sea-level curves for part of the mid-Cretaceous.

like the progradational sequence of shale described by Rice and Gautier (1983). The laminae of mudrocks in Unit 3 and the laminae and thin beds of mudrocks and sandstone in Units 2 and 1 are discontinuous and are either even and parallel or wavy and nonparallel; they apparently record variable, mainly weak currents near the seafloor and a prograding western shoreline. All three units contain burrows and Units 2 and 1 are partly bioturbated which suggests intermittent low rates of sedimentation (for this epeiric sea) in oxygen-bearing water. The estimated rate of vertical sedimentation for Units 3, 2, and 1 is about 13 cm (5.1 in.) per thousand years. This value is derived from the total thickness of the units, an estimated 50 percent compaction of the former sediments, and the radiometric ages of bounding beds of bentonite (Obradovich and Cobban, 1975; Fouch and others, 1983; Obradovich, 1993). However, Tillman proposed (Tillman and Merewether, 1994) that Unit 1 includes sequence boundaries and flooding surfaces which probably represent missing thicknesses of strata.

The diversity of trace fossils in the three units is low, typical of either dysaerobic or brackish-water environments (Ekdale and others, 1984, p. 75; Ekdale and Mason, 1988). "Low-diversity assemblages of *Planolites*, *Trichichnus* and/or *Chondrites* are commonly associated with mudrocks" that were deposited in oxygen-deficient, offshore paleoenvironments (Mieras and others, 1993). Most of the trace fossils in the units, *Planolites*, *Chondrites*, *Teichichnus*, and *Zoophycos*, reportedly are abundant in shales that accumulated in poorly oxygenated waters.

Several of the benthic foraminiferal genera in the low diversity assemblages from Units 3 and 1 (B.R. North and W.G.E. Caldwell, written commun., 1977) have been assigned to shallow-water environments (less than 30 m (100 ft) deep) of the shelf (M.A. Carey, oral commun., 1993). Bones of marine reptiles, from an ichthyosaur and an elasmosaur, were found in strata overlying the Mowry Shale in northeastern Wyoming (Nace, 1941; Massare and Dain, 1989).

No molluscan fossils of marine, brackish-water, or freshwater origin have been found in Units 3 and 2 in Johnson County or in laterally equivalent rocks elsewhere in the region (fig. 1). However, if the water in the epeiric sea was less alkaline than normal seawater or was very slightly acidic, as Gill and Cobban (1966) suggested, the paucity of calcareous fossils in these rocks might indicate only low rates of sedimentation. Nevertheless, marine molluscan fossils of late early Cenomanian age have been collected from strata of the boreal sea in west-central Canada (Warren and Stelck, 1958) and from beds of the Tethyan sea in southwestern New Mexico (Cobban, 1987) and western Texas (Böse, 1910; Young, 1958; Cobban and Kennedy, 1989) (fig.8). Marine molluscan fossils of early middle Cenomanian age were collected from the upper part of Unit 1 of the core as well as from many outcrops in the Rocky Mountains (fig. 4; Cobban, 1993).

A sequence of lower Cenomanian strata that includes Unit 2 and a lower part of Unit 1 of the core, between depths of 254 and 312 m (833–1,024 ft) (fig. 3), is confined by two conspicuous beds of bentonite. These bentonites were identified on the geophysical logs of about 300 boreholes scattered throughout northeastern Wyoming and an adjacent area of Montana, and thicknesses of the intervening strata were calculated. The thicknesses of the sequence between the bentonites (fig. 9) range from less than 40 m (130 ft) in Sheridan County, Wyo., and adjoining areas to more than 60 m (200 ft) in the vicinity of Crook County, Wyo., and in parts of Natrona, Converse, and Niobrara Counties, Wyo. The gradual changes in the thickness resemble those of a depositional shelf or possibly a basin. However, in the core hole the strata between depths of 254 m (833 ft) and 261 m (857 ft) were interpreted as tidally influenced valley-fill and those between depths of 261 m (857 ft) and 281 m (923 ft) were interpreted as distal valley-fill and open-bay deposits by R.W. Tillman (Tillman and Merewether, 1994).

Asquith (1970) estimated that the depth of water at the outer edge of a Late Cretaceous shelf in northeastern Wyoming, where the sediments were dominantly clay, is about 60 m (200 ft). Weimer (1984) reported that estimates of the water-depths for Cretaceous shelves generally range from 30 to 90 m (100 to 300 ft). The upper lower Cenomanian rocks in southern Johnson County, Wyo., were deposited near the inner edge of a shelf in shallow water, possibly less than 30 m (100 ft) deep.

Paleogeography of Some Cenomanian Rocks

The Mowry Shale was deposited in early Cenomanian time (Stelck and Armstrong, 1981; Cobban and Kennedy, 1989) in a boreal epeiric sea that extended from the Arctic Ocean to south-central Colorado (fig. 4; Haun and Weimer, 1960). In the Frontier Formation of Johnson County, Wyo., the upper part of Unit 1 accumulated during middle Cenomanian time in an epicontinental sea that extended northward from the Gulf of Mexico to the Arctic Ocean (fig. 4). This part of Unit 1 contains Tethyan molluscan fossils of earliest middle Cenomanian age (zone 6, fig. 7). The strata between the top of the Mowry and the upper part of Unit 1, assigned to Units 3, 2, and the lower part of Unit 1, record deposition generally during a marine regression and a subsequent widespread marine transgression that contributed to the opening of the Late Cretaceous transcontinental seaway (fig.4).

Studies by Eicher (1965, 1967) and Eicher and Diner (1985) of foraminifera in the outcropping lower Cenomanian beds of Colorado, Wyoming, and Montana include two fossil localities in northeastern Wyoming and one in south-central Montana. Eicher (1967) reported that about 90 percent of his samples contained only arenaceous foraminifers, and that foraminifera in northeastern Wyoming are sparse in the lowermost Belle Fourche but increase in abundance and variety upward in the sequence. From their data, Eicher (1967) and Eicher and Diner (1985) concluded that this early Cenomanian assemblage lived in a restricted seaway, probably in poorly oxygenated water of less than normal marine salinity, and that an open sea of normal salinity lay to the south. The data collected during the current investigation are consistent with most of their conclusions.

Analytical Procedures

The mineral constituents of 22 whole-rock samples of core from the lower part of the Belle Fourche Member of the Frontier

Figure 8. Locations of speculative strandlines (dotted lines) for early Cenomanian (lower Belle Fourche Shale) epeiric seas in the mid-continent of North America, of the MacKenzie salient, and of fossiliferous strata (indicated by ●) of early Cenomanian age in southwestern New Mexico and western Texas. Modified from McGookey and others (1972), Williams and Stelck (1975), and Stelck and Armstrong (1981).

Formation (Units 3, 2, and 1; figs. 1, 3) were determined by X-ray diffraction (XRD; tables 1, 2). Amounts of the oxides of major elements in 20 samples of the core (table 3) were measured by X-ray spectroscopy (Taggart and others, 1987). The 20 samples were also analyzed for many elements (table 4) by induction-coupled plasma spectroscopy (Crock and others, 1987). Amounts of sulfur and total carbon (table 5) were determined by combustion with infrared detection; the amount of carbonate carbon was determined by acidification and coulometric titration; and the organic-carbon content was calculated from the amounts of total carbon and carbonate carbon (Jackson and others, 1987).

Organic matter (table 6) was analyzed by using the Rock-Eval procedure of Espitalie and others (1977). In this procedure, amounts of hydrocarbons in the samples are estimated from pyrolysis assays and are reported as S_1 (free or absorbed hydrocarbons in the rock), S_2 (hydrocarbons produced mainly by pyrolysis of solid organic matter), S_3 (carbon dioxide produced by pyrolysis of organic matter), and $T(S_2)$ (temperature of maximum pyrolytic yield) (G.E. Claypool, written commun.,

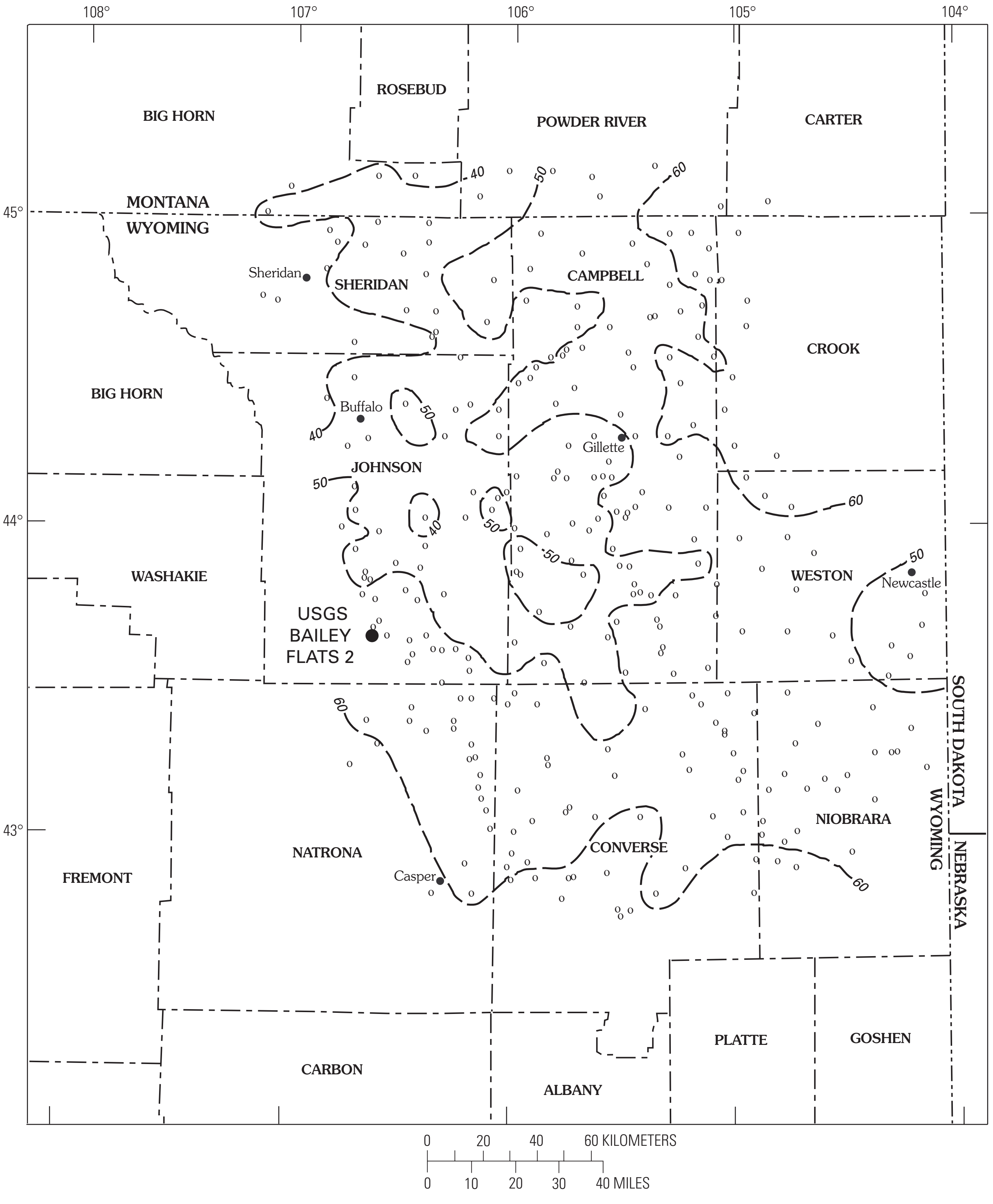


Figure 9. Contours of thickness (m) of some lower Cenomanian strata in northeastern Wyoming and an adjoining part of Montana. Thicknesses determined from geophysical logs of boreholes (o). Location of corehole, USGS Baily Flats 2, in southern Johnson County, Wyo., shown by black dot.

Table 1. Mineral constituents of shale and siltstone in Units 1, 2, and 3 from core of the Frontier Formation, Johnson County, Wyo.

[No entry indicates mineral was not found in sample. Minerals identified using X-ray diffraction. Location of core hole shown in fig. 1; stratigraphic units shown in fig. 3]

Stratigraphic unit	Depth in m	Depth in ft	Quartz	Potassium feldspar	Plagioclase	Kaolinite-chlorite	Illite-montmorillonite	Sodium-montmorillonite	Mixed layer clay	Calcite	Dolomite	Pyrite
Unit 1	222.9	731.2	X	X	X	X	X	X				X
	223	731.6	X	X	X	X	X	X		X	X	X
	228.2	748.7	X	X	X	X	X	X			X	X
	238.1	781	X	X		X	X	X	X			X
	244.9	803.4	X	X	X	X	X		X		X	X
	251.1	823.7	X	X	X	X	X	X	X		X	X
	257.6	845.1	X	X	X	X	X		X		X	X
	263.5	864.5	X	X	X	X	X		X		X	X
	266.2	873.3	X	X	X	X	X		X			X
	271.1	889.5	X	X	X	X	X		X			X
	274.4	900.2	X	X	X	X	X		X			X
	277.1	909	X	X	X	X	X		X			
Unit 2	277.7	911.2	X	X	X	X	X		X			
	282.4	926.6	X	X	X	X	X		X			
	288.5	946.6	X	X	X	X	X		X			
	296.4	972.3	X	X	X	X	X		X			
	301.4	988.7	X	X	X	X	X		X			
	307.7	1009.5	X	X	X	X	X		X			
	309.6	1015.6	X	X	X	X	X	X	X			
Unit 3	312.9	1026.7	X	X	X	X	X		X			X
	314.5	1031.7	X	X	X	X	X		X			X
	317.5	1041.7	X	X	X		X	X				X

Table 2. Mineral constituents of concretions in Unit 2 from core of the Frontier Formation, Johnson County, Wyo.

[More abundant minerals (XX), less abundant minerals (X). No entry indicates mineral was not found in sample. Minerals identified using X-ray diffraction. Location of core hole shown in fig. 1]

No. of samples	Depth in m	Depth in ft	Quartz	Potassium feldspar	Plagioclase	Clay	Calcite	Siderite
1	281.8	924.5	XX		X	X	X	XX
1	282.1	925.5	XX		X	X	X	XX
5	287.2- 287.3	942.2- 942.7	X	X		X	XX	X
6	291.7- 291.9	957.0- 957.8	XX	X	X	X	XX	XX
5	293.1- 293.2	961.6- 962	XX	XX	X	X		XX
5	306.7- 306.9	1006.2- 1006.8	XX	X	X	X	XX	XX

Table 3. Content, in weight percent, of major element oxides in shale and siltstone of Units 1, 2, and 3 from core of the Frontier Formation, Johnson County, Wyo.

[All oxides determined by X-ray fluorescence spectroscopy. Location of core hole shown in fig. 1; stratigraphic units shown in fig. 3]

Stratigraphic unit	Depth, in m	Depth, in ft	SiO_2	Al_2O_3	$FeTO_3$	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
Unit 1	223	731.6	69.3	12.6	3.11	1.49	0.98	1.53	2.27	0.5	0.16
	228.2	748.7	63.5	14.7	3.95	1.62	0.67	1.26	3.23	0.59	0.18
	238.1	781	63.8	16.2	3.81	1.25	0.64	1.41	2.88	0.55	0.14
	244.9	803.4	66.4	14.4	3.9	1.2	0.72	1.38	2.57	0.62	0.15
	251.1	823.7	64.8	14.9	4.11	1.4	0.64	1.33	2.68	0.6	0.16
	257.6	845.1	71.7	12.5	3	0.88	0.37	0.94	2.97	0.57	0.17
	263.5	864.5	72.7	11.6	3.71	1.01	0.52	1.23	2.19	0.47	0.17
	266.2	873.3	69.6	12.9	3.73	1.17	0.51	1.33	2.31	0.5	0.18
	271.1	889.5	68.7	14	3.69	1.02	0.42	1.08	3.16	0.55	0.16
	274.4	900.2	69.4	13.7	3.47	1.04	0.34	0.97	3.57	0.56	0.16
Unit2	277.7	911.2	67.1	14.8	3.77	1.2	0.46	1.21	2.96	0.52	0.14
	282.4	926.6	68.8	14.2	3.29	1.11	0.53	1.31	2.44	0.5	0.14
	288.5	946.6	68	14.7	2.92	1.01	0.44	1.11	3.56	0.58	0.13
	296.4	972.3	71.1	13.3	3.15	0.91	0.59	1.26	2.65	0.48	0.13
	301.4	988.7	70.9	13.3	3.03	0.95	0.62	1.59	1.97	0.42	0.11
	307.7	1009.5	66.8	15.4	3.36	1.03	0.38	1.18	3.1	0.52	0.1
	309.6	1015.6	64.2	16.4	4.04	1.14	0.39	1.25	2.43	0.47	0.1
Unit3	312.9	1026.7	68.8	13.9	3.61	0.97	0.47	1.1	2.84	0.49	0.12
	314.5	1031.7	66.9	14.8	3.6	1.02	0.41	1.17	2.83	0.49	0.11
	317.5	1041.7	72.8	11.9	2.21	0.94	0.45	1.89	0.84	0.18	0.07
Unit 1, mean			68	13.8	3.65	1.21	0.58	1.25	2.78	0.55	0.16
std. dev.			3.2	1.4	0.36	0.24	0.19	0.19	0.46	0.05	0.01
Unit 2, mean			68.1	14.6	3.37	1.05	0.49	1.27	2.73	0.5	0.12
std. dev.			2.4	1.1	0.41	0.11	0.1	0.15	0.52	0.05	0.02
Unit 3, mean			69.5	13.5	3.14	0.98	0.44	1.39	2.17	0.39	0.1
std. dev.			3	1.5	0.81	0.04	0.03	0.44	1.15	0.18	0.03

Table 4. Elements in shale and siltstone (in parts per million) of Units 1, 2, and 3 from core of the Frontier Formation, Johnson County, Wyo.

[Elements identified by induction-coupled plasma spectroscopy. Location of core hole shown in fig. 1; stratigraphic units shown in fig. 3]

Stratigraphic unit	Depth, in m	Depth, in ft	Mn, in ppm	Ba, in ppm	Be, in ppm	Ce, in ppm	Co, in ppm	Cr, in ppm	Cu, in ppm	Ga, in ppm	La, in ppm	Li, in ppm	Nb, in ppm	Nd, in ppm	Ni, in ppm	Pb, in ppm	Sc, in ppm	Sr, in ppm	Th, in ppm	V, in ppm	Y, in ppm	Yb, in ppm	Zn, in ppm
Unit 1	223	731.6	110	690	2	69	9	77	25	19	41	41	10	30	33	24	11	210	14	120	20	2	96
	228.2	748.7	130	630	3	62	7	75	41	18	36	41	10	29	30	20	10	200	12	100	18	2	85
	238.1	781	130	650	3	110	9	70	32	21	62	46	17	58	29	26	13	230	16	110	51	4	120
	244.9	803.4	150	640	2	79	8	56	55	18	46	36	13	36	22	21	9	220	14	85	20	2	73
	251.1	823.7	90	600	2	76	7	53	26	16	44	33	9	35	22	20	9	210	13	83	21	2	82
	257.6	845.1	100	590	2	65	9	69	25	17	39	36	7	31	28	23	10	130	12	100	20	2	96
	263.5	864.5	76	600	2	61	7	64	19	15	36	30	4	31	21	16	8	170	13	89	22	2	81
	266.2	873.3	72	620	2	65	7	68	20	17	38	30		30	23	17	8	180	14	92	22	2	78
	271.1	889.5	83	700	3	72	12	82	27	19	42	40	9	37	34	22	11	170	15	120	25	2	120
	274.4	900.2	78	640	2	66	13	78	29	19	39	37	5	32	37	23	11	150	13	120	22	2	110
Unit 2	277.7	911.2	77	680	3	75	12	93	30	21	44	41	12	37	44	24	12	190	18	110	24	3	120
	282.4	926.6	170	680	3	72	7	68	25	19	43	33	4	35	25	21	9	200	17	97	22	2	96
	288.5	946.6	250	620	3	69	10	86	32	20	41	37	8	34	34	22	12	170	12	110	22	2	110
	296.4	972.3	150	660	3	72	10	64	25	18	42	33	8	34	31	23	9	180	15	92	22	2	110
	301.4	988.7	160	680	3	77	7	52	20	19	45	27	13	37	25	23	8	220	19	75	26	3	98
	307.7	1009.5	160	580	3	73	13	84	28	22	44	40	12	36	35	20	12	180	15	100	22	2	87
	309.6	1015.6	280	560	3	72	10	71	35	22	43	44	11	34	28	22	11	180	15	90	24	2	120
Unit 3	312.9	1026.7	76	550	3	67	7	66	25	18	40	36	8	32	26	19	10	170	12	88	22	2	92
	314.5	1031.7	88	540	3	70	8	62	32	19	41	36	9	33	24	22	10	160	14	85	22	2	99
	317.5	1041.7	51	1400	4	68	4	19	11	17	38	33	9	32	10	26	5	260	22	24	37	4	64
Unit 1, mean			102	636	2	72	9	69	30	18	42	37	9	35	28	21	10	187	14	102	24	2	94
std. dev.			27	37	0	14	2	9	11	2	8	5	4	9	6	3	2	32	1	15	10	1	17
Unit 2, mean			178	637	3	73	10	74	28	20	43	36	10	35	32	22	10	189	16	96	23	2	106
std. dev.			67	51	0	3	2	14	5	2	1	6	3	1	7	1	2	17	2	12	2	0	13
Unit 3, mean			72	830	3	68	6	49	23	18	40	35	9	32	20	22	8	197	16	66	27	3	85
std. dev.			19	494	1	2	2	26	11	1	2	2	1	1	9	4	3	55	5	36	9	1	19

Table 5. Sulfur and carbon (in weight-percent) in shale and siltstone of Units 1, 2, and 3 from core of the Frontier Formation, Johnson County, Wyo.

[Total sulfur and total carbon by combustion with infrared detection; carbonate carbon by acidification and coulometric titration; organic carbon, calculated amounts of total and carbonate carbon using method of Jackson and others (1987). Location of core hole shown in fig. 1; stratigraphic units shown in fig. 3]

Stratigraphic unit	Depth, in m	Depth, in ft	Total S	Total C	Organic C	Carbonate C
Unit 1	223	731.6	0.6	1.36	1.17	0.19
	228.2	748.7	1	2.14	2.04	0.1
	238.1	781	0.84	1.82	1.8	0.02
	244.9	803.4	0.77	1.66	1.58	0.08
	251.1	823.7	0.97	1.9	1.82	0.08
	257.6	845.1	0.9	1.18	1.18	0
	263.5	864.5	1.01	1.08	1.06	0.02
	266.2	873.3	0.83	1.44	1.42	0.02
	271.1	889.5	0.64	1.26	1.24	0.02
	274.4	900.2	0.36	1.41	1.39	0.02
Unit 2	277.7	911.2	0.09	1.58	1.55	0.03
	282.4	926.6	0.06	1.43	1.38	0.05
	288.5	946.6	0.06	1.55	1.49	0.06
	296.4	972.3	0.1	1.23	1.18	0.05
	301.4	988.7	0.11	1.02	0.96	0.06
	307.7	1009.5	0.08	1.45	1.41	0.04
	309.6	1015.6	0.08	1.52	1.46	0.06
Unit 3	312.9	1026.7	0.49	1.34	1.32	0.02
	314.5	1031.7	0.44	1.68	1.66	0.02
	317.5	1041.7	0.21	0.92	0.87	0.05
Unit 1, mean			0.79	1.53	1.47	0.06
std. dev.			0.21	0.34	0.33	0.06
Unit 2, mean			0.08	1.4	1.35	0.05
std. dev.			0.02	0.2	0.21	0.01
Unit 3, mean			0.38	1.31	1.28	0.03
std. dev.			0.15	0.38	0.4	0.02

1984). The genetic potential or total hydrocarbon yield ($S_1 + S_2$) is a semiquantitative determination of the original hydrocarbon-generating capacity of the sampled rock. The hydrogen index (HI), which is the pyrolytic hydrocarbon yield (S_2) normalized by the organic carbon content, is used to determine the type of organic matter in the sample. Similarly, the oxygen index (OI) is the pyrolytic organic CO_2 yield (S_3) normalized by the organic carbon content, which also helps to evaluate the type of organic matter. The transformation ratio or production index ($S_1/S_1 + S_2$), as well as the temperature of maximum pyrolytic yield [$T(S_2)$], reflect the thermal maturity of the sampled strata.

The core of Unit 2 contains many concretions, most of which are cemented by siderite and calcite. Samples were collected from vertical profiles through most of the concretions; several samples were collected from each concretion. The samples and their depths within the core are listed in tables 2 and 7. Each sample was crushed and ground in a porcelain mill for standard mineral analysis by X-ray diffraction and for stable carbon and oxygen isotopic analysis. Amounts of carbon and oxygen isotopes were measured using a double-collecting, isotope-ratio, Finnigan MAT mass spectrometer on CO_2 generated by reacting about 50 mg of crushed sample with an excess of 100 percent phosphoric acid (McCrea, 1950). The samples of siderite were reacted for six days at 25°C and no fractionation factor was applied (as would be necessary at higher temperatures of reaction) to the δ^{18} O data; samples of calcite were treated similarly. All carbon and oxygen isotope data are reported with reference to the PDB-University of Chicago standard. For most samples, stable carbon and oxygen isotopic compositions of either calcite or siderite were measured; in several samples however, significant amounts of both calcite and siderite were recognized. In such samples, separation and collection of CO_2 gas from both carbonates was attempted by means of a differential dissolution procedure whereby CO_2

Table 6. Pyrolitic data from shale and siltstone of Units 1, 2, and 3 in core of the Frontier Formation, Johnson County, Wyo.

[Determined with Rock-Eval procedures of Espitalie and others (1977). TOC, total organic carbon in percent; Tmax, temperature of maximum yield of hydrocarbons during pyrolysis in degrees C; HI, hydrogen index (mg HC/g TOC); OI, oxygen index (mg CO_2/g TOC); PI, production index (S_1/S_1+S_2); S_1, S_2, S_3, mg of HC or CO_2/g rock]

Stratigraphic unit	Depth, in m	Depth, in ft	TOC	T_{max}	HI	OI	PI	S_1mg/g	S_2mg/g	S_3mg/g
Unit 1	223	731.6	1.29	426	51	27	0	0	0.67	0.35
	228.2	748.7	1.33	427	87	24	0.04	0.05	1.17	0.32
	238.1	781	1.47	431	68	23	0.01	0.01	1	0.35
	244.9	803.4	1.23	430	83	35	0.03	0.03	1.03	0.44
	251.1	823.7	1.34	439	59	29	0.06	0.05	0.8	0.4
	257.6	845.1	1.2	430	103	27	0.03	0.04	1.24	0.33
	263.5	864.5	1.26	425	78	28	0.03	0.03	0.99	0.36
	266.2	873.3	1.24	429	79	33	0.01	0.01	0.99	0.41
	271.1	889.5	1.45	430	60	26	0	0	0.88	0.38
	274.4	900.2	1.43	433	91	27	0.01	0.01	1.31	0.39
Unit 2	277.7	911.2	1.64	434	117	25	0.01	0.01	1.93	0.41
	282.4	926.6	1.41	432	109	28	0	0	1.55	0.4
	288.5	946.6	1.71	432	119	26	0	0.01	2.05	0.45
	296.4	972.3	1.55	431	129	27	0	0.01	2.01	0.42
	301.4	988.7	0.81	428	86	43	0.01	0.01	0.7	0.35
	307.7	1009.5	1.46	431	89	28	0.02	0.03	1.3	0.41
	309.6	1015.6	1.64	431	75	28	0.01	0.01	1.24	0.46
Unit 3	312.9	1026.7	1.09	430	112	30	0.01	0.01	1.23	0.33
	314.5	1031.7	1.42	433	179	26	0.01	0.02	2.55	0.37
	317.5	1041.7	0.76	422	88	40	0.03	0.02	0.67	0.31
Unit 1, mean			1.32	430	76	28	0.02	0.02	1.01	0.37
std. dev.			0.1	4	16	4	0.02	0.02	0.2	0.04
Unit 2, mean			1.46	431	103	29	0.01	0.01	1.54	0.41
std. dev.			0.31	2	20	6	0.01	0.01	0.5	0.04
Unit 3, mean			1.09	428	126	32	0.02	0.02	1.48	0.34
std. dev.			0.33	6	47	7	0.01	0.01	0.97	0.03

released during the first hour of phosphoric-acid digestion is regarded as being derived entirely from calcite. Any CO_2 collected between one and two hours is discarded and CO_2 collected after two hours is regarded as derived entirely from siderite.

Composition

The composition of the 20 samples of the Belle Fourche Member from Johnson County, Wyo., was compared to the composition of 134 samples of marine rocks and 58 samples of nonmarine rocks from the Upper Cretaceous Pierre Shale and equivalent strata in Montana, North Dakota, and South Dakota described by Schultz and others (1980, table 14). The shale and siltstone of the Pierre and equivalent beds were assigned to several categories of marine and nonmarine rocks. The compositions of the three units of the Belle Fourche Member are similar to those of marine rocks of the Pierre except for the amounts (arithmetic means) of SiO_2, CaO, carbonate carbon, and manganese. The mean content of SiO_2 is larger in the three units (about 68–70 percent) than in the Pierre (about 61 percent), although the SiO_2 content of the units is similar to that of marine siliceous shale (67 percent, 7 samples) in the Pierre. Average amounts of CaO in the three units are 0.44–0.58 percent; significantly less than the 1.9 percent in most marine shale and siltstone of the Pierre; however, marine shale overlying bentonite in the Pierre (6 samples) contains 0.72 percent CaO.

Silica, iron, phosphorus, and dissolved organic matter are more abundant and calcium and sulfate are less abundant in river water than in seawater, according to Liss (1976) and Berner and Berner (1996). Mean amounts of carbonate carbon in the units (0.03–0.06 percent) are also much lower than the

Table 7. Isotopic values for carbon and oxygen in calcareous and sideritic concretions of unit 2 in core of the Frontier Formation, Johnson County, Wyo.

[Values determined by mass spectroscopy. Standard NBS19 relative to PDB: Δ^{13} C+1.95/mil; Δ^{18} 0-2.20/mil]

Depth, in m (ft)	Δ^{13} C- CALCAREOUS	Δ^{18} O- CALCAREOUS	Δ^{13} C- SIDERITIC	Δ^{18} O- SIDERITIC
281.8 (924.5)			-3.82	-6.85
282.1 (925.5)			-1.42	-6
287.2-287.3	0.48	-9.57		
(942.2-942.7)	0.29	-9.71		
	0.38	-9.76		
	1.49	-9.63		
	1.17	-9.59		
291.7-291.9	-13.62	-11.6	-10.99	-10.61
(957-957.8)	-12.5	-11.27	-7.7	-7.74
			-1.77	-6.76
			-2.03	-6.32
			-6.29	-8.01
	-12.49	-11.5		
293.2 (962.0)			7.93	-9.1
			8.25	-7.97
			4.33	-8.92
306.7-306.9	-15.25	-12.09	-5.59	-9.52
(1006.2-1006.8)				
			-5.91	-7.98
			-4.53	-7.67
			-6.59	-8.95
	-18.67	-12.5	-2.13	-10.53

mean amount in marine shale and siltstone of the Pierre (0.45 percent, 134 samples), except for marine shale overlying bentonite (0.07 percent, 6 samples). The low values for CaO and carbonate carbon in the units probably reflect the dearth of calcite in the sequence and the exclusion of data from the concretions in Unit 2. The mean content of manganese in the units is 72–178 ppm. In marine shale and siltstone of the Pierre (134 samples), the average manganese content is 750 ppm, although the average manganese content of marine shale overlying bentonite (6 samples) is 135 ppm.

The lithologic differences between the concretionary strata (Unit 2 of the Belle Fourche Member) and the underlying and overlying rocks (Unit 3 and Unit 1 of the Belle Fourche, respectively), which are noticeable at outcrops, correspond to differences in the mineralogical and chemical composition of core from the three units. Mineral constituents of 22 samples of the core are listed in table 1. Samples of the laminae and beds generally contain quartz, potassium feldspar, plagioclase, kaolinite-chlorite, illite-montmorillonite, and other mixed-layer clays. Several of these samples include sodium montmorillonite. Most of the clays probably formed during early diagenesis. The three samples from Unit 3 also contain pyrite and possibly minor dolomite. Pyrite and dolomite were found in most of the samples from Unit 1 but were not confirmed in the seven samples from Unit 2. Most of the concretions in Unit 2 contain quartz, plagioclase, clay, calcite, and siderite; several of them also contain potassium feldspar (table 2).

Amounts of the oxides of major elements in 20 samples of the core are shown in table 3. The major-element compositions of samples from the three units, excluding the concretions in Unit 2, are very similar, although the content of P_2O_5 seems to decrease slightly with depth (fig. 10). The P_2O_5 in these rocks could be in constituent clay minerals, volcanogenic apatite, and biogenic apatite, as suggested by Schultz and others (1980, p. B59).

The 20 samples of core, excluding those from concretions, were also analyzed for chemical elements. Mean amounts of the elements in Units 3, 2, and 1 vary slightly, although not significantly, with the depth and age of the units (table 4). Nevertheless, the mean content of manganese is greater in Unit 2 than in Units 1 and 3 (fig. 11). Amounts of boron and vanadium in sedimentary rocks have been used to indicate the salinity of basin waters and to separate marine and nonmarine depositional environments (Potter and others, 1963). For these samples, the boron content was not determined and the vanadium content ranges from 24 ppm to 120 ppm, which is significantly less than the values (226–353 ppm) reported by Leckie and others (1990) for estuarine, restricted marginal marine, and open-marine shales of the Cretaceous Shaftesbury Formation in Alberta.

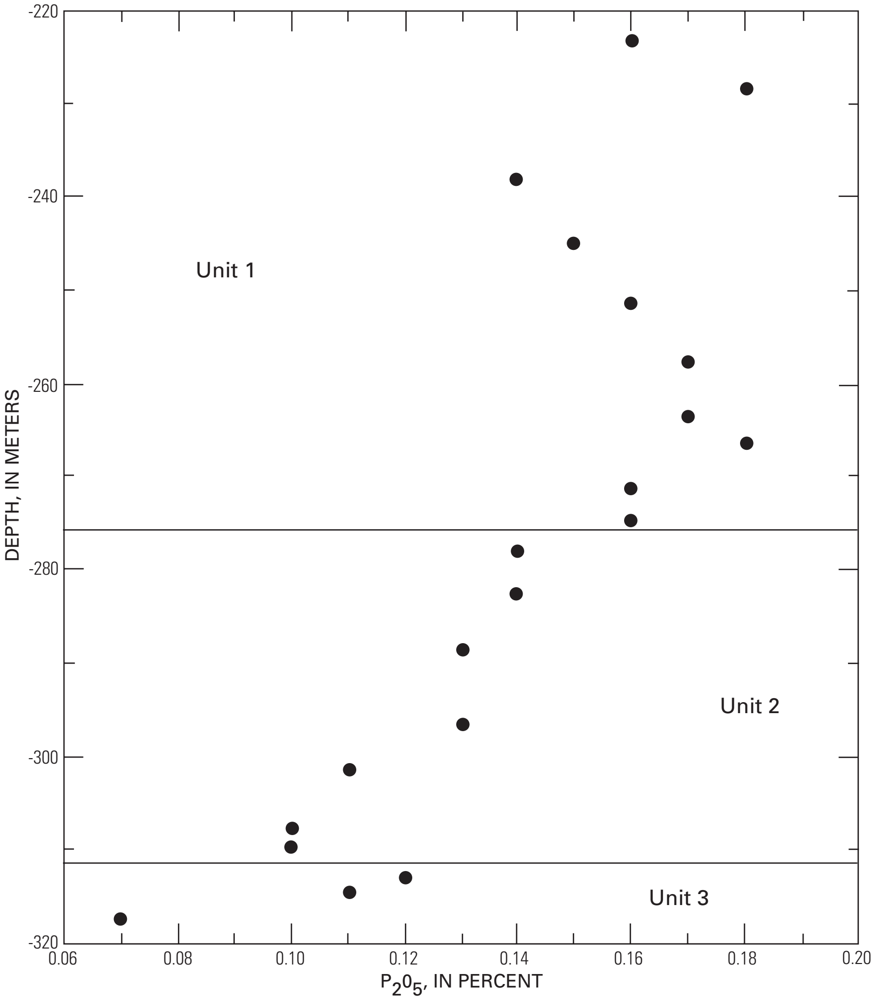


Figure 10. Depth profile for the phosphate (P_2O_5) content of 20 samples of core from the Frontier Formation of Johnson County, Wyo. Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

The amounts of sulfur and carbon in the 20 samples are listed in table 5. Mean values for total carbon, organic carbon, and carbonate carbon in each of the three units, not including data from the concretions in Unit 2, are only slightly different. The sulfur content, however, is much lower in Unit 2 than in Units 1 and 3 (fig. 12).

The amount and character of the organic matter in the three cored units are represented in table 6. The content of total organic carbon (TOC) ranges from 1.20 to 1.47 percent (mean is 1.32 percent) for Unit 1, from 0.81 to 1.71 percent (mean is 1.46 percent) for Unit 2, and from 0.76 to 1.42 percent (mean is 1.09 percent) for Unit 3. For the samples from each unit, the mean temperature of maximum pyrolytic yield (Tmax) ranges from 428°C to 432 °C, and is slightly less than the temperature of 435°C that generally represents the initial generation of oil in source rocks.

Average amounts of free or absorbed hydrocarbons in samples of the units (S_1) range from about 0.01 to 0.02 mg/g. The mean amounts of hydrocarbons produced mainly by pyrolysis of solid organic matter in the units (S_2) range from 1.01 to 1.54 mg/g. Mean amounts of carbon dioxide produced by pyrolysis of organic matter (S_3) in the three units range from 0.34 to 0.41 mg/g. The production index (PI) is S_1/S_1+S_2 and, where averaged for each unit, ranges from 0.01 to 0.02. These values are less than the PI of about 0.1 that indicates the transition from thermal immaturity to thermal maturity and the beginning of oil generation. Means of the hydrogen index (HI; S_2/organic C content) and the oxygen index (OI; S_3/organic C content) for the three units range from 76 to 126 and 28 to 32, respectively, and both indices increase with depth. The organic material in the units, as indicated by the values for HI and OI, is hydrogen poor and could be dominantly humic (Type III kerogen). The pyrolysis data suggest that the sampled beds are humic rich and gas prone but poor source rocks and thermally immature. Humic, continentally derived, organic matter is less reactive than marine organic matter which can limit the formation of pyrite in the host sediments (Davis and others, 1988). The organic carbon contents (TOC) of all samples of the three units are less than 2 percent and the hydrogen indices (HI) of nearly all of the samples from Unit 1 are less than 100 which could indicate that the organic matter in Unit 1 is refractory (Dean and Arthur, 1989). However, the nature of the organic carbon did not prevent the formation of pyrite in Unit 1.

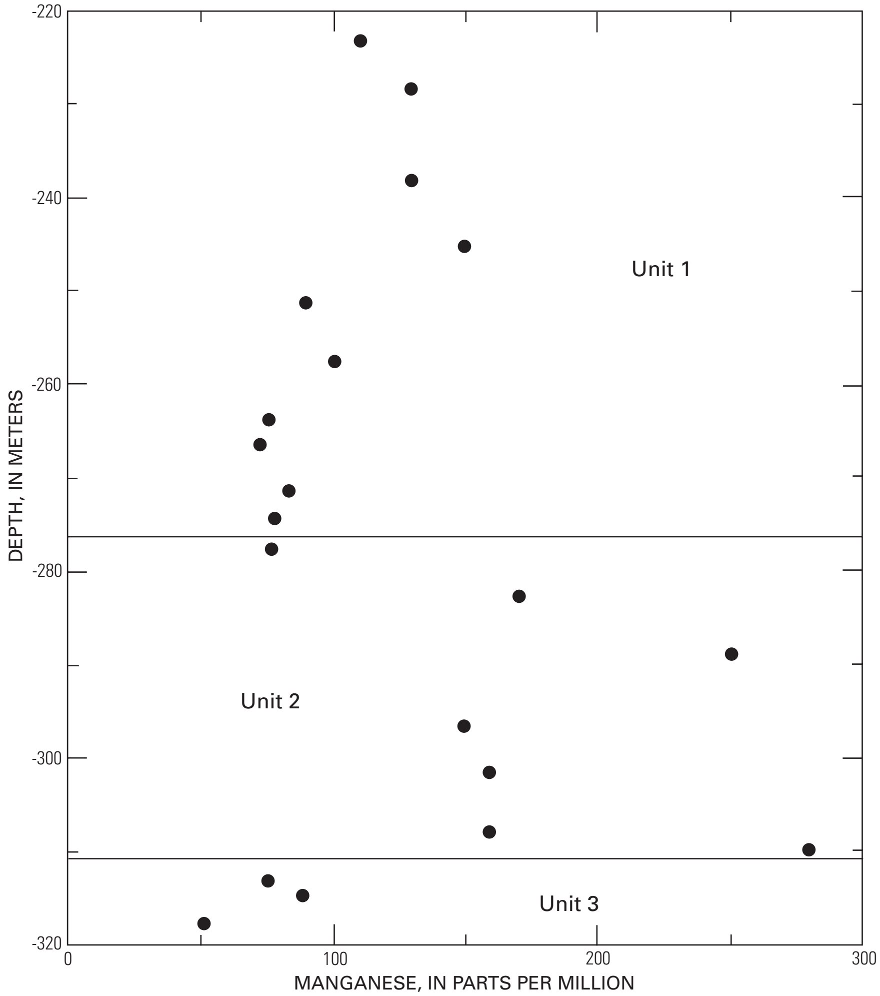


Figure 11. Depth profile for the manganese content of 20 samples of core from the Frontier Formation of Johnson County, Wyo. Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

The three samples of Unit 3 in the Belle Fourche, from the core hole in Johnson County, Wyo., contain the mean amounts of 2.23 percent Fe, 0.38 percent total S, and 1.28 percent organic carbon, and have a mean value for HI of 126 (tables 4-6). Analytical data representative of the underlying Mowry, from twenty samples of core from depths of 1,540–1,558 m (5,052–5,110 ft) in Powder River County, Mont. (fig. 1), include mean values of 2.56 percent Fe, 1.50 percent total S, and 2.80 percent organic carbon, and have a mean value for HI of 271 (Dean and Arthur, 1989, table 4). In the two groups of samples, the amount of iron is similar but the amounts of sulfur and organic carbon are generally larger in the samples from Powder River County. The HI value from Powder River County is also larger than the value from Johnson County; it suggests more hydrogen-rich, reactive, organic matter, probably of marine origin.

The chemical composition of the three units varies slightly but significantly. The amounts of iron (3.14–3.65 percent Fe_2O_3) and organic carbon (TOC, 1.09–1.46 percent) in the units are similar, but the mean values for sulfur content (0.08–0.79 percent), manganese content (72–178 ppm), and HI (76–126) are different. Sulfur is much less abundant in Unit 2 (0.08 percent) than in Unit 1 (0.79 percent) and Unit 3 (0.38 percent). Sulfur values of less than 0.2 percent are found in rocks from continental fresh-water environments (Schultz and others, 1980, p. B53, table 14). Manganese is slightly more abundant in Unit 2 (178 ppm), which contains sideritic and calcitic concretions, than in Unit 1 (102 ppm) and Unit 3 (72 ppm). The mean HI values are 76 for Unit 1, 103 for Unit 2, and 126 for Unit 3 (table 6). In mudrocks that have an organic carbon content of less than 2 percent and an HI of less than 100, the organic matter is highly refractory (Dean and Arthur, 1989). Consequently, the organic matter in at least Unit 1 apparently is highly refractory and probably not suitable for bacterial metabolism.

Geochemistry of Carbon, Sulfur, and Iron and Authigenic Carbonates

The wide geographic occurrence of the distinctive unit of nonfossiliferous, sideritic mudrocks in the lower part of the Belle Fourche Member of the Frontier Formation and in

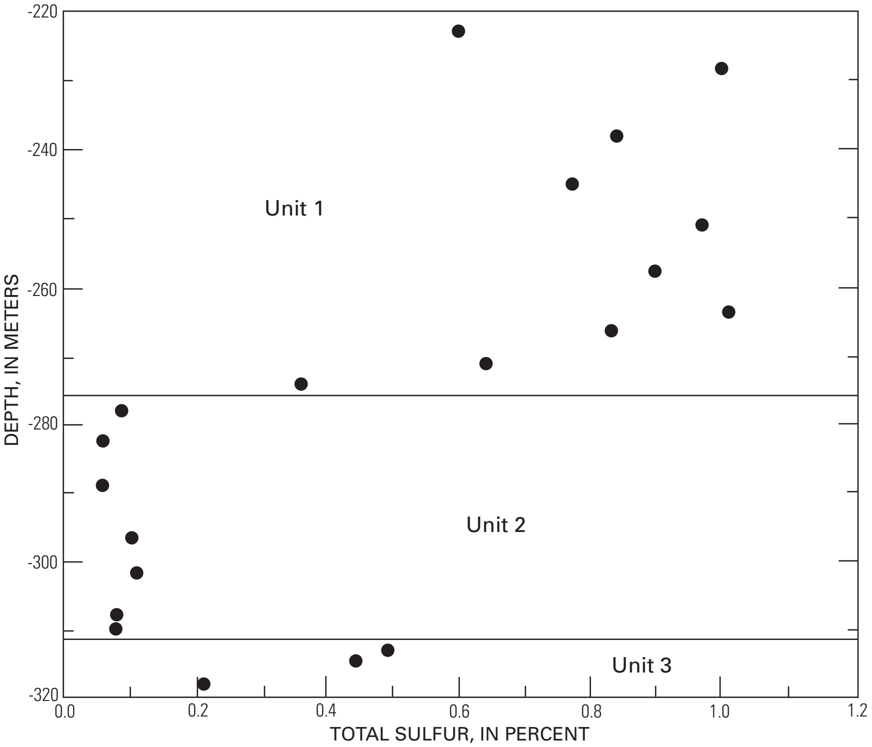


Figure 12. Depth profile for the sulfur content of 20 samples of core from the Frontier Formation of Johnson County, Wyo. Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

laterally equivalent formations indicates that the diagenetic features of these rocks reflect critical stratigraphic and paleoenvironmental changes that occurred during the transition between deposition of the marine Mowry Shale and deposition of marine beds near the middle of the Belle Fourche. In the following paragraphs, the origin of the sideritic rocks in the lower part of the Belle Fourche Member is described, discussed, and interpreted in terms of the geochemistry of carbon, sulfur, and iron in the mudstone and the mineralogic and stable isotopic compositions of the carbonate minerals.

The core of Unit 2 includes six concretions that commonly contain quartz, plagioclase, potassium feldspar, siderite, calcite, and clay (table 2). However, the mineral composition varies, both between and within the concretions. In the concretions at depths of 281.8 m (924.5 ft) and 282.1 m (925.5 ft), siderite and quartz are the most abundant minerals. At depths of 287.2–287.3 m (942.2–942.7 ft), the concretion contains a large amount of calcite but includes important amounts of siderite and quartz in the upper part. At depths of 291.7–291.9 m (957.0–957.8 ft), the lowermost and uppermost parts of the concretion contain abundant quartz, calcite, and feldspar; the middle parts contain abundant quartz, siderite, and feldspar. The concretion at depths of 293.1–293.2 m (961.6–962.0 ft) contains much quartz, siderite, and feldspar in the lower part and much quartz, feldspar, and clay in the upper part. At depths of 306.7–306.9 m (1006.2–1006.8 ft), the outermost parts of the concretion contain abundant quartz, siderite, feldspar, and calcite; the interior of the concretion contains much quartz, siderite, and feldspar.

Carbon, Sulfur, and Iron Geochemistry

All of the core samples from Johnson County contain iron far in excess of that in stoichiometric pyrite (S/Fe=1.15); iron therefore probably was not a limiting component in the diagenetic evolution of these rocks (fig. 13). Sulfur, however, exhibits significant variation, in that it is highly depleted in samples from Unit 2 of the Belle Fourche. The samples from Units 3 and 1 of the Belle Fourche contain carbon and sulfur in abundances similar to those in normal marine rocks, although as a group these samples show a large amount of scatter resulting from variations in sulfur content. Samples from Unit 2, however, are uniformly depleted in sulfur and plot on a sulfur/carbon diagram (fig. 14) and on a sulfur-iron-carbon ternary diagram (fig. 15) where values from nonmarine rocks generally occur (Berner and Raiswell, 1984; Dean and Arthur, 1989). Both the relative abundance of sulfur compared to iron and carbon and the absolute abundance of sulfur are very low in the rocks of Unit 2.

Sulfur in argillaceous rocks such as those of this study is contained mainly in pyrite that formed in the sulfate-reduction zone (Berner, 1984) during early diagenesis. Low amounts of sulfide sulfur in shale can result from several causes. (1) The organic matter in the original sediment at the onset of sulfate reduction was of such low abundance or so metabolically refractory as to be an unsuitable substrate for bacterial activity. (2) The amount of aqueous sulfate available to the sulfate-reducing

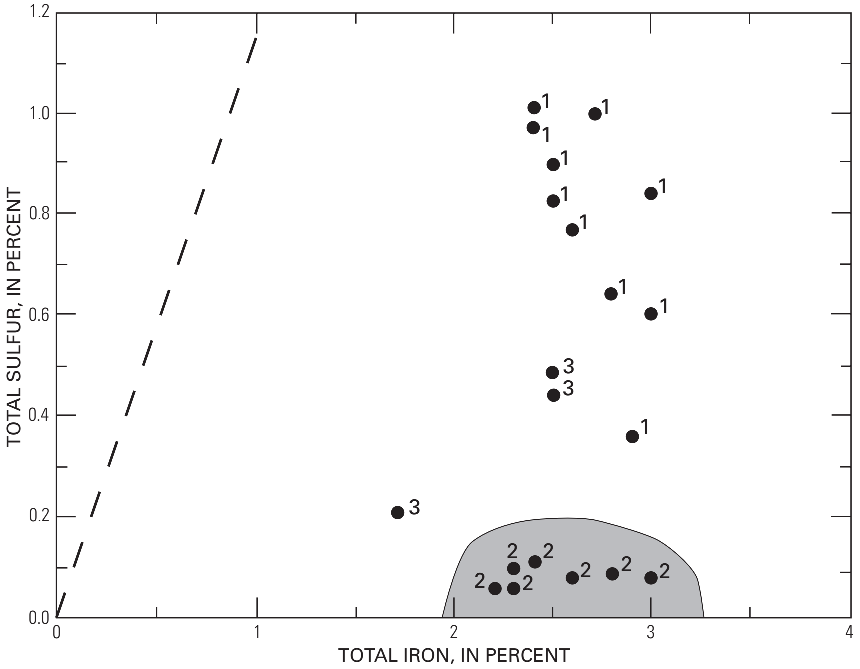


Figure 13. Comparison of the values for the amounts of total sulfur and total iron for 20 samples of core from Units 1, 2 (shaded), and 3 of the Frontier Formation, Johnson County, Wyo. The dashed line is the stoichiometric line for pyrite (FeS_2). Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

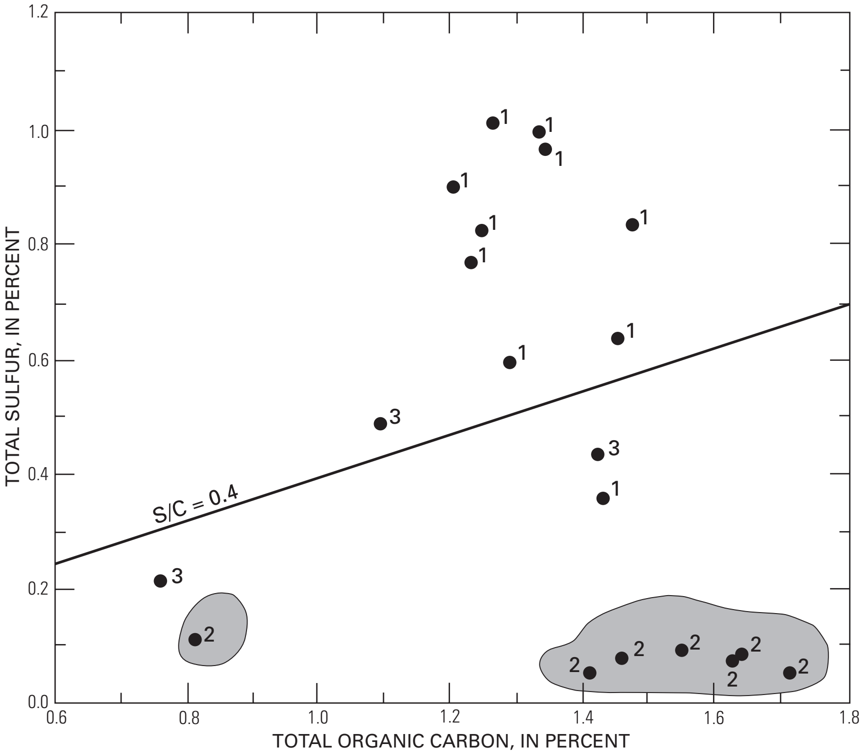


Figure 14. Comparison of the amounts of total sulfur and total organic carbon in 20 samples of core from Units 1, 2 (shaded), and 3 of the Frontier Formation, Johnson County, Wyo. S/C = 0.4, an average value for Holocene sediments that contain appreciable organic matter and were deposited in oxic marine environments (Sweeney, 1972). Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

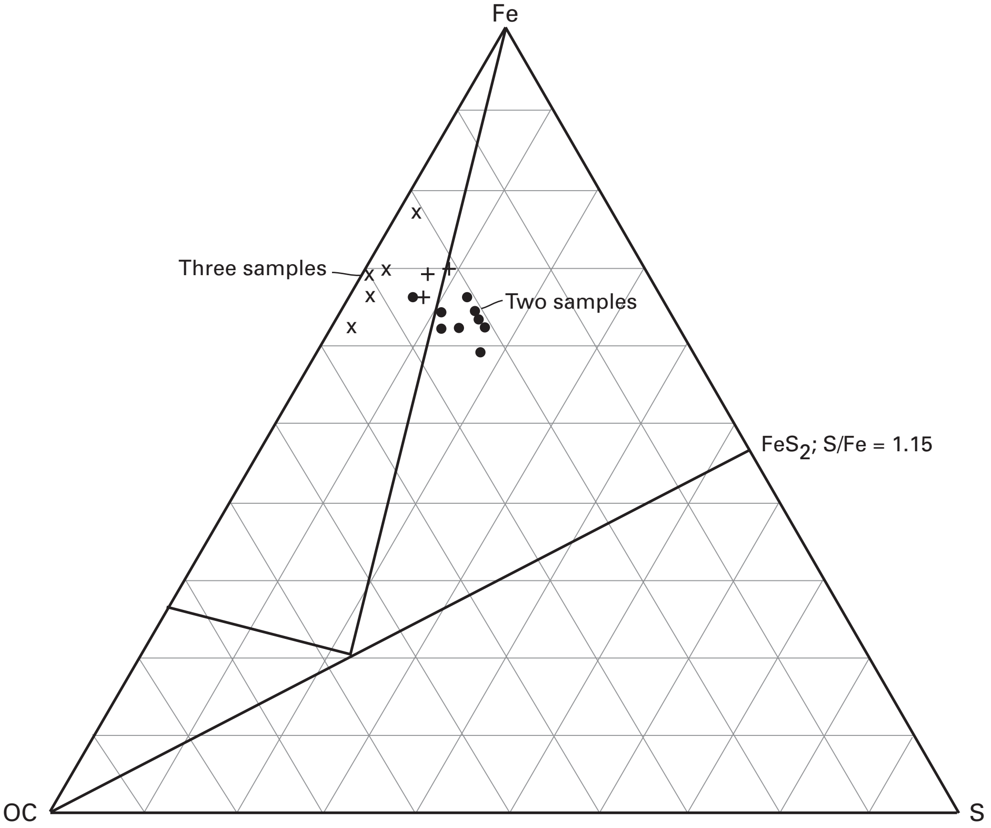


Figure 15. Comparison of the amounts of iron, organic carbon, and total sulfur in 20 samples of core rom Unit 1 (●), Unit 2 (x), and Unit 3 (+) of the Frontier Formation, Johnson County, Wyo. Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

bacteria was so low as to provide a limit on their activity and thus on the formation of pyrite. (3) Reactive iron was present in such limited amounts as to preclude the formation of significant amounts of solid iron sulfides. Cause 2 is clearly evident in the composition of the samples of Unit 2 that contain abundant iron, as indicated by the presence of sideritic cements. The hydrogen indices (HI) of organic matter in Unit 2 are, on average, higher than those of Unit 1, which contains amounts of pyrite normal for marine rocks. A plot of HI against sulfur (fig. 16) shows that variation in the quality of the organic matter probably was not the limiting factor in the formation of pyrite in these samples. Rather, the opposite seems to have been the case; that is, samples having very low sulfur contents actually have comparatively high hydrogen indices.

The carbon, sulfur, and iron chemistry strongly suggests that sulfate availability was the limiting factor in pyrite formation and sulfide incorporation in Unit 2 of the Belle Fourche. Such sulfate limitation is consistent with a water column that was brackish to fresh from top to bottom, as opposed to a stratified water column with more brackish waters at the top, as proposed for other units of the Cretaceous system in North America (Pratt, 1984). Analyses of diagenetic carbonates in the cores of Unit 2, described in the following section, further support this interpretation.

Isotopic Values for Carbon and Oxygen

In samples of the core, both siderite and calcite display a wide variation in carbon isotopic composition and a somewhat smaller variation in oxygen isotopic values (table 7). In contrast to many concretionary, fine-grained rocks, for which large variations in isotopic composition (especially for carbon) have been found within single concretions, the range in the isotopic composition of calcite carbon in these samples (from +1.49 to -18.67) includes values from several concretions rather than one. Isotopic values for oxygen in calcite similarly have a greater range between concretions than within them, with values from -9.57 to -12.50. Siderites likewise display a wide variation in the isotopic composition of carbon, ranging from +8.25 to -10.99, and most variation occurs between concretions rather than within them. The oxygen isotopic composition of siderites ranges from -6.00 to -10.61.

Mozley and Burns (1993) compiled stable isotope data that had been obtained from many concretions of marine origin. From their calcite concretions, most of the $\delta^{13}C$ values range from +3 to -22‰ PDB and most of the $\delta^{18}O$ values range between 0 and -10‰ PDB. From their siderite concretions, most of the $\delta^{13}C$ values range between 7 and -15‰ PDB and

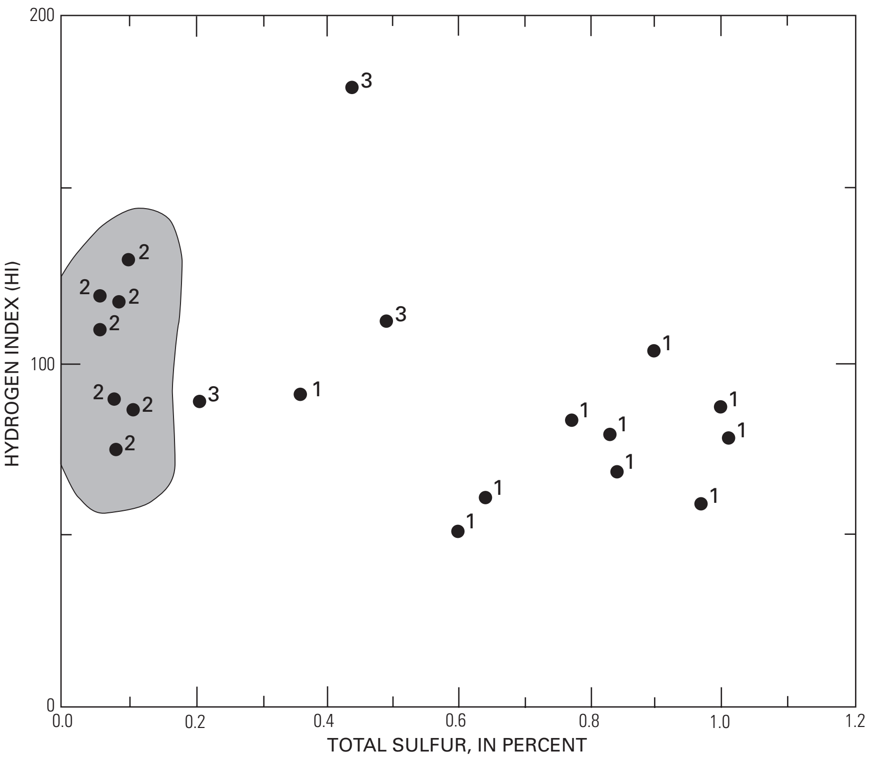


Figure 16. Comparison of the values for hydrogen index and the amounts of total sulfur for 20 samples of core from Units 1, 2 (shaded area), and 3 of the Frontier Formation, Johnson County, Wyo. Location of core hole shown in fig. 1; stratigraphy of core shown in fig. 3.

most of the δ^{18}O values range from 1 to -12‰ PDB. The initials PDB represent Peedee belemnite. Carbon dioxide obtained from belemnites from the Peedee Formation in South Carolina is used as a standard of comparison in determining the isotopic composition of carbon and oxygen. The carbon isotopic values from the calcite and siderite in the core resemble the values from marine concretions reported by Mozley and Burns (1993). However, the oxygen isotopic values from the calcite and siderite in the core contrast with those from the marine concretions described by Mozley and Burns (1993).

The oxygen isotopic composition of calcite and siderite is a function of the precipitation temperature and the ^{18}O/^{16}O ratio of the water from which the carbonate minerals precipitated. The range of oxygen isotope values from calcites suggests precipitation within a range of temperatures but at a temperature of no more than about 22°C. It seems more likely, however, that the variation in δ^{18} O values for both siderite and calcite reflects changes in the isotopic composition of waters from which siderite and calcite were precipitated. If the shale of the lower Belle Fourche was deposited in waters of normal marine salinity, the oxygen isotope values indicate either that precipitation occurred at temperatures of 70-92°C or that the oxygen isotopic composition of pore waters changed significantly prior to carbonate precipitation. Neither of these possibilities seems likely inasmuch as organic-matter maturation data indicate that temperatures this high were never present during the burial history of the Belle Fourche and that many of these cements are probably of early diagenetic origin. More likely, the shales were deposited from waters at much lower temperatures but having an isotopic composition strongly influenced by meteoric runoff, an explanation consistent with the carbon-sulfur-iron geochemical data from enclosing shales of Unit 2. Meteoric waters in Wyoming in Cenomanian time are believed to have had δ^{18} O isotopic ratios of -7 to -10‰ SMOW (Standard Mean Ocean Water; d_{PDB}=0.97006 d_{SMOW}-29.94) (Dickinson, 1984). If the cements of the lower Belle Fourche in the core from Johnson County were precipitated directly from such meteoric waters, these values suggest precipitation of calcite at temperatures of 15-28°C; temperatures reasonable for near-surface conditions of early diagenetic concretion formation in the Cretaceous.

Carbon isotopic data for the carbonates of Unit 2 of the Belle Fourche display a wide range that evidently results from multiple sources and (or) varying processes, which is typical of conditions during the formation of early diagenetic carbonates in organic-carbon-rich nonmarine rocks. Each discrete carbonate displays a comparatively narrow range of values, but differences between carbonates are large. For example, calcite from samples at a depth of about 306.6 m (1,006 ft) contains carbonate carbon that is highly depleted in the heavy carbon isotope ^{13}C, with values (-15 and -19‰) approaching those of organic carbon fixed through photosynthesis (-20 to -30‰). In contrast, calcite at a depth of 287.1 m (942 ft) contains carbonate carbon that is indistinguishable from that of marine carbonate carbon (+0.3 to +1.17). Siderites show a smaller but nevertheless disparate range of carbon isotopic compositions. The lightest (most ^{13}C-depleted) carbon isotopic values suggest the input of oxidized organic carbon, whereas the heaviest values (as much as +8.25) indicate a strong depletion in the light isotope ^{12}C, as might be expected in the presence of methanogenic microorganisms (see, for example, Gautier and Claypool, 1984). No particularly significant carbon isotopic fractionation is to be expected between calcite and siderite. Consequently, the significant differences in carbon isotopic composition between siderites and calcites in the Johnson County core strongly suggest that the calcite and siderite did not precipitate simultaneously but formed under chemically different conditions. The siderites are systematically less depleted in ^{13}C or, conversely, are more depleted in the light isotope ^{12}C than are the corresponding calcites. This trend suggests, but does not prove, that the siderites formed in conjunction with a methanic environment of early diagenesis.

Interpretations and Conclusions

Most of the sediment in Units 3, 2, and 1 in southern Johnson County (fig. 3) and in correlative rocks nearby (fig. 9) were deposited slowly in quiet-water environments on a subaqueous shelf. This interpretation is based on poor sorting, intense burrowing, the paucity of sand, the apparently low rate of sedimentation [as little as 13 cm (5.1 in.) per 1,000 years], and the gradual changes in thickness for age-equivalent rocks (fig. 9). However, the organic matter in the rocks apparently is mostly terrestrial and is thermally immature. Data from the pyrolysis assays and the variable abundance and diversity of the deposit-feeding ichnogenera (Ekdale and Mason, 1988) in these strata typify aerobic to dysaerobic environments in sediments on the sea floor. The high degree of bioturbation, especially in Unit 2 and the lower part of Unit 1 (fig. 3), might have reduced the magnitude of the HI values for those rocks. Foraminifers in the mudrocks of Units 3, 2, and the lower part of Unit 1 lived in water probably less than 30 m (100 ft) deep and in association with generally weak current action. Eicher and Diner (1985) proposed that the paucity of foraminifers in laterally equivalent rocks elsewhere suggests poorly oxygenated bottom water. From samples of outcrops in eastern Wyoming and southeastern Montana, Eicher (1967) determined that the abundance and variety of arenaceous foraminifera in lower Cenomanian strata generally increase upward. The low diversity of arenaceous foraminifers, the scarcity of filter-feeding ichnogenera, the varying diversity and abundance of deposit-feeding ichnogenera, and the absence of macrofossils in Units 3, 2, and the lower part of Unit 1 indicate an adverse benthic habitat, probably water of seasonally variable temperature, oxygen content, and salinity, with generally less than normal marine salinity.

The composition of 20 samples of core from the Belle Fourche Member has been compared to the composition of 134 samples of marine rocks and 58 samples of nonmarine rocks from the Upper Cretaceous Pierre Shale and equivalent strata in Montana, North Dakota, and South Dakota described by Schultz and others (1980, table 14). The compositions of the three units of the Belle Fourche Member are similar to those of marine rocks of the Pierre except for the amounts of SiO_2, CaO, carbonate carbon, and manganese. The mean content of SiO_2 is larger in the three units (about 68–70 percent) than in the Pierre (about 61 percent). Average amounts of CaO in the three units are 0.44–0.58 percent; significantly less than the 1.9 percent in most marine shale and siltstone of the Pierre. Mean amounts of carbonate carbon in the units (0.03–0.06 percent) are also much lower than the mean amount in marine shale and siltstone of the Pierre (0.45 percent). The low values for CaO and carbonate carbon in the units probably reflect the dearth of calcite in the sequence and the exclusion of data from the concretions in Unit 2. The mean content of manganese in the units is 72–178 ppm. In marine shale and siltstone of the Pierre, the average manganese content is 750 ppm.

For Units 3, 2, and 1, the respective mean contents are: sulfur (weight percent), 0.38, 0.08, 0.79; MgO (weight percent), 0.98, 1.05, 1.21; CaO (weight percent), 0.44, 0.49, 0.58; manganese (ppm), 72, 178, 102; and $FeTO_3$ (weight percent), 3.14, 3.37, 3.65. The MgO/CaO ratios for Units 3, 2, and 1 are 2.2, 2.1, and 2.1, respectively. These data do not indicate clear differences in the composition and origin of the three units, although a comparison of the amounts of sulfur and carbon in the three units (fig. 17) suggests that sediments in Units 3 and 1 could have been deposited in normal marine environments and sediments in Unit 2 might have been deposited in fresher water, sulfate-limited environments. However, the ternary diagram for iron, sulfur, and organic carbon in the samples (fig. 15) shows a concentration of values near Fe and between Fe and OC which resembles the concentration of values in a ternary diagram for samples of Pleistocene and Holocene silty clay from the continental slope and rise of northern California (Dean and Arthur, 1989, fig. 10).

Mozley and Wersin (1992) compiled isotopic values for carbon and oxygen in siderites that had originated in continental and marine depositional environments (fig. 18). Most of the comparable values from the siderites in Unit 2 resemble those from siderites that are either continental or marine.

All three units contain sulfur, although the percentage in Unit 2 is significantly less than the percentages in Units 3 and 1 (table 5). Nevertheless, pyrite is absent in Unit 2 and present in Units 3 and 1 (table 1). The absence of pyrite can be caused by nonreactive iron, refractory organic matter, or a reduction in the salinity of the sea (Davis and others, 1988). Mean HI values for all samples of the units are less than 130 (table 6), indicating that the organic material now in the units is nonreactive and would have limited the formation of pyrite. However, although the organic material in all of the samples is refractory only Unit 2 is without pyrite. Mean percentages of $FeTO_3$ in Units 3, 2, and 1 (table 3) are 3.14, 3.37, and 3.65, respectively. Mean prcentages of iron in Units 3, 2, and 1 are 2.2, 2.5, and 2.7, respectively.

If the differences in the amounts of P_2O_5 in the three units (table 2) represent differences in the amounts of biogenic apatite, which seems likely, then the changes in the content of P_2O_5 (fig. 10) might reflect changes in the amount of Cenomanian biotic activity. Presumably, the number of organisms, including foraminifers, palynomorphs, and burrowers, was relatively low when Unit 3 and the lowest part of Unit 2 were deposited but the number increased during deposition of the upper part of Unit 2 and the lower part of Unit 1 (fig. 10). Biotic activity in the sediments and water column apparently increased slowly during late early Cenomanian time although a corresponding increase in the abundance of fossils in the units is not evident.

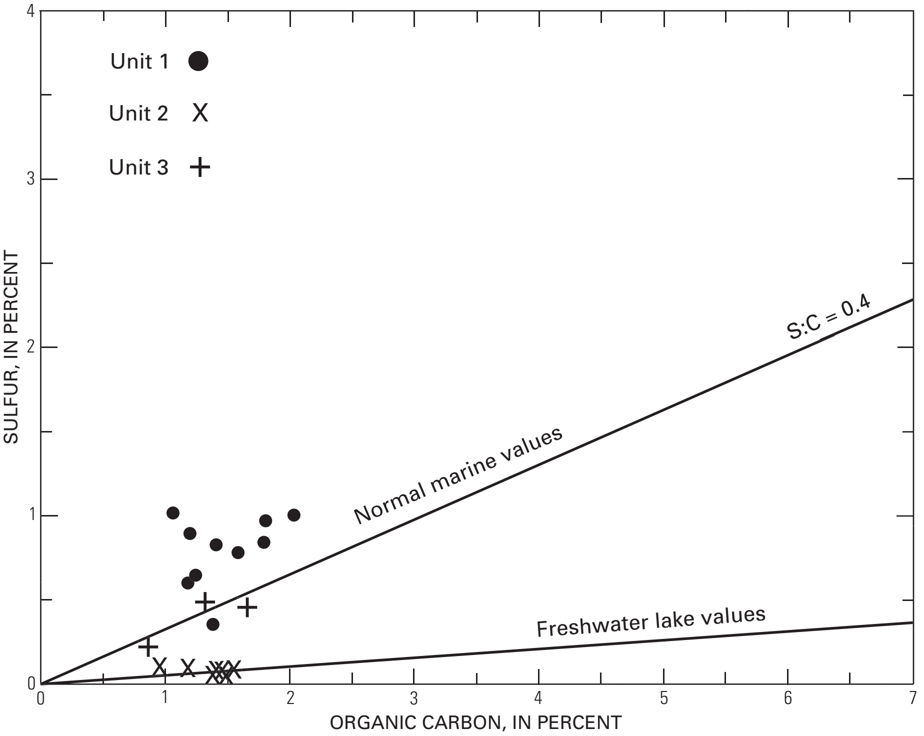


Figure 17. Organic carbon and sulfur contents of samples of the three units compared with values from well-oxygenated, normal marine sediments (Berner and Raiswell, 1983) and from fresh water lake sediments (Berner and Raiswell, 1984).

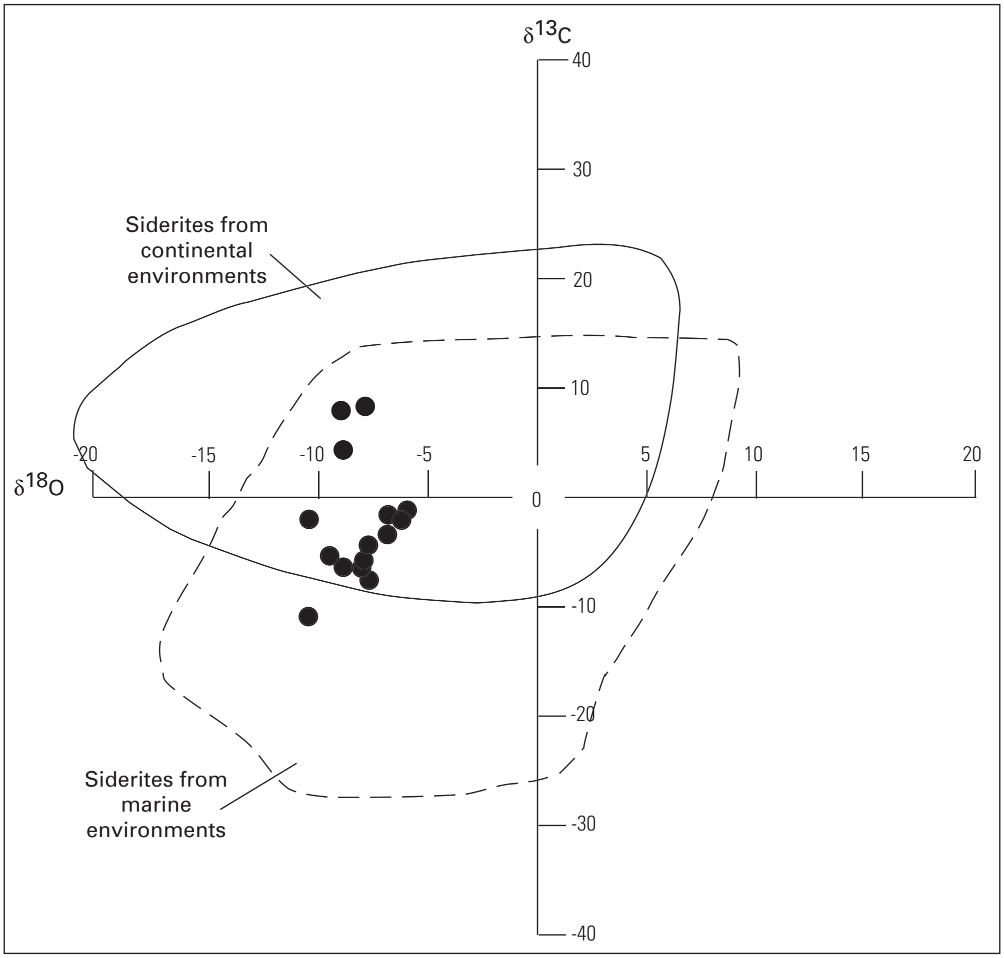


Figure 18. Comparison of isotopic values for carbon and oxygen in 15 samples of siderite from Unit 2 (table 7) of the Frontier Formation, Johnson County, Wyo., with generalized fields of published isotopic values for siderites from continental and marine depositional environments (W.E. Dean, written commun.,1995; Mozley and Wersin, 1992).

The data for carbon, sulfur, and iron, together with the mineralogic and isotopic composition of authigenic mineral species in mudrocks of Unit 2, suggest cementation during early diagenesis in a variety of microenvironments. The interstitial waters from which the minerals precipitated were far removed in elemental and isotopic composition from normal marine waters; the original pore-water composition probably was brackish to fresh, similar to conditions of the overlying waters in the Belle Fourche sea and supporting the contention of Eicher and Diner (1985) who proposed that the seaway contained poorly oxygenated water of less than normal marine salinity. Presumably, the distinctive episode of concretion formation that characterized deposition of Unit 2 was a widespread occurrence of strong dilution of the boreal epeiric sea, presumably by waters derived from uplands near the seaway. Barron (1986) concluded that the seasonal precipitation rates on mid-latitude continents of the northern hemisphere during the mid-Cretaceous were unusually high. His estimates of mid-Cretaceous precipitation rates for July in Wyoming and adjoining areas are 0.5–1.5 cm per day (72–216 in. per year). This seasonal addition of a large quantity of fresh water to the southern part of the boreal sea might also temporarily affect the temperature of the sea. For the mudrocks of Unit 2, the diagenetic features are evidently indicators of oceanographic conditions.

The widespread sideritic concretions of late early Cenomanian age (fig. 1) probably reflect the approximate lateral extent of the body of comparatively fresh water; however, saltwater is indicated in the early Cenomanian seaway of west-central Canada by the occurrence of marine molluscan fossils. If a southern part of the epeiric sea (fig. 1) was brackish to fresh, the inflow of fresh water was intermittently large, as Barron (1986) indicated, and the influx of saltwater was comparatively small. A reduction in the proportion of saltwater to fresh water could have been caused partly by a constriction of the seaway to the north, perhaps near the Mackenzie salient of northwestern Canada (Williams and Stelck, 1975) (fig. 8).

The foregoing stratigraphic, paleontologic, and geochemical data indicate that Units 3, 2, and a lower part of Unit 1, a gradational, coarsening-upward sequence, were deposited in shallow brackish to fresh water, mostly during a marine regression. This regression apparently is represented by the reduction in the area of the epeiric sea in Wyoming and Colorado during late early Cenomanian time, as depicted by McGookey and others [1972, figs. 17 (then assigned to the latest Albian) and 26]. The upper part of Unit 1 reflects the subsequent marine transgression, which is also represented by the enlargement of the epicontinental sea and the introduction of Tethyan mollusks during the earliest middle Cenomanian (fig. 4; Cobban, 1993). The boreal epeiric sea of mid-Cretaceous time in eastern Wyoming and contiguous areas contracted in the late early Cenomanian and expanded in the late early(?) and middle Cenomanian, to join the Tethyan Sea and form a north-trending transcontinental seaway. Tectonism and associated erosion in western Wyoming and adjoining areas during the late Albian and early Cenomanian and a eustatic fall during the late early Cenomanian could have caused regressions, whereas a eustatic rise in the late early(?) and middle Cenomanian probably caused the transgression.

Comparison of the ages of the units with the sea level curves of Haq and others (1987) suggests that Unit 3 could have accumulated during a gradual eustatic rise, that Unit 2 was deposited thereafter partly during a eustatic fall, and that Unit 1 subsequently accumulated mainly during a eustatic rise (fig. 7). Nevertheless, the western shore of the epeiric sea in Wyoming was evidently prograding eastward in late early to middle Cenomanian time (fig. 4), while sea level was both falling and rising. This marine regression must have been caused mostly by the Albian and Cenomanian tectonism and erosion in Montana, Idaho, and Utah reported by Wiltschko and Dorr (1983), Heller and others (1986), and Dyman and others (1988).

Acknowledgments

W.A. Cobban supplied important stratigraphic information and identified molluscan fossils of mid-Cretaceous age from outcrops and core of the region. B.R. North and W.G.E. Caldwell, while at the University of Western Ontario, London, Ontario, Canada, identified and interpreted foraminifers from core of the Frontier Formation in Johnson County, Wyoming. Additional interpretations of the foraminifers were provided by M.A. Carey. Trace fossils were identified by B.L. Mieras, a stratigraphic consultant, while at the University of Colorado, Boulder. Samples of strata from the core hole in Johnson County were analyzed for minerals by G.L. Skipp; major element and trace element compositions were determined by J.N. Taggart, A.J. Bartel, D.F. Siems, and D.L. Fey; analyses for percentages of carbon and sulfur were conducted by L.L. Jackson and E.L. Brandt. The organic composition and thermal maturity of the rocks were determined by T.A. Daws and J.G. Palacas. Samples of concretions from the core hole were analyzed for minerals by R.M. Pollastro and T.M. Finn. Isotopic analyses were performed by C.N. Threlkeld and A.K. Vuletich. Thoughtful and constructive reviews of this report were contributed by Walter E. Dean, Karen J. Franczyk, and Michele L. Tuttle. The essential and generous contributions of effort and information by these scientists and technicians of the U.S. Geological Survey, the University of Western Ontario, and the University of Colorado are gratefully acknowledged.

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