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DISTRIBUTION AND ORIGIN OF ORGANIC CARBON IN THE UPPER CRETACEOUS NIORARA FORMATION AND SHARON SPRINGS MEMBER OF THE PIERRE SHALE, WESTERN INTERIOR, UNITED STATES

by

Glen S. Tanck

A Dissertation Submitted to the Faculty of the DEPARTMENT OF GEOSCIENCES In Partial Fulfillment of the Requirements For the Degree of DOCTOR OF PHILOSOPHY In the Graduate College THE UNIVERSITY OF ARIZONA

1997
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Glen S. Tanck entitled DISTRIBUTION AND ORIGIN OF ORGANIC CARBON IN THE UPPER CRETAEOUS NIOMBRARA FORMATION AND SHARON SPRINGS MEMBER OF THE PIERRE SHALE, WESTERN INTERIOR, UNITED STATES and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Judith T. Parrish
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SIGNED: [Signature]
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ABSTRACT

The Upper Cretaceous Niobrara Formation and the overlying Sharon Springs Member of the Pierre Shale are two of several organic-carbon (OC) rich units deposited in the Western Interior seaway. A key to assessing the validity of models proposed to account for OC enrichment in these units is understanding the three-dimensional (3D) distribution of OC within these units. Within the study area abundant subsurface data in the form of geophysical well logs are available. These logs were used in two key ways: (1) to divide the Niobrara and Sharon Springs into regionally correlatable chronostratigraphic horizons and (2) to estimate OC-content. By combining these elements a 3D picture of the OC-distribution was obtained. This distribution was compared to changes in lithology, sedimentation rate, and tectonic activity.

The Niobrara and Sharon Springs contain local and regional disconformities which indicate water depths were near an estimated storm-wave base depth of 100 m. Local disconformities in the Niobrara are indicative of basinal tectonic activity that may be linked to Sevier thrusting to the west.

There is a regular vertical pattern of OC enrichment in the Niobrara, but no pronounced regional patterns are evident. Estimated paleoproductivities are moderate, except to the southeast where higher productivities may have been a consequence of upwelling. Small-scale chalk/marl cycles result from alternation of high productivity during periods of fairly vigorous circulation (chalks) with low productivity during periods of more sluggish circulation (marls).

The regional diachroneity of the Sharon Springs facies was a result of clastic dilution associated with progradation from the west and the paleobathymetry.
Paleoproducivities were moderately high during Sharon Springs deposition, but there is no conclusive evidence of upwelling.

Both units were deposited beneath bottom waters that were on average dysoxic, but oxygenation levels varied intermittently from fully oxic to anoxic. These changes were climatically modulated. At short time scales they may have been seasonal and at longer time scales they may have been driven by Milankovitch cyclicity.
CHAPTER 1
INTRODUCTION

THE WESTERN INTERIOR SEAWAY

The Cretaceous Western Interior Seaway (WIS) of North America was a 6000-km-long shallow marine basin that extended from present-day Arctic Canada to the Gulf of Mexico from the late Albian (100 ma) to early Maastrichtian (70 ma) (McGookey et al., 1972). (Fig. 1.1). The WIS reached its maximum extent in the Cenomanian when it was 1200 km to as much as 2000 km wide (Kauffman, 1975) and, at times it may have been as deep as 500 m (Asquith, 1970).

The development of this epicontinental sea and the accumulation of its sedimentary record was a consequence of two separate factors. The first of these was the formation of a foreland basin due to crustal loading produced by eastward-vergent thrust faulting (Beaumont, 1981; Beaumont et al., 1982; Jordan, 1981). In the United States this thrust faulting was associated with the Sevier orogeny (Armstrong, 1968) and in Canada with the correlative Columbia orogeny (Douglas et al., 1970).

Although the development of the foreland basin was essential to the creation of the WIS, it is important to differentiate the two, as the basin had a longer history than the seaway. The distinction between the two is in part a consequence of the other factor that was instrumental in the development of the WIS—the large eustatic rise of sea level that occurred during the Upper Cretaceous (e.g., Vail et al., 1977). Estimates of the sea level rise range from 228 m (Kominz, 1984) to 600 m (Hancock and Kauffman, 1979). The sea-level highstand resulted in the long-term marine flooding of what otherwise would have been simply a continental foreland basin.

The Western Interior foreland basin was asymmetrical with the greatest subsidence occurring close to the thrust belt. It can be divided into four zones from west
Figure 1.1. Paleogeographic map of the Western Interior seaway during maximum Niobrara transgression, Middle Santonian (from Hay, 1993).
to east: following the terminology of DeCelles and Giles (1996): a wedge-top depozone, a foredeep depozone, a forebulge depozone, and a back bulge depozone (Fig. 1.2). The wedge-top depozone was an area where synorogenic thrusting, erosion, and deposition took place and it is characterized by progressive deformation and erosion of shallowly buried synorogenic sediments (DeCelles and Giles, 1996). The foredeep depozone was to the east of the frontal edge of the orogenic wedge and it was flanked on the east by a forebulge and then a back-bulge depozone. However, the distinction between these zones was lost in the Campanian when the forebulge disappeared (e.g., Cross, 1986). In addition to these zones that are directly related to the thrust belt, a stable eastern platform was flooded by the Cretaceous sea-level rise.

Sedimentation rates were high near the tectonically active western edge of the basin and were generally able to keep pace with the subsidence. Thus the foredeep was not a topographic basin, and deposition there consisted mainly of non-marine and near-shore sediments. To the east the rate of subsidence diminished, but so did the sedimentation rate as terrestrial sediment sources became more distant. As a result water depths were often greatest well to the east of the foredeep (axial basin of Kauffman, 1984). Deposition in this region was primarily marine and often pelagic or hemipelagic. Most of the eastern edge of the seaway has not been preserved, but marine sediments extended far to the east (see Fig. 1.1) and terrestrial sediment input from the east was limited. Superimposed upon this general pattern were laterally widespread and large-scale cycles of deposition that have been attributed to second- and third-order eustatic changes in sea level (Kauffman, 1969; 1977; Caldwell, 1984).

ORGANIC-CARBON RICH STRATA IN THE WESTERN INTERIOR SEAWAY

Rock units rich in organic carbon (OC) (>1.0% organic carbon) form a large proportion of the strata deposited in the central and eastern portions of the WIS. The
Figure 1.2. Schematic cross-section through the Western Interior basin, Utah to eastern Kansas (after DeCelles and Giles, 1996).
organic-rich units encompass a range of lithologies, and each of the units is believed to have been an important petroleum source rock in one or more of the petroliferous basins that make this region an important petroleum-producing province (e.g., North, 1985). Extensive subsurface control, along with generally good outcrop exposures, has allowed these units to be studied in considerable detail. As a result, their basic stratigraphic, petrologic, and sedimentologic characteristics are quite well documented (McGookey et al., 1972; Kauffman, 1977; Pratt et al., 1985).

OC-rich units deposited in the WIS share three general characteristics besides OC-richness: they were generally deposited during transgressions, often near transgressive peaks (Kauffman, 1969); their apparent rates of deposition were slow or moderate (Gill et al., 1972; Pratt et al., 1985; Davis et al., 1989; Eicher and Diner, 1989; Parrish and Gautier, 1993); and they were deposited in the central and eastern portions of the basin (e.g., McGookey et al., 1972). In addition, they were all deposited during a relatively short time period (about 20 m.y.) (Fig. 1.3). However, as noted above, they encompass a range of lithologies. For example, the Mowry is a siliceous, radiolarian-rich shale (Rubey, 1928; Davis, 1970; Cluff, 1976); the Greenhorn and the Niobrara are predominantly calcareous shale and chalk (e.g., see papers in Pratt et al., 1985); and the Sharon Springs is typically a phosphatic shale (Gill et al., 1972). Partly as a result of these differences, the depositional environments of these units are controversial, particularly when consideration is given to those aspects of the environment that may have promoted the preservation of organic matter (Eicher and Diner, 1989; Zelt, 1990; Parrish and Gautier, 1993; Pratt et al., 1993).

DISCUSSION OF THE PROBLEM

The lithologic variability of the strata in the WIS must be attributable to changes in some or all of a variety of environmental factors, including eustatic sea level, tectonic
Figure 1.3. Generalized stratigraphic column for the Cretaceous Western seaway showing marine OC-rich strata. Organic-carbon contents are generalized from numerous sources.
activity, paleocirculation patterns, and climate. It is well established that changes in these factors can account for dramatic changes in lithology, but for OC-rich units of variable lithology, these changes have to fit within a depositional model consistent with OC-richness. Thus models used to explain the depositional environments for units like the Niobrara and the Sharon Springs must also consider those factors that can account for their OC-richness.

Depositional models for OC-rich rocks are of two general types: those that require high organic productivity and relatively rapid burial (Parrish, 1982) and those that require water-column density stratification with consequent stagnation, oxygen depletion, and enhanced preservation of organic matter beneath the pycnocline (Demaison and Moore, 1980. Modern examples of these two types are typified respectively by the high-productivity upwelling zone off Peru and the salinity-stratified Black Sea (Deuser, 1971; Burnett et al., 1983).

The stratified basin model has been most often invoked to account for OC-rich intervals in the WIS (Nixon, 1973; Pratt, 1984; Sageman, 1985; Barlow, 1986). The argument for this begins with the recognition that the OC-rich intervals generally lack benthic fauna and bioturbation. This indicates anoxia (or at least dysoxia) (Shafer, 1972; Byers, 1977) which in turn is used to suggest sluggish circulation or stagnation of bottom water and probable density stratification of the seaway.

Periodic density stratification of the WIS is presumed to result from development of a brackish-water cap during periods of humid climate and high runoff (Kauffman, 1975; Fischer, 1980; Pratt, 1981, 1984). Pratt (1984), in particular, developed this model for OC-rich intervals in the Greenhorn Formation. Milankovitch-type climatic variations are called upon to produce the cyclic variations in lithology and organic matter content observed in some sections (Gilbert, 1895; Fischer, 1980; Pratt, 1984), including the Niobrara.
The brackish-water-cap model is supported by several lines of evidence. The OC-rich intervals are associated with the shale-rich intervals in the Greenhorn (Pratt, 1984) which can in turn often be associated with progradational deltaic tongues farther to the west (Sageman, 1985). Oxygen isotope values appear to be too negative in OC-rich intervals to be accounted for other than by low salinities (Arthur et al., 1985; Barron et al., 1985; Pratt, 1984; Pratt and Barlow, 1985), despite evidence for diagenetic lowering of the $\delta^{18}O$ values (e.g., Pratt et al., 1993). Finally, planktonic faunas during times of OC-rich sediment deposition sometimes are not of normal marine affinities (Kauffman, 1984).

Each of the above lines of evidence has problems, however. In contrast to the Greenhorn, for example, in the Niobrara carbonate-rich zones are occasionally just as OC-rich as shaly zones (Barlow, 1985; Pratt and Barlow, 1985). This is not consistent with the runoff/salinity-stratification model. The oxygen isotope values even in carefully selected samples may have been diagenetically altered (Miskell-Gerhardt and Dunbar, 1989). Furthermore, the isotopic values obtained from inoceramids in OC-rich intervals (inoceramids were benthonic and believed to have been adapted to low-oxygen environments) are problematic. Their low $\delta^{18}O$ values seem to imply that the bottom waters were low salinity, thus indicating that mixing with surface waters took place. However, such mixing would have transferred oxygen to bottom waters. In addition, Laferriere (1992) has shown that $\delta^{18}O$ values do not vary significantly between the shale (OC-rich) and limestone (OC-poor) beds in the Fort Hays Member of the Niobrara.

Faunal evidence for a brackish-water cap is also equivocal. Eicher and Diner (1985, 1989) found that abundant planktonic foraminifera in shaly, OC-rich beds of the Greenhorn Limestone are indicative of normal marine salinities, contradicting the "brackish cap" model. These same intervals are ones that have strongly negative $\delta^{18}O$ values (Pratt, 1985), so a low-salinity interpretation of these isotope values can be called.
into question. Absence of benthic faunas in some units might have resulted from lack of a firm substrate (e.g., Hattin, 1986) and not lack of oxygen.

On the basis of the faunal evidence, Eicher and Diner (1985) proposed a variation of the stratified-basin model that involves a global rather than a regional mechanism. They adapted the warm saline bottom water model of Brass et al. (1982), which suggests that during the highest sea level stands evaporation in shallow, low-latitude epeiric seas would produce warm saline water dense enough and in sufficient amounts to replace normal ocean bottom water. This would result in vertical mixing, enhanced upwelling, and increased productivity in portions of the world's oceans (including the WIS, according to Eicher and Diner, 1985). During periods of wetter climate or lower sea level the production of warm saline bottom water would have been shut off, the ocean would restratify, and preservation of organic matter would be enhanced. Eicher and Diner (1989) did not, however, suggest a specific mechanism for the stratification of the WIS. Eicher and Diner (1989) critically examined the brackish-cap model for cyclicity in the Bridge Creek Member of the Greenhorn and concluded that the evidence contradicts the model. They suggested instead that episodic enhanced productivity tied to conditions in Tethys were the cause of the cyclic strata of the Bridge Creek.

Another type of stratified-basin model calls for the occasional incursion of an oxygen minimum zone into the WIS from the open ocean to the south. This model was used by Frush and Eicher (1975), for example, to explain the disappearance and sudden reappearance of benthic foraminifera in the Boquillas Formation of the Big Bend area. Incursion of an oxygen minimum zone deep into the WIS could account for at least some episodes of OC-rich sedimentation.

High-productivity models are not commonly applied to OC-rich intervals in the WIS, probably in part because sedimentation rates are perceived to be too low for this mechanism of preservation (e.g., Zelt, 1985). Davis et al. (1989), for example,
suggested that Mowry sedimentation rates imply low productivity, though they did not propose a particular preservation model. However, Mowry sedimentation rates do not appear to be lower than some modern high-productivity, siliceous depositional environments (Miskell-Gerhardt, 1989).

A high-productivity, upwelling model has been applied to the Sharon Springs Member of the Pierre Shale. Parrish and Gautier (1993) argued that the high phosphatic content, lateral facies associations, abundant vertebrate remains and fecal pellets, and the displacement of the OC-rich facies away from the basin center are indicative of high productivity and upwelling.

Although numerous models have been applied to the OC-rich units, none is entirely satisfactory. The models are designed around particular units and thus limit comparison among the units. This might be taken to mean that each OC-rich unit is so unique as to require its own model. Such a stance would contradict the many attempts to classify depositional mechanisms for OC-rich units, attempts that have resulted from the limited number of fundamentally different environments in which OC-rich sediments are being deposited today (Demaison and Moore, 1980; Pedersen and Calvert, 1990).

RESEARCH PURPOSE

As the above discussion illustrates, a general lack of consensus exists concerning the origin of OC-rich strata in the WIS. This is indicative of the controversy concerning the origin of most marine OC-rich rocks. While many lines of evidence bear on the problem, one fundamental key to interpreting the origin of OC-rich strata is understanding the distribution of OC vertically, laterally, and with respect to facies, as this critically bears on the possible origins of a given OC-rich unit. For example, in the stratified basin model the key to OC-enrichment is enhanced preservation beneath a pycnocline. In this model OC-rich strata will be concentrated in the bathymetric lows (beneath the pycnocline) and lateral OC
variation will be limited. In contrast, high productivity is seldom basin-wide and it is often concentrated in upwelling zones at the flanks of the basin. Data from existing studies are insufficient, however, to delineate OC distribution in any strata of the WIS. In a few studies, detailed vertical profiles have been made for a particular outcrop or core (e.g., Pratt et al., 1993). However, models of OC-enrichment developed from single stratigraphic sections cannot account for potential regional variations in OC-content that could be of great significance. In others studies, regional distributions of OC have been mapped, but only for OC values averaged across an entire formation without regard for vertical variations (e.g., Burtner and Warner, 1984). In these instances, potentially significant temporal variations in OC-content are ignored. To fully understand the origin of OC enrichment in these strata, both the regional and vertical (temporal) pattern of OC distribution is needed.

This study examines the distribution of OC both in a regional and in a vertical (time) sense in the Niobrara and the overlying Sharon Springs. In order to accomplish this, the study utilizes the vast amount of subsurface, primarily well log, data that are available in the greater Rocky Mountain region. These data are used in four primary ways: (1) to determine lithologic facies, (2) to define regionally correlative, chronostratigraphic horizons that can be used to subdivide the individual formations into narrower depositional time frames, (3) to quantitatively determine OC-content, and (4) to use the association of uranium with OC to help assess sedimentation rates and bottom-water oxygenation levels.

**Methods**

(1) **Lithology.** Modern geophysical methods can be used to access the lithology of subsurface strata with accuracy (e.g., Burtner and Warner, 1984; Hurst et al., 1992; Hurst et al., 1990; Rider, 1991; Schlumberger, 1989). Not only can they be used to identify basic lithologies (i.e., shale, sandstone, limestone, etc.), they can also be used to identify subtler variations, such as shale percentage or even, in some cases, the types of clays that are most
abundant (Schlumberger, 1989). The density-neutron log combination, for example, is particularly useful in a limestone and shale unit like the Niobrara where it can define vertical changes in relative proportions of the lithologies down to the vertical resolution of the logs. In addition, this log combination can be used to calculate porosity, which has to be known if sedimentation rates are to be calculated.

(2) Chronostratigraphic horizons. Regionally correlative chronostratigraphic horizons have been documented in a number of the Cretaceous marine units of the WIS. These horizons have been recognized both in outcrop, for example, in the Greenhorn (Hattin, 1971, 1985; Elder, 1985; Zelt and Gautier, 1985) and in the Niobrara (Hattin, 1982; Barlow, 1985; Barlow and Kauffman, 1985; Rodriguez, 1985), and in the subsurface, for example, in the Niobrara (Laferriere et al., 1987; Laferriere and Hattin, 1989) and in the Mowry (Nixon, 1973).

Numerous chronostratigraphic horizons can be recognized in the subsurface Niobrara and some of these can readily be tied to surface sections where they can be integrated with biostratigraphic control. Many prominent chronostratigraphic horizons can be recognized over hundreds of thousands of square kilometers. Frequently, these horizons encompass significant variations in thickness and facies. Sometimes the chronostratigraphic horizons merge, and the zones defined by them become so thin, as to become unidentifiable (Laferriere et al., 1987). The thinning occurs, in particular, over structurally positive areas (Weimer, 1978; Laferriere and Hattin, 1989). Those chronostratigraphic horizons that can be identified over large areas are extremely useful, because they can be used to divide strata into individual chronostratigraphic units. With this temporal information, lateral changes in relative sedimentation rates, OC content and mass accumulation rates, and lithofacies can be mapped. These rates can be converted to absolute values by estimating the age span for each individual chronostratigraphic unit. This can be done by using a combination of biostratigraphy, the isotopic dating of
Obradovitch (1993), and patterns of probable Milankovitch cyclicity, at least for the Niobrara (e.g., Fisher et al., 1985; Fisher, 1993). The Sharon Springs does not contain as many horizons which can be widely correlated chronostratigraphically as the Niobrara, but it does contain the widespread Ardmore Bentonite zone which can be used to divide the Sharon Springs into an upper and lower unit. Because lateral thickness variations in strata of the WIS are often due to tectonic influences (e.g., Sonnenburg and Weimer, 1981; Weimer, 1978), changes in tectonic patterns can be assessed in a narrower time frame than is typically possible. In addition, where tectonic influences can be discounted, lateral variations in terrigenous influx and/or productivity may become apparent.

(3) **Organic-carbon content.** A variety of methods has been utilized in the effort to estimate organic carbon (OC) content from well logs. These have included the use of gamma-ray logs (Schmoker, 1980; Schmoker, 1981), density logs, (Schmoker, 1979; Schmoker and Hester, 1983), spectral gamma-ray logs (Fertl and Rieke, 1980; Zelt, 1985), pulsed neutron logs (carbon/oxygen) (Herron, 1986), and various combinations of logs (Autric and Dumesnil, 1985; Carpentier et al., 1991; Mendelson and Toksoz, 1985; Meyer and Nederlof, 1984; Passey et al., 1991). The accuracy of these methods varies and is constrained to a degree by the complexity of natural rock systems and inherent limitations in geophysical logging methods. Nevertheless, in many instances accuracy is quite good (e.g., Carpentier et al., 1991) and more than sufficient to document regional changes in OC content (e.g., Schmoker and Hester, 1983).

In this study the CARBOLOG® method of Carpentier et al. (1991) is used to estimate OC content in the Niobrara and Sharon Springs. This method uses sonic and resistivity logs and secondarily incorporates the density log. The method relies on the fact that organic matter (OM) has a very slow sonic velocity, while at the same time being very resistive. This is in contrast to most other rock constituents, so the effect of OM on log response can be predicted and quantified with proper calibration.
(4) **Uranium content versus OC content.** Uranium content typically correlates quite closely with OC content (Beers and Goodman, 1944; Russell, 1945; Swanson, 1961). In the subsurface, uranium content can be measured with a spectral gamma-ray log. The spectral gamma-ray log divides total gamma ray radiation into its potassium, uranium, and thorium components (actually radiation from daughter products is measured) (i.e., see Zelt, 1985; Schumberger, 1989). Because of the close association of uranium and OC, the spectral gamma-ray log has been used to estimate OC-content (Fertl and Rieke, 1980; Supernaw et al., 1978; Zelt, 1985). However, the uranium/OC ratio is not constant; for example, the ratio of uranium to OC increases with decreased sedimentation rate (Arthur et al., 1990; Mangini and Dominik, 1979), and it appears that bottom-water oxygenation levels affect the ratio as well. In the Niobrara and Sharon Springs it is sometimes possible to separate these factors and thus assess relative changes in sedimentation rates and/or bottom-water oxygenation levels.

**Application**

The combination of basic lithofacies data, a more finely resolved regional chronostratigraphic zonation, estimates of OC content, and estimates of sedimentation rate forms a powerful framework to aid in interpreting the depositional history and the origin OC enrichment of the Niobrara and Sharon Springs. This integrated approach has produced a number of significant conclusions.

Niobrara deposition occurred in a more dynamic setting than has heretofore been recognized, as disconformities are common in many parts of the Niobrara. These disconformities were produced by differential tectonic movement of the basin floor during Niobrara deposition and this basinal tectonic activity can be related to episodes of Sevier thrusting to the west. Large-scale chalk/marl cycles in the Niobrara may also be linked to
episodes of Sevier thrusting. The disconformities also suggest that Niobrara deposition was frequently at or near an estimated storm-wave base of 100 m.

Niobrara paleoproductivities were on average moderate, but periods of higher productivity alternated with periods of low productivity to produce the characteristic cyclicity (cm to m chalk/marl couplets) characteristic of the Niobrara. No strongly pronounced regional trends in OC content are observed in the Niobrara, but an area of higher estimated paleoproductivities to the southeast may have resulted from upwelling. Authigenic uranium to organic carbon ratios indicate the Niobrara deposition occurred beneath bottom water that was on average dysoxic.

The regional distribution of the OC-rich Sharon Springs facies is documented and related to changes in the sedimentation rate and paleobathymetry. The diachrony of this facies is shown to be the result of progradation and clastic dilution to the west and paleobathymetrically controlled levels of oxygenation to the east. An extensive disconformity at the top of the lower Sharon Springs corresponds to a well-documented sea-level fall, but it also indicates that Sharon Springs deposition was frequently close to storm-wave base.

Sharon Springs paleoproductivities are estimated to be quite high and appear to be cyclic, but there are no strong regional variations over the time periods considered. Authigenic-uranium to organic-carbon ratios indicate the Niobrara deposition occurred beneath bottom water that was on average dysoxic.

This dissertation is structured as follows. Chapter 2 establishes a chronostratigraphic framework for the Niobrara Formation by dividing the Niobrara into a series of units bounded by regionally correlative chronostratigraphic horizons that are readily identified on well logs. Isopach maps of these units are used to document regional and temporal changes in sedimentation. The role of sediment flux, tectonics, and paleobathymetry in creating these patterns is addressed. Chapter 3 is devoted to adapting
a method by which OC contents can be estimated from well logs, specifically to the Niobrara and Sharon Springs. Chapter 4 documents the principle controls on the authigenic-uranium to organic-carbon ratio and shows how this ratio can be used to help ascertain levels of ancient bottom-water oxygenation. Chapter 5 integrates elements of the first three chapters to document how OC content varies in the Niobrara and what factors may have produced these variations. Chapter 6 also draws on the earlier chapters and documents regional trends in Sharon Springs deposition and OC content and it demonstrates what controls produced these trends. Finally, a brief summary is presented in Chapter 7.
CHAPTER 2
CHANGES IN TECTONIC ACTIVITY AND SEDIMENTATION DURING DEPOSITION OF THE NIOBRARA FORMATION

INTRODUCTION

The Upper Cretaceous (Coniacian-Campanian) Niobrara Formation was deposited in the Western Interior seaway (WIS) during a second order (Kauffman and Caldwell, 1993) transgression (third order of Kauffman, 1977; 1985). The Niobrara is divided into two members: the Fort Hays and the overlying Smoky Hill (Scott and Cobban, 1964). The formation is a shaly chalk to the east, where it is typically about 200 m (650 ft) thick (Hattin, 1982). To the west, it grades into several hundred meters of calcareous shale (McGookey et al., 1972; Fig. 2.1).

The Niobrara exhibits cyclic sedimentation on scales ranging from less than a millimeter to many tens of meters in thickness (e.g., Dean and Arthur, 1989; Pratt and Barlow, 1985; Pollastro, 1992; Pratt et al., 1993). These cycles may have formed over periods ranging from one year for those at the smallest, submicroscopic scale (Tyson and Pearson, 1991) to 800,000 years or more at the largest scale (Pratt et al., 1993). Intermediate cycles have been attributed to Milankovitch rhythms (Pratt, 1985; Barron et al., 1985; Arthur et al., 1985; Fischer et al., 1985). These cycles are important to this study, because they occur basinwide and can serve as time lines. The large scale, chalk/shaly chalk cycles in the Niobrara are readily recognized along the Front Range of Colorado, where they are used to divide the Smoky Hill Member of the Niobrara into 7 informal members (Scott and Cobban, 1964). These cycles have been attributed to changes in eustatic sea level (e.g., Kauffman, 1985; Kauffman and Caldwell, 1993), but the role that tectonics might have played in generating these cycles has not been adequately addressed.
Figure 2.1. Map showing paleogeography near peak Niobrara transgression (middle Santonian) and area of present study. Gray area is land. Line X-X' denotes location of key cross section. Map is adapted from Hattin (1982) and (Cobban et al. 1994)
Large-scale cyclicity in marine sedimentary rocks can be the result of several factors. Foremost among these factors are changes in eustatic sea level and/or tectonic activity. Distinguishing between the relative importance of these factors in a particular depositional setting is often difficult. Changes in tectonic activity are usually expressed on time scales of several millions of years, but even the large-scale Niobrara sedimentary cycles (e.g., the 4th order cycles of Barlow and Kauffman, 1985) are typically an order of magnitude shorter in duration (100's of ka). These cycles are not readily tied to episodes of tectonic activity and they are often attributed to sea-level change even when independent evidence for this is lacking. By examining tectonic activity in as narrow a time frame as possible, changes in tectonic activity can be related to contemporaneous changes in sedimentation.

Although pronounced thickness variations in basinal sediments are often attributed to tectonic activity, they can also be the result of variations in sediment input. Such variations may be tied to regional differences in terrigenous input or in marine paleoproductivity.

This part of the study uses subsurface data in the form of geophysical well logs to divide the Niobrara into 14 chronostratigraphic units (Fig. 2.2) in a portion of the Western Interior seaway (Fig. 2.1). Isopach maps of these units are used to assess regional as well as relatively local variations in thickness. The purpose of this part of the study is to identify the effects of tectonics, terrigenous influx, and paleoproductivity in creating these thickness changes.

**PREVIOUS WORK**

A number of authors have evaluated the evidence for syndepositional tectonic movements during Niobrara Formation deposition. The focus of these studies has been confined to looking at tectonic effects on either (1) the thickness of the Niobrara as a
Figure 2.2. Composite gamma-ray log of the Niobrara section showing formal and informal Niobrara divisions used in this study. Logs from several wells were combined to produce this composite section. Sections were chosen on the basis of their stratigraphic completeness and thickness, so the resulting section is thicker than any actual section.
whole, (2) a single, thin interval within the Niobrara (i.e., the Fort Hays Member), or (3) an area of very limited lateral extent.

Reeside (1944) mapped an area of Niobrara thinning extending from south-central South Dakota to southwestern Colorado and noted that it corresponded to the trend of the Paleozoic transcontinental arch. Weimer (1978, 1984) and Sonnenberg and Weimer (1981) looked at regional thickness patterns within the Niobrara and also concluded that a band of northeast-southwest trending thinning was related to the Paleozoic Transcontinental arch. They postulated that the thinning was due to renewal of recurrent tectonic movement along this broad structural high during Niobrara deposition. This interpretation is supported by the presence of significant unconformities and the absence of some faunal zones in the area of thinning (Weimer, 1978, 1984). Shurr and Sieverding (1980) and Shurr (1984) noted the effects of the Transcontinental arch on Niobrara sedimentation patterns, but they did not specifically address the tectonic aspects.

Laferriere and Hattin (1989) used detailed subsurface correlations of chronostratigraphic horizons in the Fort Hays Member in eastern Colorado and northwestern Kansas to create detailed isopach maps of the Fort Hays and two separate intervals within the Fort Hays. Their maps illustrate a pattern of northeast-southwest trending thick and thin areas. The authors related this pattern to syndepositional tectonic movements along and parallel to the Transcontinental arch. Overall, however, the magnitudes of the thickness changes are modest and only minor tectonic movement is needed to account for them. The Fort Hays represents only about 10% of the entire Niobrara section, so the results of their study do not adequately represent the formation as a whole.

A number of authors have noted the role of tectonics in creating oil or gas accumulations in the Niobrara (e.g., Sonnenberg and Weimer, 1981; Davis, 1985; Pollastro, 1992). They commonly attributed the structural aspects of these accumulations
to Laramide and/or later tectonics. However, a few authors have noted the presence of numerous syndepositional Niobrara faults as well. Cockerham (1982) and Jeffrey (1982), for example, noted the presence of numerous listric normal faults that are largely confined to the Niobrara (and sometimes part of the overlying Pierre Shale) in two Niobrara gas fields in eastern Colorado. Jeffrey (1982) concluded that these faults are probably growth faults. The density of drilling in fields allows some of these faults to be mapped in detail within relatively localized areas. Davis (1985) was able to identify listric normal faults on seismic profiles in the Niobrara in the Boulder-Wattenburg-Greeley area. He interpreted these as reflecting recurrent movement on underlying basement faults.

The studies of Laferriere et al. (1987) and Laferriere and Hattin (1989) demonstrated that well logs could be used to trace chronostratigraphic horizons in the subsurface within the Fort Hays Member of the Niobrara. The Fort Hays consists of rhythmically-interbedded pelagic limestones and thin shales. Laferriere (1987) demonstrated that these depositional cycles were regionally synchronous by tying them to distinctive bentonite beds. Although individual cycles cannot be recognized on well logs, the thicker shales produce distinctive and consistent well-log signatures.

The recognition of widespread, correlatable chronostratigraphic horizons in the Niobrara is not confined to the Fort Hays Member, however. Such horizons have been recognized in the Smoky Hill Member as well on the basis of outcrop studies (Hattin, 1982; Barlow, 1985; Rodriguez, 1985; Barlow and Kauffman, 1985). These authors noted thickness changes in some of the informal Smoky Hill members, but did not attempt to isopach them. Though all these studies were based on outcrop examination, Rodriguez (1985) and Barlow (1985) made some correlations from the outcrop into the subsurface by utilizing core and well logs. Their use of subsurface data was limited, but their work demonstrated the potential utility of well logs to make correlations in the Smoky Hill as well as in the Fort Hays.
METHODS

Correlations and Establishment of Time Lines

I correlated subsurface geophysical well-logs in the vicinity of Pueblo and Lyons, Colorado with nearby surface Niobrara sections (those described at Pueblo by Scott and Cobban, 1964 and Pratt et al., 1985 and at Lyons by Pratt and Barlow, 1985). It is difficult to correlate individual Niobrara beds from the surface to the subsurface, though use of outcrop gamma-ray logging can be very helpful (e.g., Slatt et al., 1995). However, thicker units with distinctive differences in lithology are easy to correlate. The members of the Niobrara—the Ft. Hays and the informal members of the Smoky Hill (Scott and Cobban, 1964)—proved to be readily recognizable on the nearby geophysical logs. (Division of these members in this study is essentially the same as that shown by Pratt et al., 1993). The stratigraphic boundaries defining the members were readily correlated to geophysical logs at greater distances from the outcrops. These boundaries are both lithostratigraphic and chronostratigraphic. Numerous other chronostratigraphic horizons can be recognized on the well logs. These horizons are sometimes bentonites but, more typically, they are subtle vertical facies changes that are caused by variations in shale, organic-carbon content, or most importantly uranium content (to be discussed further below). A few of these horizons were used to further subdivide the Niobrara into a total of 14 different units (Fig. 2.2).

Detailed subsurface cross-sections were constructed and correlated in the greater Denver Basin region (Fig. 2.3-2.11). Two-hundred and thirty-one well logs were directly utilized in these sections, but thousands of other logs were examined in the process of constructing them. Gamma-ray logs were the principle type used in correlation, but other log types were also used, including induction, density, and sonic logs. Cross-sections were tied to one another with common logs. Correlations made from a single starting point were carried along successive cross-sections until they were returned to the starting
Figure 2.3. Index map showing cross-section network and other wells used in this study
(for a listing of wells used see Appendix A).
Figure 2.4. North-south stratigraphic cross-section of the Niobrara Formation, A-A', southeastern Colorado to northeastern Wyoming. Section utilizes gamma-ray logs and is about one sixth original scale. Section is continued on the following two pages.
Figure 2.4 (cont.)
Figure 2.4 (cont.)
Figure 2.5. North-south stratigraphic cross-section of the Niobrara Formation, B-B', southeastern Colorado to northwestern Nebraska. Format and scale as in Figure 2.4.
Figure 2.6. North-south stratigraphic cross-section of the Niobrara Formation, C-C', east-central Colorado to central South Dakota. Format and scale as in Figure 2.4.
Figure 2.7. North-south stratigraphic cross-section of the Niobrara Formation, D-D', northwestern Kansas to southcentral South Dakota. Format and scale as in Figure 2.4.
Figure 2.8. East-west stratigraphic cross-section of the Niobrara Formation, E-E', north-central Colorado to southwestern Nebraska. Format and scale as in Figure 2.4.
Figure 2.9. East-west stratigraphic cross-section of the Niobrara Formation, F-F', north-central Colorado to south-central Nebraska. Format and scale as in Figure 2.4.
Figure 2.10. East-west stratigraphic cross-section of the Niobrara Formation, G-G', east-central Colorado to northwestern Kansas. Format and scale as in Figure 2.4.
Figure 2.11. East-west stratigraphic cross-section of the Niobrara Formation, Niobrara stratigraphic cross section H-H', east-central Colorado to west-central Kansas. Format and scale as in Figure 2.4.
point. Correlations in the resultant closed, cross-section "loops" (see Fig. 2.3) proved to be internally consistent. This demonstrated that the regional correlation of the Niobrara units could be made with confidence in the subsurface. The study area was largely defined by the regional limits of confident correlation.

Gamma-ray logs were the principle well logs used to correlate horizons in the Niobrara Formation. Gamma-ray logs record the combined gamma-ray emissions of potassium 40, thorium, and uranium (and their daughter products). Because clays usually contain much more of these radioactive minerals than do carbonates or quartz sandstones, gamma-ray logs are often used to quantify shale content in sedimentary sections (e.g., Schlumberger, 1989). Though the Niobrara in the area of study occasionally contains as much as 60% shale (e.g., Pollastro, 1991), most of the gamma-ray radiation (50-80%) in the Smoky Hill Member is due to authigenic uranium that is tied to the organic-matter content of the Niobrara (see Chapter 4). The authigenic-uranium content is a function of several factors and some of these factors (e.g., bottom water oxygenation and organic-carbon flux—discussed in Chapter 4) are climatically modulated and thus basinwide in extent. Therefore, variations in authigenic uranium content and by extension total gamma-ray emissions typically represent synchronous events (see Appendix C).

The physical log correlations used in this study were checked against biostratigraphic control where possible. For example, log correlations were checked against biostratigraphic correlations between Niobrara sections at Pueblo, Colorado (Scott and Cobban, 1964; Pratt et al., 1985) and Kansas (Hattin, 1982) and found to be consistent. However, the time resolution of Niobrara biostratigraphy is not particularly good, in large part because of the paucity of ammonites in many areas (Hattin, 1982).

In a majority of cases, the well-log correlations were made using a single, readily identifiable horizon or bed. In other cases, convergence of beds (to below the resolution of the well logs) or the presence of disconformities prevented the use of a single bed.
character to make the correlations. Despite this, errors in correlation are estimated to be only a meter or two at most.

In the southeastern part of the study area, the middle marl and middle chalk sections are greatly expanded in thickness. Horizons used to divide these units elsewhere are difficult to recognize in this area because characteristic log signatures are lost in the expanded section (largely because contrasts in shale and uranium contents are reduced). However, numerous bentonites can be recognized, particularly on the dual induction logs. Bentonites are recognized by their lack of permeability when compared to the adjacent chalk and by their lateral continuity in recognizable bundles over hundreds of square kilometers. Though individual bentonites are much too thin to be fully resolved within the vertical resolution of the well logs, they affect shallow resistivity and micrologs enough to be recognizable in areas where the Niobrara has not been deeply buried (i.e., is very porous and permeable).

Construction of Isopach Maps

Once the correlations were completed, thickness values for each unit were calculated and these were used to construct isopach maps. Over 700 wells were utilized in the construction of the maps (Fig. 2.3). This was enough to define regional thickness trends for each of the units, and many local thickness variations as well. Structural dips are nearly always very low in the area of study, so vertical log thicknesses were taken as true thicknesses. In a few cases, values for individual horizons were excluded when they were obviously cut by faults of likely Laramide origin.

Figures 2.12-2.26 are a series of isopach maps that illustrate thickness changes in the Niobrara Formation. These maps were contoured by hand and they have not been corrected for differential compaction. Because burial depths have varied in the study area, this factor needs to be considered. Porosity ranges from a maximum of about 30% in
Figure 2.12. Isopach map of the Niobrara Formation.
Figure 2.13. Isopach map of the Fort Hays Member unit 1.
Figure 2.14. Isopach map of Fort Hays Member unit 2.
Figure 2.15. Isopach map of the shale and limestone member and laterally equivalent upper Fort Hays Member of Kansas and central Nebraska.
Figure 2.16. Isopach map of the lower marl member.
Figure 2.17. Isopach map of the lower chalk member unit 1.
Figure 2.18. Isopach map of the lower chalk member unit 2.
Figure 2.19. Isopach map of the lower chalk member unit 3.
Figure 2.20. Isopach map of the middle marl member.
Figure 2.21. Isopach map of the middle chalk member unit 1.
Figure 2.22. Isopach map of the middle chalk member unit 2.
Figure 2.23. Isopach map of the upper marl member unit 1.
Figure 2.24. Isopach map of the upper marl member unit 2.
Figure 2.25. Isopach map of the upper marl member unit 3.
Figure 2.26. Isopach map of the upper chalk member.
shallowly buried sections in western Kansas, for example, to less than 10% in the deeper parts of the Denver Basin. This means that thicknesses in the Denver Basin are reduced by about 25% compared to those in western Kansas. Though this factor should be kept in mind, interpretation of the Niobrara isopach maps is not greatly affected by it. The effect of differential compaction is a broadly regional one. In contrast, most thickness patterns considered herein are more local.

RESULTS

The isopach map of the entire Niobrara Formation (Fig. 2.12) shows significant thinning of the formation from more than 200 m (656 ft) in the southern part of the Denver Basin to less than 100 m (328 ft) in portions of the northern Denver Basin. An area of thin Niobrara extending from north of Denver to the northeast across western Nebraska is coincident with the Transcontinental arch.

The individual Niobrara units exhibit a variety of isopach patterns. These can be grouped into four types: (1) thin units that vary little in thickness, but may be regionally absent (e.g., Fort Hays units 1, Fig. 2.13, and 2, Fig. 2.14), (2) units with low-frequency thickness variations (e.g., shale and limestone, Fig. 2.15), (3) units that have high-frequency thickness variations without consistent preferred orientation (e.g., lower chalk unit 3, Fig. 2.19), and (4) units that have high-frequency thickness variations with a strongly preferred orientation (e.g., upper marl units 2 and 3, Figs. 2.24, 2.25). Classifications of the Niobrara units into these categories is shown in Table 1, along with summaries of the most important aspects of the individual isopach maps.

DISCUSSION

The isopach map of the entire Niobrara (Fig. 2.12) illustrates the pronounced thickness change in the Niobrara that is believed to be the result of Cretaceous reactivation
<table>
<thead>
<tr>
<th>Unit</th>
<th>Type</th>
<th>Description</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Chalk</td>
<td>1</td>
<td>&lt;5 to &gt;10 m thick, locally absent</td>
<td>return to lower levels of tectonic activity, carbonate deposition ends as regression continues</td>
</tr>
<tr>
<td>Upper Marl - 3</td>
<td>4</td>
<td>0 to 25 m thick, SW-NE pattern of thick and thin areas</td>
<td>high level of tectonic activity characterized by syndepositional faulting and erosion on &quot;horsts&quot; paralleling the Transcontinental arch, sea level fall</td>
</tr>
<tr>
<td>Upper Marl - 2</td>
<td>4</td>
<td>0 to 30 m thick, SW-NE pattern of thick and thin areas</td>
<td>level of tectonic activity increases with more syndepositional faulting, S.L. fall continues, disconformity SE of Denver moves to SE, detrital input increases</td>
</tr>
<tr>
<td>Upper Marl - 1</td>
<td>3</td>
<td>0 to 30 m thick, thick in W. Kan. and adj. Neb., absent SE of Denver</td>
<td>differential subsidence/upsift(?) and sea level fall continues, disconformity SE of Denver moves to SE, detrital input increases</td>
</tr>
<tr>
<td>Middle Chalk - 2</td>
<td>3</td>
<td>absent SE of Denver, thickens to over 20m further to SE</td>
<td>differential subsidence/upsilt(?) along with the start of sea level fall initiates a disconformity SE of Denver</td>
</tr>
<tr>
<td>Middle Chalk - 1</td>
<td>2</td>
<td>thin in Denver area (5-10 m), thickens to &gt;60m to SE</td>
<td>cont. subsidence and probable high productivity to SE flanking bathymetric high produced by middle marl deposition, sea level rise slows</td>
</tr>
<tr>
<td>Middle Marl</td>
<td>2</td>
<td>thin to N. of and near Denver (10m), thickens to &gt;60 m to south</td>
<td>subsidence to SE, limited tectonic activity but disconformities present near Denver, detrital input from SSW, locally high productivity, cont. S.L. rise</td>
</tr>
<tr>
<td>Lower Chalk - 3</td>
<td>3</td>
<td>0 to 15 m thick, locally absent, thickens to &gt;15 m to SW</td>
<td>continued basinal tectonic activity reflected in local areas of erosion/non-deposition, differential subsidence/upsilt, cont. sea level rise</td>
</tr>
<tr>
<td>Lower Chalk - 2</td>
<td>3</td>
<td>0 to 20 m thick, gen. &gt;2 m thick, thickens to &gt;15 m to SW</td>
<td>continued basinal tectonic activity reflected in local areas of erosion/non-deposition, differential subsidence/upsilt, cont. sea level rise</td>
</tr>
<tr>
<td>Lower Chalk - 1</td>
<td>3</td>
<td>0 to 8 m thick, thin in area near Denver, pinches out to NW</td>
<td>increased basinal tectonic activity reflected by differential subsidence assoc. with Sevier tectonism, cont. sea level rise</td>
</tr>
<tr>
<td>Lower Marl</td>
<td>2</td>
<td>thin in Denver area (&lt;5 m), thickest to SW (30 m), thins to N.</td>
<td>maximum terrigenous input, thicknesses reflect underlying depositional topography, little tectonic activity, cont. sea level rise</td>
</tr>
<tr>
<td>Shale &amp; Limestone</td>
<td>2</td>
<td>thick near Denver (30 m) and to S. (40+m), thins to N. in Neb.</td>
<td>increased terrigenous input from west associated with Sevier tectonism, creation of depositional relief, cont. sea level rise</td>
</tr>
<tr>
<td>Fort Hays - 2</td>
<td>1</td>
<td>6 to 8 m thick, pinches out and is absent in NW Nebraska</td>
<td>continued sea level rise, transgression, and onlap; little basinal tectonic activity</td>
</tr>
<tr>
<td>Fort Hays - 1</td>
<td>1</td>
<td>2 to 6 m thick, pinches out and is absent in most of Neb. and Kan.</td>
<td>transgression begins with sea level rise, depositional area limited by bathymetric highs to north, east, and west (?), little tectonic activity</td>
</tr>
</tbody>
</table>

Table 1. Summary and interpretation of key aspects of individual Niobrara isopach maps. Categories explained in text.
of the Transcontinental arch (Weimer 1978, 1984). This map is similar to Sonnenberg and Weimer's (1981) Niobrara isopach map, though their map shows several thin areas that are not as apparent in Figure 2.12 because the contour interval used here is larger—20 meters versus 50 feet (15.2 m). Sonnenberg and Weimer (1981) interpreted the areas of Niobrara thinning to be structural highs during Niobrara deposition. This logically follows from the assumption that tectonically controlled accommodation space determines the variations seen in formation thicknesses. Thus the Niobrara isopach map illustrates the cumulative effects of structural activity during Niobrara deposition—a period of about 7.5 Ma and variation in tectonic activity is averaged over this lengthy time period.

The isopach maps of individual units (Figs. 2-13-2.26) illustrate significant regional and local thickness changes during deposition of the Niobrara Formation. These thickness changes can be due to several factors as outlined below.

**Controls on Pelagic Sediment Thickness**

The Niobrara is an organic-rich chalk deposited in a basinal setting well away from land (Fig. 1). It consists of whole and fragmented coccoliths, planktonic foraminifera, terrigenous clay and silt, and benthic micro- and megafossils, in order of abundance (Hattin, 1981; Pollastro and Martinez, 1985). The latter are volumetrically minor, so sedimentation was dominated by pelagic settling of autochthonous biogenic and subordinate allochthonous components throughout the water column.

In pelagic settings, sedimentation usually occurs in relatively uniform layers, particularly when compared to sedimentation in more dynamic settings. Nevertheless, significant lateral variations in sediment accumulation can occur. Controls on pelagic sediment thickness can be divided into two broad categories: those related to currents (especially bottom currents) and those related to spatial differences in sediment supply (e.g., Gorsline, 1984). These two controls are often linked.
Surface and intermediate currents will influence the distribution of pelagic sediments, but bottom-water currents are more important. Variations in bottom-water-current strength control deposition by limiting it, preventing it, or eroding previously deposited sediments (e.g., McCave, 1984). Often this control follows bathymetry. Bathymetric lows tend to accumulate more sediment than bathymetric highs. If the depositional slope is great enough, the thicker sediments in the lows might consist of sediments derived from downslope movement (slumping, etc.) and resedimentation (Gorsline et al., 1984). Sediments are thinned over bathymetric highs by higher-velocity bottom currents. These currents may be generated by wave activity where the bottom reaches normal- or storm-wave base or they may result from acceleration of currents over bathymetric highs. In either case, the currents may be sufficiently strong to either prevent sedimentation or to erode pre-existing sediment. Eroded sediment will be redeposited in the bathymetric lows.

A bathymetric high can be produced by several factors (Fig. 2.27). Pre-existing subaerial surfaces may be drowned by a rise in sea level. Tectonic activity, that is, faulting or folding with differential uplift and subsidence, may produce shoal areas. Both of these were undoubtedly important during Niobrara deposition (Merewether and Cobban, 1986). Underlying sediments may undergo differential compaction and subsidence (see, for example, Gastaldo et al., 1991), although this is less likely where grain size and composition do not change much. Finally, spatial variations in sediment supply may produce bathymetric relief on the sea floor (e.g., Gorsline et al., 1984).

Spatial variations in sediment supply can have several causes. Upwelling and in some places the resultant high biologic productivity can produce dramatic increases in the biogenic component of pelagic sedimentation and in sedimentation and accumulation rates (Hay and Brock, 1992; Berger et al., 1993). Because upwelling areas are usually related to long-term patterns of circulation and/or physiographic factors, these areas tend to
Figure 2.27. Schematic diagram, with vertical exaggeration, of mechanisms that can produce bathymetric highs and and/or thick sediment accumulations in a pelagic setting. Open arrows denote surface currents.
remain relatively stationary for long periods of time. This can produce areas of thick sediment accumulation. Spatial variations in terrestrial sediment influx to a basin are controlled by the size and position of rivers discharging into the basin and current strength and direction within the basin. The fine-grained component may be deposited preferentially by sediment plumes that occur in the surface water (Fig. 2.27), in deeper water along pycnoclines, or in the bottom nepheloid layer (e.g., Gorsline et al., 1984). Wind introduced a large amount of fine-grained terrigenous material into the WIS, particularly as volcanic ash (Bloch et al., 1993), but such material would be broadly distributed and of modest thickness (e.g., Elder, 1988), so it would be unlikely to have produced bathymetric highs.

If sediment supply in a particular area exceeds the increase in accommodation space from tectonic subsidence or eustatic sea level rise, the bottom may reach a local or regional base level (e.g., storm wave base). Then the area of maximum sediment deposition will be progressively displaced and a time transgressive disconformity can result as shown in Figure 2.28. The Niobrara has such a feature, which will be further discussed in a following section.

**Significance of Thickness Variations in the Niobrara Formation**

The Niobrara isopach maps illustrate that significant variations in thickness occur in units that are demonstrably chronostratigraphic. The thickness patterns of these individual units are compared to those expected from the above factors. Although it is not possible to distinguish which of the factors was most important in producing all the thickness variations in each unit, it was possible to do so for many. Clues to the origin of the thickness variations are provided by the thickness pattern of each unit, the relative amounts of carbonate versus clastic sediment in thick versus thin areas, disconformities,
Figure 2.28. Cross-sectional example of a time-transgressive disconformity produced solely by differential sedimentation rates and (a) eustatic sea-level change. (b) Model allows an area of high sedimentation to build up (arrow) until an arbitrary storm-wave base is reached, after which the area of maximum sedimentation is progressively displaced. Sedimentation can resume as accommodation space again increases. The evolution of the paleobathymetry is shown in (b) and the resultant stratigraphy is shown in (c). Model accounts for sediment compaction and water/sediment loading (Airy isostatic correction with regionally averaged loading). Sea-level curve and amount of tectonic subsidence are arbitrary.
and the relationship of thickness changes between units. These factors provide key information concerning the depositional/tectonic history of Niobrara deposition.

Interpretations of the thickness variations in units of the Niobrara Formation are given in the following sections. In all cases, it is assumed that areas of zero thickness result from erosion and/or non deposition of sediment due to intermittent bottom-water currents. In addition, continuous, but spatially and temporally irregular, increases in accommodation are assumed. These increases reflect the combined effects of eustacy and subsidence due to sediment/water loading and tectonics. As discussed in a previous section, thicknesses have not been corrected for differential compaction, but this does not materially affect the conclusions presented below. Discussion of the isopach maps is organized by the categories presented in Table 1 and presented in chronological order from oldest to youngest.

Fort Hays Member—type I

The Fort Hays of this study does not include the uppermost Fort Hays of Kansas because this section is time equivalent to the shale and limestone member along the Front Range (see Fig. 2.10, for example). This result is consistent with the biostratigraphy and correlations presented by Laferriere and Hattin (1987). In Kansas the Fort Hays/Smoky Hill contact is near the base of the *Inoceramus (Volviceramus) grandis* zone (Hattin, 1982), in contrast, at Pueblo the contact is within the *Inoceramus deformis* zone (Scott and Cobban, 1964). At Pueblo the base of the *Inoceramus (Volviceramus) grandis* zone occurs within the shale and limestone member (Scott and Cobban, 1964).

The Fort Hays Member (Figs. 2.13 and 2.14) is thin, and thickness variations are not particularly large. Laferriere and Hattin (1989) attributed the thickness variations to either erosional/depositional or diagenetic thinning over northeasterly trending structural highs that parallel the Transcontinental arch. They suggested that these may have been
structurally active areas during Fort Hays deposition. Any tectonic activity was probably limited, however, because thickness variations are modest. Most of the thickness variation within the Fort Hays Member occurs in its lower portion (Fort Hays unit I, Fig. 2.13). The thickness changes in this unit may reflect depositional relief on the basal Fort Hays disconformity and/or differential compaction in the thick underlying Cretaceous sedimentary section. The uniformity of the Fort Hays in most of the study area suggests that much of the seaway was quite flat-bottomed during early Niobrara deposition.

The lower Fort Hays unit is absent to the east and both Fort Hays units are absent in the northern part of the study area. This is consistent with the loss of lower Niobrara biostratigraphic zones to the northeast (Hattin, 1975; 1982; Shurr, 1984) and the pinchout of the "lower chalk tongue" (equivalent of Fort Hays through lower chalk of this study) of Shurr (1984).

The absence of the Fort Hays in northern Nebraska is the result of nondeposition rather than erosion, as younger Fort Hays beds onlap the basal disconformity in this direction (Laferriere and Hattin, 1989; and cross sections in Figs.2.6-2.7). This structurally positive area was probably not subaerially exposed, but it was probably above wave base. In contrast, most of the Fort Hays was deposited below wave base as indicated by the continuity of its rhythmic bedding and general lack of erosional indicators (Hattin, 1982). Continued onlap of overlying Niobrara units to the northeast suggests that some previous interpretations that Fort Hays deposition marked maximum sea level during the Niobrara transgressive cyclothem (e.g., Kauffman, 1977) are in error, as Kauffman and Caldwell (1993) now suggest (see their figure 4). Water depth during initial Fort Hays deposition is uncertain, but probably was 15 to 50 meters (Hattin, 1982).
Shale and limestone member/lower marl member—type 2.

The isopach map of the shale and limestone member is shown in Figure 2.15. This member is recognized near the Front Range (e.g., Scott and Cobban, 1964; Barlow and Kauffman, 1985), but as noted above, the lateral equivalent toward Kansas is the upper part of the Fort Hays (Figs. 2.9-2.10). Because this study is concerned with time-equivalent strata, this facies change is ignored and the units are grouped together as the shale and limestone member. Like the Fort Hays, the shale and limestone member onlaps the positive area in northern Nebraska, indicating continued transgression. This unit is quite uniform in thickness in the eastern part of the study area, but has three thick areas to the west along the Front Range (Fig. 2.15). The thick areas occur near the western edge of the mapped area and thicken towards the west, implying that the sediment source was there. Although this area was presumably far from the western shoreline at this time (e.g., McGookey et al., 1972; see their figure 37), the pattern is consistent with the distal edges of a prodelta. Indeed, the shale and limestone member is differentiated from the coeval upper Fort Hays by its higher shale content (about 40% versus 20%), which increases to the west.

Although the shale content is higher in the western part of the study area where the limestone and shale is thickest, the proportion of carbonate decreases much less than can be accounted for by simple clastic dilution. Thus the carbonate flux to the seafloor must also have been higher in this area. This would reflect greater productivity of the overlying water compared to areas farther to the east.

Initiation of shale and limestone member deposition (middle Coniacian) is coincident with an unconformity in the San Juan Basin (King, 1974; Bottjer and Stein.

1Well established well-log methods are used to estimate the proportion of carbonate and clay in the Niobrara (see p. 32-33).
1994) that expands to become an extensive depositional lacuna in southwestern Colorado and southeastern Utah (Peterson et al., 1980; Molenaar, 1983). This unconformity is indicative of a relative fall in sea level (Bottjer and Stein, 1994) and probably resulted from movement of deep-seated structures in the area (Elder and Kirkland, 1994), rather than eustatic sea-level change, because a complete section is present farther to the north (Elder and Kirkland, 1994). Because of the lacuna, fine-grained sediments probably bypassed southwestern Colorado and to be deposited farther to the east, including the southwestern part of the study area. Thus it seems likely that deposition of the shale and limestone member is related to increased clastic input that is in turn related to tectonic activity to the west.

The thickness of the shale and limestone/upper Fort Hays unit is uniform in the eastern part of the study area, reflecting limited basinal tectonic activity. This, along with the depositional interpretation expressed above, implies that the thick areas (e.g., near Denver) were expressed as bathymetrically shallow areas on the Niobrara sea floor. This interpretation is supported by the isopach pattern of the overlying lower marl member (Fig. 2.16), discussed next.

A comparison of the lower marl isopach map (Fig. 2.16) to that of the underlying shale and limestone member (Fig. 2.15) reveals an inverse thickness relationship. The prominent thick area near Denver in the shale and limestone unit is overlain by thin lower marl (less than 5 m) and is fringed by thick areas in the lower marl (to more than 20 m., see Fig. 2-10). This pattern is consistent with distal deltaic deposition. Where sediment buildup is great enough, storm wave base is reached, sediment bypassing begins to occur, and sediment accumulation is then greatest at the flanks of the previous high. Thus, much of the thickness variation in the lower shale unit is probably depositional in origin.
Lower marl member deposition is the culmination of the increased clastic input to the Colorado-Wyoming portion of the Western Interior seaway that began with shale and limestone member deposition. As such, it marks end of the first fourth-(Kauffman, 1985) or third-(Kauffman and Caldwell, 1993) order cycle in the Niobrara Formation.

Lower chalk member — type 3

The isopach pattern of the lower chalk unit 1 (Fig. 2.17) is roughly similar to that of the lower marl. A thin area near Denver (less than 2 m) is flanked by thicker areas (2 to 6 m) to the north, east, and south. These thick areas again flank the underlying thick area in the limestone and shale member, and the pattern appears to reflect continued infilling in of the low areas of that unit. A thickening of this unit to more than 8 m near the Kansas border may have resulted either from greater subsidence or higher productivity in this area. In other areas the unit is locally absent, probably reflecting tectonically produced bathymetric highs due to differential subsidence.

Lower chalk member unit 2 has a similar but more subdued pattern compared to unit 1, except for an increased thickness of the unit in easternmost-central Colorado (Fig. 2.18). Deposition of thick chalk continues in that region in lower chalk member 3 and a band of thick chalk appears in unit 33 near the southwest corner of the Nebraska panhandle (Fig. 2.19). Units 2 and 3 are both absent just west of Denver and all three units are absent in an area about 100 kilometers southeast of Denver, with the area of erosion or non-deposition increasing from unit 1 to unit 3. The thick area in units 2 and 3 about 180 km southeast of Denver probably indicates a bathymetric low formed by differential subsidence (see also cross section H-H', Fig. 2.11).

Basinal tectonic activity increased during deposition of the lower chalk compared to the underlying units as evidenced by the increase in high frequency thickness variations and the development of disconformities.
Middle marl member and middle chalk member unit 1—type 2

The isopach pattern changes dramatically with deposition of the middle marl member (Fig. 2.20). This unit is less than 20 m thick over most of the study area and is less than 10 m in places, but thickens to more than 60 m in the southwestern part of the mapped area (see cross sections in Figs. 2.10, 2.11). This thick area extends in a northeasterly direction to the Colorado-Kansas-Nebraska border. It also extends to the south. At Pueblo the unit is 85 m thick (Scott and Cobban 1964) and in the Raton Basin, northern New Mexico, it is even thicker (Scott et al., 1986). Part of this thick area flanks and overlaps one of the underlying bathymetric highs. Effective accommodation space must have increased in this region to allow renewed deposition. However, overlying Niobrara units are thin or absent over this same area (see Figs. 2.21, 2.22), so if accommodation space for the middle marl was created by subsidence, sediment accumulation must have equaled or exceeded the subsidence. It is likely that the thick area in the middle marl unit reflects, not a trough, but higher depositional rates along a bathymetric slope produced by greater subsidence to the southeast and progradation of deltaic sediments from the southwest, where this unit becomes sandy (Scott et al., 1986).

Deposition of the middle marl member was limited near Denver by storm-induced bottom currents over a shoal area (disconformities occur in the middle marl in an area east of Denver, for example— see Fig. 2.10, wells 7 through 12). These currents would have transported sediment to quieter, deeper water flanking the shoal area. Thus some of the thick upper marl may be the result of resedimentation. The carbonate content of the middle marl is somewhat greater in the area where it is thickest (based on corrected gamma-ray and neutron-density log analyses). This is evidence of mixing of resedimented marl with local carbonate production, and the area of thick middle marl may also represent an area of increased carbonate flux. This increased carbonate flux may be a response to input of nutrients from the delta or localized, bathymetry-induced upwelling.
Terrigenous flux from the delta must also have been higher in this area, however, as an increase in the carbonate flux alone would have diluted the shale content to below that actually observed.

Bathymetry-induced upwelling has been recognized along portions of the southeast coast of the United States where it accounts for episodes of enhanced productivity (Blanton et al., 1981; Atkinson and Targett, 1983; Riggs, 1984). Average sedimentation rates for the Niobrara range from 1 to 3 cm/ka uncorrected for compaction or 3 to 6 cm/ka corrected to 60% porosity. In contrast, sedimentation rates in the area of thick middle marl deposition range from 20 to as much as 40 cm/ka (with 60% porosity). These values correspond to carbonate productivities of 195 to 390 gCaCO₃ m⁻² a⁻¹ (assuming sediment is 70% carbonate). These high productivity values are consistent with upwelling as are organic-carbon (OC) productivity estimates of over 200 gCorg m⁻² a⁻¹ (see Chapter 5).

The thick middle marl area is overlain by a thin area in the middle chalk unit 1 (Fig. 2.21). The thickest area in the middle chalk unit 1 is southeast of the thickest area of the middle marl along the Colorado-Kansas border (see cross section H-H', Fig. 2.11). Paleoproductivity values in this area of middle chalk unit 1 are comparable to those of the middle marl.

Middle chalk member unit 2 and upper marl member unit 1 — type 3

The pattern in the middle chalk unit 2 (Fig. 2.22) is similar to that of the underlying middle chalk unit 1, for example, both units thicken to the southeast. However, unit 2 begins a trend towards higher-frequency variations in thickness, and it is absent over much of the area occupied by the thickest part of the middle marl. The isopach map of upper marl unit 1 (Fig. 2.23) continues elements of the isopach map of
the underlying middle chalk unit 2. Again there is an area of zero thickness to the southeast of Denver and the frequency of thickness variations has increased.

**Upper marl units 2 and 3—type 4**

Isopach maps of the two upper marl units continue elements of the isopach maps of the underlying units, except that the thickness variations show strongly oriented, northeast-southwest trends (Figs. 2.24, 2.25). Each of these units has an area of very thin or zero thickness roughly overlying the thickest areas in the underlying middle marl and middle chalk unit 1. The area of zero thickness has migrated to the southeast with time and is the product of a time-transgressive disconformity, which at its maximum extent represented more than a million years. This disconformity is seen on cross-sections A-A', B-B', and H-H' (Figs. 2.4, 2.5, and 2.11). On these cross sections the disconformity is quite obvious. It is generally represented by many meters of missing section and a thin zone with a very high gamma-ray reading. In addition, the disconformity is typically characterized by increased density (reduced porosity) compared to adjacent zones. This reflects penecontemporaneous cementation and resultant hardground formation—a process that is favored by long periods of contact between the sediment and seawater (Scholle et al., 1983). Frequently, the high-density zone can be seen to truncate underlying horizons.

Initiation of the disconformity occurs in the upper part of the Niobrara middle chalk. The middle chalk is the most extensive chalk zone in the Niobrara (this study and Shurr 1984) and it represents the maximum transgression of the Niobrara sea. The initiation of the disconformity occurs at about 85 Ma. This follows the maximum Niobrara transgression shown by Kaufman and Caldwell (1993) and corresponds to the fall in sea level at 85 Ma shown by Haq et al. (1987).
Basinal tectonic activity became more common during deposition of the upper marl. Local disconformities become more common in this part of the section, listric normal faulting is common in some areas (Cockerham, 1982; Jeffrey, 1982; Davis, 1985), and thickness variations become more pronounced and regular in pattern. The latter is particularly evident in upper marl unit 3 (Fig. 2.25). The northeast-southwest trending thickness pattern probably reflects reactivation of basement faults paralleling the Transcontinental arch.

Upper chalk member—type 1

The upper chalk member (Fig. 2.26) is not as variable in thickness as the underlying upper marl unit 1 (Fig. 2.25), although the maximum thickness in both units is about the same. This is an interesting result, as Cockerham (1982), Jeffrey (1982), and Davis (1985) all reported that much of the listric faulting discussed in the previous section extends through the Niobrara into the lower part of the Pierre Shale. The contrast in thickness variability between the upper chalk and underlying upper marl unit 1 could be the result of two separate factors: (1) It could mean that the faulting was concentrated during deposition of the upper marl and that tectonic activity diminished during deposition of the upper chalk or, (2) that tectonic activity continued at a steady rate, but is not reflected in the thickness pattern of the upper chalk. Either scenario is plausible as outlined below.

In scenario one above, a peak in basinal tectonic activity would have resulted in nondeposition or erosion in areas of differential uplift. Deposition would have been concentrated in the bathymetric lows. A reduction in tectonic activity during upper chalk deposition would have resulted in a reduction of basin topography and a return to more regionally continuous sedimentation, resulting in the regionally more uniform thickness of the upper chalk. Alternatively, changes in sea level might have produced the isopach
patterns observed. Sea level reached its maximum during deposition of the middle chalk (Kauffman and Caldwell, 1993 and this study) and was falling during deposition of the upper marl. As sea level fell, areas of nondeposition and erosion became more common as the storm wave base approached bottom. This enhanced the difference in net sedimentation rates between bathymetrically (i.e., tectonically) high areas and bathymetrically low areas. If the upper chalk represents a rise in sea level as has been proposed (e.g., Kauffman and Caldwell, 1993), then such differences would have been reduced and the resulting isopach map would reflect less thickness variation.

It is not possible to unequivocally determine which of the above scenarios is correct. However, in many places where the upper marl 3 unit is highly variable in thickness, it is overlain by a normal upper chalk section with no significant thinning suggesting that basinal tectonic activity reached a peak during upper marl deposition (see wells 7 through 15 in Figure 9, for example). In addition, thinning of the upper chalk is often the result of erosion that post-dates upper chalk deposition and thus the thinning is unrelated to syndepositional tectonics (see wells 50 to 51 in Figure 4, for example).

SYNTHESIS

Tectonics

A brief summary of the level of basinal tectonic activity during Niobrara deposition is presented here and in Table 1. The four categories of isopach patterns are used to distinguish varying levels of and responses to tectonic activity. These are: (1) low levels of basinal tectonic activity (Fort Hays), (2) low levels of basinal tectonic activity, but with increased detrital input (e.g., lower marl), (3) moderate levels of basinal tectonic activity, and (4) high levels of basinal tectonic activity including strongly oriented faulting (e.g., upper marl 3). These divisions closely correspond to those based on isopach patterns (summarized in Table 1).
During early Niobrara deposition (Fort Hays through the lower marl) basinal tectonic activity was limited. Basinal tectonic activity increased during lower chalk deposition, but appears to have diminished again during middle marl deposition. Then tectonic activity increased in the upper part of the Niobrara, particularly during deposition of middle chalk unit 2 and the overlying upper marl.

Niobrara deposition (Late Turonian to Early Campanian) occurred during a period of active thrusting in the Sevier orogenic belt to the west (Armstrong and Oriel, 1965; Armstrong, 1968; McGookey et al., 1972) and basinal tectonic activity is likely to be linked to this thrusting (Merewether and Cobban, 1986; Weimer, 1986). Previously, I linked periods of Niobrara tectonic activity to specific thrust events of short duration (Tanck and Parrish, 1996). For example, differential uplift during lower chalk deposition is coincident with the Coniacian-Early Santonian age of the Echo Canyon Conglomerate (Jacobson and Nichols, 1982), the deposition of which has been attributed to major movement along the Crawford thrust (Armstrong and Oriel, 1986c). However, the linking of basinal tectonic activity to specific, well-timed, thrust events is problematical. Although precise dating of thrusting is often implied by published figures (e.g., Kauffman, 1984; Armstrong and Oriel, 1986c; Villien and Kligfield, 1986), the dating of thrust fault movement is typically not very precise (Armstrong and Oriel, 1986a; Armstrong and Oriel, 1986b; Peter G. DeCelles, personal communication). For example, according to DeCelles (1994) movement along the Crawford thrust was likely from the Late Turonian through the Santonian.

Upper marl deposition began during the Late Santonian (at about 84.5 Ma). This marked a period of increased basinal tectonic activity that culminated during deposition of upper marl unit 3. The increase in tectonic activity during Upper Niobrara deposition was previously recognized by Weimer (1986) and he linked it to major thrusting on the Meade-Crawford thrusts in Wyoming and Utah. Although this linkage is problematical, the upper marl was deposited during a period of increased volcanic activity that is well
documented by an increase in volcanic ash abundance (figure 3 of Kauffman and Caldwell, 1993). Thus it seems likely that upper marl deposition occurred during a period of increased tectonism in the Western Interior.

The striking pattern of northeast-southwest trending thickenings and thinning of the upper marl unit 3 (Fig. 2.25) was probably produced by the syndepositional listric normal faulting that has been documented to occur in the upper part of the Niobrara (Cockerman, 1982; Jeffrey, 1982; Davis, 1985). Unlike faulting during Pierre Shale deposition that has been attributed to growth faulting (Davis and Weimer, 1976), the listric faulting in the Niobrara has been attributed to underlying faulting of the basement (Davis, 1985). Although listric normal faults typically occur in extensional settings (e.g., Shelton, 1984), the basement faults shown on seismic lines in Davis (1985) may be steeply dipping reverse faults consistent with the overall east-west compressional stresses that existed during most of the Upper Cretaceous (Gries, 1983). The orientation of the basement faults, SW-NE, suggests that they may be related to the Transcontinental Arch, which was probably a zone of weak, hetrogenous basement that was subject to recurrent tectonic movement (Weimer, 1978).

In addition to secular changes in the level of basinal tectonic activity there were distinct regional variations as well. In particular, there was a strong east-west gradient in the level of tectonic activity. Syndepositional faulting and disconformities were common in the western part of the study area (Colorado, western Wyoming, western Nebraska), but rare in the eastern part (central Nebraska and western Kansas; Compare isopach patterns in the two areas and note differences between the western and eastern portions of the east-west cross sections; Figs. 2.9-2.12). The western areas were in greater proximity to the ancient Transcontinental Arch and probably inherited structural weaknesses along and paralleling this trend.

To accommodate Niobrara deposition (and all of Upper Cretaceous deposition), a considerable degree of tectonic subsidence is required. Models of foreland basin subsidence have typically focused on subsidence produced by lithospheric flexure caused
by crustal loading produced by imbricate thrust faulting in the orogenic belt (Beaumont, 1981; Jordan, 1981). In these models, significant subsidence is restricted to a zone about 300 to 400 km wide between the orogenic belt and the forebulge (Beaumont, 1981; Jordan, 1981), but significant thicknesses of sediment accumulated well to the east of this zone in the WIS, thus an additional mechanism to account for this more distal subsidence is required. Models by Mitrovica et al. (1989) and Gurnis (1992) are able to account for this additional subsidence by appealing to dynamic slab effects associated with subduction.

Disconformities in the Niobrara

Disconformities are common in the Niobrara Formation. With the exception of the basal Fort Hays disconformity, these are typically relatively local in extent. Their limited areal extent and the significant time span represented (a minimum of 200 Ka for lower chalk units 1 and 2, for example) suggests that they were not a result of lack of sediment (i.e., no productivity). Instead these disconformities must been caused by bottom currents of sufficient strength to prevent deposition or cause erosion.

Strong bottom currents could be density or tidal driven, but neither factor is likely to have accounted for the disconformities in the Niobrara section. Strong density currents would have been confined to the deepest parts of the basin and erosion would have tended to occur in continuous bands, not isolated areas. Though there is some evidence of tidal currents in the Western Interior seaway (Klein and Ryer, 1978), such evidence is largely confined to rocks deposited in sheltered nearshore environments (Ericksen and Slingerland, 1990). Ericksen and Slingerland (1990) concluded that tides were microtidal within the seaway and that storm-influenced deposition was more important.

The disconformities in the Niobrara are therefore probably the result of storm currents affecting bathymetric highs. Storms produce geostrophic currents as well as gravity-wave oscillatory currents. Either can have significant depth implications. Storm-wave base in the Western Interior seaway has been estimated to be at a depth of 100 to
150 m (Winn et al., 1987). No evidence for this depth is provided by Winn et al. (1987), although it is consistent with the common observation that only the very largest waves (>10 s period) cause significant motion below 100 m (e.g., Ross, 1977).

**Water Depth**

To better ascertain the effective depth of storm-wave base in the Western Interior seaway it is necessary to consider the likely size of storm-generated waves and the depth to which they could erode sediment. The size of wind-generated waves is a function of wind velocity, wind duration, and fetch. The chart in Figure 2-29 plots wave period *versus* wind velocity, assuming a fetch of 600 km (values are from a wave prediction chart in Collins, 1976). Prevailing winds were from the west in the Cretaceous Western Interior seaway (Parrish et al., 1984) and 600 kilometers is the distance from eastern Colorado to the western paleoshoreline. Winds are assumed to be unidirectional and durations range from about four days for the smallest wind velocities to one day for the highest wind velocities. These durations produce near-maximum wave sizes for the given wind velocities and fetch (increasing durations and/or the fetch beyond 600 km has only a small effect on increasing the wave size).

Figure 2-30 is a plot of water depth *versus* maximum wave-orbital velocity (only velocities less than one m/s are plotted) for waves of various periods (from equation 1 in Clifton, 1976). Typical wave heights and wavelengths for waves of these periods are assumed (from charts in Collins, 1976). As expected, only waves with periods of greater than 10 s produce significant velocities below 100 m.

Data on the velocities needed to erode pelagic calcareous oozes are limited, but Southard et al. (1971) conducted flume experiments with a calcareous ooze of very similar composition to the Niobrara. The authors found that critical erosion velocities varied from about 8 to 20 cm/s at 6 cm above the bed. Critical velocities were found to be roughly proportional to the elapsed time from bed preparation to the time of the experiment, reflecting the rapidity of initial dewatering and compaction. Highest critical
Figure 2.29. Graph of wave period versus sustained wind velocity (four days for lowest wind velocities to one day for highest) for a fetch of 600 km. Fetch of 600 km is the approximate distance of eastern Colorado from the western paloshoreline (see Figure 1), which was in the direction of the prevailing westerly winds. Graph is derived from wave prediction chart in Collins (1976).
Figure 2.30. Chart of water depth versus wave orbital velocity for waves of various periods. Chart is based on equation 1 in Clifton (1976).
velocities were close to 20 cm/s in sediments that had 20 hours to "set." Porosities in these samples were approximately 70%, a value that is consistent with surficial carbonate oozes in deep ocean settings (e.g., Shipboard Scientific Party, 1989). Southard et al. (1971) estimated that a 20 cm/s velocity in their flume was equivalent to a velocity of about 36 cm/s one meter above the ocean floor where bottom frictional effects are minimized.

Based on the above, a wave-orbital velocity of 40 cm/s is used here to test which combinations of waves and paleobathymetry could have eroded newly deposited Niobrara chalk. This value should be considered an absolute minimum for Niobrara erosion as it does not account for the likely consolidation of sediment in a natural setting owing to the influences of microbial or algal mats. The latter can greatly increase the critical shear velocities needed to erode sediment (e.g., McCave, 1984).

Figure 2.31 combines Figures 2.29 and 2.30 in a plot of wave-orbital velocities versus sustained wind speeds for various depths. Predicted Cretaceous wind velocities can be used to estimate near-bottom wave orbital velocities from this chart. Cretaceous atmospheric circulation can be predicted by analogy to modern circulation (e.g., Parrish and Curtis, 1982; Parrish et al. 1984) and/or by numerical modeling (e.g., Barron and Washington, 1982).

Ericksen and Slingerland (1990) presented a general circulation model (GCM) for the Cretaceous WIS that is relevant to this study. They modeled two types of winter storms, one with maximum wind velocities approaching 20 m/s and one with maximum wind velocities of 28 m/s. These results are consistent with Recent winter storms in temperate latitudes. A 20 m/s wind speed does not produce the 40 cm/s minimum wave-orbital velocity necessary to erode newly-deposited Niobrara chalk except at depths of 50 m or less. A 28 m/s wind speed produces the critical velocity at depths of 80 m or less. Hurricane-force winds of 33 m/s produce the critical velocity at depths to 100 m. Stronger hurricane winds of 50 m/s can produce the critical velocity to depths of 160 m.
Figure 2.31. Chart of sustained wind velocities versus "bottom" wave orbital velocities. Chart based on same data used in Figures 34 and 35.
Ericksen and Slingerland's (1990) GCM simulations also predicted geostrophic current velocities. For the first winter storm scenario, maximum geostrophic currents in the seaway were predicted to be 27 cm/s at 100 m depth. In eastern Colorado the maximum predicted values were about 15 cm/s. Geostrophic current vectors were not presented for the second, stronger, winter storm scenario, but the authors reported a modeled "massive" geostrophic flow of 40 cm/s to a depth of 100 m. This value is consistent with winter-storm produced geostrophic currents on the Recent Atlantic Shelf (Beardsley and Butman, 1974; Swift et al., 1986), and it just reaches the minimum critical velocity for erosion of Niobrara sediment.

Hurricanes may have entered the WIS and influenced sedimentation (Duke, 1985; 1987), though their importance compared to winter storms has been downplayed by Klein and Marsaglia (1987) and Swift and Nummedal (1987). Though hurricanes could have produced short periods of deep oscillatory current flow, they are unlikely to have produced strong geostrophic currents because of their limited areal extent (Swift and Nummedal, 1987). Finally, hurricanes would have occurred during the summer and fall—periods when seasonal density stratification would have tended to dampen the effect of surface waves.

Given all of the above, it seems probable that disconformities in the Niobrara were formed by waves on bathymetric highs at or near winter-storm-wave base at depths of 100 m or less, though deeper erosion by geostrophic currents cannot be totally discounted. Stratal patterns suggest that water depths away from the disconformities were not substantially greater. During most of Niobrara deposition water depths were greatest in the southeastern portion of the study area.

Origin of the Time-Transgressive Disconformity

The time-transgressive disconformity initiated in the upper part of the middle chalk has interesting connotations for Niobrara deposition. Though regional tectonics, such a migrating forebulge zone (e.g., Allen and Allen, 1990) can form a similar
disconformity, such a mechanism is not likely in this case. The area encompassed by the disconformity is about 750 km from the Sevier thrust belt, well to the east of the forebulge zone suggested by Kauffman (1985) and is relatively local in extent. Figure 2-28 presented a conceptual model for production of a time-transgressive disconformity, but it cannot completely account for the one seen in the Niobrara.

To model the disconformity, a 250-km cross section was constructed across the disconformity along a line from just south of Denver to the Colorado-Kansas border to the southeast (Figs. 2-32). Present-day thickness values for each of the Niobrara units were picked from the isopach maps at 21 equally spaced points along the section. These thickness were decompacted and then recompacted as each unit was successively added to the previous one to model the Niobrara sedimentation along the cross section. A sea level curve (Fig. 2-33) consistent with previous literature (e.g., Kauffman, 1977; Haq et al., 1987) was used incorporated into the model. Subsidence due to water and sediment loading was accounted for using standard techniques (e.g., Allen and Allen, 1990). The lithosphere was assumed to be rigid (given the length of the the cross section and small differences in sediment loading along the section, this is a valid assumption), so sediment thicknesses were averaged over the entire section and these values were used for calculation of sediment loading. Tectonic subsidence in this model includes true tectonic subsidence as well as that caused by sediment loading outside the extent of the cross section. This is because the model includes the critical assumption that disconformities in the Niobrara formed at a uniform depth of 100 m, so wherever the cross section contains a disconformity, the local paleobathymetry was adjusted to this depth by varying the tectonic component of the subsidence as needed. The actual values for sea level change and tectonic subsidence are not critical to the model as it was designed to test the differential tectonic subsidence/uplift needed to meet the paleobathymetric criteria above.

Figure 2.34 shows the evolution of the paleobathymetry with time. Note the greater degree of subsidence of the basin to the southeast and the differential subsidence/uplift needed to create the disconformity. Figure 2.35 shows a series of
Figure 2.32. Niobrara Formation cross section X-X' showing present day thicknesses of Niobrara units used in this study. Datum is the base of the Fort Hays Member Note disconformity. Increase in thickness to the southeast is largely, but not entirely, due to decreased burial depth. Thicknesses from this cross section were used to model Niobrara deposition.
Figure 2.33. Sea-level curve used in the model of Niobrara deposition. The values and exact timing of the sea-level rise are arbitrary, but are consistent with sea-level curves for this interval (e.g., Haq et al., 1987).
Figure 2.34. Model of bathymetric evolution of Niobrara deposition along cross-section X-X' following deposition of: (a) shale and limestone, (b) lower chalk, (c) middle chalk unit 1, (d) upper marl unit 1, and (e) upper chalk (end of Niobrara deposition). Zero datum is sea level. Initiation of time transgressive disconformity during middle chalk unit 2 deposition is indicated by unannotated arrow in (d). Note how the disconformity migrates to the southeast with time.
Figure 2.35. Tectonic profiles at equal intervals along section X-X' showing "tectonic" subsidence/uplift at each location plotted against time. Vertical lines represent zero subsidence/uplift. Deflection to the left indicates subsidence and deflection to right indicates uplift. Each tick mark represents 2 cm/ky of tectonic movement.
"tectonic" profiles through time for points along the cross section. The vertical lines represent zero tectonic uplift or subsidence. Deviation from this line to the left indicates subsidence and deviation to the right indicates uplift.

Periods of greater subsidence seem to have occurred during marl deposition. This may result from increased tectonic subsidence or from sediment loading produced by the progradation of thick clastic wedges from the west or south (middle marl). Alternatively, sea level could be rising and creating the increased accommodation space, although this would be contrary to the view that marl deposition occurred during eustatic sea-level falls (see above).

**Sea Level Change**

The presence of areas of nondeposition/erosion during lower and middle chalk deposition suggests that the paleobathymetry was at or near storm-wave base much of the time. This is inconsistent with a sea-level rise of 50 to 100 meters during chalk deposition as postulated by Kauffman and Caldwell (1993) even if a more open seaway and/or increased size of storms resulted in a lowering of storm-wave current depths. Thus it is likely that the third-order chalk/marl cycles in the Niobrara (e.g., Kauffman and Caldwell, 1993) are largely the result of regional tectonics and/or autocyclic processes and not large-scale eustacy as generally thought (e.g., Barlow and Kauffman, 1985; Kauffman and Caldwell, 1993). If correct, this interpretation of the chalk/marl cycles eliminates the problem of finding a plausible mechanism for sea level change on a time scale of 100's of ka in an ice-free Cretaceous world.

**SUMMARY AND CONCLUSIONS**

Geophysical well-log correlations were used to demonstrate the presence of numerous chronostratigraphic horizons in the Niobrara within the study area. Certain of these horizons were used to divide the Niobrara into a total of 14 chronostratigraphic units. Isopach maps of these members were used to document variations in sedimentation
patterns and basinal tectonic activity during Niobrara deposition. A number of significant conclusions arise from this work.

(1) Areas of nondeposition and erosion throughout much of the Niobrara section suggest that deposition was never far below storm-wave base (100-150 m). Basinal tectonic activity and differential subsidence resulted in areas of nondeposition and erosion in the Niobrara.

(2) Chalk/marl cycles were not the result of large fluctuations in sea level as previously proposed.

(3) Levels of basinal tectonic activity are low during lower Niobrara deposition, increase during middle Niobrara deposition, and culminate during upper marl deposition at a time of maximum volcanic activity.

(4) Some Niobrara isopach patterns can be related to distal deltaic deposition (sediment plumes?) and possible variations in paleoproductivity.

(5) An extensive time-trangressive disconformity to the southeast of Denver was triggered by sea-level fall in the Late Santonian that exposed middle chalk sediments to storm-wave-base erosion. The disconformity propagated upsection and to the southwest as the locus of sedimentation and differential subsidence moved in that direction.
CHAPTER 3

WELL-LOG ESTIMATION OF ORGANIC-CARBON CONTENT
IN THE NIOBRA FORMATION AND SHARON SPRINGS MEMBER OF THE
PIERRE SHALE

INTRODUCTION

Study Rationale

The Upper Cretaceous Niobrara Formation and overlying Sharon Springs
Member of the Pierre Shale are two of several rock units deposited in the Western Interior
seaway (WIS) that are rich in organic carbon (OC). The Niobrara Formation in the greater
Denver Basin study area ranges from 80 to 100 m in thickness. It consists of alternating
chalk and marl units and is divided into two formal members, the Fort Hays and the
Smoky Hill, and several informal members (Scott and Cobban, 1964). With the
exception of thin shale interbeds the Fort Hays Member is OC-poor with total organic
carbon (TOC) values of less than 1.0% (Pratt and Barlow, 1985). In contrast, TOC
values in the overlying Smoky Hill Member range from about 2.0 to 6.0% with an
average of about 3.0% (Hattin, 1982; Rice, 1984; Rodriguez, 1985; Dean and Arthur,
1989).

The Sharon Springs Member of the Pierre Shale is a dark brown to black, OC-
rich shale that is resistant to weathering. In the greater Denver basin region, it varies in
thickness from a few meters to over 100 m. TOC values in the Sharon Springs are
variable, typically ranging from 3.0 to 10.0% (Gill et al., 1966; Gill et al. 1972; Zelt and
Gautier, 1985).
As discussed Chapter 1, the origin of organic enrichment in these units has been the subject of considerable controversy (e.g., Gautier et al., 1984; Barlow and Kauffman, 1985; Pratt et al., 1985; Eicher and Diner, 1989; Parrish and Gautier, 1993). Although these rocks are quite well studied, one aspect that has not previously been examined in any detail is the three dimensional (3D) distribution of OC within these units. Yet this factor is of critical importance in assessing the potential models that can account for the origin of the organic enrichment. Stratified basin models require that OC-rich rocks be centered in the deepest part of the basin and that the OC-enrichment be widespread at any given time. As stratification may be periodic, temporal variation in OC content is possible, but lateral variations should be minimal. In contrast, high productivity is seldom basin-wide. Instead, it occurs in areas prone to upwelling and perhaps off the mouths of rivers. Upwelling zones may be episodic, and over long periods of time upwelling zones can migrate with changes in circulation and/or physiography. The OC content of rocks produced in seas with upwelling zones can than be expected to be both temporally and spatially variable. By determining the 3D distribution of OC, it may be possible to distinguish between the models.

The Cretaceous WIS rocks are among the best-studied in the world, yet insufficient core samples exist to reconstruct the 3D geometry of OC-rich layers. Well logs are abundant, however, and provide the only source of data that is extensive enough for such reconstructions. This chapter demonstrates that the Carbolog method of estimating OC-content (Carpentier et al., 1991), in particular, can be successfully applied to the Niobrara and Sharon Springs. The methodology for adapting this method to the Niobrara and Sharon Springs is developed in this chapter for application in subsequent chapters. This chapter is organized as follows: the effect of OM on a variety of specific well logs is summarized, the Carbolog method is explained, the method is calibrated to
sample data from the Niobrara and Sharon Springs, and finally its predictive capabilities are tested.

This chapter shows that varying degrees of organic maturity can be accounted for by calibrating the Carbolog method to the burial depth of the Niobrara and Sharon Springs. Past applications of the method have not done this. Further, equations for the use and calibration of the method are provided. By combining estimated OC contents with high resolution stratigraphic control (Chapter 2), it is possible to reconstruct the 3D distribution of OC-rich within the Niobrara and Sharon Springs.

**Use of Well Logs to Estimate Organic-Carbon Content**

Organic matter (OM) has physical properties that are quite different from those of most rock constituents. Because of these differences, the petrophysical properties of rocks containing OM are somewhat different from those lacking OM. Modern geophysical (wireline) well logs are sensitive enough to detect these changes even when relatively small amounts of OM are present. Given the importance of OM-rich rocks to petroleum exploration, it follows that geophysical logs have been utilized in an effort to estimate OM content (and by extension, OC content).

Previous investigators have used a variety of methods to estimate OC content from well logs. Types used include: gamma-ray logs (Schmoker, 1980; 1981), gamma-ray spectra logs (Fertl and Rieke III, 1980; Zelt, 1985), density logs (Schmoker, 1979, 1993; Schmoker and Hester, 1983), pulsed neutron (carbon/oxygen) logs (Herron, 1986), and various combinations of logs (Meyer and Nederlof, 1984; Mendelson and Toksoz, 1985; Autric and Dumesnil, 1985; Carpentier et al., 1991; Passey et al., 1991). Each of the methods has advantages and disadvantages, depending in large part on the availability of suitable logs and the nature of the rock strata being investigated.
A more detailed discussion of some of these "log OC" methods follows, but first there are some common problems associated with every method of estimating OC from well logs that need to be considered. These problems revolve around four facts: (1) the complex natural variability of rock strata, (2) the inherent inaccuracies and limitations of geophysical logging methods, (3) the variability of organic matter, and (4) the difficulty in calibrating log-derived OC values with measured OC values.

Of necessity, most log-OC methods assume the rock formation surrounding the borehole to be a simple, three- or perhaps four component system. This simplification means that variations in minor constituents are not accounted for. Though variations in these constituents may be small, they will affect log response and lead to inaccuracies in log-derived OC values. An example is the potential vertical variability in formation fluid resistivities, especially when some zones contain hydrocarbons. For log-OC methods that use the deep-resistivity log, this can be a source of error.

Modern geophysical well logs are carefully calibrated and generally quite accurate, but are subject to variations in the environment in which they operate. Borehole size affects some log readings, for example, as does drilling mud weight. Corrections can usually be made for these particular variations. Other variations are difficult to correct for, including those caused by the statistical variations in radioactive decay (i.e., gamma-ray logs).

One problem that most log-OC methods share is the great variability in OM. Most minerals have well-defined compositions and structures, and therefore have physical properties that fall within narrow ranges. In contrast, organic matter can vary substantially in composition and physical structure (Tissot and Welte, 1978). Thus the physical properties of OM are variable. Even when the OM type is constant over a wide
area, the level of organic diagenesis (maturity) will vary with burial depth, producing changes in OM physical properties.

Finally, it is important to examine the compatibility of log-OC values with those obtained by conventional sampling for laboratory analyses. This is critical as log-OC methods must be calibrated to actual OC data. Laboratory analyses of OC content are usually reported as total-organic-carbon (TOC) in weight percent of the dry rock (Waples, 1985). TOC data, then, are calibrated to log-derived values for OC.

Geophysical well logs vary in vertical resolution, but about two feet (0.6 m) is typical. Log measurements average the physical properties of the rock measured over this interval. Because the geophysical measurements are made with a moving sonde, the resulting log records a "running average" of the rock property(ies) being measured. Log-calculated OC values will then also be a running average with similar resolution. This contrasts with the kind of TOC data obtained from cores or outcrops. Usually only a few samples are taken in any particular stratigraphic interval, and at best samples represent only an inch (centimeter or two) of section every few feet. If vertical variations in OC content are small and gradual, this sampling strategy may accurately reflect OC values for the entire sampled interval, and thus be compatible with log-OC values. More typically, however, vertical variations in OC occur on centimeter or even millimeter scales. Figure 3.1 illustrates this for a 2.5 foot (0.8 m) section in the Niobrara. In this case, a dense sampling strategy serves to illustrate the large and rapid variations in organic-carbon content can occur within a thin stratigraphic interval.

Ideally, the calculated log-OC value for the interval shown in Figure 3.1 would be

---

1 Feet will be used in this chapter as that is the historical standard unit of measurement in the U.S. oil industry and some figures herein reproduce well logs that are calibrated in feet.
Figure 3.1. TOC values for a 2.5 foot (0.8 m) Niobrara interval in the Coquina Oil Co. #4-Berthoud State well, Larimer Co., Colorado. Data from Dean and Arthur (1989).
close to the actual average OC content of about 3.0% as determined from laboratory analysis of the samples. This would lend credence to the log method chosen. But, if for example, the only sample available for calibration was from 3042.25 feet (927.2 m), where the TOC value is about 4.7%, the log method would be assumed to be in error by 1.7%. The systematic sampling in Figure 3.1 is not a universal practice. Rather, geologists sometimes concentrate on sampling the richest-appearing horizons. Thus the skewness cited here as an example is likely to be the case in many wells.

The problem demonstrated by Figure 3.1 is nearly universal and this makes calibration and accuracy assessment of log-derived OC values very difficult. TOC values obtained from well cuttings are potentially more compatible with log OC values, as cuttings presumably contain rock fragments representing a substantial interval. However, depth control for most cuttings is poor, they are subject to caving from upsection, and they usually are not representative of the complete section of interest.

Though both the Niobrara Formation and Sharon Springs Member of the Pierre Shale are discussed in this chapter, the Niobrara receives more emphasis especially in the following section. This is because there are very few cores available from the Sharon Springs and cores are critical to fully calibrating and testing the Carbolog method.

A brief background summary of the common geophysical logs that have been used to estimate OC content is presented below. To illustrate the effect of OC on these logs, I first collected TOC data from a well that was cored through much of the Niobrara section and that has a full suite of geophysical logs. The TOC data from the core were compared to the geophysical-log responses and used to calibrate the log-derived OC data. The effect of OM on the common geophysical logs is described with reference to these data and the calibration.
Calibration

I selected two cores for sampling and total-organic-carbon (TOC) analyses. These cores were provided by the United States Geological Survey Core Research Center in Denver. Sample analyses were provided courtesy of Conoco, Inc., Ponca City, Oklahoma. One of these cores, a 238 foot (72 m) Niobrara core from the Golden Buckeye #2-Gill well in Weld County, Colorado, is particularly important, because it has a full log suite, including gamma-ray, gamma-ray spectra, sonic, density, neutron, spontaneous potential, and dual induction (resistivity) logs. This means that a number of different log-OC methods could be tested. Further, the core covers most of the Niobrara section (Fig. 3.2).

To make the core samples as compatible as possible with log measurements, continuous sampling was conducted. Longitudinal (vertical) slices of each core piece were cut, crushed, and proportionately mixed to produce composite samples, each representing two feet (0.6 m) of section. (Unfortunately, missing core intervals meant that most samples did not represent a full two feet). The TOC content of the samples was determined using a LECO carbon analyzer. The samples were also subjected to Rock-Eval analyses. These analyses were done at DGSI, The Woodlands, Texas, courtesy of Conoco, Inc., Ponca City, Oklahoma.

Gamma-Ray Logs

Gamma-ray logs have been used alone or in combination with other logs to estimate OC content. The gamma-ray log records the emission of gamma rays due to the radioactive decay of potassium 40 and the thorium and uranium series (Schlumberger, 1989). The use of gamma-ray logs to estimate OC content is based upon the well-known association of authigenic uranium with OM (Beers and Goodman, 1944; Russell, 1945;
Figure 3.2. Gamma-ray and sonic log on the Golden Buckeye #2-Gill Land Co. well, (22-6N-64W), Weld Co., Colorado. Cored interval is shown along with the formal and informal members of the Niobrara.
Swanson, 1960). This association will be discussed in detail in Chapter 4, where controls on the ratio of authigenic uranium to organic carbon will be addressed. In addition, use of this ratio to assess levels of bottom-water oxygenation will be demonstrated.

Typical shales have uranium contents of about 3 ppm (Schlumberger, 1989), representing perhaps 20 to 30% of total gamma-ray emissions. In OC-rich shales, however, the uranium content is commonly 20 to 40 ppm or more and may represent as much as 70 to 80% of total gamma-ray emissions. Thus OC content will correlate fairly well to total gamma-ray readings. In shales with uniform clay mineralogy (nearly constant amounts of K, Th, and allogenic U), this correlation may be quite strong. Further, in OC-rich carbonate rocks nearly all of the gamma-ray emissions are due to uranium associated with OC, and thus the OC/gamma-ray correlation can be very strong. With calibration to laboratory measured OC values, gamma-ray determined OC values can be reasonably accurate, in some rock units (Schmoker, 1981). Because gamma-ray logs have been run on almost all oil and gas exploratory wells for many decades, they are widely available and this is one of their main advantages. A number of factors can affect the accuracy of gamma-ray logs. Many of these, such as mud weight and hole size, are subject to correction. Nevertheless, it is important to keep in mind that the compromise between logging speed and accuracy necessarily results in some statistical variation in the recorded gamma-ray readings. For a further discussion of these issues see standard well log company manuals, such as Schlumberger (1989).

Figure 33 illustrates the correlation between gamma-ray readings and TOC in the Golden Buckeye #2-Gill Land Company well used in this study (Fig. 3.2). The strong positive correlation is apparent, despite considerable scatter.
Figure 3.3. Log gamma-ray values versus TOC. Golden Buckeye #2-Gill Land Co. well. Weld Co., Colorado.
**Gamma-Ray Spectra Log**

The gamma-ray spectra log carries the measurement of gamma rays one step further than the standard gamma-ray log. Gamma-ray emissions vary in their energy and the gamma-ray spectra log separates these into an energy spectrum. The individual radioactive components have different energy spectra and these can be distinguished (Schlumberger, 1969; Hurst et al., 1990). Abundances of potassium, uranium, and thorium can then be computed and plotted on the log.

The uranium trace of the gamma-ray spectra log should better reflect OC content than the standard gamma-ray log because variable thorium and potassium contents are not a complicating factor. The mineral (allogetic) uranium content may be variable, but in OC-rich rocks this fraction is typically small compared to the authigenic component associated with the OC. Authigenic uranium is derived from the water column and most of it is complexed with organic matter just below the sediment/water interface, where anoxic conditions are developed due to organic-matter degradation (Anderson et al., 1989b).

Uranium can become remobilized in the subsurface, particularly when fluid movement is high and the fluids are oxidizing. For example, it is sometimes enriched in fractures (Fertl and Rieke, 1980; Fertl et al., 1980). In general though, uranium is relatively immobile in the reducing conditions prevalent in the subsurface.

Figure 3.4 is a plot of log uranium content versus TOC using the same well and TOC data as in Figure 3.3. The improvement in the correlation over Figure 3.3 is quite small. This is probably because most (70-80%) of the gamma-ray emissions recorded by the standard log are from uranium associated with the OC. Changes in the U/OC ratio then are more important than gamma ray variations produced by changes in shale content.
Figure 3.4. Gamma-ray spectra uranium values versus TOC. Golden Buckeye #2-Gill Land Co. well, Weld Co., Colorado.
The uranium content measured by the gamma-ray spectra log includes both allogenic uranium associated with detrital minerals and authigenic uranium associated with organic matter (and to a lesser extent phosphorite). The allogenic uranium content can be estimated by assuming a constant level of uranium (i.e., 2 ppm) for 100% shale and multiplying this by the clay percentage, which can be estimated from the potassium and/or thorium content or from neutron/density logs. The allogenic uranium component can then be subtracted from the total uranium, leaving only the authigenic component which is closely tied to the OC content. In the Niobrara, this correction is fairly small, averaging about 0.6 ppm, compared to an average uranium content of about 12 ppm. A plot of authigenic uranium content versus TOC for the Golden Buckeye well is shown in Figure 3.5. No improvement in the uranium/TOC correlation is evident.

Some of the scatter in Figure 3.5 is probably the result of inaccuracies in both the log uranium content and in the measured OC values. However, uranium-to-OC ratios are not always constant (e.g., Calvert, 1976) and thus most of the scatter is probably from variations in this ratio. The U/OC ratio may be influenced by several possible factors, including the Eh and pH of the bottom water, the type of organic matter (Leventhal, 1981; Mann and Fyfe, 1984), the uranium content of the water, and the sedimentation rate (Mangini and Dominik, 1979; Arthur et al., 1990). The two most important of these factors are the bottom-water oxygenation level and the sedimentation rate. When these two factors can be accounted for, better OC-estimates from uranium logs can be obtained. A discussion of the role of bottom-water oxygenation and sedimentation rate in controlling the ratio of uranium to OC is presented in Chapter 4.
Figure 3.5. Authigenic uranium values versus TOC. Golden Buckeye #2-Gill Land Co. well, Weld Co., Colorado.
Density Logs

Density logs record bulk formation density and as such they are affected by every formation constituent. In sedimentary rocks, matrix density usually ranges from about 2.65 g/cm\(^3\) (quartz) to 2.71 g/cm\(^3\) (calcite). In contrast OM density varies from about 1.00 to 1.3 g/cm\(^3\). This means that formation density should be inversely proportional to OM content. Schmoker had considerable success in using this relationship to estimate OC content in eastern U.S. Devonian shales (Schmoker, 1979, 1981; 1993) and in the Bakken Formation in the Williston Basin (Schmoker and Hester, 1983; Schmoker, 1993).

More typically, particularly in carbonate source rocks, porosity variations will affect bulk rock density more than OC content. In the Niobrara, for example, TOC is weakly proportional to density (Fig. 3.6). Density variations in the Niobrara result in part due to the variable porosity, so it appears that zones with lower porosity (i.e., denser) tend to contain more OC. The density log by itself then is not useful in estimating the OC-content of the Niobrara.

Appropriate data are limited for the Sharon Springs, but Figure 3.7 indicates that the relationship between TOC and formation density is stronger than in the Niobrara, but in this case it is again the opposite of what is expected. In this case, the increase in density is caused by pyrite associated with the OM (this factor can be important and will be discussed in greater detail below).

In formations where the porosity is variable, the density log must be used in conjunction with another log, usually the resistivity log (e.g., Passey et al., 1991). Density logs are widely available and this is advantageous, but they are affected by significant variations in borehole size (washouts). This can limit their usefulness in some zones unless density values can be accurately corrected.
Figure 3.6. TOC versus rock density (from density log) in the Niobrara Formation. Golden Buckeye #2-Gill Land Co. well, Weld Co., Colorado.
Figure 3.7. TOC versus rock density (from density log) in the Sharon Springs Member of the Pierre Shale. Kansas-Nebraska Natural Gas #1-32 Whomble and Mountain Petroleum #1-29 State wells, Yuma Co., Colorado. TOC data are from Rice (1984).
Sonic Logs

Sonic logs measure the velocity of sound through rock strata adjacent to the borehole. Because sound velocity is dependent on rock elastic properties that are closely tied to density, the sonic log is used in some of the same ways as the density log, for example, in the estimation of porosity. Sonic logs plot the inverse of the sound velocity — the interval transit time (ΔT) in ms/ft or ms/m. Because ΔT values for OM are much higher than ΔT values for typical matrix minerals, the presence of OM significantly affects sonic log response. In some cases, sonic logs may be used alone to assess OM-content, but as with density log-derived estimates, the failure to consider porosity variations will typically make the estimates more qualitative than quantitative. A way to take porosity into account is needed, and this can be accomplished by combining the sonic log with a resistivity log (Carpentier et al., 1991; Passey et al., 1991).

Resistivity Logs

Resistivity logs measure the electrical resistivity of rock strata near the borehole. By using induction coils (or electrodes) with different spacings, it is possible to design the logging tool to investigate to different depths away from the borehole (for a full treatment of these logs refer to standard logging company manuals, such as Schlumberger, 1989). The resistivity measurement used in estimates of OC content is the deep resistivity curve. This curve is assumed to measure the true formation resistivity (far enough away from the borehole to be unaffected by normal invasion of the drilling fluid). The inverse of deep resistivity (i.e., formation conductivity) is often plotted as an additional curve on resistivity logs.

By itself the deep resistivity log is of little use in estimating OC content, though the two may roughly correlate in rocks where OM (nonconductive) tends to reduce
porosity (filled with conductive formation water) and thus increase the formation resistivity. The deep resistivity log can, however, be used to roughly assess OM maturity in some shales (e.g., Davis, 1994). When the OM maturity is great enough to generate petroleum, formation water is displaced, the petroleum is trapped, and the formation resistivity increases. As the amount of petroleum generated from a rock with a given OC content is proportional to the OM maturity, the effect on resistivity will also be roughly proportional.

THE CARBOLOG METHOD AND ITS APPLICATION

Method

The Carbolog method of Carpentier et al. (1991) is used in this study. This method is theoretically sound as it is based on actual rock properties and is readily adaptable to different rock types and conditions. The method and conditions for its use are described in detail in Carpentier et al. (1991), though the authors did not publish a complete equation or derivation. An equation for OC-estimation is derived in Appendix D, so only a brief summary will be given here. The Carbolog method has been successfully applied in other studies of OC-rich rocks (e.g., Bessereau et al., 1995), however to my knowledge, it has not been applied to the WIS, nor has it been coupled with a method to predict values for key OM properties, as is done in this study.

The Carbolog method utilizes $\Delta T$ (transit-time) values from the sonic log along with the corresponding deep formation resistivity ($R_f$) values from the resistivity log. These values can be plotted on a graph of $1/R_f^{1/2}$ ("conductivity") versus $\Delta T$ (Fig. 3.8). On this plot are shown three poles: a matrix pole, a water pole, and an OM pole.

In a chalk like the Niobrara, the matrix pole is defined by the properties of calcite — nonconductive with a $\Delta T$ of 47.5 $\mu$s/ft. Formation water has a fairly constant
Figure 3.8. Plot showing effects of major rock constituents and organic matter (OM) on the response of sonic and resistivity logs. Point A shows possible offset of a OM-containing rock from the matrix/water line. Diagram after Carpentier et al. (1991).
ΔT of about 189 μs/ft (this varies somewhat with changes in salinity, temperature, and pressure), but its conductivity will vary considerably with salinity and temperature changes. Organic matter is nonconductive and has a ΔT that is much higher than the matrix. In this simple system, a chalk with some porosity but no organic matter, will plot somewhere along the line between the matrix pole and the water pole. The presence of organic matter will offset the point to the lower right towards the OM pole. It is this offset that can be used, if properly calibrated, to estimate OM content. The Niobrara contains variable amounts of clay (0-70%), and variations in shale content can be accounted for in the Carbolog method (Carpentier et al., 1991), but in the Niobrara this shale is dispersed within the chalk matrix and experience shows that it can be ignored without significantly affecting the results.

The equation for estimating the volume percent OM (VOM %) is:

\[
VOM\% = 100 \frac{(\Delta T - m(1/R_t^{1/2}) - \Delta T_m)}{(\Delta T_{om} - \Delta T_m)}
\]

where:

- ΔT is the transit time of the formation from the sonic log
- m is the slope of the matrix pole/water pole line
- R_t is the deep formation resistivity from the resistivity log
- ΔT_m is the transit time of the matrix
- ΔT_{om} is the transit time of the organic matter.

This equation is based on a simple derivation (Appendix D) from the graph shown in Figure 3.8. A second equation modified from Carpentier et al. (1991), converts the volume OM % to weight percent OC:
OC % = \frac{1}{f} (\partial_{\text{om}}/\partial_{r}) \text{VOM}

where:

- \( f \) is the OM/OC conversion factor
- \( \partial_{\text{om}} \) is the density of the organic matter
- \( \partial_{r} \) is the formation density obtained from the density log—the wet bulk density (WBD) of the rock

The above expresses the OC content as a weight percent of the water-saturated rock. Because TOC values are normally reported as weight percent of dry rock, it is necessary to make a final conversion. The dry bulk density of the rock can be estimated as:

\[
\text{DBD} = \partial_{r} - ((\partial_{\text{ma}} - \partial_{\text{r}})(\partial_{\text{ma}} - \partial_{\text{wtr}}) - \text{VOM}/\partial_{\text{om}})
\]

where:

- \( \text{DBD} \) is dry bulk density
- \( \partial_{\text{ma}} \) is density of the matrix
- \( \text{VOM}, \partial_{\text{om}}, \partial_{r}, \) as above
- \( \partial_{\text{wtr}} \) is water density (usually 1.0)

The above equation converts the WBD of the rock to DBD by removing the water component of the rock. Because the presence of OM mimics porosity, the normal porosity calculation \([(\partial_{\text{ma}} - \partial_{r})/(\partial_{\text{ma}} - \partial_{\text{wtr}})]\) is corrected to a true porosity by subtracting out the influence of the OM. Then weight percent OC % (DBD) is:

\[
\text{OC % (DBD)} = \frac{\text{OC % (WBD)} \times \text{WBD}}{\text{DBD}}.
\]
Unlike most minerals, OM is quite variable in its geophysical properties. For the most part, properties, such as sonic transit time and density cannot be determined directly. Appropriate values must be determined by calibration with existing lab-measured OC values. The conversion factor (f) usually falls within a range of 1.12 to 1.57, depending on the type and maturity of the OM (Tissot and Welte, 1978). This value can be estimated from pyrolysis data, as outlined below.

The presence of pyrite adds a complicating factor to the Carbolog method (indeed to most log-based methods of estimating OC), and pyrite is typically present in OC-rich rocks. In the Niobrara, pyrite can range as high as 5% by weight of the whole rock, but typically it is less than 2% (Gill et al., 1972; Pollastro and Martinez, 1985). Pyrite's physical properties are opposite to those of OM. (i.e., pyrite is conductive, very dense, and it has a high sonic velocity). Therefore, its presence tends to reduce the expected log response to any OM present in the rock. But pyrite is not a very significant factor in the Niobrara because (1) it is typically less than one percent by volume, and (2) its abundance tends to be strongly positively correlated with OM abundance (Gautier et al., 1984). The latter means that the effect of the pyrite on the logs tends to be directly inversely proportional to the effect of the OM. In practical terms, this means that log response is still directly related to OM abundance, but OM density will be somewhat overestimated and transit time will be somewhat underestimated owing to the presence of pyrite.

Calibration of the Carbolog method is further complicated by additional factors. Tissot and Welte (1978) noted, for example, that different labs can test the same sample for OC and produce results that vary by as much as ±0.3 wt. %. The lab that performed the analyses for this study has demonstrated reproducibility to within 10% (oral communication). Additionally, in this study, the Golden Buckeye core was on average
only about 73% complete owing to missing and fragmented sections, with a few intervals less than 25% complete. Finally, it is difficult to assure that the very small amount of sample analyzed, about 0.1 g, actually includes rock fragments from the entire sampled interval. Thus despite the sampling strategy, a sampling bias may still exist.

**Application of the Carbolog Method to the Niobrara**

The Carbolog method was calibrated and tested with existing and new TOC data from the Niobrara. The sampling strategy for the Golden Buckeye #1 Gill well was designed to make the laboratory measured values as compatible as possible with log-derived estimates. Values for sonic transit time, deep resistivity, and density were read from the appropriate logs at the centers of the two-foot core intervals selected for sampling (care was taken to assure that log and core depths matched). The value for formation-water resistivity was calculated from a porous zone within the OC-poor Fort Hays member of the Niobrara using a standard derivation of Archie's (1942) equation: 

\[ R_w = R_t / f^2 \]

Rock Eval pyrolysis (Espitalié et al., 1977) data (Appendix F) were used to calculate the appropriate value for \( f \), the OM/OC conversion ratio. This was done by converting the average hydrogen index (HI) and the average oxygen index (OI) for the Golden Buckeye core to the elemental H/C and O/C ratios respectively. These in turn can be used to estimate the conversion ratio based on data presented in Tissot and Welte (1978) The equation is:

\[ f = 0.00013 \times \text{HI} + 0.0056 \times \text{OI} + 1.087 \]
This equation is not strictly accurate as the relationship between hydrogen and oxygen indices to elemental H/C and O/C ratios, respectively, is not exact. Also, the equation does not consider other elements present in the OM, such as sulfur and nitrogen. However, these occur in limited amounts (Tissot and Welte, 1978), and have only a very small effect on the conversion factor. The calculated f for the Golden Buckeye well, 1.175, was then applied to the Carbolog equations, leaving only two unknowns, $\Delta T_{om}$ and $\partial_{om}$. Arbitrary but reasonable, values for these two parameters were selected and adjusted until the calculated Carbolog OC values most closely matched lab measured TOC values. At this point the values for $\Delta T_{om}$ and $\partial_{om}$ are not unique, but as outlined in Appendix E, further independent calibration can produce unique values for each of these parameters. For the Golden Buckeye well, these are $\Delta T_{om}$ = 275 $\mu$s/ft and $\partial_{om}$ = 1.16 g/cm$^3$. Calibration was done across the entire cored interval and not for individual zones. This was done to derive average values for the OM parameters.

Figure 3.9 compares the calibrated Carbolog values for TOC (henceforth these records will be simply called "Carbolog") with those obtained from the laboratory analyses on the Golden Buckeye core. Though the agreement is generally quite good, there are some intervals where the differences are notable. Figure 3.10 is a histogram showing the percent deviation of the Carbolog from the lab values. The distribution is positively skewed. This skewness reflects the apparent overestimation of OC values by the Carbolog method at certain depths. For example, overestimation of OC content in a couple of zones near the top of the section is probably the result of bentonites several centimeters thick, which tend to increase the sonic interval transit times over those zones. Other zones of overestimation are in carbonate-rich zones that contain liquid hydrocarbons (this well was oil productive from the underlying Codell Sandstone). The presence of liquid (or gaseous) hydrocarbons lowers the resistivity and decreases the
Figure 3.9. Comparison of Carbolog with lab-measured TOC values in the Niobrara. Golden Buckeye #2-Gill Land Co. well, Weld Co., Colorado.
Figure 3.10. Histogram showing percent deviation of Carbolog-OC values from lab values for the Golden Buckeye #2-Gill Land Co. well. Positive categories are where Carbolog values are greater than lab values.
sonic velocity of the rock, thereby leading to an overestimation of the OC still in the rock matrix.

Most of the Carbolog estimates (86 of 104) fall within 30% of the laboratory values and 70 of these are within 20%. Given the limitations on laboratory analyses discussed previously, the agreement between the Carbolog and the laboratory measured values is remarkably good.

Once calibrated, the Carbolog method can be applied to wells lacking sample analyses. However, if the level of organic maturity varies significantly, this factor has to be considered. It has been demonstrated that the OM to OC conversion factor (f) varies with organic maturity (Tissot and Welte, 1978), and it is logical to assume that both ΔT_{om} and δ_{om} vary with organic maturity as well. The Niobrara section in the Golden Buckeye well is in a relatively deep portion of the Denver Basin (top of Niobrara is at 6641 feet, 2024 m) and the Golden Buckeye Niobrara section is in the oil generation window, with an average T_{max} value of 439°C. Most of the Niobrara has not reached this level of maturity.

To account for the variable OM factors, the Carbolog method was also calibrated to wells in shallower portions of the Denver Basin. Calibration of the Carbolog method to two additional wells was accomplished using published data. One of these was the Excelsior #1-Alice Nay well, Weld County, Colorado. Log-derived TOC values were calibrated to Rock-Eval data obtained from a core in this well (Rice, 1984) (Figure 3.11).

2 In the Rock-Eval method of assessing petroleum-source-rock potential, a sample undergoes a programmed pyrolysis (Espitalié, et al., 1977). As heating of the sample progresses, carbon dioxide is emitted. An initial peak in CO2 is generated by hydrocarbons already present in the sample and a second peak occurs when kerogen in the sample begins to break down. The temperature at this second peak is the T_{max} value. This value depends on the burial history (time and temperature) of the rock and it is a measure of OM-maturity. A T_{max} value greater than 435°C puts OM into the mature stage.
Figure 3.11. Comparison of Carbolog (COC) values calibrated to upper Niobrara TOC values from the Excelsior Oil #1-Alice Nay well (14-9N-58W), Weld Co., Colorado. TOC data from Rice (1984). Individual TOC values are quite different than the log-estimated values, but averaged values are similar. This is an example of the problem illustrated by Figure 3.1 (p. 112) and discussed on pages 111 and 113.
The top of the Niobrara section in this well is at 5400 feet (1646 m) and the average $T_{\text{max}}$ value of 420°C puts the Niobrara in the immature zone of oil generation. The OM-to-OC conversion ratio is calculated to be 1.28 and the calibration process outlined above and in Appendix E produces values of 310 $\mu$S/ft for $\Delta T_{\text{om}}$ and 1.13 g/cm$^3$ for $\delta_{\text{om}}$. Log-derived TOC values were also calibrated to Rock-Eval data for a second well, the Kansas-Nebraska Natural Gas #1-33 Powell, Yuma County, Colorado (Rice, 1984) (Figure 3.12). The top of the Niobrara in this well is at a depth of 2803 feet (854 m) and the average $T_{\text{max}}$ is 404°C. The following key values for the OM were obtained: $\phi$=1.55, $\Delta T_{\text{om}}$ = 370, and $\delta_{\text{om}}$=1.09 g/cm$^3$.

Plots of the $\phi$, $\Delta T_{\text{om}}$, and $\delta_{\text{om}}$ values obtained above versus corresponding $T_{\text{max}}$ values reveal their dependency on OM maturity (Figures 3.13-3.15). If the level of OM maturity is known, then the values for $\phi$, $\Delta T_{\text{om}}$, and $\delta_{\text{om}}$ can be estimated from these charts and applied to the Carbolog method for the Niobrara. Without suitable geochemical analyses, however, the level of OM maturity usually is not known.

OM maturity is a function of both time and temperature (e.g., Tissot and Welte, 1978). The time factor does not vary greatly for the Niobrara, because the time span it encompasses (about 7.8 Ma), is small compared to its age of about 90 Ma. Temperature, however, is a function of burial depth (and burial history) of the rock, so burial depth can be considered a proxy for maturity. However, present day burial depths do not necessarily reflect past burial history. A better proxy for maturity is porosity, which is highly dependent on past burial depth, particularly in chalks such as the Niobrara (Lockridge and Scholle, 1978). This means that porosity logs can serve as a proxy for OM maturity. Certainly, this is an inexact proxy, as other things (e.g., OM content, secondary porosity) effect porosity log readings, but the relationship is quite strong as indicated by a plot of $T_{\text{max}}$ values versus average $\Delta T$ values (averaged over the entire
Figure 3.12. Comparison of calibrated Carbolog (COC) values to TOC values for the Kansas-Nebraska Natural Gas Co. #1-33 Powell well (33-3N-47W). Yuma Co., Colorado. TOC data from Rice (1984).
Figure 3.13. Graph showing relationship of the OM to OC conversion ratio (f) to OM maturity as expressed by $T_{\text{max}}$ values. Squares are data from wells discussed in text. Circles are additional data from this study, Rice (1984), and Rodriguez (1985).
Figure 3.14. Graph showing relationship of $\Delta T_{om}$ to maturity as expressed by $T_{\max}$ values. Data are discussed in text.
Figure 3.15. Graph showing relationship of OM density ($\rho_{om}$) to maturity as expressed by $T_{\text{max}}$ values. Data are discussed in text.
Niobrara section) in several Niobrara wells (Fig. 3.16). This means that average Niobrara \( \Delta T \) values can be used to estimate the OM parameters that are used in the Carbolog method (Figs. 3.17-3.19), and thus the level of OM-maturity can be taken into account. Unfortunately, some of these graphs are limited to only three points, because of the very limited amount of data available for calibration, and the need to reserve additional data to test the method.

The reader will notice that portions of Figures 3.11 and 3.12 show wide discrepancies between measured and estimated OC. These illustrate two of the complications in using the Carbolog method. In Figure 3.11 the wide dispersion of TOC values suggests that they represent samples from thin intervals, much thinner than the resolution of the well logs (see Fig. 3.1). Calibration in this case was done by comparing the average TOC and Carbolog values across the sampled interval. In Figure 3.12 the Carbolog overestimates the OC content in the upper 15 feet of the log. In this instance the discrepancy is readily accounted for as the upper portion of the interval is gas saturated (as evidenced by crossover of the neutron-density log). The gas content increases \( \Delta T \) and formation resistivity, so the Carbolog method overestimates OC.

**Niobrara Tests of the Carbolog Method**

The Carbolog method was tested on the Niobrara Formation with log data from two additional wells. Wells with a full suite of logs plus core and TOC data, such as the Golden Buckeye well, are unusual. Hence to test the Carbolog method, it was necessary to extrapolate data in some cases. Dean and Arthur (1989) published a set of TOC values from samples obtained from a core in the Coquina #4-Berthoud well, Larimer County, Colorado. The samples were taken at approximately three-foot (one-meter) intervals over most of the Niobrara section. Unfortunately, although this well had a sonic log, it did not
Figure 3.16. Graph showing correlation between Niobrara $\Delta T$ values (from sonic logs) with Niobrara $T_{\text{max}}$ values in the same wells.
Figure 3.17. Graph of Niobrara ΔT values (averaged over the entire Niobrara section) versus the OM to OC conversion factor (f). This graph can be used to estimate f from the sonic log in the Niobrara Formation.
Figure 3.18. Graph of Niobrara ΔT values (averaged over the entire Niobrara section) versus the ΔTom values obtained by calibration of the Carbolog method to TOC data. This graph can be used to estimate ΔTom values from the sonic log in the Niobrara Formation.
Figure 3.19. Graph of Niobrara $\Delta T$ values (averaged over the entire Niobrara section) versus OM density ($\delta_{om}$) values obtained by calibration of the Carbolog method to TOC data. This graph can be used to estimate dom values from the sonic log in the Niobrara Formation.
have resistivity or density logs. However, a nearby well, the Coquina #3-Berthoud well, did have resistivity and density logs as well as a sonic log. The Niobrara sections in the two wells are very similar (Fig.3.20). An exception to this is the basal 25 feet (6 m) of sampled section in the #4 well. This section is different in the two wells, therefore it is excluded in the following analyses.

The logs were carefully correlated and resistivity and density log values from the #3 well were used along with sonic values from the #4 well to make Carbolog TOC estimates for the #4 well. The Rw value of 0.12 ohms was also obtained from the #3 well. Given the average Niobrara AT value of 79.3 in the #4 well, estimated values for the key OM parameters are: f=1.29, ATom = 320, and dom=1.13 g/cm³ (from charts in Figs. 3.17-3.19). These values are used in the Carbolog equations to calculate OC and the results are compared to the published values (Dean and Arthur, 1989) in Fig. 3.21. The agreement between the two data sets is excellent. The average calculated OC value of 3.15 % is very close to the average TOC value of 3.05% (63 samples). Further, the Carbolog OC value across the densely sampled interval shown in Figure 1 is 3.03% which is exactly the TOC average across this interval.

A histogram (Fig.3.22) illustrates how well the Carbolog-predicted OC values match the published TOC values. Forty-nine (49) of 63 values (78%) are within 20% of the laboratory measured values and only 3 values differ by more than 50%.

The Coquina #4-Berthoud State well was sufficiently porous and oil saturated for oil to be produced from the Niobrara. Drill stem test (DST) results indicate high oil saturations through most of the Niobrara section. Oil greatly increases the formation fluid

3Drill stem tests provide data on formation pressures and fluids through the use of a testing tool that is attached to the base of the drill string. Packers are used to isolate specific zones of interest.
Figure 3.20. Comparison of the gamma-ray and sonic logs through the Niobrara section in the Coquina Oil Co. #3 and #4 Berthoud State wells, Larimer Co., Colorado.
Figure 3.21. Comparison of Carbolog-predicted OC values with TOC values. TOC data from Dean and Arthur (1989).
Figure 3.22. Histogram showing percent deviation of Carbolog-OC values from lab TOC values for the Coquina Oil Co. #4 Berthoud State well. Positive categories are where Carbolog values are greater than lab values.
resistivity. This means that the presence of oil (or gas) would normally lead to an overestimation of OC via the Carbolog method (see Fig. 3.12), but this would only be the case if the resistivity log through the oil saturated section is used along with formation water resistivity. In this example, both the Rw value and the log resistivity are from the nearby, but non-productive #3 well (structurally 50 meters lower). The oil saturation in the #4 well is thus not a factor. Oil also affects the sonic log by increasing the formation transit time, but this effect is small unless porosity is very high.

Another well, the Murfin Drilling #1-19 Bida Walters, was also selected for Carbolog testing. This well is in Wallace County, Kansas (19-14S-40W) not far from a stratigraphic test well (Guy Holland test hole at 36-13S-40W) drilled and sampled by the U.S.G.S. Cuttings at 5-foot (3-m) sample intervals from this well were analyzed for OC-content in both the Sharon Springs and upper Niobrara (Gill et al., 1972). In both of these wells the Niobrara section is at a shallow depth and, because of their proximity to each other, they can be expected to have very similar sections.

The average Niobrara ΔT value of 132 μs/ft is indicative of the shallow burial history of the Niobrara in western Kansas, and consequently the OM is very immature in this area. Using the charts in Figures 3.17-3.19, values for the OM parameters are expected to be: f=1.64, ΔTom =430, and δom=1.05. However, when these values are used in the Carbolog equations and calibrated as outlined above and in Appendix E, it clear that the ΔTom is about 490 μs/ft. This is not surprising as the initially selected value was obtained from projecting a line defined by only three points. The new point can be used to modify the correlation shown in Figure 3.18. This new point defines an upper limit for ΔTom in shallowly buried Niobrara sections.

Figure 3.23 compares the Carbolog OC values for the Murfin well to those measured in the Guy Holland well. The general agreement between the two sets of values
Figure 3.23. Graph comparing predicted Niobrara Carbolog-OC values in the Murfin Drilling #1-19 Bida well (19-14S-40W), Wallace Co., Kansas to measured values in the nearby U.S.G.S. Guy Holland test well (39-13S-40W). TOC values in the Guy Holland well are from cuttings sampled at 5- or 10-foot intervals (Gill et al., 1972). Depths shown on the graph are for the Guy Holland well. Sections are correlated based on a small overlap in the resistivity logs on the two wells (log extends only 20 feet into the Niobrara in the Guy Holland well and casing is set near the top of the Niobrara in the Murfin well). However, the correlation appears to be valid, as it matches a low OC content in the Murfin well to a similar low OC content in the Guy Holland well at a depth of 280 feet.
is good. The results again confirm the validity of the Carbolog method in assessing OC contents in the Niobrara.

**Carbolog estimation of OC in the Sharon Springs**

The Sharon Springs Member of the Pierre Shale is an OC-rich shale that occurs directly above the Niobrara Formation in most of the area studied (to the west, other shale units separate the two units) (Gill et al., 1972; McGookey et al., 1972). The OC content in the Sharon Springs ranges from 2% to >10% (Gill et al., 1972; Schultz et al., 1980; Rice, 1984; Gautier et al., 1984). Given the high OC content, the Sharon Springs should have considerable effect on geophysical logs and indeed this is the case. Sonic transit time and resistivity are higher in the Sharon Springs compared to the overlying OC-poor Pierre Shale. These responses should make the unit a good candidate for Carbolog analyses.

However, the Sharon Springs presents problems that complicate the use of the Carbolog method. The matrix pole used is that for quartz ($\Delta T_m=56$ $\mu$s/ft) which makes up about 20% of the Sharon Springs (Gill et al., 1972), but it is difficult to calculate an appropriate resistivity value for the formation water in this shale section. There are several reasons for this. (1) It is harder to accurately calculate porosity (and hence resistivity) in shales as matrix densities vary with changes in mineralogy. (2) The relative amount of bound water affects the total formation water resistivity (e.g., Schlumberger, 1989). And (3), where the OM has reached thermal maturity, evolved (and trapped) hydrocarbons will tend to raise the apparent resistivity. The resistivity of the Sharon Springs formation water is probably close to that of the underlying Niobrara, so this value is used as a starting point.

I assumed that the OM in the Sharon Springs is similar to the OM in the Niobrara. This means that the OM parameters used in estimating OC contents in the Sharon Springs can be determined in the same way as they were for the Niobrara.
Appropriate OC data from the Sharon Springs to adequately test the Carbolog method is limited; nevertheless, several wells have at least some TOC data that can be used as a test.

The Enserch Exploration 1-19 Koenig well in Weld County, Colorado, is located on the western flank of the Denver Basin in an area where the "type" Sharon Springs facies is absent or reduced due to dilution by a high sedimentation rate (Gautier et al., 1984) (Fig. 3.24). Despite dilution, the Sharon Springs equivalent is enriched in OM compared to the overlying Pierre Shale. A ΔT value of 74 μs/ft for the Niobrara in this well produces the following values for the OM parameters (from Figs. 3.17-3.19): f=1.21, ΔT_{om} = 300 μs/ft, and δ_{om}=1.15. These values are used in the Carbolog equations to produce the Carbolog shown in Figure 3.25. Three composite cuttings samples from the Enserch well at depths of 6430 to 6550, 6550 to 6640, and 6640 to 6680 feet were analyzed and their TOC values of 1.03%, 1.66%, and 2.15%, respectively, are also shown on this log. The agreement between the values is good, especially in the upper part of the section. OC values in the lower part of the section appear to be overestimated by Carbolog, but if a substantial portion of the analyzed cuttings were samples from shallower depths, as is likely, this result is not surprising.

In western Kansas the Sharon Springs facies is well developed. In the Guy Holland test hole, the unit is 220 feet (67m) thick (Gill et al., 1972). This matches the thickness of the Sharon Springs in the nearby Holden Energy 1-29 Burk well (29-12S-41W), so it is assumed that the sections are similar. Again the appropriate Carbolog parameters were initially determined from the graphs in Figures 3.17-3.19 and used with the log data across the Sharon Springs section to produce a Carbolog of the section. In this case, initial results underestimated the OC content compared to the TOC values reported from the Guy Holland well (not shown). Calibration of the data as previously outlined and with the Guy Holland data revealed that the ΔT_{om} value derived from the
Figure 3.24. A portion of the gamma-ray and sonic log on the Enserch #1 Koenig well (19-5N-67W), Weld Co., Colorado. Lower Pierre Shale section and uppermost Niobrara Formation are shown. The interval above 6556 feet is typical of Pierre Shale log response, in contrast, the interval from 6556 to 6640 feet with slightly higher gamma-ray values represents poorly developed Sharon Springs facies. Higher gamma-ray readings in the section from 6640 to the top of the Niobrara reflect better-developed Sharon Springs facies. Intervals for which TOC analyses were made are shown by the numbered vertical bars.
Figure 3.25. Carbolog and sample TOC values for the Sharon Springs section in the Enserch #1-19 Koenig well.
Niobrara was too high (490 μs/ft vs 410 μs/ft). This results from two factors: (1) the
Sharon Springs contains proportionally more pyrite than the Niobrara and (2) immature
OM in the Sharon Springs is different in character than that in the underlying Niobrara.

As indicated above, pyrite partially counteracts the effect of OM on the sonic log. This does not affect the actual ΔT_{om} value, but it does change the value that is appropriate for use in the Carbolog calculations, as pyrite is not independently corrected for. Evidence for the difference in the OM between the Niobrara and the Sharon Springs is provided in Figures 3.26 and 3.27. As a result of the above factors the values used for ΔT_{om} are different in the Sharon Springs from those in the Niobrara.

Final Carbolog results are compared to TOC values from 5-foot (3m) cuttings samples in the Guy Holland well (Gill et al., 1972) in Figure 3.28. The agreement between the two sets of values is good and the results help establish the appropriate parameters for estimating the OC content in the Sharon Springs. Figure 3.29 shows how ΔT_{om} for the Sharon Springs varies with maturity (the ΔT Niobrara proxy).

Another example of applying the Carbolog method to the Sharon Springs is shown in Figure 3.30. A Carbolog of the Sharon Springs section in the Sohio #7-1 Creech well, Lincoln County, Colorado, is compared to TOC values from composite cuttings samples across three separate intervals. The average predicted values across these intervals is in good agreement with the laboratory values.

In general, the Carbolog method of estimating OC-content appears to work quite well in the Sharon Springs. However, OC-contents may be underestimated when the method as outlined above is applied to sections where the Sharon Springs is especially thin or condensed. An example is given below.

Gautier et al. (1984) and Rice (1984) published TOC data from a core through part of the Sharon Springs section in the Kansas-Nebraska 1-32 Whomble well, Yuma
Figure 3.26. Modified van Krevelen diagram plotting the hydrogen and oxygen indice of OM from the Kansas-Nebraska Natural Gas #1-32 Whomble well (32-2S-43W) Yuma Co., Colorado. Data are from Rice (1984) and Gautier et al. (1984). Note that hydrogen indices for the Sharon Springs and Niobrara are similar, but that oxygen indices for the Niobrara are higher.
Figure 3.27. Plot of average Niobrara $\Delta T$ versus the OM to OC conversion factor ($f$) for the Niobrara Formation and Sharon Springs Member of the Pierre Shale. ($\Delta T$ values for the underlying Niobrara are plotted against $f$ values for the Sharon Springs in the same wells). At the same $\Delta T$, $f$ is displaced towards lower values in the Sharon Springs compared to the Niobrara, particularly for immature OM. This reflects differences in the OM as demonstrated in Figure 3.26.
Figure 3.28. Comparison of Holden Energy #1-23 Burk Carbolog to 5 foot (3 m) TOC values from the Guy Holland test well (Gill et al., 1972).
Figure 3.29. Plot of average Niobrara $\Delta T$ values (maturity proxy) versus $\Delta T_{om}$ for the Sharon Springs Member of the Pierre Shale.
Figure 3.30. Carbollog of the Sharon Springs section in the Sohio Petroleum #7-1 Creech well (7-12S-55W), Lincoln Co., Colorado. Vertical bars represent the TOC values from composite cuttings across the intervals indicated.
County (32-2S-43W). This well does not have a sonic log, but a well in a nearby section, the Mountain 1-29 State (29-2S-43W), does. Both wells have thin lower Sharon Springs sections that are nearly identical (Fig. 3.31), so it is assumed that OC contents should also be very similar. When the Carbolog method is applied to the Mountain State well, however, the OC content is apparently grossly underestimated (Fig. 3.32). Only when the $\Delta T_{om}$ value used is reduced to 260 $\mu$s/ft (versus the 370 $\mu$s/ft used in Fig. 3.32) is the TOC data matched (Fig. 3.33). The size of this disparity means it must be due to real differences in this Sharon Springs section compared to those previously discussed rather than some type of error.

The answer probably lies in the thinness of the Sharon Springs section in this area. The sampled lower Sharon Springs (between the base of the Ardmore bentonite zone and the top of the Niobrara) is only 22 feet (6.7 m) thick in the Whomble well, compared to 116 feet (35.4 m) in the Holden Energy 1-29 Burk well, for example. The thinness of the lower Sharon Springs section in the Whomble well is due to a very slow depositional rate (a condensed section). This could produce differences in the properties of the OM. For example, an increase in the residence time of the OM in the near-surface diagenetic zone and greater microbial degradation could produce a more refractory OM. This could account for the low $\Delta T_{om}$ value needed to calibrate the Carbolog to the data. Another key factor is probably the pyrite content. The inverse relationship between density and OC content previously noted for the Whomble well (Fig. 3.7) is due to a high pyrite content (pyrite may reach as much as 20% by weight based on its affect on the density log). The high pyrite content partially accounts for the lower $\Delta T_{om}$ value needed to calibrate the log data to the TOC values. Rather limited data indicate that there is an inverse relationship between the pyrite content and the thickness of the lower Sharon
Figure 3.31. Gamma-ray and density log comparison of the Sharon Springs section in the Mountain Petroleum #1-29 State well (29-2S-43W) and Kansas-Nebraska Natural Gas #1-32 Whomble well (32-2S-43W), Yuma Co., Colorado.
Figure 3.32. Comparison of Carbolog-predicted OC values with $\Delta T_{\text{om}}$ equal to 370 $\mu$s/ft in the Mountain Petroleum #1-29 State well to TOC values from the equivalent section in the nearby Kansas-Nebraska #1-32 Whomble well. Estimated OC values are well below actual values. TOC values are from Rice (1984) and Gautier et al. (1984).
Figure 3.33 Comparison of Carbolog-predicted OC values with $\Delta T_{om}$ equal to 240 $\mu$s/ft in the Mountain Petroleum #1-29 State well to TOC values from the equivalent section in the nearby Kansas-Nebraska #1-32 Whomble well. Estimated OC values are close to actual values (compare with Fig. 3.32). TOC values are from Rice (1984) and Gautier et al. (1984).
Springs. This relationship can tentatively be used to adjust the $\Delta T_{\text{om}}$ used in thin Sharon Springs sections, but further work is needed to see if this is valid.

The Carbolog method appears to work in much of the Sharon Springs, but it was not able to accurately predict TOC values in a condensed section owing, probably, to changes in the physical properties of the OM and abundant pyrite. Recalibration of the method to the condensed zone means values in other similarly condensed zones can be estimated accurately, at least locally. It may be possible to account for levels of intermediate condensation, though data to test and demonstrate that notion are at present insufficient.

CONCLUSIONS

Well-log methods of estimating OC have in the past been applied to a variety of different OC-rich formations with some success. Typically, these methods have been successful only when applied to units with fairly constant thicknesses, compositions, porosities, and OM-maturity levels. Thus they are unable to predict OC values in the more usual case where these factors are highly variable. The Carbolog method as used in this study can account for most of these variations and thus can be more broadly applied. The methods' accuracy is limited by a number of factors, but as demonstrated, the method can be used quite successfully to predict OC content in the the Niobrara Formation and Sharon Springs Member of the Pierre Shale. Additional TOC data are needed to fully test the method, especially in the Sharon Springs where cores are almost nonexistent.

Few cores are taken even in the best-studied regions. Therefore, it has been impossible to delineate with any confidence the three-dimensional distribution of organic carbon. The significance of the work presented here is that, with a few representative wells throughout a region for calibration, the method can be used to assess both lateral and vertical variations in OC content in tens, perhaps hundreds of wells.
CHAPTER 4
CONTROLS ON THE AUTHIGENIC-URANIUM/ORGANIC-CARBON ASSOCIATION

INTRODUCTION

The association of uranium (U) with organic carbon (OC) in "black shales" was recognized as early as 1893 by Nordenskiöld in his studies of the alum shales in southern Sweden (cited in Swanson, 1961). However, it was not until the mid-1940s and early 1950s that this association was fully documented. Confirmation of the U/OC association was largely the result of the greatly accelerated search for sources of uranium that occurred during the dawning of the nuclear age. Several papers, including those by Beers and Goodman (1944), Beers (1945), and Russell (1945), demonstrated that U was enriched in marine carbonaceous rocks. These early papers were followed by extensive government-sponsored investigations on more than 200 formations containing black shales in the United States from 1944 to 1957. These investigations were conducted by a variety of academic and federal agencies, but especially by the United States Geological Survey (a summary of these is provided in Swanson, 1961).

Although none of the investigated shales ultimately proved to be an economical source for U, many were nevertheless very enriched in U, and the strong association of OC with U was fully demonstrated. In the OC-rich Chattanooga Shale, for example, the U content was found to average about 60 to 70 ppm (Swanson, 1961). Values in this general range are common in many OC-rich shales (e.g., Tournelot, 1956; Landis, 1958, 1959; Kepferle, 1959; Swanson, 1961; Matthews, 1993). In contrast, shales that lack significant OC typically have U contents of only 3 or 4 ppm (Swanson, 1960). This is close to the average U content in the earth's crust of about 3 ppm (Baturin, 1973; Schlumberger, 1989).
On average, OC-rich shales have U contents of about 20 to 40 ppm. This is a 100-fold enrichment over typical pelagic sediments and a $10^4$ increase in concentration compared to the 3.3 ppb of U present in sea water (Rona et al., 1956; Ku et al., 1977). Thus some mechanism(s) concentrates U in the marine depositional environment.

This chapter first reviews the origin of uranium enrichment in OC-rich marine shales, and this is followed by a discussion of the principle controls on the ratio of authigenic uranium ($U_A$) to OC. The two key controls are shown to be the sedimentation rate and the bottom-water oxygen content. Examples of how the $U_A$/OC ratio can be utilized to assess ancient levels of bottom-water oxygenation are then presented. The significance of $U_A$/OC ratios in the Niobrara and Sharon Springs is presented in the following two chapters.

**ORIGIN OF URANIUM ENRICHMENT**

The U content of fine-grained marine sediments can be the result of several factors (Fig. 4.1). In broad categories, these include processes that operate in three environments: terrestrial, within the water column, and in sediments at or below the sediment-water interface. Although U enrichment takes place in the sediments, the importance of each of the possible U sources is briefly reviewed below for background.

**Terrestrial Sources of Uranium**

A portion of the U in fine-grained marine sediments is allochthonous and derived from the terrestrial environment. This component can be associated with three types of material: clays, heavy minerals, and plant material. Most clay minerals include trace amounts of U as a result of ionic substitution. The common clay mineral, illite, for example, contains 1.5 ppm U (Bateman, 1985). Thus in OC-poor shales the U contained in the clays accounts for most of the U.
POSSIBLE SOURCES OF URANIUM IN MARINE SEDIMENTS

A. LAND DERIVED
   1. Clays
   2. Resistates
   3. Plant fragments

B. FROM WATER COLUMN
   1. Absorbed by plankton
   2. In phosphatic fossils (fish bones etc.)
   3. Complexed with humic acids

C. ADSORBED OR PRECIPITATED AT OR BELOW SEDIMENT-WATER INTERFACE
   1. Adsorbed by organic matter
   2. Ionic exchange in clays
   3. Ionic substitution in phosphate
   4. Direct precipitation of uraninite

Figure 4.1. Diagram showing possible sources of uranium in fine-grained marine sediments. After Swanson (1960) in part.
Heavy minerals can contain significantly larger amounts of U, with values ranging from 300 ppm to as much as 3000 ppm for zircon (Bateman, 1985), for example. However, these minerals are present in such small quantities in pelagic and hemipelagic sediments that their contribution to the overall U-content is minor, perhaps 1 ppm (Swanson, 1961).

Terrestrial plants usually contain U in ppb quantities or less (Hoffman, 1942), although in unusual circumstances concentrations can reach low ppm values (Vine, 1962). In terrestrial carbonaceous sediments (i.e., carbonaceous shale, humus, peat, lignite, and coal) the concentration of U is typically low (<1 ppm), but values of 10-50 ppm are present in some settings (e.g., Vine, 1962), and occasionally U concentrations can be an order of magnitude higher (Vine, 1962). Therefore in marine shales that contain a significant component of humic (terrestrial) organic matter, at least some U enrichment can result from this component of the terrestrial input. It should also be noted that much of this U may be lost through weathering and oxidation before it can reach offshore marine environments.

Although the above factors all contribute to the U content of marine shales, they are insufficient to account for the 10- to 100-fold enrichment of U observed in OC-rich shales compared to average shales. Thus most U enrichment of these sediments must occur in the marine environment. This is further supported by the fact that the isotopic composition of the U is usually consistent with a sea water origin (e.g., Anderson et al., 1989b), indicating that the U is authigenic.

**Uranium Enrichment within the Water Column**

Uranium is highly soluble in oxidizing environments. In oxic sea water, U occurs in the hexavalent state, U(VI), as part of a soluble carbonate complex $[(\text{UO}_2\text{CO}_3)^4]$ (e.g., Langmuir, 1978). In reducing environments U is reduced to an insoluble
tetravalent state, U(IV). Despite U's solubility in oxic settings, it could be removed by active biological uptake or by chemical adsorption or complexation with particulate matter (organic or inorganic). These mechanisms were suggested by Swanson (1960), but only in more recent years have they been adequately tested.

Degens et al. (1977) invoked biological uptake of U by plankton to explain the U enrichment in Black Sea sediments. Algae are known to concentrate U in laboratory and natural waters as Mann and Fyfe (1984, 1985) have demonstrated. Although they cited an enrichment factor on the order of $10^4$, algal U contents cited by Swanson were an order of magnitude lower. In either case (i.e., a few ppm to a few 10's ppm), the amount is far too low to account for the whole-rock U-enrichments cited above.

Kochenov et al. (1965), Kolodny and Kaplan (1973), and Mo et al. (1973) proposed that particulate organic matter adsorbed U from the water column before settling to the bottom. However, studies of the particulate flux of U in the Black Sea (Anderson et al., 1989a) and other areas (Kuznetsov et al., 1968; Anderson et al. 1989b) have shown that very little U is removed from seawater within the water column itself. This is the case even in the anoxic water column of the Black Sea where reducing conditions might be expected to accelerate U removal from the water (Anderson et al., 1989a). Anderson et al. (1989a) found that the kinetics of the U reduction process are extremely slow under the chemical conditions of the Black Sea-bottom water.

Uranium Enrichment within the Sediments

Several studies have demonstrated that U-uptake is a syngenetic process that occurs at or below the sediment-water interface in a reducing environment (e.g., Yamada and Tsunogai, 1984; Anderson et al., 1989a; Thomson et al., 1990). Anderson et al. (1989b), for example, demonstrated that U is progressively depleted in sediment pore-waters with increased depth while the U content (solid phase) of the sediments increases
with depth. It is known that beneath anoxic bottom waters U enrichment occurs at or very near the sediment-water interface (Anderson et al., 1989a, 1989b). Beneath oxic bottom waters the enrichment occurs just beneath the redox boundary within the sediment (e.g., Thomson et al., 1990). If the redox boundary is beneath the zone of effective diffusion very little U enrichment occurs (Thomson et al., 1990; Rosenthal et al., 1995a).

The precise mechanism by which U-enrichment occurs in marine sediments is not well understood. It is generally assumed that at some point U(VI) is reduced to U(IV) with the consequent formation of uraninite (UO$_2$). However, intermediate stages may be involved, including the formation of U(VI)/organic complexes (Natashima et al., 1984; Cochran et al., 1986) and insoluble U(V) species (Kniewald and Branica, 1988). These may later be reduced to U(IV) in the sedimentary column (Disnar and Sureau, 1990). In contrast, Olson (1982) suggested that urano-organic complexes may last until a high level of thermal maturity (for kerogens) is reached.

The fact that U(IV) does not form in the bottom water of the Black Sea (Anderson, 1989a) is consistent with experimental evidence that mineral surfaces may be needed to catalyze the U reduction (Kochenov et al., 1977; Mohogheghi and Goldhaber, 1982). And although reduction of U(VI) in the presence of hydrogen sulfide has long been a traditional explanation for U precipitation in anoxic environments (e.g., Swanson, 1961), it is now recognized that sulfate-reducing bacteria play a direct role in the process (Lovley et al., 1991, 1993). Experimental work by Lovley et al. (1993) indicates that some sulfate-reducing bacteria enzymatically reduce U(VI) in the Fe(III) reducing zone above the zone of significant sulfide accumulation. This latter result is consistent with observations by Cochran et al. (1986) and Rosenthal et al. (1995a).

In summary, although the exact mechanism that enriches U in OC-rich sediments is still poorly understood, the importance of OM is unquestioned. At the least, it is instrumental in producing the anoxic environment needed to reduce U(VI) and it probably
directly aids in the extraction of U from sea water by adsorbing and complexing U in some way. Most likely this occurs due to the direct enzymatic reduction of soluble U(VI) to insoluble U(IV) by sulfate-reducing bacteria.

Uranium is often highly correlative with phosphorite (Baturin, 1974; Veeh et al., 1974; Calvert and Price, 1983; Ingall and Van, 1990). In part, this is because areas with abundant phosphorite are also typically enriched in OM. However, U can substitute for Ca in the apatite crystal structure. Baturin (1974) reported U levels of 10 to 700 ppm in phosphorite nodules and bone detritus. In areas with abundant phosphorite this component of U enrichment may be significant, though even then, U associated with OM seems to be more abundant.

CONTROLS ON URANIUM/ORGANIC-CARBON RATIOS

Although the correlation of authigenic U ($U_A$) with OC is strong, the $U_A$/OC ratio is highly variable. This probably accounts for the fact that some studies have found no significant correlation between U and OC even within a single basin (e.g., Veeh et al., 1974; Weber and Sackett, 1981). An early explanation for this was that only terrestrial OC was likely to be enriched in U and that variation in the $U_A$/OC ratio was then a function of varying amounts of terrestrial OC (Swanson, 1960). However, much work has since shown that marine OC is just as frequently enriched in U (e.g., Rona and Joensu, 1974; Kalil, 1976; Mangini and Dominik, 1979), so other factors must be involved to account for the variability of the ratio.

Possible controls on the $U_A$/OC ratio are the sedimentation rate, bottom-water oxygenation, U content of the sea water, OM flux, OM maturity, and sediment type and texture. These are briefly discussed in the following sections.
Sedimentation Rate

Sedimentation rate should play an important role in controlling the $U_A/$OC ratio (e.g., Swanson, 1961, Thomson et al., 1990; Anderson and Fleisher, 1991). This follows logically from the assumption that $U_A$ will have more time to accumulate if sedimentation rates are slow. In addition, lower sedimentation rates result in lower OC contents as more OM is oxidized in the near-surface diagenetic zone (Müller and Suess, 1979; Müller and Mangini, 1980). The combination of these two factors results in a higher $U_A/$OC ratio in slowly deposited sediments. Mangini and Dominik (1979) quantitatively demonstrated this relationship in a study of Late Quaternary sapropels in the Mediterranean. The authors used the $^{230}$Th excess method (Dominik and Mangini, 1979) to calculate sedimentation rates and then combined these with $U$ and OC data to illustrate the inverse relationship of $U_A/$OC to sedimentation rate (Fig.4.2).

Bottom-Water Oxygenation

Bottom-water oxygenation levels (i.e., oxygen supply) control the $U_A/$OC ratio by partly determining the level of the redox boundary within the sediment (e.g., Thomson et al., 1990). The OC-flux (i.e., $O_2$ consumption) also controls this boundary (see below). In fully oxic settings with limited OC input, the redox boundary is as deep as 40-120 cm (e.g., Yamada and Tsunogai, 1984; Thomson et al., 1990; Rosenthal et al., 1995a, 1995b). A deep redox boundary limits $U$ uptake because diffusion of $U$ to depths below the boundary is limited.

Uranium Content of the Sea Water

Variations in the $U$ content of sea water could account for variation of the $U_A/$OC ratio. However, given authigenic $U$ enrichment factors of $10^4$ and more, such variations would have to be large to significantly influence the $U_A/$OC ratio. Variations in $U$ content
Figure 4.2. UA/OC ratios versus sedimentation rates (corrected to 60% porosity) in Late Quaternary Mediterranean sapropels (data from Mangini and Dominik, 1979). Authors used the $^{230}$Th excess method (Ku, 1976; Dominik and Mangini, 1979) to calculate sedimentation rates and assumed a 1.5 ppm detrital U component.
do occur in the world's oceans, but they are small in the open ocean and attributed to variations in salinity (Ku et al., 1977). The conservative behavior of U and the fact that the salinity of the world's oceans has varied little during the Phanerozoic (Rubey, 1951; Redfield, 1958) suggests that the U content was also relatively constant.

Some depletion of U has been observed in the anoxic water columns of the Saanich Inlet (Todd et al., 1988) and Black Sea (Anderson et al., 1989a), but the depletion is 30% or less compared to the surface waters. Thus it is unlikely that variation in the U content of sea water plays a significant role in controlling the U/S/OC ratio.

Organic-Matter Flux

Variations in the OM flux may produce variations in the U/S/OC ratio depending in part on the role of OM in extracting U from sea water. OM may only serve to create the reducing environment necessary for U precipitation. If so, any excess OM flux beyond that needed to create a reducing condition at the sediment water interface will not result in additional U precipitation, and the U/S/OC ratio will be lowered as OM sedimentation continues. If the OM adsorbs or complexes the U directly in some way (biologically mediated or not), as seems more likely, then the U/S/OC ratio would tend to remain constant with an increased OM flux.

The OM flux into the sediments also has a direct role in determining the level of the redox boundary. A high OM flux with consequent high O2 consumption will result in a shallow redox boundary. This would tend to increase the U/S content and the U/S/OC ratio. It may also lead to less oxidation of the OM, producing the opposite effect on the U/S/OC ratio. The latter effect is less certain, however, as the relative ability of aerobic versus anaerobic bacteria to degrade OM is the subject of dispute (e.g., Calvert et al., 1992; Canfield et al., 1993; Tyson, 1995). On balance it seems likely that a high OM flux will increase the U/S/OC ratio.
Organic-Matter Maturity

Thermally mature organic matter may have an increased $U_{A}/OC$ ratio due to the loss of OM during the generation of petroleum and the preferential retention of $U$ (Mann and Müller, 1988), at least to the late catagenic or early metagenic stage (Olson, 1982). However, at very high maturity levels urano-organic complexes may break down and decrease the $U_{A}/OC$ ratio (Olson, 1982).

Sediment Texture and Type

Sediment texture may influence the $U_{A}/OC$ ratio as it determines the depth to which diffusion occurs as well as the reactive surface area of the sediment. The combined effect of these variables on the $U_{A}/OC$ ratio are difficult to assess, but as marine OC-rich rocks are all fine-grained, the effect may be minor.

The composition of the sediment could also influence the $U_{A}/OC$ ratio to some degree. Because of the paucity of Fe in carbonate sediments, OC-rich carbonates generate and preserve more $H_2S$ than do clay-dominated sediments (Jones, 1984). An expanded sulfide zone could effect both $U_{A}$ formation and OM degradation.

Changes in the Depth of the Redox Boundary

Changes in the depth of the redox boundary can help control the preserved $U_{A}/OC$ ratio. This control is related to bottom-water oxygenation and OM flux as discussed above. Temporal changes in these factors result in fluctuating redox levels within the sediment. These fluctuations will tend to average out over time, however, an oxidation front that moves downward will remobilize and concentrate $U$ in the underlying sediment (e.g., Thomson et al., 1990; Rosenthal et al., 1995b; Piper and Isaacs, 1996). This zone
of concentrated U will be preserved when the redox boundary again stabilizes or rises. The resulting $U_A/OC$ ratio can be exceptionally high.

METHODS

To document controls on $U_A/OC$ ratios I conducted a literature search for relevant data on both Recent offshore marine sediments and their ancient counterparts. Ideally, the data included: OC content, U content, carbonate content, sedimentation rate, and level of bottom-water oxygenation. Data on the depth to the redox boundary would have been very useful, but most studies did not include this parameter. From these data, I determined $U_A/OC$ ratios and compared them to estimated sedimentation rates and levels of bottom-water oxygenation. In practice, it was difficult to find published data that completely met all the above requirements.

Organic-Carbon Content

Data on the OC content of modern and geologically recent sediments are common. These data include both surficial and core data from a variety of marine environments. Measurement of OC content is almost routine in the Ocean Drilling Program (ODP) and ODP reports served as a major source of data in this study. Data on OC content is also common for ancient rocks, primarily because of the importance of OC-rich rocks as the source for petroleum.

Uranium Content

Unlike the OC content, the U content of sediments is not routinely measured in the laboratory. Generally, U content is determined only for very specific studies that concern the geochemistry of U or its use in dating. Commonly, but not always, OC content is also obtained in these studies. Fortunately, in recent years the gamma-ray
spectra log (e.g., Schlumberger, 1989) has come into fairly common use. This log records gamma rays at energy levels that are most characteristic of the different gamma-ray energy spectra of uranium, potassium 40, and thorium. The gamma-ray emissions are directly proportional to the abundances of these elements and the logging tool is carefully calibrated in test pits containing known concentrations of uranium, potassiuim 40, and thorium. The gamma-ray spectra log is quite commonly run in boreholes drilled for petroleum exploration and it has been routinely run on ODP boreholes in recent years.

**Sediment Composition**

Sediment composition is an important consideration in estimating the $U_A$ content. Calcite and quartz have extremely low U contents compared to the clay minerals comprising fine-grained clastic sediments (e.g., Schlumberger, 1989). Clastic muds and shales typically have allogenic U contents of 2 or 3 ppm and this has to be corrected for to obtain the authigenic component of the U. A 2 ppm allogenic U content is assumed for the purposes of this study. For example, if a sediment consists of 50% clay and the clay has an U content of 2 ppm, one ppm is subtracted from the measured U content to obtain the $U_A$ component. In most cases this correction was minor as the $U_A$ component was generally much larger than the allogenic U associated with the clay content.

**Sedimentation Rates**

Sedimentation rates for the literature data were taken from published estimates, generally from the same paper as OC/U data. In Recent and Pleistocene rocks sedimentation rate estimates are probably fairly accurate if mass accumulation rates are given. However, many times estimates of sedimentation rate are not presented along with porosity (or bulk density) data. This can make comparisons between sediments at
different levels of compaction difficult. Sedimentation rates are generally not so well
cstrained in ancient rocks because geochonological resolution is lower. All
sedimentation rates were adjusted to a common porosity of 60% whenever possible (most
modern and all ancient data) to account for wide differences in sediment compaction. In
some cases, porosity values were inferred and no attempt was made to consider the effect
of cementation in ancient rocks). The choice of 60% porosity was arbitrary, but it does
reflect a typical porosity for shallowly-buried marine sediments for which sedimentation
rates are often reported.

**Bottom-Water Oxygenation**

This factor is the least constrained of all the factors considered in this study. Only
in the modern is it possible to actually measure the bottom-water oxygenation and such
measurements may sometimes reflect transient O₂ levels rather than normal or average O₂
levels. The presence or absence of a benthic fauna can be used as a proxy for O₂
measurements in many cases. In ancient sediments, bottom-water oxygenation can only
be inferred. Lack of bioturbation is commonly taken as a sign of bottom-water anoxia,
however, bioturbation may be limited by other factors including soupy substrates (Hattin,
1986) and high sedimentation rates (Rhoads, 1974; Chanton et al., 1987). So although
inferences concerning ancient levels of bottom-water oxygenation are included in this
study, they are not treated as data.

**RESULTS**

Figure 4.3 shows U_A/OC values plotted against sedimentation rates. These values
were obtained from a compilation of published data (references for and notes on this data
are given in Appendix G). The figure includes data from a variety of Recent and ancient
marine depositional environments. Despite the scatter the inverse relationship between
U_A/OC and sedimentation rates is apparent.
Figure 4.3. Graph showing relationship of the UA/OC ratio to sedimentation rate from a variety of Recent and older sediments. Data are from the literature, and sources and notes on this data are presented in Appendix G.
Figure 4.3 (cont.). Key to graph showing relationship of the $U_A/OC$ ratio to sedimentation rate from a variety of Recent and older sediments. Data are from the literature, and sources and notes on this data are presented in Appendix G.
The data in Figure 4.3 include depositional environments with a broad range of bottom-water oxygenation levels. To test the effects of oxygenation, the data were separated into three settings using the Tyson and Pearson (1991) terminology: oxic (>2.0 ml/l O_2), dysoxic (0.2 to 2.0 ml/l O_2), and anoxic (0.0 ml/l O_2). Only Recent sediments are included. U_A/OC values from each setting are plotted against sedimentation rate in Figures 4.4-4.6.

Data from anoxic settings (Fig. 4.4) cover a relatively narrow range of sedimentation rates, but they clearly define the inverse relationship between U_A/OC values and sedimentation rates. Results for oxic settings (Fig. 4.5) also produce a clearly defined inverse trendline, but U_A/OC ratios are several times smaller than they are in anoxic sediments with similar sedimentation rates. Dysoxic settings (Fig. 4.6) mostly plot between the trendlines established for the anoxic and oxic settings.

DISCUSSION

Figures 4.3 through 4.6 illustrate the two primary controls on the U_A/OC ratio: the sedimentation rate and the level of bottom-water oxygenation. As expected the U_A/OC ratio is inversely proportional to the sedimentation rate and the bottom-water oxygenation level. Despite the somewhat limited Recent data, tentative trendlines for oxic and anoxic environments are established on U_A/OC versus sedimentation rate charts. The trendlines are statistically different in elevation (P<0.001), but not in slope. Potentially these can be used to help infer ancient bottom-water oxygenation levels when sedimentation rates are known or sedimentation rates when bottom-water-oxygenation levels can be inferred.

Gulf Of California Example

A plot of U_A/OC ratios versus sedimentation rates from five basins in the Gulf of California is shown in Figure 4.7 (data from Kalil, 1976). Data used for this plot are
Figure 4.4. Graph showing relationship of the U/OC ratio to sedimentation rate from Recent anoxic environments. Correlation line does not include Sal Si Puedes and Pettasquamscutt plots, as sedimentation rates for these are poorly constrained (see appendix).
Figure 4.5. Graph showing relationship of the UA/OC ratio to sedimentation rate from Recent oxic environments.
UA/OC RATIOS vs. SEDIMENTATION RATES
RECENT* LOW OXYGEN ENVIRONMENTS

unless otherwise noted

Anoxic

Oxic

Sedimentation Rate (cm/ka)

UA/OC (ppm/wt. %)

Figure 4.6. Graph showing relationship of the UA/OC ratio to sedimentation rate from Recent dysoxic environments. Trendlines from Figures 4.4 and 4.5 are also shown.
Figure 4.7. Graph of UA/OC ratios versus sedimentation rates for various basins in the Gulf of California (Data from Kalil, 1976). Plots include only data between depths of 20 to 100 cm (see text).
restricted to the depth range of 20 to 100 cm within the sediments. This strategy eliminated a few near-surface samples for which an U/OC equilibrium may not have been reached and restricts the samples to a time span of less than 1000 ka. (The importance of this is addressed below). Estimated sedimentation rates in these basins are not greatly different (there is uncertainty in some of these estimates—see Appendix G), but the $U_{\lambda}/OC$ ratios vary by a factor of more than 10. Samples from the shallower basins (i.e., Sal Si Puedes and Guaymas) have higher $U_{\lambda}/OC$ ratios compared to those from deeper basins (i.e., Carmen and Pescadero). The control on the $U_{\lambda}/OC$ ratio in this instance is the bottom-water oxygenation level. A bathymetric profile of the Gulf of California through these basins indicates that the position of the oxygen minimum zone relative to the sample depth is key (Figs. 4.8 and 4.9). The shallower basins have lower bottom-water oxygenation levels and hence higher $U_{\lambda}/OC$ ratios.

The $U_{\lambda}/OC$ ratios of some the basins (i.e., Farallon, Guaymas, and Sal Si Puedes) appear to be anomalously high given their estimated sedimentation rates. This is particularly true of the marginally dysoxic (just below 2.0 ml/l O$_2$) Farallon Basin sample. This could be due to overestimation of the sedimentation rate or to an expanded and more intense oxygen-minimum zone in the past.

There is evidence that bottom-water-oxygenation levels were lower in at least some of the Gulf of California basins in the past, as demonstrated in Figure 4.10. This figure plots $U_{\lambda}/OC$ ratios against sample depth for 4 of the basins (the Guaymas Basin is not included as the data were not suitable, see figure caption). In three of the basins (Pescadero, Farallon, and Sal Si Puedes), the $U_{\lambda}/OC$ ratio increases with sample depth. In the Sal Si Puedes Basin, it increases from a low (<1.0) value near the surface to a much higher value (≈3.0) at 80 cm. In the Pescadero and Farallon Basin, there is an increase at 100 cm depth and in the Farallon Basin there is an abrupt increase again at 200 cm depth (see Fig. 4.10).
Figure 4.8. Index map showing location of Gulf of California basins and location of bathymetric profile shown in Figure 4.9 (map from Van Andel, 1964).
Figure 4.9. Schematic bathymetric profile through Gulf of California basins used in Figure 4.6 showing sample depths and position of oxygen minimum zone (sample depths from Kalil, 1976; bathymetry from Van Andel, 1964).
Figure 4.10. $U_{\text{A}}/\text{OC}$ ratios versus depth below the sediment/water interface in the Carmen, Farallon, Pescadero and Sal Si Puedes Basins, Gulf of California. The Guaymas Basin is not included as most individual samples in this basin were analyzed for TOC or uranium, but not both. (Data from Kalil, 1976).
The Farallon Basin $U_{\lambda}/OC$ profile is especially interesting because of its location. At present this core site lies in marginally dysoxic water below the oxygen-minimum zone. The $U_{\lambda}/OC$ profile suggests that this site was more intensely dysoxic or anoxic in the past, especially prior to 2000 B.P., if Kalil's (1976) sedimentation rate estimate of 100 cm/ka is correct.

Upwelling intensity is known to have been greater in the Gulf of California in the past (DeMaster and Turekian, 1987; Juillet-Leclerc and Schrader, 1987) and this would have expanded the oxygen-minimum zone. Juillet-Leclerc and Schrader (1987) combined varve stratigraphy along with diatom $\delta^{18}O$ values from two cores in the Guaymas Basin to produce a curve that records variations in upwelling in the Gulf of California for the last 3000 years. The authors also presented a curve showing variations in the abundance of the silicoflagellate, *Dictyocha messanesis*, which is considered to be an indicator of low productivity. These curves along with the $U_{\lambda}/OC$ and TOC profiles of the Farallon Basin core are presented in Figure 4.11. The Juillet-Leclerc and Schrader (1987) curves are plotted against time and the Farallon Basin curves are plotted against depth, but with an estimated 100 cm/ka sedimentation rate (see above) for the 280 cm Farallon core, the two sets of curves span a very similar time period.

The Guaymas Basin upwelling/productivity curves can be correlated to the Farallon Basin curves (Fig. 4.11). For example, the high productivity interval from 2000 to 1500 B.P. corresponds to a zone of higher than average TOC in the Farallon Basin core (140 to 205 cm). The Farallon TOC curve fits the productivity/upwelling curves quite well below the 100 cm depth, but above this the Farallon basin samples are too widely spaced for a meaningful comparison.

By tying the two sets of curves, it is possible to estimate sedimentation rates for individual zones within the Farallon core. These are combined with average $U_{\lambda}/OC$ ratios over the same intervals and presented in Figure 4.12. The results suggest that Farallon
Figure 4.11. Comparison of the absolute abundance of *Dictyocha messanensis* and diatom δ18O values versus age from the Guaymas Basin to U4/OC and TOC profiles from the Farallon Basin. Guaymas Basin curves are reproduced from figure 3 of Julliet-Leclerc and Schrader (1987) and include only their smoothed curves. Farallon Basin data are from Kalil (1976).
Figure 4.12. $U_{\text{A}}$/OC ratios versus sedimentation rates for Farallon Basin: zones 1 through 6 as defined in Figure 4.11. The most recent sediments (zone 1) plot in dysoxic zone. Older sediments plot as dysoxic to anoxic. The zone with highest paleoproductivity (zone 4—see Figure 4.11) plots with highest sedimentation rate.
Basin bottom-water was dysoxic to anoxic in the past at the location of this core. Also, with the exception of intervals 1 and 2, higher-productivity episodes are associated with higher sedimentation rates as expected.

Southeastern Indian Ocean

$U_A/OC$ ratios versus sedimentation rates for Holocene and Pliocene sediments at a site in the subtropical of southeastern Indian Ocean are shown in Figure 4.13 (Rosenthal et al., 1995b). Sedimentation rates are well constrained and quite constant, so changes in the $U_A/OC$ ratio should reflect changes in the bottom-water oxygenation and/or the depth of the redox boundary within the sediments. At present the area is overlain by oxic waters with a deep redox boundary of 70 to 75 cm beneath the sediment surface (Rosenthal et al., 1995a). The authors suggested that during glacial stages increased OC-productivity resulted in the shoaling of the redox boundary and increased $U$ precipitation. The $U_A/OC$ ratios shown in Figure 4.13 are consistent with this interpretation, though the very high $U_A/OC$ ratios, particularly for stages 2 and 6, would seem to indicate that the bottom water was anoxic at these times. Rosenthal et al. (1995a) suggest bottom-water oxygen levels were lower during glacial periods, but do not infer complete bottom-water anoxia. The high $U_A/OC$ ratios of stages 2 and 6 are, in part, likely to reflect post-depositional remobilization of $U$ when the redox front was migrating downward as a result of increased oxygenation of the bottom water and/or a decreased OM flux.

$U_A/OC$ MODEL

Previous sections have discussed and illustrated the controls on the ratio of $U_A$ to OC in fine-grained marine sediments. In this section a simple qualitative model is presented that accounts for the main controls on the $U_A/OC$ ratio. First, the nature of
Figure 4.13. UA/OC ratios versus sedimentation rates for Pleistocene and Recent sediments in the southeastern Indian Ocean. Numbers refer to glacial stages. Data from Rosenthal et al. (1995a).
these controls is further illustrated with examples of porewater and sediment profiles showing U content (Figs. 4.14, 4.15).

The porewater U profiles in Figure 4.14 are grouped by degree of bottom-water oxygenation. The profiles from anoxic basins show that porewater U decreases abruptly within the first few cm of the sediment indicating rapid U uptake. In contrast, profiles in oxic settings show a more gradual decline in porewater U content over a broader depth range. Abrupt decreases in porewater U in these settings correspond to the level of the redox boundary within the sediment.

Profiles of sediment U content (Fig. 4.15) demonstrate the rapid increase in $U_A$ that occurs just below the redox boundary. The shape of the U profile below this boundary can be related to depositional history. For example, the relatively flat U profile in core 11147 #1K (Fig. 4.15b) form 65 to 150 cm indicates steady-state conditions. In contrast, the $U_A$ peak between 40 and 65 cm in this same core has been attributed to a slowing of the sedimentation rate and a lowering of the redox boundary (Thomson et al., 1990).

The relationship between U content in sediments and porewater U is illustrated by Figure 4.15c in which both profiles are plotted for a single core. The abrupt decrease in porewater U and increase in sediment U at about 7 cm corresponds to the level of the redox boundary.

The principle controls on the $U_A$/OC ratio in marine sediments are summarized in Figure 4.16. This figure schematically illustrates how the sedimentation rate, the oxygen supply, and the OM-flux affects the $U_A$/OC ratio. In summary, the amount of U in the sediments is determined by two primary factors: (1) the residence time of the sediment in the zone at or below the redox boundary and above the zone of effective diffusion and (2) the amount of OM present in this zone. The first of these factors is a function of the sedimentation rate and the position of the redox boundary. The position of the redox
Figure 4.14. U porewater profiles from both anoxic and oxic marine settings. Anoxic settings include: (a) Saanich Inlet (from Anderson et al., 1989b), (b) Cariaco Trench and (c) Black Sea (from Barnes and Cochran, 1990). Oxic settings (d) are from the NW Atlantic (from Barnes and Cochran, 1990). In the anoxic settings, the porewater U profile records an abrupt drop from normal seawater values (2.4 dpm $^{238}$U) in the first few cm of sediment. In the oxic settings, the drop in porewater U is much less and spread out over a greater depth even though the sediments themselves are described as being suboxic (Barnes and Cochran, 1990). One dpm $^{238}$U = 1.34 ppm U.
Figure 4.15. Profiles of U content in marine sediments from (a) the eastern Atlantic and (b) NE Atlantic (Thompson et al., 1990). Profiles of both sediment U and porewater U (c) are from a core on the California shelf (Klinkhammer and Palmer, 1991). Abrupt increase in U content in each core denotes the depth of the redox boundary.
Figure 4.16. Simple model of the primary controls on the $U_A/OC$ ratio in marine sediments. Anoxia is shown by dark shading and the level of the redox boundary (RDB) is shown. Key to diagram follows.

Low OM Flux

1a. Deep redox boundary (RDB) and long residence time in oxic zone means only small amounts of highly refractory OM are preserved. Diffusion of $U$ to RDB is very limited. $U_A/OC$ ratio is low.

1b. A high sedimentation rate (SR) reduces the residence time of OM in the near surface oxic (and anoxic) diagenetic zone, so some additional OM is preserved. $U$ has limited time to be incorporated with the OM. $U_A/OC$ ratio is very low.

1c. Dysoxic bottom water (e.g., impingement of $O_2$ minimum) raises RDB. Some additional OM may be preserved. $U$ readily diffuses to and below the RDB. $U_A/OC$ ratio is high.

1d. High SR results in additional OM preservation and reduces time for $U$ to diffuse to RDB. $U_A/OC$ ratio is moderate.

1e. Stratified basin results in anoxic bottom water. OM preservation may be increased. $U$ has very long time to be incorporated with the OM. $U_A/OC$ ratio is very high.

1f. High SR results in additional OM preservation and reduces time for $U$ to diffuse to RDB. $U_A/OC$ ratio is moderate to high.
High OM Flux
2a. A high OM flux raises the redox boundary. OM preservation may be increased compared to 1a. U content increases. $U_A/OC$ ratio is moderate.
2b. High SR results in additional OM preservation and reduces time for U to diffuse to RDB. $U_A/OC$ ratio is low to moderate.
2c. A high OM flux raises the RDB probably to at or near (slightly above or below) the sediment water interface. OM preservation may be increased. U has a long time to be incorporated with the OM. $U_A/OC$ ratio is high.
2d. High SR results in additional OM preservation and reduces time for U to diffuse to RDB. $U_A/OC$ ratio is moderate.
2e. OM preservation is high. $U_A/OC$ ratio is very high unless U in the bottom water becomes depleted in U.
2f. OM preservation is very high. $U_A/OC$ ratio is moderate.
Low OM Flux

Oxygen Supply

1

Sed. Rate

Low

a

High (Active circulation)

Water

low UA/OC

b

High

Water

v. low UA/OC

c

Low to Moderate (Sluggish circulation)

Water

high UA/OC

d

Water

mod. UA/OC

e

Very Low (Stratified Basin)

Water

v. high UA/OC

f

Water

mod. to high UA/OC

High OM Flux

Oxygen Supply

2

Sed. Rate

Low

a

High (Active circulation)

Water

mod. UA/OC

b

High

Water

low to mod. UA/OC

c

Low to Moderate (Sluggish circulation)

Water

high UA/OC

d

Water

mod. UA/OC

e

Very Low (Stratified Basin)

Water

v. high UA/OC

f

Water

mod. UA/OC
boundary is controlled by the level of bottom-water oxygenation (O₂ supply) and the OM flux (O₂ consumption). From the above it follows that the U₄/OC ratio is largely a function of factor (1) above, as the data presented demonstrate.

SUMMARY AND CONCLUSIONS

The association of U₄ with OC is ubiquitous in fine-grained marine sediments. Reducing conditions within these sediments are created by the oxidation of OM. Consequently, soluble U(VI) from the water column is reduced to U(IV) in the presence of the OM, probably by sulfate-reducing bacteria. The correlation of U₄ with OC is usually strong, but there are a number of factors that can influence the ratio of U₄ to OC. The most important of these are the sedimentation rate and the bottom-water-oxygenation level as Figures 4.3 through 4.6 demonstrate.

The U₄/OC ratio can be very useful in interpreting ancient depositional environments as demonstrated by the examples presented. And although other trace elements are concentrated in OC-rich rocks and many of these are useful or potentially useful in paleoenvironmental interpretations (e.g., Calvert, 1993), use of U has the significant advantage over other trace elements in that uranium contents are often recorded by geophysical well-logs both in ancient sedimentary basins and in more recent marine depositional environments.

In the next chapter, the U₄/OC relationships established in this chapter, are applied to the Niobrara to help assess bottom-water oxygenation during Niobrara deposition. In Chapter 6, these relationships are used in a similar fashion for the Sharon Springs.
CHAPTER 5
CONTROLS ON ORGANIC-CARBON DISTRIBUTION, ACCUMULATION RATES, AND PALEOPRODUCTIVITY IN THE NIOPRARA FORMATION

INTRODUCTION
In this chapter the three dimensional (3D) distribution of organic carbon (OC) within the Niobrara Formation is examined. The chapter begins with a review of the relationship of OC content to vertical facies changes in the Niobrara. This includes a brief discussion of how these facies changes manifest themselves on certain geophysical logs. Then the Niobrara chronostratigraphic framework established in Chapter 2 is coupled with well-log estimation of OC as outlined in Chapter 3. Together these elements are used to produce a 3D picture of OC distribution in the Niobrara. Organic-carbon accumulation rates and paleoproductivity estimates are then compared to the variety of factors that both reflect and potentially control OC enrichment in the Niobrara. These include the sedimentation rate, paleobathymetry, bottom-water oxygenation, and general paleoceanographic setting. U\textsubscript{A}/OC ratios are used to help assess levels of bottom-water oxygenation during Niobrara deposition. Finally, the data are synthesized and used to put constraints on the model(s) that can best account for the OC enrichment of the Niobrara. A similar treatment of the Sharon Springs is presented in Chapter 6.

ORGANIC-CARBON CONTENT AND FACIES
A number of previous studies have looked at the relationship between facies and OC content in the Niobrara (Pollastro and Martinez, 1985a; Pratt et al., 1993; Pratt and Barlow, 1985; Rodriguez, 1985). Most of these studies have focused on a limited number of stratigraphic sections, often a single outcrop or core; nevertheless, taken together, the studies provide evidence of a consistent vertical pattern of OC enrichment in
the Niobrara Formation. This pattern is closely tied to the vertical facies changes that are used to divide the Niobrara into formal (Fort Hays and Smoky Hill) and informal members. This pattern is summarized below, and then a detailed examination of the relationship of OC content to a variety of factors is discussed.

**Vertical Changes in OC Content**

The pattern of vertical (temporal) variation in OC content within the Niobrara is consistent between localities, at least throughout the region included in the study area. Figure 5.1 illustrates this by comparing TOC profiles through two Niobrara sections. The data are from long Niobrara cores taken from wells about 53 km apart (Fig. 5.2). The lower TOC values in the Golden Buckeye well are a consequence of the greater thermal maturity of the OM in this well, but the overall pattern of OC content in these wells is the same. Other data are also consistent with this pattern, although these data are generally confined to smaller stratigraphic intervals at any given locality. A summary of the general pattern is presented below along with additional supporting references where relevant.

The OC content of the Fort Hays Member of the Niobrara is generally less than 1.0%, as shown in Figure 1. In the thick limestone beds (typically 0.2 to 0.8 m (Barlow and Kauffman, 1985)) values are generally much less than 1.0% (Pratt and Barlow, 1985). In the thin shale interbeds, however, values are about 1.0% higher on average. This pattern continues into the shale and limestone member, but OC contents gradually increase upwards as do the thickness of the shale beds (Pratt and Barlow, 1985).

OC contents in the lower shale unit are in the 3.0 to 5.0% range (Pratt and Barlow, 1985). They decrease to 2.0 to 3.0% in the lower chalk (Pratt and Barlow, 1985). They are typically 3.0 to 5.0% in the middle marl, 2.0 to 4.0% in the middle
Figure 5.1. Comparison of TOC logs from the Coquina #4-Berthoud State well, Larimer Co., CO (16-4N-69W), and the Golden Buckeye #2-Gill Land Co. well, Weld Co., CO (22-6N-64W). See Figure 2 for locations. Data for the Coquina well are taken from Dean and Arthur (1989) and Pratt et al. (1993). Samples in this well were taken at one meter intervals from a core through the Niobrara section. Data for the Golden Buckeye well are part of this study. Each sample in this data set is a composite of finely crushed rock fragments spanning 0.6 m (2 ft) intervals along the length of the core (see Chapter 2 for details). Data for the upper chalk and Fort Hays through lower marl sections are from Carbollog OC values. (The lower part of the Golden Buckeye core is fragmented with missing sections and uncertain sample depths, so TOC values obtained for this part of the section [dashed line] are problematical).
<table>
<thead>
<tr>
<th>Layer</th>
<th>Coquina Oil Corp.</th>
<th>Golden Buckeye</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#4 Berthoud St.</td>
<td>#2 Gill Land Co.</td>
</tr>
<tr>
<td></td>
<td>16-4N-69W</td>
<td>22-6N-64W</td>
</tr>
</tbody>
</table>

- **Upper Chalk**: 3
- **Upper Marl**: 2
- **Middle Chalk**: 2
- **Middle Chalk**: 1
- **Lower Chalk**: 3
- **Lower Marl**: 2
- **Shale & Lms**: 1
- **FORT HAYS**: 1

**Graphical Representation**

- **10 m**
- **TOC %**

The diagram shows the layers and their thickness at two different locations, with the TOC percentage indicated on the right side.
Figure 5.2 Index map showing location of key cores and the cross section discussed in this chapter.
chalk (Pollastro and Martinez, 1985a), 3.0 to 6.0% in the upper marl, and 1.0 to 4.0% in the upper chalk (Rodriguez, 1985).

OC Content and Carbonate Content

The overall pattern in the Niobrara is one of higher OC contents in the marl units and lower OC contents in the chalk units. This pattern is generally duplicated at smaller scales as well. For example, a number of authors have demonstrated a strong inverse relationship between OC content and carbonate content down to the scale of thin individual bedding couplets (Pollastro and Martinez, 1985a; Pollastro and Martinez, 1985b; Precht and Pollastro, 1985; Rodriguez, 1985; Pollastro, 1992; Pratt et al., 1993).

OC Content and Bioturbation

The inverse relationship between OC content and the intensity of bioturbation in the Niobrara is well documented (Pratt and Barlow, 1985; Savrda and Bottjer, 1989b). At the extremes, laminated zones generally have high OC values (3.0-5.0%), whereas intensively bioturbated zones (largely confined to the Fort Hays and part of the shale and limestone member) have low OC values (<1.0%). Bioturbation in most of the Smoky Hill member of the Niobrara is restricted to thin, lightly burrowed zones. The level of bioturbation in the Niobrara can be directly related to the level of bottom-water oxygenation (Savrda and Bottjer, 1989a; Savrda and Bottjer, 1989b; Savrda and Bottjer, 1993). The very limited bioturbation in the Smoky Hill implies that oxygen levels at the bottom of the Niobrara sea were generally too low to support most bottom-dwelling organisms. The origin of this oxygen-depleted bottom water is a key to understanding OC deposition in the Niobrara. A stably stratified water column may lead to bottom-water anoxia which then enhances preservation of OM (Demaison, 1991; Demaison and Moore, 1980; Tyson, 1987). Or alternatively, anoxia/dysoxia may result from high productivity
and a high OM flux which then depletes oxygen near the bottom even in the absence of stagnant bottom water (Calvert et al., 1992; Calvert and Pedersen, 1992; Pedersen and Calvert, 1990). These alternatives are evaluated at the end of this chapter in light of evidence to be presented below.

Organic Matter Type

The OM in the Niobrara is dominated by type II (Tissot et al., 1974) marine organic matter (Fig. 5.3). Exceptions are the Fort Hays and the shale and limestone members where type III organic matter is abundant. This indicates that for most of the Smoky Hill member variations in OC content were not produced by variations in terrestrial OM input.

Relationship of Facies to Log and Rock-Eval Data

A generalized description of the Niobrara core from the Golden Buckeye #2-Gill Land Co. well is shown in Figure 5.4, along with a series of geophysical and Rock-Eval logs (see Chapter 2). A summary of some of the more important aspects of this figure follows.

OC Content and Facies

A comparison of the Niobrara facies to the OC content in the Golden Buckeye well (Fig. 5.4a-c) confirms previously published relationships. The chalk units have lower OC contents than the marl units, dark laminated sections have high OC contents, and bioturbated zones generally have the lowest OC contents.
Figure 5.3. Modified van Krevelen diagram (HI versus OI plot) after Espitalié et al. (1977), showing maturation trends for the principal kerogen types (I, II, and III) along with Rock-Eval data for the Niobrara. Sources of the data are as follows. (1) Lower marl through upper marl and (2) Fort Hays Member and shale and limestone member in the Golden Buckeye #2 Gill Land Co well, 22-6N-63W, Weld Co., CO (this study). (3) Upper chalk member, Mesa #1-5 Federal well, 29-4N-46W, Yuma, Co., CO (this study). (4) Outcrop samples from the upper marl member, 8-1N-15W, Franklin Co., NE (this study). (5) Upper chalk member at Lyons, CO from Rodriguez (1985). (6) Upper marl member at Lyons, CO from Rodriguez (1985). (7)-(11) Upper chalk member from Rice (1984) with data from the (7) Kansas-Nebraska #1-32 Whomble well, 32-2S-46W, Yuma Co., CO; (8) Excelsior #1 Nay well, 14-9N-58W, Weld Co., CO; (9) Mountain Petroleum #1-29 State, 29-2S-43W, Yuma, Co., CO; (10) J.W. Operating Co. #1 Brophy, 29-4N-46W, Yuma, Co., CO; and Kansas-Nebraska #1-33 Powell, 33-3N-47W, Yuma Co., CO.
Figure 5.4. Core description, OC, log, and Rock-Eval data for the Niobrara, Golden Buckeye #2-Gill Land Co. well, Weld Co., CO (22-6N-64W).

(a) Niobrara stratigraphic column.

(b) Generalized core description (entire section was not cored).

(c) TOC data from core sample analyses (lower chalk through the upper marl) and well-log estimates (remainder of section). Well-log estimates were used in lieu of sample analyses for the lower part of the core because of its fragmented condition.

(d) Corrected gamma-ray log (U component removed). Log values are roughly proportional to the clay content (i.e., 40 API units equals approximately 40% clay). (e) Uranium (U) content from gamma-ray spectra log. Note similarity between this curve and the TOC curve.

(f) Ratio of authigenic uranium to OC content (see $U_A$/OC text section).

(g) Hydrogen index of OC samples.

(h) Oxygen index of OC samples.

(i) Tmax values (maturity) of samples. Values between about 436°C and 458°C are within the hydrocarbon-generation window (Tissot and Welte, 1974)

(j) Ratio of hydrogen index to oxygen index.

(k) Production index. This index is the ratio of the hydrocarbons already produced to the genetic potential of the rock (see Chapter 2).
OC and Clay Content

A comparison of the TOC curve (c) to the corrected gamma-ray curve (d) in Figure 5.4 confirms the fact that OC content tends to correlate with clay content as noted above. A notable exception is the lower marl member. On average, this unit contains less clay than does the underlying shale and limestone member.

OC and Uranium Content

As expected, the OC content correlates quite well with the uranium content (compare curves c and e in Fig. 5.4). The U content is only 2 to 3 ppm in the OC-poor Fort Hays Member, whereas it averages about 12 ppm in the Smoky Hill Member where it is of mostly authigenic origin. The $U_A/OC$ ratio (curve f) generally falls between 3 and 6 (ppm/wt.%). Highly variable values near the base of the section reflect the interbedded shales and limestones of the Fort Hays and shale and limestone member. $U_A/OC$ values gradually increase to a maximum in the middle chalk and remain constant in the remainder of the section. As noted in Chapter 4, the $U_A/OC$ ratio is largely dependent on the sedimentation rate and the level of bottom-water oxygenation. Its significance for the Niobrara will be discussed in a subsequent section.

OC Content and Rock-Eval Data

Curves g through k in Figure 5.4 plot various Rock-Eval parameters against depth. The first of these curves is a log of the hydrogen index (HI). Most of the values fall between 120 and 160. These values are consistent with type II OM that is in the thermally mature, hydrocarbon-generation zone (see Fig. 2). The HI gradually increases upwards into the middle chalk member, then declines. This pattern is temporally coincident with the rise and fall of Niobrara sea level outlined in Chapter 2. When sea level was highest, terrestrial OM input to the basin was likely to be most limited and type
II marine OM most dominant. This pattern is not observed in the Coquina #4 Berthoud State well, however, as hydrogen indices in this well are relatively constant.

Values for the oxygen index (OI), log (h), are typically between 10 and 20. Again these values are typical of type II organic matter that has reached the thermally mature stage. Values in the shale and limestone member and Fort Hays Member, in contrast, fall between 100 and 300. These values are consistent with terrestrial OM (i.e., type III). Average OI values are slightly higher in the chalk members than they are in the marl members. Peaks in OI correspond to zones with the lowest OC contents. These zones also tend to have the highest carbonate contents and the greatest degree of bioturbation.

\( T_{\text{max}} \) values are plotted in Figure 5-4(i). Values generally fall between 440°C and 450°C, which puts the section near the middle of the oil window (Tissot et al., 1974). Values in the shale and limestone member and the Fort Hays Member are less than 430°C reflecting the influence of OM type (II vs. III) on the \( T_{\text{max}} \) value (Tissot et al., 1974). \( T_{\text{max}} \) values are also lower in some of the same chalk zones that have higher than average OI values. Although a minor part of this decrease in the \( T_{\text{max}} \) values could result from a change in the kerogen composition in these zones, most of it probably results from the presence of migrated hydrocarbons, which tend to lower \( T_{\text{max}} \) values (Peters, 1986).

Although conventional core analyses on the (jolden Buckeye well were not obtained, migrated hydrocarbons are clearly present in the Niobrara in this well, particularly in the chalk units, as noted in Chapter 2. This is further confirmed by the production index (PI) plot (Fig. 5-4k), as PI values are high, given the level of maturity indicated by the \( T_{\text{max}} \) values. PI values above 0.4 generally occur in the wet gas zone in conjunction with \( T_{\text{max}} \) values greater than 460°C (Tissot et al., 1974). PI values in the Golden Buckeye well are highest (>0.5) in carbonate rich zones that often have the greatest porosity and/or permeability. As pointed out by (Pollastro, 1992), carbonate-rich zones in the Niobrara
tend to be more brittle than adjacent marls and therefore are more subject to fracture-produced porosity and permeability.

**DISTRIBUTION OF ORGANIC CARBON IN THE NIOBRARA**

In this section, Carbolog-estimated OC values are combined with the chronostratigraphy to document the 3-D distribution of organic carbon in the Niobrara. First, however, a two-dimensional picture of the OC distribution is presented in Figure 5.5 to illustrate the type of data that were used. This figure utilizes a series of 13 Carbologs (including two directly calibrated to sample data) to create a cross section extending from the Boulder area to west-central Nebraska (see Figure 5.2). The cross section demonstrates the regional consistency of the vertical (temporal) pattern of OC-enrichment in the Niobrara. Note, however, lateral variations in the OC content within time-equivalent strata. For example, OC values are generally lower in the wells near the west end of the cross section than they are farther to the east. This result is largely a consequence of burial depth. Wells at the west end of the section are in the deep Denver Basin, and the Niobrara section in these wells (e.g., the Golden Buckeye well) is at maturity levels sufficient to have converted some of the kerogen into petroleum, thus lowering the OC content (even if the petroleum is unmigrated, the more volatile hydrocarbons are often lost before analyses are made).

In order to assess lateral and vertical changes in OC contents within the Niobrara, geophysical logs from 58 wells were used to estimate average OC contents in each of the chronostratigraphic units discussed in Chapter 2 (the Fort Hays was not subdivided). The wells used are tabulated in Appendix H. Maps showing the regional distribution of OC in each of these zones were produced, and two of these are reproduced herein as examples. OC values for the lower chalk unit 1 (LC-1) are shown in Figure 5.6 and those for lower chalk unit 2 (LC-2) are shown in Figure 5.7. OC values in LC-2 are generally somewhat
Figure 5.5. East-west Carbolog cross section extending 365 km from Boulder, CO to west-central Nebraska (see Figure 2).
Figure 5.6. Average OC values in the lower chalk unit 1. Contour interval is 1.0%.
Figure 5.7. Average OC values in the lower chalk unit 2. Contour interval is 1.0%. 
higher than they are in the LC-1 (on average 0.7% higher). The two maps exhibit some broadly similar patterns, including an area of higher OC contents to the southeast and northeast and an area of low OC in an area directly north of Denver. The latter area corresponds to the deep Denver Basin where OM maturity levels are high. The most consistent pattern on all the maps (other than the lowered OC values north of Denver) is a trend towards higher OC values to the southeast.

**OC Content, OCARs, and Sedimentation Rates**

A number of studies have noted a positive correlation between OC contents and sedimentation rates (Health et al., 1977; Müller and Suess, 1979). The positive correlations noted by the above authors have been attributed to the preservational effect of the more rapid burial of OC (e.g., Müller and Suess, 1979).

To a large extent the strong positive correlation between OC and sedimentation rate noted by Health et al. (1977) and Müller and Suess (1979) was produced by combining modern data from slowly deposited deep-sea sediments with that from much more rapidly deposited continental shelf and slope deposits. Deep-sea sediments have low OC contents in the modern for the following reasons: they underlie areas of low productivity, the depth limits the OM flux that makes it to the bottom, and the bottom water is well oxygenated. In contrast, continental shelf and slope sediments are deposited in shallower water beneath areas of moderate to high productivity, and bottom water oxygen levels are often low. If the data are restricted to environments that are more directly comparable (upwelling zones, normal continental shelf, etc.), the correlation between OC and sedimentation rate breaks down, see figures in Stein (1990) and discussion in Pelet (1987), for example.
Niobrara Sedimentation Rates

Time spans for individual units were initially estimated by combining the physical subsurface stratigraphy with the published biostratigraphy (e.g., Scott and Cobban, 1964; Hattin, 1982; Pratt et al., 1985) and the latest absolute-age determinations of Obradovich (1993) (Fig. 5.8). However, given the limited number of absolute ages in this section and the lack of biostratigraphic resolution in this ammonite sparse section (e.g., Hattin, 1982), there was still considerable latitude for deciding on exact age boundaries between most units.

To make estimates of the age spans for each individual unit two additional steps were taken. A composite section was created by combining the averaged thicknesses of each individual unit in the east-central part of the study area. In this area sedimentation rates are probably quite uniform as evidenced by the lack of disconformities and significant facies change. Further, by averaging several sections localized variations in sedimentation rate could be minimized. A constant sedimentation rate was assumed for this composite Niobrara section. Then time spans could be estimated for individual units by assuming a 7.8 Ma (±1.0) time span for Niobrara deposition (see Fig. 5.8). The estimated time spans were then compared to patterns of likely Milankovitch cyclicity. Such cycles have been previously noted in the Niobrara (Gilbert, 1895; Fischer et al., 1985; Fischer, 1993; Pratt et al., 1993), although they have not been particularly well documented. Major cycles in the Niobrara were found to have a timing at or very close to the 100 ka eccentricity cycle. It was then assumed that these were 100 ka cycles and time spans were adjusted accordingly.

Sedimentation rates were standardized by using density logs to determine present day porosities and converting these to a common 60% porosity value.
Figure 5.8. $^{40}$Ar/$^{39}$Ar ages of Obradovich (1993) plotted against the Western Interior ammonite zones spanning the Niobrara and Sharon Springs sections. Boundaries between individual units are inferred (see text).
Organic-Carbon Accumulation Rates

OC contents were combined with estimated sedimentation rates to produce organic-carbon accumulation rates (OCARs). Figures 5.9 and 5.10 are maps showing OCARs for LC-1 and LC-2 respectively. These two maps are quite similar, as they reflect the broadly similar pattern of OC contents in these two zones, as well as their similar thickness patterns (see isopach maps in Chapter 2). The close correspondence between OCARs and thickness in these units is not surprising as the OC flux can be expected to vary in phase with the carbonate flux (this topic will be expanded upon in a subsequent section).

OC Content versus Sedimentation Rates

In Figure 5.11 plots of OC versus sedimentation rate are shown for several Niobrara units. Correlations between OC and sedimentation rate are only weakly positive and in the case of the lower marl, the correlation is weakly negative. The lack of any significant correlation suggests that at best there is only a modest preservational effect attributable to increased rates of sedimentation.

Organic-Carbon Accumulation Rates versus Sedimentation Rates

Organic-carbon accumulation rates are plotted against sedimentation rates in Figure 5-12. In this case, the correlations are strongly positive for each of the units plotted. This is not surprising as the sedimentation rate is a partially dependent variable of the OCAR (the OC flux contributes to the overall sediment flux). Furthermore, as biogenic carbonate is the dominant constituent (60-70%) in the Niobrara, it follows that there should be a positive relationship between the carbonate flux (CaCO₃ productivity) and the OC flux (OC productivity). The correlation is not one to one, however. A doubling of the sedimentation rate does not quite produce a doubling of the OCAR. This
Figure 5.9. Organic-carbon accumulation rates in the lower chalk unit 1.
Lower Chalk 2 - OCAR (g/cm²/ka)

Figure 5.10. Organic-carbon accumulation rates in the lower chalk unit 2.
Figure 5.11. Organic-carbon content versus sedimentation rates for selected units in the Niobrara Formation. Best-fit correlation lines are shown, although none is statistically significant.
Figure 5.12. Organic-carbon accumulation rates versus sedimentation rates for selected units in the Niobrara Formation. Values to the lower right are the slopes of the correlation lines. A slope of 0.05 is a one-to-one correlation between the two sets of values.
suggests that dilution of the OC is a somewhat more important effect of increased sedimentation rates than is preservation. No significant difference between marl and chalk units is apparent.

Because it is possible to estimate shale (clay) contents in the Niobrara using well logs (either the corrected gamma-ray log or the neutron density combination), it is also possible to estimate the mass accumulation rates (MARs) of the carbonate and clay components separately. Figure 5.13 is a plot of carbonate and clay MARs against corresponding OCARs for a series of upper marl unit 2 sections. The OCAR correlates strongly with the carbonate accumulation rate, but only weakly, if at all, to the clay accumulation rate. It is clear that in this unit at least, regional changes in thickness are largely a function of the carbonate flux and that the OC flux is closely tied to this flux. This seems to firmly establish the relationship between carbonate and OC productivity.

PALEOPRODUCTIVITY

Estimation of Paleoproductivity

A number of different equations have been developed to provide estimates of paleoproductivity for ancient OC-rich sediments (for a review of many of these, see Tyson, 1995). Researchers have tried to isolate the key controls on OC content in modern environments and then provide best-fit mathematical equations to account for these controls. These equations have then been used to estimate past productivity. Such estimates are inherently suspect, given the number of potential controls on OC preservation, the uncertainty in establishing some important parameters for the ancient record (water depth, sedimentation rates, etc.), and the probable lack of modern analogs for at least some ancient OC-rich rocks. Nevertheless such estimates can be useful, at least in denoting regional and/or temporal changes in paleoproductivity, if not absolute paleoproductivity.
Figure 5.13. Clay and carbonate mass accumulation rates (MARs) versus OCARs for the upper marl unit 2. Values are averages for the entire unit at each of 26 widely spaced subsurface sections.
For this study, estimates were made by combining the formula of Betzer et al. (1984) which relates OC flux to water depth and productivity, with that of Henrichs and Reeburgh (1987) which relates burial efficiency to the sedimentation rate. The latter equation was found to be especially accurate for slowly deposited sediments (less than 10 cm/ka) in pelagic and hemipelagic settings by Tyson (1995), so it is well suited to the Niobrara Formation (average sedimentation rate of 2-3 cm/ka). The Betzer et al. (1984) equation is:

\[ \text{OC flux} = 0.409 \times \text{productivity}^{1.4} \times \text{depth}^{-0.63} \quad (r = 0.92, \ n = 26) \]

where productivity is g/m^2/a

and depth is in meters

The Henrichs and Reeburgh (1987) equation is:

\[ \text{Burial efficiency (BE)} = \text{LSAR}^{0.4}/2.1 \quad (r = 0.95, \ n = 32, \ \text{Henrichs and Reeburgh, 1987}; \ r = 0.79, \ n = 79, \ \text{Tyson, 1993}) \]

where LSAR is the linear sedimentation rate in cm/a

and BE = preserved OC/OC flux to bottom

These two equations can be combined and solved for productivity with the following result (see Appendix I for the derivation):

\[ \text{PP} = (51.3 \times \text{OCAR}/((\text{LSAR} \times 0.001)^{0.4} \times \text{depth}^{-0.63}))^{0.71} \]

where PP = productivity in g/m^2/a

OCAR = organic carbon accumulation rate in g/cm^2/ka

LSAR = linear sedimentation rate in cm/ka

and depth is in meters

The above equation combines two different sets of data, however as both formulas used to produce this equation are highly significant (p < 0.001), the equation is assumed to be valid. A similar equation was devised by Sarnthein et al. (1987) from the
same OC-flux data versus depth data that Betzer et al. (1984) used (from Suess, 1980) and a set of OCAR versus sedimentation rate data initially published by Müller and Suess (1979).

The derivation above was chosen instead of the Sarath Hein et al. (1987) equation, because of the apparent accuracy of the Henrichs and Reeburgh's (1987) equation in predicting burial efficiencies in slowly deposited sediments (see above). It is also noted, that although the accuracy of the Betzer et al. (1984) equation appears to be good over a broad depth range, it may be less so at shallow depths alone (i.e., <150m).

Niobrara Paleoproductivity

The above equation was applied to Niobrara OCAR and sedimentation rate data to produce a series of paleoproductivity maps (Figs. 5.14 to 5.26). A water depth of 120 m was assumed and no attempt was made to account for changes in sea level or paleobathymetry. Although the arguments presented in Chapter 2 provide some important insights into both regional and temporal changes in the paleobathymetry, it was decided that including these would only complicate the discussion to follow. However, including these estimates would only tend to enhance the regional contrasts in the estimated paleoproductivities shown in Figures 5.14 to 5.26, because the paleoproductivities tend to be highest in the areas interpreted to be over the deepest water (including depths greater than 120 m would increase the paleoproductivity estimates, for example, a 200 m depth would increase these estimates by about 25%.

Most paleoproductivity values for the Niobrara fall between 100 and 200 gC/m²/a. Although they may not accurately reflect the actual Niobrara paleoproductivity, they are certainly reasonable values. Productivity values in this range are typical of shelf areas in the modern ocean (Berger, 1989). A brief discussion of each paleoproductivity map with frequent references to the isopach maps shown in Chapter 2 follows.
Fort Hays

Estimated paleoproductivity values for the Fort Hays appear to be unreasonably low (Fig. 5.14). This unit was deposited in shallow (15-50 m), well-oxygenated waters (e.g., Hattin, 1982 and see Chapter 2). For such shallow depths the equation used is not accurate, as Betzer et al's. (1984) formula was developed for depths beneath the mixing zone.

Shale and Limestone Member

Paleoproductivity estimates for the shale and limestone member vary from less than 100 (mostly in the upper Fort Hays equivalent) to more than 200 gC/m²/a (Fig. 5.15). The highest values occur in the southwestern part of the study area where the shale and limestone facies is best developed and thickest. Enhanced productivity in this area is consistent with observation in Chapter 2 that carbonate productivity must have been higher in this area as well.

Lower Marl

Paleoproductivity estimates for the lower marl average 150 gC/m²/a (Fig. 5.16). The pattern of paleoproductivity on this map begins to show the influence of paleobathymetry. As noted in Chapter 2 the area to directly southeast of Denver was probably a shoal area at this time, over which sedimentation was limited. Thus the pattern of productivity shown in Figure 5.16 may in large part reflect the preferential deposition of OM in deeper water flanking this shoal area.

Lower Chalk

The paleoproductivity patterns in lower chalk units 1 and 2 are similar (Figs. 5.17 and 5.18). A band of higher productivity (150 to 250 gC/m²/a) extends across northeast
Figure 5.14. Paleoproductivity map of the Fort Hays Member of the Niobrara Formation.
Figure 5.15. Paleoproductivity map of the shale and limestone member of the Niobrara Formation (includes upper Fort hays of Kansas).
Figure 5.16. Paleoproductivity map of the lower marl member of the Niobrara Formation.
Figure 5.17. Paleoproductivity map of the lower chalk unit I of the Niobrara Formation.
Lower Chalk 2 - Inferred Paleoproductivity (gC m\(^{-2}\) a\(^{-1}\))

Figure 5.18. Paleoproductivity map of the lower chalk unit 2 of the Niobrara Formation.
Colorado and into western Kansas. Again this pattern may result from preferential deposition of OM in deeper water flanking the shoal area previously mentioned. If the pattern does replicate the actual pattern of productivity at this time, it could be an area of bathymetrically induced upwelling.

The paleoproductivity pattern changes somewhat in the overlying lower chalk unit 3 (Fig. 5.19). Areas of highest paleoproductivity on this map largely correspond to areas where this unit is thickest. Overall paleoproductivity estimates for the lower chalk average about 140 gC/m²/a.

Middle Marl

Middle marl paleoproductivity averages 180 gC/m²/a (Fig. 5.20). The pattern of paleoproductivity is largely independent of the thickness of this unit. The highest values occur just to the north of the thick middle marl tongue that is shown on Figure 2.20. Higher productivity in this area could have been produced by increased nutrient input from the same currents that deposited the thick distal deltaic tongue of sediment shown on the isopach map.

Middle Chalk

Paleoproductivity patterns for middle chalk units 1 and 2 are broadly similar (Figs. 5.21 and 5.22). The highest paleoproductivity values occur to the southeast along a paleobathymetric slope to the southeast (see Chapter 2). This may have been an area of dynamic upwelling caused by the change in paleobathymetry. However, once again higher OCARs in this area may have resulted from the preferential settling of OM in deeper water. Both maps have areas of apparent low paleoproductivities just to the northwest of the area of high paleoproductivity. These areas correspond to the areas of
Lower Chalk 3 - Inferred Paleoproductivity (gC m\(^{-2}\) a\(^{-1}\))

Figure 5.19. Paleoproductivity map of the lower chalk unit 3 of the Niobrara Formation.
Middle Marl - Inferred Paleoproductivity (gC m\(^{-2}\) a\(^{-1}\))

Figure 5.20. Paleoproductivity map of the middle marl member of the Niobrara Formation.
Middle Chalk 1 - Inferred Paleoproductivity (gC m\(^{-2}\) a\(^{-1}\))

Figure 5.21. Paleoproductivity map of the middle chalk unit 1 of the Niobrara Formation.
Figure 5.22. Paleoproductivity map of the middle chalk unit 2 of the Niobrara Formation.
non- or limited deposition associated with the disconformity documented in Chapter 2. Thus the low estimated paleoproductivities in this area are probably spurious.

Upper Marl

Paleoproductivity patterns in the upper marl units (Figs. 5.23–5.25) are difficult to decipher. Differential tectonic movement of the basin floor during deposition of the upper marl, especially during unit 3 deposition, produced a series of bathymetric highs and lows that strongly influenced sedimentation rates. As a result it is probably not possible to discern any regional paleoproductivity trends for this unit. Average paleoproductivity values for the upper marl range to 185 gC/m²/a (in unit 2), the highest in the Niobrara.

Upper Chalk

Paleoproductivity estimates in this unit are lower than they are for the underlying middle marl (Fig. 5.26). The highest values occur to the southeast. The area of high paleoproductivity in western Nebraska may be an artifact of an over estimation of the OC content in this area because of partial gas saturation of this zone.

Significance of Niobrara Paleoproductivity Estimates

It is clear that a series of factors other than actual paleoproductivity can and do affect paleoproductivity estimates. In the Niobrara, a key factor is the control that paleobathymetry exerts, but not only in the sense that it determines the OC flux that survives degradation in the water column, as accounted for in the Betzer et al. (1984) formula. Instead, fine-grained sediments were preferentially directed to bathymetric lows, presumably by higher current velocities over the bathymetric highs.
Figure 5.23. Paleoproductivity map of the upper marl unit 1 of the Niobrara Formation.
Figure 5.24. Paleoproductivity map of the upper marl unit 2 of the Niobrara Formation.
Figure 5.25. Paleoproductivity map of the upper marl unit 3 of the Niobrara Formation.
Figure 5.26. Paleoproductivity map of the upper chalk member of the Niobrara Formation.
This paleobathymetric effect on the paleoproductivity estimates is often relatively local in extent, so these estimates can be averaged over a larger area. At times, regionally large-scale variations in sediment thickness could reflect regional variations in paleoproductivity rather than paleobathymetry. However, nearly all such areas in the Niobrara contain disconformities, suggesting that the paleobathymetry was at least partially responsible for the area of thin sediment accumulation.

The paleoproductivity maps do not convincingly demonstrate that there were any consistent upwelling areas within the study area, with the possible exception of the area to the southeast, where paleoproductivity values are consistently high. The moderate to high paleoproductivity values along with regional variations do suggest that the water column was sufficiently dynamic to sustain a moderate to fairly high nutrient flux to the upper water column. Thus it is unlikely that the seaway was continuously stratified.

**U_A/OC RATIOS IN THE NIOBRA RA**

**Authigenic-Uranium Content**

Estimation of $U_A$

$U_A$ contents in the Niobrara were estimated from the uranium curve on gamma-ray spectra logs (see Fig. 5.27) or from standard gamma-ray logs. In wells with gamma-ray spectra logs, the allogenic U component was assumed be 2 ppm for 100% shale. In the Niobrara, the allogenic component of U was assumed to be proportional to the clay content of the formation. The clay content was derived from the corrected gamma-ray log or the neutron-density log (e.g., Schlumberger, 1989). When standard gamma-ray logs were used, it was assumed that gamma-ray API values greater than 100 units for 100% shale were due to $U_A$ (this value represents the average for the overlying OC-poor parts of the Pierre Shale). The estimated gamma-ray component due to the clay content was
Figure 5.27. Gamma-ray spectra log through the Niobrara section in the Golden Buckeye #2 Gill Land Co. well, Weld Co., CO. Note how uranium accounts for most of the gamma-ray emissions in most of the Niobrara section. The SGR (standard gamma-ray) curve includes the uranium component, whereas the CGR (corrected gamma-ray) curve includes only the thorium and potassium 40 components of the gamma-ray emissions.
then subtracted from the total gamma-ray reading and the difference was converted to the \( U_A \) content.

Possible Sources of Error

The \( U_A \) values are derived from gamma-ray logs. If it is reasonably assumed that these logs are properly calibrated and standardized, then errors in gamma-ray measurement will result from either variations in the borehole or statistical variations in radioactive decay (e.g., see Schlumberger, 1989). The former includes variations in the borehole diameter and in drilling-mud weight. Bit sizes and drilling-mud weights used in the Denver basin region generally do not vary enough to significantly affect gamma-ray measurements. The second possible error is a function of logging speed and the discontinuous nature of radioactive decay. In my experience, repeat gamma-ray log runs seldom produce differences of more than 10%. Further, as these variations in radioactive decay are random and not systematic, they tend to cancel out over intervals of a few meters.

The correction from total U content to \( U_A \) content is another source of error. Changes in clay mineralogy may include variations in the content of radioactive isotopes including U, but these variations are likely to be small, especially in hemipelagic and pelagic rocks like the Niobrara and overlying Sharon Springs.

Estimates of clay content from well logs are subject to error. However, even if the estimate of the clay content is very inaccurate, the error in the estimated \( U_A \) is likely to be small. For example, if the clay content is estimated to be 20% and it is actually 40%, the allogetic component of U only varies from 0.4 ppm to 0.8 ppm (using 2 ppm for 100% clay). U contents in the Niobrara are usually 20 to 50 times this value. The 0.4 ppm difference would become significant only when \( U_A \) contents are very low.
Although the U estimates produced by the methods presented above are subject to error, this error is not likely to be large because in most of the studied section, the U content is the largest component of the total gamma-ray emissions. Figure 5.27 demonstrates this with a gamma-ray spectra log covering the Niobrara section in the Golden Buckeye #2-Gill Land Company well. Note that the U content of the Smoky Hill Member ranges to 20 ppm and that the U content usually accounts for 50 to 90% of total gamma-ray emissions in this member.

**Accuracy of \( U/VOC \) Ratios**

It must be noted that the \( U/VOC \) ratios in this study are subject to considerable error as they combine the potential inaccuracies of both the measured or estimated OC and \( U \) values. For example, in a typical case a Niobrara interval may contain 3.0% OC and 12 ppm \( U \). These values produce a \( U/VOC \) ratio of 4. If the OC and \( U \) values are both subject to a potential 10% error then the actual \( U/VOC \) ratio may range from a minimum of 3.27 (10.8/3.3) to a maximum of 4.89 (13.2/2.7). These values could only result in situations where the errors in the two data sets are systematic and in the opposite sense. In practice, this is unlikely to be the case.

**Post-Burial Changes in \( U/VOC \) Ratios**

Use of \( U/VOC \) ratios to make inferences about the original depositional conditions of a particular unit requires that there be no wholesale remobilization and redistribution of either \( U \) or OC after burial. OC is not readily subject to dissolution and redistribution until burial depths are sufficient for catagenesis (hydrocarbon generation) to occur.

Uranium can be remobilized in the near surface by oxidizing waters as discussed in Chapter 4, but it can also be remobilized at depth. Although formation waters in petroliferous basins usually have a negative redox potential (e.g., Fertl and Rieke, 1980).
downward movement of meteoric waters can sometimes occur to considerable depths. These waters can remobilize and move uranium. The uranium is sometimes reprecipitated along fractures and this means that gamma-ray spectra logs can sometimes be used in fracture detection (Fertl et al., 1980; Fertl and Rieke, 1980; Fertl, 1983b).

Although fractures are common in parts of the Niobrara (e.g., Pollastro, 1992), significant U enrichment along these fractures is not common. In only a few areas has this author noted small zones of U enrichment in the Niobrara that are probably fracture related (in the highly faulted Wattenburg Field area, for example). Most highly U-enriched zones in the Niobrara are traceable over 100's of square kilometers and are demonstrably chronostratigraphic and therefore depositional in origin.

Niobrara $U_A$/OC Ratios versus Sedimentation Rates

A plot of $U_A$/OC ratios versus estimated sedimentation rates for a number of complete Niobrara sections is shown in Figure 5.28. The values fall between the oxic and anoxic trend lines that were defined in Chapter 4. This result is consistent with previous interpretations that the Niobrara was deposited under conditions that were frequently dysoxic with extremes ranging from completely oxic to anoxic (Pratt and Barlow, 1985; Savrda and Bottjer, 1989b; Pratt et al., 1993).

Figure 5.28 averages the $U_A$/OC ratios across the entire Niobrara section. However, it can be expected that the ratios will vary with stratigraphic position depending on bottom-water-oxygenation levels and sedimentation rates. For example, with the exception of thin shale interbeds, the Fort Hays Member of the Niobrara is extensively bioturbated and OC-poor (Pratt and Barlow, 1985; Savrda and Bottjer, 1989b). Thus it has been interpreted to have been deposited largely under well-oxygenated conditions (e.g., Savrda and Bottjer, 1989b). As $U_A$/OC ratios in this part of the Niobrara should reflect these well-oxygenated conditions, they should be lower than ratios for the
Figure 5.28. $U_\alpha/OC$ ratios versus sedimentation rates for the Niobrara. The majority of the values fall between the oxic and anoxic trendlines defined in chapter 4, suggesting that the Niobrara was deposited in bottom water that was on average dysoxic.
formation as a whole. This is indeed the case as the average Fort Hays $U_{A}/OC$ ratio is about 2.4 compared to 3.4 for the Smoky Hill.

Average $U_{A}/OC$ ratios are plotted against average sedimentation rates by zone in Figure 5.29. With the exception of the lower marl, the marl units tend to plot somewhat closer to the anoxic line than do the chalk units. This is consistent with the fact that the units are typically almost devoid of bioturbation while the chalks units generally are at least partly bioturbated, especially lower chalk units 1 and 3 (numbers 4 and 6 on the plot). The Fort Hays plots unexpectedly far off the oxic line, but the very low OC and U contents in this unit make the calculated $U_{A}/OC$ ratios for this unit subject to considerable error.

Individual $U_{A}/OC$ and sedimentation rate values for the same set of wells are plotted against each other in Figure 5.30 for two separate units: the lower chalk unit 1 and upper marl unit 2. These units were selected to provide a contrast in the probable level of bioturbation (lower chalk 3—partly bioturbated—upper marl 2—laminated). Although there is considerable overlap, lower chalk 1 has numerous values that plot at or near the oxic line. Nearly all of these are from northwest Nebraska in an area that was probably shallow at this time (this unit pinches out to the north on the flanks of a paleobathymetric high—see Chapter 2). Thus the bottom water may have been more oxygenated than in deeper areas further to the south.

Organic-matter maturity and $U_{A}/OC$ Ratios

As pointed out in Chapter 2, the level of organic maturity affects the $U_{A}/OC$ ratio. In rocks that have reached the catagenic stage (Tissot and Welte, 1978) organic matter begins to be converted to petroleum. As petroleum migrates away from its source area, the organic-matter content of the source rock is reduced while the uranium remains. The resulting increase in the $U_{A}/OC$ ratio should be evident in the Niobrara. In most of the
Figure 5.29. $U_{\text{A/OC}}$ ratios versus sedimentation rates for individual zones in the Niobrara (values are averages from approximately 50 wells). (1) Fort Hays. (2) Shale and limestone. (3) lower marl. (4) lower chalk 1. (5) lower chalk 2. (6) lower chalk 3. (7) middle marl. (8) middle chalk 1. (9) middle chalk 2. (10) upper marl 1. (11) upper marl 2. (12) upper marl 3. (13) upper chalk.
5.30. $U_{AA}/OC$ ratios versus sedimentation rates for the lower chalk unit 1 and upper marl unit 2. Values are from individual wells. Circled value is from the Golden Buckeye #2 Gill land Co. well.
study area, the Niobrara has not reached the oil window, but in deeper parts of the Denver Basin it has reached this level of thermal maturity.

In the Golden Buckeye #2-Gill Land Company well, for example, the $T_{\text{max}}$ value for organic matter in the Niobrara averages 444°C, which places the Niobrara section in the upper portion of the oil window (Tissot and Welte, 1978). Niobrara sections buried to similar or greater depths should also be in the oil window. In contrast, more shallowly buried sections are not likely to have reached the oil window.

Figure 5.31 is a plot of $U_A/OC$ ratios versus sedimentation rates for a single chronostratigraphic horizon in the Niobrara (lower chalk-unit 2). The data are divided by burial depth (Niobrara porosity is used as a proxy for burial depth) into mature and immature levels of organic-matter maturity. The higher $U_A/OC$ ratios for sections with mature organic matter confirm the effect of maturity on this ratio.

The $U_A/OC$ ratio and the Production Index

The production index (also called transformation ratio) is the ratio of petroleum actually formed to the maximum amount of petroleum the organic matter is capable of generating (i.e., the genetic potential (Tissot and Welte, 1978)). This ratio is usually obtained from Rock-Eval pyrolysis (Espitalie et al., 1977), however, it may be possible under the right circumstances to use $U_A/OC$ ratios. For example, the circled point on the graph in Figure 5.31 is from the Golden Buckeye well. The present $U_A/OC$ ratio is about 4.8, but based on the graph, the original $U_A/OC$ ratio should have been about 3.1. As the $U_A$ is 10.8 ppm for this interval, the original OC content should have been about 3.5%. This compares to a present OC value of 2.29%. Therefore, 35% of the original OC has been lost. This compares quite favorably to pyrolysis data from the Golden Buckeye well which indicates an average transformation ratio of about 0.4. (This is an over
UA/OC RATIOS vs. SEDIMENTATION RATES

5.31. Plot of $\text{UA}/\text{OC}$ ratios versus sedimentation rates by level of organic-matter maturity in the lower chalk unit 2. Circled value is from the Golden Buckeye #2 Gill land Co. well.
simplification, as the genetic potential is not the same as OC content. However, the two values are highly correlative).

Effect of Maturity Factor on Niobrara $U_A/OC$ Data

Because the Niobrara $U_A/OC$ data include some wells that are in the oil window, there is bit of a bias towards higher $U_A/OC$ values than would be due to purely depositional controls on the $U_A/OC$ ratio. However, this bias is very small as only a few wells in this study have reached the oil window. This factor can be corrected for to some extent, if Rock-Eval data is available. For example, the circled point on the graph in Figure 5.30 is from the Golden Buckeye well. This point plots quite high on the graph considering the fact that this zone is quite well bioturbated. Present OC values in this zone average 1.7 %, but with a PI of about 0.4 for this zone the original OC content would have been 2.8%. If this value is divided into the $U_A$ content of 4.6, the resulting $U_A/OC$ ratio is 1.64 – a number that plots much closer to the oxic line in Figure 5.30.

DISCUSSION

Dilution or Productivity?

Well-defined bedding couplets are a notable feature of the Niobrara, especially in the chalk units. As noted previously, OC content in the Niobrara is highest in marl units and lowest in chalk units. Within units of either type OC content tends to be inversely proportional to the carbonate content (e.g., Dean and Arthur, 1989; Ricken, 1993). This relationship has important implications for the origin of organic enrichment in the Niobrara.

Two end member models that attempt to explain both the bedding couplets and their OC content have been proposed. The first of these suggests that the marl couplets were produced during periods when wet climate produced high river discharges (e.g.,
Pratt et al., 1993). In this model, buoyant plumes of sediment-laden brackish water would extend across the seaway, increasing the clay flux to the sea floor to produce the marl couplets (dilution cycle). In addition, the brackish water would serve to stratify the seaway, restrict vertical mixing, and promote depletion of bottom-water oxygen, thus promoting the preservation of organic matter. The second model suggests that the bedding couplets were produced by cycles of increased carbonate productivity (e.g., Fischer, 1993). In this view, the terrigenous flux would be relatively constant (productivity cycle).

In the dilution model, sedimentation rates would be highest during marl deposition, whereas in the productivity model they would be highest during chalk deposition. It has been argued that because the chalk couplets are thicker than the marl couplets, the chalk couplets probably represent carbonate productivity cycles (Fischer, 1993). This was based largely on the Fort Hays Member, however, and the thickness difference between chalk/marl couplets in this unit may be partly diagenetic in origin (Laferriere, 1992). In other parts of the Niobrara the thickness variations between marl/chalk couplets are not as great. To test which of these models is likely to be correct, the element of time needs to be added, so carbonate and terrigenous flux rates can be calculated.

The following three subsections systematically tie probable Milankovitch cyclicity in outcrop to that in subsurface well logs, and then to a key, densely-sampled core interval. This helps to establish a probable chronology for bedding couplets in the core, which in turn allows flux rates to be calculated. In addition, the sections below demonstrate that the cyclicity observed on well logs can be tied to outcrop.
Milankovitch Cycles

As noted in Chapter 2, the Niobrara is cyclic on several scales ranging from centimeters to tens of meters. The exact mechanism responsible for these cycles is uncertain, although the cycles are generally attributed to climatic changes, and the analysis in Chapter 2 supports this interpretation. The timing of the cycles is often attributed to variations in solar insolation which are produced by variations in the Earth's orbital parameters (i.e., Milankovitch cycles –Gilbert, 1895; Barron et al., 1985; Fischer, 1993; Fischer et al., 1985; Pratt et al., 1993; Kauffman and Caldwell, 1993). Cyclicity at all scales is apparent in outcrop and core, and the larger-scale (meter-scale) cyclicity is also very apparent on geophysical well logs (Fisher, 1993; Pratt et al., 1993; and see Chapter 2 and Appendix D). Based on the examination of hundreds of geophysical well logs throughout the greater Denver basin region, it seems probable that the observed cycles are of Milankovitch origin (as previously noted this assumption was used to refine the age-span estimates for individual units). The patterns of cyclicity seem to meet the appropriate criteria that is bundling and timing of cycles (e.g., Fischer et al., 1985; Fischer, 1993).

In the following section, the lower chalk unit described at Pueblo (Barlow and Kauffman, 1985) is tied to regionally-correlative horizons that have been identified on well logs. The lower chalk was chosen for this analysis because of its very distinctive log character (see Appendix C), and because cyclicity in the lower chalk in outcrop has been attributed to Milankovitch cyclicity (Barlow and Kauffman, 1985).

From Outcrop to Subsurface Log

The Niobrara section has been described in detail at Rock Canyon Anticline, Pueblo, Colorado, by Scott and Cobban (1964) and Barlow and Kauffman (1985). The extremely thick and well-exposed section at this locality has made it a classic and well-
studied section. Particular attention has been paid to the spectacular bedding couplets of the Fort Hays that are so well exposed at Rock Canyon, but bedding couplets are also well developed in the lower chalk (lower limestone of Pratt et al., 1985). Barlow and Kauffman (1985) described a total of 43 individual beds in this unit, ranging in thickness from about one meter to less than a centimeter (Fig. 5.32a). The beds range in composition from nearly pure chalk to shale. Three of the beds are bentonites and two are limonite beds of problematic origin. As the lower chalk unit was assigned a depositional time span of 800 ka in this study (see discussion above and Fig. 5.8), the remaining 38 to 40 beds (excluding the bentonites and possibly the limonite beds) would perfectly fit the obliquity cycle (~40 ka – 20 ka/bed).

To test the match of the Pueblo cycles to those exhibited by subsurface geophysical logs a "synthetic" gamma-ray log for the lower chalk section at Pueblo was constructed. This was done by assigning an arbitrary, but reasonable, gamma-ray intensity to each centimeter of lower chalk section based on the lithologic description, then producing a 0.5 m running average of these intensities to roughly mimic an actual gamma-ray log (Fig. 5.32b). In thin-bedded sections the synthetic log averages several beds of varying lithology, but where thick beds are present, it accurately reflects the expected (relative) gamma-ray intensity for that particular lithology.

The Pueblo section was divided into 8 chronostratigraphic units (with initiation of lower chalk deposition equal to zero) on the assumption that 5 beds represent 100 ka (2.5 obliquity cycles). These divisions were tied to the synthetic gamma-ray log, which was in turn, correlated to a gamma-ray log from a well 25 km to the north (Fig. 5.32c). The correlation between the two is excellent (remember thickness changes in the lower chalk are common—see Chapter 2 and Appendix D) and the correlation supports the age spans used in this study for individual lower chalk units (i.e., LC-1 = 200 ka, LC-2 = 200 ka, and LC-3, = 400 ka).
Figure 5.32. (a) Stratigraphic section of the lower chalk member at Pueblo, Colorado, (from Pratt et al., 1985). Vertical scale in meters. Thick limestone beds are highlighted and thick beds are numbered for reference to the Pratt et al. (1985) description. Chronostratigraphic horizons based on inferred Milankovitch cyclicity (see text). (b) Synthetic gamma-ray intensity log for the Pueblo section (see text for details). (c) Gamma-ray log through the lower chalk section from the Placid #1 36 State well. (d) Gamma-ray log and sonic log from the Coquina #4 Berthoud well. "A" points to a densely sample interval from a core on this well. LC1, LC2, and LC3 refer to the lower chalk units used in this study.
Subsurface Log to Core

The correlation of the 100-ka chronostratigraphic units is extended another 200 km to the north to the Coquina #1 Berthoud State well (near Lyons, Colorado,–Fig. 5.32d). This correlation is supported by dozens of intervening well logs. Again the correlation is made to the gamma-ray log, but a portion of the sonic log on this well is also included. The sonic-log peaks (high transit times/low velocities) tie very well to the 100-ka boundaries. In each instance the correlation falls at, or just above, the sonic-log peaks. The sonic log is recording chalk/marl cycles that are consistent with a 100 ka periodicity.

The Niobrara section in the Coquina #4-Berthoud State well was cored and numerous samples from this core have been analyzed (Dean and Arthur, 1969). Dean and Arthur (1989) also sampled an interval of this core with three-pronounced bedding couplets approximately every three centimeters over a 0.75 m interval and analyzed the samples for TOC and carbonate content (see also Pratt et al., 1993) (Fig.5.33). This interval is located near the top of the section shown in Figure 5.32d, where it is highlighted. The sampled interval spans a 100-ka boundary (the 700-ka boundary traced from Pueblo). If the 100 ka periodicity is valid, then sedimentation rates averaged about 2.5 cm/ka (2.5 m/100-ka) below this boundary and about 1.0 cm/ka (1.0 m/100 ka) above it. Sedimentation rates for the sampled interval are probably nearer the lower end of this range, perhaps 1.0 to 1.5 cm/ka, as sedimentation rates apparently declined in the uppermost lower chalk (note the uppermost 100 ka unit is much thinner than the one below it). If the 1.0 to 1.5 cm/ka estimate is valid, then the 72 cm thickness of the three bedding cycles shown in Figure 5-33 represents a time span of 48 to 72 ka. Further if the three cycles are of uniform length, each cycle would represent from 16 to 24 ka—meaning the cycles are consistent with orbital precession (approx. 20 ka).
Figure 5.33. Vertical profiles of organic-carbon and carbonate contents through three bedding cycles (chalk/marl couplets) in the upper part of the lower chalk member, Niobrara (data from Dean and Arthur, 1989).
Now that a possible chronology for the cycles has been established, allowing flux rates to be calculated, the relative merits of the dilution and productivity models can be better evaluated. This is done in the following section.

**Flux Rates and Their Significance**

If the bedding couplets in Figure 3.33 are Milankovitch (probable precession) cycles, flux rates for the carbonate, clay (here to include the insoluble residue minus OC), and OC components of the Niobrara can be calculated. There are several possibilities. These are that the hemicycles are (1) of equal length (there is no *apriori* reason to think they are), (2) variable in length with chalk cycles having the higher sedimentation rates, and (3) variable in length with marl cycles having the higher sedimentation rates. In addition, the base of each cycle can begin with either a chalk or a marl, so the total number of possibilities is six. Whether each cycle begins with a chalk or a marl is not critical to the analysis of these couplets, so only three possibilities are considered. Each of these possibilities is outlined below and then their significance is presented. The arguments below apply as long as the cycles are assumed to be periodic, so whether or not the cycles are, in fact, precession cycles does not materially affect the conclusions presented.

**Hemicycles of Equal Length**

In Figure 5.34, three cycles are designated, each beginning with a marl couplet. Each couplet is assumed to represent 10 ka. An average sedimentation rate for each couplet is then used along with the compositional data (Fig. 5.33) and density to calculate mass-accumulation rates (MARs) for carbonate, clay, and organic carbon. The results are shown in Figure 5.34 c and d. Under this scenario, variations in the carbonate flux
Figure 5.14. Vertical profiles of (a) OC content, (b) carbonate percentage, (c) mass accumulation rates (MARs) for carbonate (CAR), "clay" (SAR), (d) organic carbon, (e) paleoproductivity, and (f) burial efficiency. Profiles (c) through (f) based on the assumption that each hemicycles represents a 10 ka time span (see text). Paleoproductivity is in gCm\(^{-2}\)a\(^{-1}\).
produce the chalk/marl cyclicity. The OCAR reaches its maximum in the basal marl of cycle 2.

An OC-paleoproductivity curve is also shown in Figure 5.34e. Unlike the earlier estimates of paleoproductivity, these estimates are derived from the carbonate flux, so they are independent of the organic-carbon flux (OCAR). The curve was calculated by assuming that 90% of the carbonate is composed of coccoliths, and that coccolithophorids represented 10% of total phytoplankton, as has been reported for the Black Sea (Izdar, 1987). These assumptions are simplistic, as the ratio of carbonate to OC-productivity is variable (see below). This is not critical, however, as the purpose of the curve was to allow potential values for OC-burial efficiency to be calculated.

A curve of OC-burial efficiencies are shown in Figure 5-34d. This curve was calculated by comparing the OCAR to the OC flux reaching the sea floor using the Betzer et al. (1984) formula and the paleoproductivity curve. Burial efficiencies are higher during marl deposition under this scenario, reflecting the higher OC content of the marls.

Figure 5.35 is a plot of (a) the carbonate (CAR) and clay accumulation rate (SAR) against the OCAR and (b) the CAR against the SAR for the above scenario. The OCAR is positively correlated with SAR and also with CAR, but only when the field of high CAR values are excluded. The CAR versus SAR plot shows no correlation, again, unless the high CAR values are excluded, then there is a positive correlation.

Productivity Cycles

Scenario two assumes that the carbonate couplets were deposited in a shorter time span than the marl couplets (Fig. 5.36). The particular sedimentation rates that were used were arbitrary and constant over each hemicycle, but chosen so that each cycle totaled the requisite 20 ka. Calculations and plots are the same as for Figure 5.34. Under this scenario, the contrast between the carbonate and clay accumulation rates is enhanced, the
Figure 5.35. (a) Carbonate and clay accumulation rates versus OCARs and (b) Carbonate accumulation rates versus clay accumulation rates for scenario one (see text).
Figure 5.36. (a) Mass accumulation rates (MARs) for carbonate (CAR), clay (SAR), (b) organic carbon, (c) paleoproductivity, and (d) burial efficiency. Profiles (a) through (d) based on the assumption that carbonate cycles are shorter than marl cycles. Units are the same as in Figure 5-34.
OCAR and carbonate paleoproduction increase in the chalk couplets, and the contrast in burial efficiencies between couplets is greater.

Figure 5.37a indicates that there is a fairly strong correlation between the OCAR and the SAR under this scenario and a weak correlation between OCAR and CAR (when both prominent CAR groupings are considered). There is at best a weak correlation between CAR and SAR in Figure 5.37b.

Dilution Cycles

Scenario three assumes that the marl couplets were deposited in a shorter time period than the chalk couplets (Fig. 5.38). Plots and calculations are the same as before and again sedimentation rates were arbitrary and constant across each hemicycle. This time the carbonate and clay accumulation rates are both higher during the marl cycles, as are the OCARs. Paleoproduction values are also highest during the marl cycles, but burial efficiencies are only marginally greater. It follows from the above that correlation among all three components is strong under this scenario, so the plots are not shown.

Significance of the Coquina Cycles

Scenarios one and two above are both plausible, but scenario two is most plausible as it does not require hemicycles of equal length. Under this scenario, the chalk/marl cycles are clearly the result of variations in the carbonate productivity. The carbonate flux varies by a factor of four, while the clay flux remains relatively constant. The OCAR is not as variable as the OC content (compare to Fig. 5.33), but it tends to be higher in zones where the sedimentation rate is highest. Paleoproduction varies in concert with the carbonate accumulation rate by definition, as noted above. Actual OC productivity would not so closely track carbonate productivity, as the carbonate-to-OC-productivity ratio varies (see discussion in Tyson, 1995; p.104, for example), but the OC
Figure 5.37. (a) Carbonate and clay accumulation rates versus OCARs and (b) Carbonate accumulation rates versus clay accumulation rates for scenario two (see text and Figure 5.36).
Figure 5.38. (a) Mass accumulation rates (MARs) for carbonate (CAR), clay (SAR), (b) organic carbon, (c) paleoproductivity, and (d) burial efficiency. Profiles (a) through (d) based on the assumption that marl cycles are shorter than carbonate cycles. Units are the same as in Figure 5-34.
and carbonate productivities are likely to be in phase with one another (Berger and Keir, 1984). Thus the burial efficiency plot probably does reflect the relative amount of produced OC that actually was buried in chalk versus marl hemicycles.

Scenario three is very unlikely. This scenario corresponds to the brackish-water cap model discussed previously. In this model, episodes of increased clastic influx are called upon to produce marl cycles that are deposited more rapidly than then the chalk cycles. Brackish-water sediment plumes can provide the increased clastic influx associated with this scenario, but what accounts for the increased carbonate productivity (Fig. 5.38), when the basin is interpreted to be stratified? These are much more likely to be times of low carbonate productivity and total productivity as well.

The scenarios above are based on only three small bedding cycles, but scenarios 1 and, in particular 2, are consistent with the larger-scale relationships between carbonate, clay, and OC previously documented for the Niobrara (e.g., in Figs. 5.11-13). These include the following: OC content correlates strongly with clay content, OCAR correlates with both the clay- and carbonate-accumulation rates, but the correlation is stronger with the carbonate-accumulation rate (see Fig. 5-13).

**Origin of Organic-Carbon, Marl, and Chalk Patterns in the Niobrara**

Several key points emerge from the above discussion and observations made earlier in this chapter. (1) Small-scale centimeter-to-meter scale carbonate/marl cycles resulted from variations in productivity, not from variations in clastic input. (2) Periods of high productivity (carbonate cycles) were characterized by vertical mixing of water within the WIS, as has often been suggested (e.g., Eicher and Diner, 1985, 1989; Fischer, 1985, 1993), although this does not mean mixing was continuous. (2) Periods of low productivity (marl cycles) were characterized by less vertical mixing, but not continuous stagnation. (3) Carbonate cycles were accompanied by increased OC
productivity and OC flux to the sea floor. (4) This accounts for the strong correlation between organic-carbon accumulation rates and carbonate accumulation rates. (5) The increased vertical mixing during the carbonate cycles reduced OC burial efficiencies. (6) As a result the OC content is inversely proportional to the carbonate content.

Cycles of chalk/marl deposition were almost certainly modulated by climate as is evident from the lateral continuity of even very thin beds on a regional scale (Chapter 2). These cycles probably developed in response to changes in solar isolation associated with Milankovitch cyclicity.

SUMMARY AND CONCLUSIONS

Estimates of OC content, based on the method outlined in Chapter 3, were combined with the chronostratigraphy developed in Chapter 2 to create a (3D) picture of the OC distribution in the Niobrara. Coupling these data with sedimentation rates enabled estimation of OCARs and paleoproductivities.

This study demonstrates that OC content in the Niobrara correlates weakly, if at all, with sedimentation rate, but that the OCAR correlates strongly with the sedimentation rate. The latter correlation is mostly a function of the strong correlation of OCAR to the carbonate-accumulation rate, although OCAR is also positively correlated to the clay-(terrigenous) accumulation rate. The correlation of OCAR to the carbonate-accumulation rate is indicative of a close linkage between carbonate and OC paleoproductivity.

The widely recognized inverse relationship between the OC and carbonate contents at the bedding scale is indicative of greater preservation during periods of low carbonate flux. Marl beds with high OC contents were deposited during periods of sluggish circulation; in contrast, chalk beds with lower OC contents were deposited during periods of more vigorous circulation. The latter periods were characterized by increased productivity, but increased levels of bottom-water oxygen and the episodic
establishment of benthonic communities reduced OC burial efficiencies compared to times of marl deposition. Consistent with fluctuating levels of bottom-water oxygen, Niobrara $U_A/OC$ ratios suggest that deposition occurred beneath water that was on average dysoxic.

Paleoproductivity estimates for the Niobrara indicate that it was moderate to high on average. Paleoproductivity patterns are complicated by the paleobathymetry making it difficult to ascertain whether or not they are real. Nevertheless, it appears that upwelling may account for high productivity values observed to the southeast.

The moderate to high paleoproductivity estimates, the $U_A/OC$ ratios, the cycles of high productivity, and the evidence for frequent exposure of the bottom to current activity (documented in Chapter 2): all suggest that the WIS was a much more dynamic system that is suggested by the deep water, stably-stratified model for OC enrichment of the Niobrara Formation.
CHAPTER 6.

CONTROLS ON THE DISTRIBUTION OF ORGANIC-CARBON RICH STRATA IN THE SHARON SPRINGS MEMBER OF THE PIERRE SHALE

INTRODUCTION

The Campanian-age Sharon Springs Member of the Pierre Shale is a dark brown to black, organic carbon (OC)-rich shale that is resistant to weathering (Gill et al., 1966; 1972; Gautier et al., 1984). The distinctive character of this unit was recognized by a number of early geologists (for historical background, see Gill et al., 1972), but the Sharon Springs name was first applied by Elias (1931) to a section of dark, hard, buttress-weathering shale at the base of the Pierre Shale near the town of Sharon Springs in Wallace County, Kansas. The Sharon Springs is recognized over a large area of the Western Interior and is equivalent to the lithologically identical Pembina Member of the Pierre Shale in eastern North Dakota and Canada (Fig. 6.1).

The Sharon Springs is characterized by a depauperate faunal assemblage (e.g., Gilbert, 1897; Griffits, 1949; Gill et al., 1966), with the exception of ammonites preserved in calcareous concretions and vertebrates. Vertebrate remains include the large fish and swimming reptiles (e.g., Nichols, 1988; Russell, 1993) that had already made the unit famous more than a century ago (e.g., Cope, 1868, 1872). Benthonic macroinvertebrates are virtually absent in the Sharon Springs, with rare exceptions having been reported by Gill et al. (1966) and Schultz et al. (1980).

At the type area, the Sharon Springs includes 6 ammonite zones and is about 70 m thick (Figs. 6.2, 6.3). In most areas, however, the section is thinner and contains fewer ammonite zones (e.g., Gill et al., 1966). In much of the study area, the Sharon Springs directly overlies the Niobrara Formation, but in the western part of the study area it is
Figure 6.1. Regional distribution of the Sharon Springs Member of the Pierre Shale at its maximum extent during *Baculites obtusus* time. Solid line is the approximate western limit of the OC-rich facies and the shaded line is the eastern erosional limit of rocks of this age. Map adapted in part from Gill et al. (1972) and Parrish and Gautier (1993).
Figure 6.2. Composite Sharon Springs type section from near Sharon Springs, Kansas (section and data from Gill et al., 1972). OC contents are from 5 foot (1.5 m) cutting samples on the U.S.G.S. Guy Holland test well (36. 13S., 40W.) in Wallace County, Kansas. Abbreviations represent the following ammonite zones: S.H.-Scaphites hippocrepis, B.SS.-Baculites sp. (smooth), B.W.-Baculites sp. (weak flank ribs), B.O.-Baculites obtusus, B.M.-Baculites maclearni, B.A.-Baculites asperiformis, B.S.-Baculites sp. (smooth), and B.P.-Baculites perplexus. Biozone boundary B.W./B.O. modified slightly from that of Gill et al. (1972). Position of Ardmore Bentonite zone based on correlation with nearby well logs. Bentonites are represented by B's.
Figure 6.3. Index map of study area, showing key outcrop localities and cross sections.
separated from the Niobrara by other units, including the Gammon Shale in Wyoming (Gill et al., 1966; 1972) and the transitional member of the Pierre Shale in the Pueblo-Cañon City area of Colorado (Scott and Cobban, 1975; 1986; Gautier et al., 1984).

The OC content of the Sharon Springs ranges from 3.0 wt.% to 10.0 wt.% (Gill et al., 1966; 1972; Gautier et al. 1884; Zelt and Gautier, 1985). This makes the Sharon Springs the richest of several OC-rich units that were deposited in the Cretaceous Western Interior seaway (WIS). As noted in Chapter 1, two end-member depositional models have been used to account for OC-rich rocks in the geological record: those related to exceptional preservation beneath anoxic bottom waters in salinity-stratified basins and those produced by high primary productivity beneath upwelling zones. The stratified basin model has been most often applied to Sharon Springs (Griffits, 1949; Leroy and Shiektz, 1958; Gautier et al, 1984; Loutit, 1990a; 1990b; Zelt, 1990), but evidence in support of the upwelling model has also been presented (Parrish and Gautier, 1993).

This study examines the relative merits of these models by looking at the three-dimensional distribution of OC in the Sharon Springs and the relationship of this distribution to locale, sedimentation rate, and paleobathymetry. Geophysical well logs serve as a major source of data for this study. Well logs are abundant in the area of study and the Sharon Springs is readily identifiable on these logs. The OC-rich Sharon Springs facies is recognized by its high gamma-ray readings (Landis, 1959; Zelt, 1985), its high resistivity (Gill et al., 1972), low density, and slow sonic velocities when compared to adjacent OC-poor shales (Fig. 6.4). A combination of these logs is used to estimate the OC content of some subsurface Sharon Springs sections (see Chapter 3) and these estimates are integrated with the physical stratigraphy to provide constraints on the depositional models proposed for the Sharon Springs.
Figure 6.4. Geophysical well-log traces through the Sharon Springs section in the J.W. Huber Corporation #16-1 Baldwin well in Yuma County, Colorado (8-2N-43W). Note in particular the pattern of the gamma-ray and resistivity logs through the Sharon Springs section (increase in gamma-ray intensity and resistivity). A.B.Z. is the Ardmore Bentonite zone.
SHARON SPRINGS STRATIGRAPHY

Type Section

In Elias's original (1931) description of the Sharon Springs type section, he divided the member into an Upper and Lower Sharon Springs. This division was based upon the abundance of concretions in the upper part of the section and their scarcity in the lower part as well as on the slightly more numerous beds resistant to weathering in the upper part of the section. In Gill et al. (1972) this basic division was retained, but a third unit was added at the top of the section—a 10 foot (3.3 m) section of "hard platy-weathering slightly phosphatic shale that contains numerous layers of soft highly weathered phosphate nodules" (p 11).

In stratigraphic succession the three units of Gill et al. (1972) are the dark soft shale, the organic-rich shale, and the phosphatic shale (Fig. 6.2). The nomenclature is unfortunate as it tends to overstate the difference in OC content between the lower, dark soft shale, and the middle, organic-rich shale. Based on Gill et al.'s (1972) own sample analyses the organic-rich shale contains an average of 5.0 % OC, whereas the dark soft shale contains an average of 4.0 % OC (Fig. 6.2). If one sample containing almost 10% OC from near the top of the section is excluded, the difference in OC content between the two units is minimal (0.3%). This "clarification" is one key in helping to correct a misconception that OC-rich shale deposition began earlier in western areas and then migrated east with time (Gill et al., 1972; Parrish and Gautier, 1993). (This topic will be addressed in much more detail in a subsequent section).
Regional Variations

Lithology

The lithology of the Sharon Springs is relatively constant over a large area. Regional changes generally involve differences in resistance to weathering and color which reflect OC content, percentage of bentonites, and sedimentation rate. As the Sharon Springs facies is often transitional with more typical shale facies both vertically and laterally, perceived regional variance in lithology can be related to differences in the way the Sharon Springs is defined at different localities.

The phosphatic shale unit described by Gill et al. (1972) at the type section appears to be developed at many localities (Parrish and Gautier, 1993), but not at others (e.g., Gill and Cobban, 1965). In particular, this unit appears to be absent to the west (Gill et al., 1966; Izett et al., 1971).

Thickness

The Sharon Springs varies from a few meters in thickness near its western depositional limits to more than 70 m in western Kansas at the type section (Gill et al., 1972). Typical thicknesses in outcrop are: 15 m near Kemmerling, Colorado (Izett et al., 1971); 10 m at Cañon City, Colorado (Scott and Cobban, 1975); 35 m at Pueblo, Colorado (Scott, 1969); 40 m at Red Bird, Wyoming (Gill et al. 1966); and 25 m in eastern North Dakota (Pembina Member) (Gill and Cobban, 1965).

Age

Both upper and lower contacts of the Sharon Springs are regionally diachronous (Fig. 6.5). At the type area in western Kansas the Sharon Springs directly overlies the Niobrara and includes ammonite zones ranging in age from *Baculites sp.* (smooth) to
Didymoceras nebrascense
Baculites scotti
Baculites gregoryensis
Baculites perplexus (late)
Baculites glabratus
Baculites perplexus (early)
Baculites sp. (smooth)
Baculites asperiformis
Baculites macleani
Baculites obtusus
Baculites sp. (wk flank ribs)
Baculites sp. (smooth)
Scaphites hippocrepis III
Scaphites hippocrepis II

AMMONITE
ZONES

Figure 6.5. Time span of the OC-rich Sharon Springs at a variety of locations (modified from Gill et al., 1972). Age assignments based on radiometric dating of Obradovich (1993).
Baculites perplexus (Figs. 6.2, 6.5). In contrast, at Cañon City the Sharon Springs encompasses the Baculites obtusus through the base of the Baculites perplexus (early) zone, and at Red Bird, Wyoming, the Sharon Springs is restricted to the Baculites obtusus and Baculites maclearni zones.

The cause(s) of this regional diachrony has not been fully addressed in previous studies. Gautier et al. (1984) suggested at least some of the diachrony resulted from the dilution of the organic-rich Sharon Springs facies in areas of more rapid sediment accumulation. In contrast, Parrish and Gautier (1993) proposed that the apparent time-transgressive nature of the OC-rich facies (see their figure 1) can best be accounted for by an eastward migrating belt of high productivity. Controls on the timing and distribution of the Sharon Springs will be examined in detail below as they have direct bearing on the origin of the OC enrichment in the Sharon Springs. First, however, it is necessary to develop a stratigraphic framework.

Subdivision of the Sharon Springs

Ardmore Bentonite Zone

The Ardmore Bentonite zone consists of a series of bentonites concentrated within a few meters of section. The thickest of these, the Ardmore Bentonite Bed, exceeds one meter in thickness at the type locality near Ardmore, South Dakota (Spivey, 1940). The individual bentonite beds are difficult to correlate from outcrop to outcrop (Spivey, 1940; Gaines, 1986), but the zone as a whole serves as an excellent stratigraphic marker in both the surface and subsurface over an extensive area of the Western Interior (Asquith, 1970; Gill et al., 1966; Gill et al., 1972). The zone encompasses the lower part of the Baculites obtusus zone (Gill, et al., 1966), so it is generally within the Sharon Springs facies.
In the subsurface, the Ardmore Bentonite zone is readily recognized on geophysical well logs by reduced gamma-ray readings and reduced resistivity compared to bentonite-free Sharon Springs (Gill et al., 1966; Gill et al., 1972). The characteristic low resistivity is especially important in recognizing the Ardmore Bentonite zone, and where this section is thick many individual bentonites can be recognized (Fig. 6.6).

Upper and Lower Sharon Springs

Although the Ardmore Bentonite zone contains several potential time-lines in the form of individual bentonites, in much of the study area the zone is too thin for these to be individually resolvable on well logs. In this study the base of the Ardmore bentonite zone is used to divide the Sharon Springs into an informal upper and lower unit (Fig. 6.6).

The informal lower Sharon Springs unit of this study encompasses the section between the top of the Niobrara and the base of the Ardmore Bentonite zone. Because the top of the Niobrara is isochronous in nearly all of the study area (see Chapter 2), the lower Sharon Springs is an isochronous unit within most of the study area. The lower Sharon Springs by this definition and for this study includes strata not formally defined as Sharon Springs, including the Gammon Shale of eastern Wyoming and the transition member of the Pierre Shale in the Pueblo area.

There is no single, convenient isochronous surface that can serve as a time line to define an upper "Sharon Springs" isochronous unit as was done for the lower Sharon Springs. Nevertheless, there are some isochronous horizons that can be used to put time constraints on upper Sharon Springs deposition.
Figure 6.6. Subsurface cross section illustrating the response of dual induction logs to the Ardmore bentonite zone (A.B.Z.) and individual bentonites in eastern Colorado. Line of section closely parallels that of cross section L-L' shown on Figure 6.3. The logs used are from the following wells: (1) Amoco Prod. Co. Richard Hein Unit, Weld Co. (1-1N-67W), (2) Lomita Operating Co. #1-8 State, Weld Co. (8-1N-63W), (3) Energy Minerals #7 Anne State, Weld Co. (7-3N-61W), (4) Bensen Mineral Group #26-13 Club, Morgan Co. (26-4N-58W), and (5) J-W Operating Co. #2-20 Mekelburg, Yuma Co. (20-4N-46W). Line of section closely parallels that of cross section L-L' shown on figure 6.5.
CHRONOSTRATIGRAPHIC FRAMEWORK

Biostratigraphy and Absolute Ages

Ammonites are relatively scarce in most Sharon Springs sections, although they are sometimes preserved in abundance in limestone concretions (e.g., Gill et al., 1972). Ammonites are abundant enough to identify which biozones are present within a particular section, but they are seldom abundant enough to define zonal boundaries to an accuracy better than a few meters (e.g., Gill et al., 1966; 1972; Izett et al., 1971). Despite this limitation, ammonite biozones help to establish a very good biochronostratigraphic framework for the Sharon Springs.

Absolute Ages

Figure 6.7 combines the biochronology spanning the Sharon Springs section with the recently published $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometry of Obradovich (1993). The estimated 600 ka age span of the lower Sharon Springs is particularly well constrained by the closely spaced $^{40}\text{Ar}/^{39}\text{Ar}$ ages bracketing this unit. Although less well constrained, estimates of the age span of the upper OC-rich Sharon Springs varies from a maximum of about 3 Ma to a minimum of 600 ka or less depending on location (see Fig. 6.4) with each ammonite zone representing 500 ka to 600 ka.

STRATIGRAPHIC FRAMEWORK AND CONTROLS ON SHARON SPRINGS DEPOSITION

This section uses a series of subsurface well-log and diagrammatic cross sections to document stratigraphic relationships within the Sharon Springs and equivalent sections. These cross sections also demonstrate important controls on Sharon Springs deposition, including the sedimentation rate and paleobathymetry.
Figure 6.7. $^{40}\text{Ar}^{39}\text{Ar}$ ages of Obradovich (1993) plotted against the Western Interior ammonite zones spanning the Sharon Springs section. The OC-rich Sharon Springs facies is diachronous and the shaded area illustrates the range in its age span (data derived from numerous sources). Range in ammonite zones can be read directly, but to get absolute age ranges, a horizontal line must be projected to the correlation line and then down to the age scale. (Note the dashed-line examples). Age span of phosphatic facies based on Gill et al.'s (1972) description of the type section in western Kansas.
Cross Section L-L'

East-west cross section L-L' extends from Boulder to a point near the Colorado/Kansas state line (Fig. 6.8). It includes the top of the Niobrara (the datum) and the lower 300 m of the of the Pierre Shale, including the Sharon Springs section at the base of the Pierre Shale. Low-resistivity zones are traced from east to west along the line of section. These are contiguous silty zones that climb section to the west. They are interpreted to be the result of relatively rapid depositional events (storms?) and therefore serve as timelines within the section. This appears to be substantiated as the section ties very well with the biostratigraphy at either end (Fig. 6.8b). Sedimentation rates were much higher to the west. For example, the interval from the top of the Niobrara to the top of the *Baculites asperformis* zone ranges from 30 m at the east end of the section to 300 m at the west end.

As documented by Gautier et al. (1984), the Sharon Springs facies is absent in areas of rapid sedimentation. This includes outcrops from Boulder to Colorado Springs where the Sharon Springs is not recognized (Scott and Cobban, 1965). In this area more than 600 m of section is time equivalent to only 30 m of Sharon Springs section at Cañon City (Gautier et al., 1984). The absence of OC-rich Sharon Springs in this area is attributed to clastic dilution (Gautier et al., 1985).

Figure 6.8 convincingly demonstrates the effect of clastic dilution on the Sharon Springs facies. As the lower Pierre Shale prograded to the east sedimentation rates also increased in that direction. This limited deposition of OC-rich shales to areas progressively farther east as shown in Figure 6.8c, where the top of the Sharon Springs is shown to cross progressively younger time lines to the east. At the eastern end of the section, in the Kansas-Nebraska No. 1-32 Whomble well, the top of the Sharon Springs
Figure 6.8. (a). East-west cross section L-L' extending from just east of Boulder to near traces with an average spacing of about 10 km. The top of the underlying Niobrara forma from east to west across the section are highlighted. Horizon labeled "S" is coincident with diagrammatic representation of cross section L-L'. Section has been extended slightly to the at Boulder is from Scott and Cobb (1965). (B.O.-Baculites obtusus, B.A.- Baculites obtusus from Parrish and Gautier, (1993). (c) Expanded diagrammatic view of the lower portion
near the Colorado/Kansas state line. The section is constructed of 24 resistively and conductivity log formation forms the datum at the base of the section. Low resistivity beds (silty zones) that can be traced ent with the top of the Sharon Springs at the east end of the section. (b) Horizontally-scaled,ly to the east include the Kansas–Nebraska #1-32 Whomble well (32-2S-43W). Biostratigraphic section lities asperformis, and B.P.- Baculites perplexus). Biostratigraphy at western edge of cross section is portion of section L-L' showing the Sharon Springs section (shaded).
is near the top of *Baculites asperformis* zone (Parrish and Gautier, 1993), whereas just to the east of Boulder it occurs in the *Baculites sp.* (smooth) and *Baculites sp.* (weak flank rib) zones. Sharon Springs deposition along section L-L' spanned about 2.2 Ma (east) to 0.6 Ma (west). Sedimentation rates for these Sharon Springs sections are 1.7 cm/ka and 3.5 cm/ka respectively, whereas for the section above the Sharon Springs near Boulder the sedimentation rate is 14.3 cm/ka.

**Cross Section M-M'**

North-south cross section M-M' (Fig. 6.9) extends from east-central Colorado to northwest Nebraska (see Fig. 6.3). This cross section illustrates several key aspects of Sharon Springs deposition, including cyclicity, stratigraphic condensation, and erosional truncation.

Regionally correlative patterns of cyclicity are demonstrable in the Sharon Springs, particularly on gamma-ray logs. In the lower Sharon Springs there is a consistent pattern of gamma-ray intensity increasing from the base upwards, then decreasing, then increasing, and finally decreasing again into the Ardmore Bentonite zone (see wells 3, 4, and 5 on Figure 6.9a). This pattern appears to continue into the upper Sharon Springs, although it is less apparent. The cyclicity creates a natural three-fold subdivision of the lower Sharon Springs into zones that can be traced over much of the study area. In areas of thick lower Sharon Springs (relatively high and continuous sedimentation), these zones are roughly the same thickness and so are interpreted to represent equal time spans. In areas with very thick lower Sharon Springs sections, the gamma-ray contrast is diminished and the cyclicity is less obvious (e.g., wells 1 and 2 on section M-M'). Because the lower Sharon Springs encompasses about 600 ka, each
Figure 6.9. (a) North-south for location. The cross section of Sharon Springs. This is a chronostratigraphic. (b) subdivisions of the Sharon Springs. (2) the truncation and con
9. (a) North-south cross section M-M' extending from east-central Colorado to northwest Nebraska (see Fig. 3 on). The cross section uses dual induction logs with gamma ray traces. Datum for the section is the top of the springs. This is a lithostratigraphic horizon, whereas other lines tie correlative horizons that are interpreted to be stratigraphic. (b). Horizontally-scaled, diagrammatic representation of cross section M-M' showing stratigraphic zones of the Sharon Springs. Key features are as follows: (1) the three-fold division of the lower Sharon Springs, incision and condensation of these zones to the north, and (3) the time transgressiveness of the top of the Sharon
individual zone is interpreted to span 200 ka. The cyclicity could reflect the 400 ka orbital eccentricity cycles of Milankovitch (1941), although it is difficult to test this possibility.

As shown on Figure 6.8, the lower Sharon Springs section thins substantially to the north. This results from two factors: (1) stratigraphic condensation of the section (slower, but still continuous sedimentation), and (2) non-deposition or erosion associated with a major disconformity at the top of the lower Sharon Springs section. In some places the lower Sharon Springs is entirely absent (wells 9 and 11, for example). The origin and significance of this disconformity will be discussed in a subsequent section.

Along section M-M' the upper Sharon Springs varies from less than 2 m to 40 m in thickness. Whereas thickness variation of the lower Sharon Springs is primarily a function of sedimentation rate and erosion, the thickness variation in the upper Sharon Springs along section M-M' (and in general) is only partly a function of sedimentation rate. Although the thin upper Sharon Springs sections in wells 1 and 2 are the result of very slow sedimentation (note the very high gamma-ray readings reflecting a very high uranium content), much of the rest of the thickness variation along the section is the result of its diachrony. This diachrony appears to result from the persistence of conditions favorable to OC-rich deposition in some areas longer than in others, rather than progradation of the Pierre Shale section, as it was for section L-L', or from erosional truncation, as there is no evidence of a widespread disconformity at the top of the Sharon Springs section.

Cross Section N-N'

Cross section N-N' (Fig. 6.10) is located in east-central Colorado (see Fig. 6.3). It illustrates many of the same features as cross section M-M', including the thinning and
Figure 6.10. (a) The section uses dual representation.
Correlative horizon labels are shown.
Figure 6.10. (a). Southwest-northeast cross section N-N' in eastern Colorado (see Figure 3 for location). The cross section uses dual induction logs (with gamma ray traces) and the datum for the section is the top of the Sharon Springs. Correlative horizons are the same as those in section M-M' (Fig. 6-9). (b). Horizontally-scaled, diagrammatic representation of cross section N-N'.
truncation of the lower Sharon Springs, the diachrony of the upper Sharon Springs, and the stratigraphic condensation of the upper Sharon Springs.

At the southwest end of the section, the upper Sharon Springs section above the Ardmore Bentonite zone is very thin, and in well number 7 it is entirely absent. This part of the upper Sharon Springs is absent over an area of about 650 km². To the southwest, this section gradually thickens, but to the northeast, the equivalent section abruptly thickens to 50 to 60 m. This occurs as a result of more rapid sedimentation and an increased depositional time span.

The area where the Sharon Springs above the Ardmore Bentonite zone is absent is interpreted to be a paleobathymetric high that resulted from syndepositional uplift of this area following Ardmore Bentonite deposition. The abrupt thickening of the section to the northeast reflects the presence of an northwest-to-southeast-trending fault that was responsible for the uplift. This paleobathymetric high was probably above a layer of dysoxic to anoxic bottom water, so the absence of part of the Sharon Springs facies in this area, lends support to the anoxic bottom water model for Sharon Springs deposition.

PATTERNS OF SHARON SPRINGS SEDIMENTATION

**Description**

**Lower Sharon Springs**

An isopach map of the lower Sharon Springs (the chronostratigraphic unit defined above) is shown in Figure 6.11. Two aspects of this map are noteworthy. One is the large area of very thin or absent lower Sharon Springs in western Nebraska and in parts of northeastern Colorado. The other is the substantial increase in thickness of the unit to the south (though not fully shown, this unit also increases greatly in thickness to the west and north where it becomes the Gammon Shale).
Figure 6.11. Isopach map of the lower Sharon Springs.
Upper Sharon Springs

Like the lower Sharon Springs isopach map, the upper Sharon Springs isopach map (Fig. 6.12) includes strata not in the Sharon Springs facies. However, unlike the lower Sharon Springs, it does not portray a regionally isochronous interval. As previously noted, the lower boundary of the upper Sharon Springs is defined as the base of the Ardmore Bentonite zone, the approximate base of *Baculites obtusus* zone (Gill et al., 1966), but a comparable regionally traceable chronostratigraphic horizon is lacking at the top of the Sharon Springs, so the upper Sharon Springs isopach map combines elements of both lithostratigraphy and chronostratigraphy (see figure caption). East of the dashed line the map includes only strata in the Sharon Springs facies. West of this line the map uses a thin silty horizon that can be traced from the top of the *Baculites asperformis* zone on the east to the top of the same zone on the west.

Four features of the isopach map stand out: (1) the very thin area covering most of western Nebraska, (2) the thickening of the unit to the south into Kansas and far eastern Nebraska, (3) the thin area at the southern edge of the map, and (4) the rapid thickening of the interval to the west. The first two of these areas mimic the basic pattern of the underlying lower Sharon Springs (Fig. 6.11), whereas the latter two are quite different from the pattern in the lower Sharon Springs.

Interpretation

Lower Sharon Springs

The area of thin or absent lower Sharon Springs in western Nebraska is a result of stratigraphic condensation (convergence of time lines) and erosion (truncation of time lines). Much of the thinning is due to the presence of a widespread disconformity that is coincident with the base of the Ardmore Bentonite zone (and base *Baculites obtusus*...
Figure 6-12. Isopach map of the upper Sharon Springs. The dashed line indicates a change in the upper boundary of the mapped interval from a lithostratigraphic one (top Sharon Springs facies) to a chronostratigraphic one (approximate top of *Baculites asperformis* zone). See text for details.
This disconformity was produced by a period of sustained sea level fall followed by a sea level rise during *Baculites obtusus* time (McGookey et al., 1972). This disconformity has been attributed to subaerial erosion by DeGraw (1975). His detailed isopach map of a unit roughly equivalent to the lower Sharon Springs in northwestern Nebraska illustrates a pattern of north-south trending thicks and thins. DeGraw (1975) attributed these to paleovalleys produced by subaerial erosion. A bit farther to the west in eastern Wyoming, Van Wagoner et al. (1990) suggested that subaerial erosion produced a similar incised valley pattern (and type I sequence boundary) beneath the Ardmore Bentonite zone. The authors postulated that the sea retreated from a large area of the North American craton at this time (the 80-Ma sea level fall of Haq et al., 1987) and that this was followed by a large-scale sea-level rise that resulted in marine shales directly onlapping the subaerial unconformity.

Neither Van Wagoner et al. (1990) or DeGraw (1975) cited evidence (paleosols, root zones, etc.) that would support the subaerial exposure of this extensive area. Gill et al. (1966) in their detailed description of the lower Pierre Shale section at Red Bird, Wyoming cite no evidence for an unconformity at the base of the Ardmore Bentonite zone (base Sharon Springs); in fact, they noted that the Gammon Shale is transitional with the overlying Sharon Springs. McGookey et al. (1972) noted that there is no evidence of a regional withdrawal of the sea from the Rocky Mountain region at this time (early Campanian–pre-*Baculites obtusus*). Thus it is much more likely that the pattern of thickening and thinning (that DeGraw, 1975; and Van Wagoner et al., 1990; noted) was produced by submarine erosion, possibly of bathymetric highs produced by differential tectonic movement (and/or differential compaction-induced subsidence) of the basin along the transcontinental arch, i.e., a continuation of the pattern in the upper part of the Niobrara (Chapter 2). Older disconformities in the upper Niobrara and lower Sharon
Springs occur at several stratigraphic levels and locations. This pattern is consistent with intermittent, relatively localized tectonic movement of the basin floor.

Van Wagoner et al. (1990) were correct in attributing the disconformity at the base of the Ardmore bentonite zone to a fall and subsequent rise of sea level. Their designation of this horizon as a sequence boundary is probably valid, although it represents a basinal rather than a subaerial expression of that boundary. Further, it is a relatively local expression of the sequence boundary, because it cannot be recognized along basinal strike as has been well documented (Krystinik et al., 1994).

It is often assumed that thin Sharon Springs sections are due to constant, but extremely slow, sedimentation in deep-water areas with very little sediment flux from the overlying water column. However, as pointed out above much of the regional thinning in the lower Sharon Springs is the result of erosional truncation. Thus the areas of thin lower Sharon Springs on the isopach map (Fig. 6.11) are likely to represent paleobathymetric highs rather than deep basinal settings. This is supported by the pattern observed in the underlying Niobrara Formation.

The areas of thin or absent lower Sharon Springs correspond to similar areas of thinning in the underlying Niobrara. These areas contain disconformities and eroded sections that were presumably deposited at or above storm-wave base (Chapter 2). If the deep, stagnant-basin model for Sharon Springs deposition is valid, then the Ardmore bentonite zone, which overlies the lower Sharon Springs, should be present in the entire area, especially as this zone corresponds to the major transgression that is inferred to have occurred at this time (McGookey et al., 1972; Gill and Cobban, 1973; Kauflman, 1977; Schultz et al., 1980). However, the Ardmore Bentonite zone is absent in some areas of western Nebraska and northeastern Colorado, despite the fact that it is well developed in northwestern Kansas at greater distances from the presumed source area of the bentonites.
in western Montana (Gill and Cobban, 1973). Taken together these observations suggest that current activity related to paleobathymetry was responsible for limiting deposition of the lower Sharon Springs in western Nebraska and northeastern Colorado. Sedimentation was probably episodic and punctuated by erosional episodes and not simply slow and continuous in these areas. The same arguments concerning the depth of maximum storm-wave base that were used for the Niobrara (Chapter 5), can be used to suggest that Sharon Springs deposition probably occurred at depths of 100 to 150 m within the study area.

The lower Sharon Springs interval thickens to the south. This thickening reflects in part a continuation of the paleobathymetric pattern of the underlying Niobrara (southward-sloping basin floor). Sediment accumulation in this area was not limited by shoal-water erosional episodes, as it presumably was farther to the north, so sedimentation was more continuous. The disconformity at the base of the Ardmore Bentonite zone is not present in this area, so the sequence boundary of Haq et al. (1988) noted above would not be recognized. The rapid thickening of the unit to the southwest (Pueblo–Cafion City area) reflects higher sedimentation rates at the distal edges of a regional progradational episode. This episode includes the maximum northeastward progradation of the Point Lookout Sandstone in the San Juan Basin during *Baculites sp.* (weak flank ribs) time (e.g., Elder and Kirkland, 1994) and the northward progradation of the Menefee Formation during *Baculites sp.* (smooth) (McGookey et al., 1972) in New Mexico.

**Upper Sharon Springs**

Several factors account for the differences in the sedimentation patterns of the lower Sharon Springs (Fig. 6.11) and the upper Sharon Springs (Fig. 6.12). The area of
most rapid sedimentation moved to the north, reflecting a regional change in
transgressive/ regressive patterns that resulted in regression in northwest Colorado and
Wyoming (the Mesaverde/Rock Springs) and transgression in New Mexico.
Sedimentation rates were still slow in the bathymetrically high area in western Nebraska,
although the rise in sea level that accompanied upper Sharon Springs deposition
accommodated renewed sedimentation, so that nearly the entire area is covered by the
upper Sharon Springs. The east-west trending thick area in east-central Colorado reflects
the presence of a bathymetric low that formed between the bathymetric high to the north
in Nebraska and a high formed to the south by both the syndepositional faulting
previously mentioned and the thick tongue of lower Sharon Springs that had prograded
from the southwest.

Although a large component of the thickness variation shown on the upper Sharon
Springs isopach map is the result of regional changes in sedimentation rates, the
diachronous nature of the upper Sharon Springs contact also plays a role in most of the
study area (east of the dashed line in Fig. 6.12). Unlike the east-west diachrony produced
by sediment dilution of the Sharon Springs facies, diachrony in the eastern part of the
study area appears to be a function of paleobathymetry. Sharon Springs deposition
appears to have terminated earlier over paleobathymetric highs. This result probably
reflects the presence of a stratified water column with a bottom layer of dysoxic to anoxic
water as has often been postulated for the Sharon Springs (e.g. Gautier et al., 1984).
Falling sea levels following a maximum transgression, probably during late Baculites
obtusus time, lowered the pycnoclines and gradually restricted Sharon Springs deposition
to bathymetric lows of increasingly smaller extent. In the next section, a cross section is
used to model this and other controls on Sharon Springs deposition.
Cross-Sectional Model

Cross section P-P' shown in Figure 6.13 uses a series of gamma-ray log traces through the Sharon Springs section. The section extends from east-central Colorado to northwest Nebraska (Fig. 6.3). Figure 6.14 (a through f) models the deposition of the Sharon Springs along this section by breaking it down into a series of time slices beginning with the end of Niobrara deposition.

In summary, OC-rich Sharon Springs deposition is inferred to have begun beneath oxygen-depleted bottom waters following Niobrara deposition. Subsidence to the south sustained higher rates of sedimentation as falling sea level increasingly limited sedimentation to the north. By the end of lower Sharon Springs deposition, a submarine erosional base level was reached (storm wave base?) in the north and pre-existing sediments were eroded to create the disconformity at the base of the Ardmore Bentonite zone. Rising sea levels during the Claggett transgression (*Baculites obtusus* zone) re-established sedimentation along the entire section. High sea levels maximized OC-rich sedimentation as oxygen-depleted bottom water reached its maximum extent. Finally, falling sea levels restricted OC-rich sedimentation to increasingly restricted areas of deep water where oxygen depletion could be sustained.

**ORGANIC-CARBON IN THE SHARON SPRINGS**

**OC Distribution**

This section combines new and published TOC values for the Sharon Springs along with those estimated from well logs (Chapter 3) to document regional and temporal changes in OC content. In Figure 6.15, cross section O-O' is shown extending from Cañon City, Colorado, to Sharon Springs, Kansas. This cross section is composed of
Figure 6.13. Gamma-ray log cross section P-P' through the Sharon Springs section. Section extends from east-central Colorado to northwest Nebraska. This section was used to reconstruct a sequential set of cross sections depicting the evolution of Sharon Springs deposition.
Figure 6.14. A series of 6 time slices portrays the evolution of Sharon Springs deposition along cross section P-P' (Fig. 6.13). The Sharon Springs is divided into a series of units along inferred chronostratigraphic horizons. Beginning with initial Sharon Springs deposition at the top of the Niobrara the deposition of these units is reconstructed in a series of steps. As the section is thin, compaction is not taken into account nor is basin subsidence except where it was needed to create accommodation space.

(a). This section shows a possible bathymetric profile of cross section P-P' at time zero (T-0) immediately following Niobrara deposition. Paleobathymetry was assumed to be well below the 100 m storm wave base (see Chapter 2), except at the southern end of this section where it is set at 100 m to accommodate a disconformity at the top of the Niobrara. Sea level is set at an arbitrary level of zero.

(b). At T-1 corresponding to the top of lower Sharon Springs zone 1, sea level has fallen and subsidence (growth faulting?) has increased accommodation space to the south. Density stratification (possibly periodic) of the water column results in oxygen depletion of the bottom water and enhanced preservation of organic matter.
a) P T O Top Niobrara - 81.2 Ma (est.)

- Sea Level
- Storm Wave Base
- (Pycnocline?)
- Disconformity

b) T I (81.0 Ma est.)

- Sea Level
- Storm Wave Base

Niobrara
(c) T-2 corresponding to the top of lower Sharon Springs. A continued fall in sea level has increasingly slowed sedimentation to the north, whereas continued subsidence to the south sustains relatively rapid sedimentation. A submarine erosional base level is reached (storm wave base?) and pre-existing sediments are eroded to create the widespread disconformity at the base of the Ardmore Bentonite zone.

(d) T-3 By this time sea level has risen (the Claggett transgression) and the Ardmore bentonites have been deposited as sedimentation of OC-rich Sharon Springs resumes along the entire section. Sedimentation rates remain slow to the north. Maximum water depths at this time result in widespread oxygen depletion of the bottom water and maximum preservation of organic matter.
T2 (80.6 Ma est.)

Sea Level

Meters

Niobrara

T3 (79.8 Ma est.)

Sea Level

- Storm Wave Base

Meters

Niobrara
Figure 6.14 (cont.).

(e) At T-4 sea level is falling again following maximum transgression. To the north the shoaling bottom intercepts the pycnocline and the OC-rich facies no longer is deposited, whereas in the deeper water to the south its deposition continues.

(f) T-5 marks the end of OC-rich Sharon Springs deposition along section P-P' as Sharon Springs deposition is limited to increasingly limited deep water settings. By this time sedimentation rates begin to increase along the northern part of the section as lower Pierre Shale progradation accelerates and silty zones become more common.
Niobrara 

Sea Level

Pycnocline

SWB

Meters

-500

-450

-400

-350

-300

-250

-200

-150

-100

-50

0

T 4 (79.4 Ma est.)

T 5 (79 Ma est.)

Niobrara
Figure 6. OC-log cross section O-O' from Cañon City, Colorado, to Sharon Springs, Kansas. Wells and data sources as follows. (1) Thicknesses from the Cambria Oil Co. #14-26 Phillips well (26-19S-69W). Average TOC values from Parrish and Gautier (1993) for the OC-rich section and from composite cuttings samples from the nearby Brehm #1 Schiel well (this study) for the sections above and below. (2) Log-calculated OC values from the Sohio #7-1 Creech well (7-12s-55W), calibrated to TOC values obtained from cuttings. (3) Log-calculated OC values from the Murfin Drilling Co #1-34 James Hill well (34-11S-53W). (4) Log-calculated OC values from the Charter Production Co. #1 Carvila well (15-14s-46W). (5) Log-calculated OC values from the Holden Energy Corp. #23-1 Burk well (23-12S-41W) calibrated to OC values from the U.S.G.S. Guy Holland well. (6) OC values from 5 foot cuttings samples from the U.S.G.S. Guy Holland well (data from Gill et al., 1972).
OC logs that include TOC data from a variety of sources as well as estimated OC values from geophysical well logs.

This cross section illustrates both vertical and lateral variations in OC content. Along this section OC values are typically highest near the top of the Sharon Springs section, especially where the uppermost Sharon Springs (above the A.B.Z.) is thin, as in wells 1 and 2. East-west changes in OC content along this line of section are not large, but there is somewhat of a reduction in the OC content to the west in the lower Sharon Springs.

Figures 6.16 and 6.17 illustrate regional variations in the OC content of the lower and upper Sharon Springs respectively. There is no clear pattern to the distribution of OC values in either unit, though a careful comparison with the isopach maps (Figs. 6.11 and 6.13) reveals that there is a tendency for the thinnest sections to have the highest OC values. This is confirmed in Figures 6.18 and 6.19, which plot sedimentation rates against OC % for the lower and upper Sharon Springs sections respectively.

Both of these plots indicate that there is a weak trend towards increased OC values with lower sedimentation rates. This result is contrary to the often reported result that higher OC contents correlate with increased sedimentation rates (e.g., Heath et al., 1977; Müller and Suess, 1979; Stein, 1986) up to the point where dilution becomes important (Ibach, 1982). This correlation is frequently attributed to the increased preservation of OM that can result from its more rapid burial (Müller and Suess, 1979). It should be pointed out, however, that some of these studies (e.g., Müller and Suess, 1979) have combined data from environments that are not readily comparable to each other (i.e., deep-sea and shelf environments).

Figures 6.20 and 6.21 reveal that there is a positive correlation between sedimentation rates and organic-carbon accumulation rates (OCARs). The correlation is
Figure 6.16. Average OC values in the lower Sharon Springs section.
Figure 6.17. Average OC values in the upper Sharon Springs section.
Figure 6.18. Sedimentation rates versus average OC for the lower Sharon Springs.
Figure 6.19. Sedimentation rates versus average OC for the upper Sharon Springs.
Figure 6.20. Sedimentation rates versus organic-carbon accumulation rates for the lower Sharon Springs.
Figure 6.21. Sedimentation rates versus organic-carbon accumulation rates for the upper Sharon Springs (lower correlation line excludes two locales with high sedimentation rates, including one off scale).
especially strong for the lower Sharon Springs. This indicates that areas with higher sedimentation rates were (a) areas of higher productivity or (b) greater preservation. However, a four-fold increase in the sedimentation rate only produces a somewhat less than three-fold increase in the OCAR. These results are less than the doubling of OCAR values for each 1.6 fold increase in sedimentation rate (Müller and Suess, 1979) that are usually attributed to a purely preservational effect, so increased productivity was unlikely to have been a factor.

As Sharon Spring OCARs do increase with increasing sedimentation rate, there may be a preservational effect. However, as the preservational effect is not as great as could expected (i.e., from data of Müller and Suess, 1979), this suggests that dilution of the OM was the net effect of the increased sedimentation rate. This result is consistent with deposition under anoxic or highly dysoxic bottom water (Stein, 1986).

Paleoproductivity

Absolute Values

Estimates of paleoproductivity during Sharon Springs deposition are shown in Figures 6.22 and 6.23. As for the Niobrara these estimates were made by combining the equation of Betzer et al. (1984), relating OC flux to water depth, with that of Henrichs and Reeburgh (1987), relating burial efficiency to the sedimentation rate. The values average about 320 gC m\(^{-2}\) a\(^{-1}\) for the lower Sharon Springs and about 230 gC m\(^{-2}\) a\(^{-1}\) for the upper Sharon Springs. These are moderately high productivity values typical of those found in coastal settings with moderate upwelling or in estuaries (e.g., Berger, 1989).

The moderately high paleoproductivity estimates are consistent with other evidence. In the Sharon Springs, the abundance of fish scales and higher vertebrate fossils argue for a productive environment (Parrish and Gautier, 1993). Bakker (1993)
Figure 6.22. Estimated paleoproduction values (in gC m\(^{-2}\) a\(^{-1}\)) for the lower Sharon Springs. Values were calculated by combining the equations of Betzer et al. (1987) and Henrichs and Reeburgh (1987) (see text). A uniform depth of 150 m is assumed.
Figure 6.23. Estimated paleoproductivity values (in gC m$^{-2}$ a$^{-1}$) for the upper Sharon Springs. Values were calculated by combining the equations of Betzer et al. (1987) and Henrichs and Reeburgh (1987) (see text). A uniform depth of 150 m is assumed.
has even used the overwhelming dominance of mosasaurs over plesiosaurs in the Niobrara and Sharon Springs to argue that the WIS was a dense algal forest. He based this on the fact that the long-bodied mosasaurs (ambush predators) would be better adapted to such conditions compared to the fast-swimming plesiosaurs. In the modern oceans, OC-rich sediments are almost always associated with high productivity.

Thus it is likely that the paleoproductivity estimates shown on the maps (Figs. 6.22 and 6.23) are reasonable. If so, it is unlikely that Sharon Springs deposition took place in a stagnant, stably stratified basin. Nutrient renewal in the photic zone is very limited in such settings and productivity values are typically low. It is more likely that the water column was periodically (seasonally?) unstable. During periods of vertical mixing nutrients would be added to the photic zone, thereby sustaining productivity. The high OM flux to the sea floor would deplete any oxygen introduced during these periods in a short time (weeks or months).

Changes in Sharon Springs Paleoproductivity

The paleoproductivity maps (Figs. 6.22 and 6.23) do not show any consistent regional trends. Thus within the study area, there is no evidence of any long-term upwelling centers, nor is there any evidence of migration of upwelling from west to east with time as proposed by Parrish and Gautier (1993). Paleoproductivity values for the upper Sharon Springs are apparently somewhat lower than they are for the lower Sharon Springs, but this could a consequence of uncertainty in the sedimentation rate estimates, particularly for the upper Sharon Springs.

The above estimates are averages over very long periods of time (100's of ka to over 1 Ma). Significant temporal changes in productivity, including regional ones, may be averaged out of these estimates. It may be possible to further subdivide the Sharon
Springs and paleoproductivity estimates for these shorter time scales could provide additional insights into regional changes in paleoproductivity.

**UA/OC RATIOS**

As demonstrated in Chapter 4, UA/OC ratios can be useful in assessing paleo-oxygenation levels. The ratios use average OC and UA values for each unit. UA/OC ratios for the Sharon Springs were determined by combining sample and geophysical-log derived OC values with geophysical-log derived UA values. UA values were derived from the uranium curve on gamma-ray spectra logs (e.g., Schumberger, 1989) or from standard gamma-ray logs. When gamma-ray spectra logs were used, the allogenic U component was assumed to be 2 ppm. This value was subtracted from the total U to produce the UA. When standard gamma-ray logs were used, it was assumed that gamma-ray API values above 100 units were produced by UA (this value is typical of the overlying OC-poor Pierre Shale section. Although variations in clay content and composition can be expected to produce variations in both the allogenic U content and total gamma-ray emissions, such variations are minor compared to those produced by variations in the UA content.

UA/OC ratios for the lower and upper Sharon Springs are plotted in Figures 6.24 and 6.25. The ratios use average OC and UA values for each unit. Both sets of data plot between the oxic and anoxic trends established in Chapter 4. This suggests that the bottom water was on average dysoxic. Therefore the suggestion that the bottom water was completely anoxic (e.g., Gautier et al., 1984), is unlikely.

A single point (circled) on Figure 6.25 is from the section above the Sharon Springs. This point plots below the oxic trend line and suggests that conditions became fully oxic following Sharon Springs deposition. This is consistent with the faunal
6.24. Plot of $U_A/OC$ ratios versus sedimentation rates for the lower Sharon Springs. OC values taken from samples or calculated using geophysical logs. $U_A$ values are obtained from gamma-ray spectra logs or standard gamma ray logs (see text).
Anoxic

6.25. Plot of $U_A$/OC ratios versus sedimentation rates for the upper Sharon Springs. Circled point is from the section directly above the Sharon Springs. OC values taken from samples or calculated using geophysical logs. $U_A$ values are obtained from gamma-ray spectra logs or standard gamma ray logs (see text).
evidence and provides support for the supposition that dysoxic bottom water was a key control in producing the OC-rich Sharon Springs.

**DISCUSSION**

Contrary to suggestions that the Sharon Springs was deposited in a deep, stagnant basin, this study suggests that the water depth was not great and that permanent stagnation (anoxia) did not exist. Instead the environment was more dynamic. Paleobathymetry was important as extensive areas of the bottom were exposed to submarine erosion, particularly at the sea level lowstand predating Ardmore Bentonite deposition. In these areas, primarily western Nebraska and northeastern Colorado, sedimentation was often episodic and punctuated by erosional episodes.

The above interpretation would seem to be in conflict with both the organic-rich nature of the Sharon Springs and its high pyrite content (Gautier et al. 1984), as currents would presumably introduce oxygen to the bottom. Oxygen would tend to oxidize the OM and limit pyrite precipitation. However, bottom currents were probably intermittent and thus not continuously supplied to the bottom. Further, in high-productivity settings the OM-flux can re-establish anoxia at the bottom in relatively short periods of time. Two aspects of the organic matter in the Sharon Springs suggest that this could be the case: (1) the low oxygen-index values for immature Sharon Springs OM when compared to subjacent Niobrara OI values and (2) the abundance of fecal pellets.

Figure 6.26 is a modified van Krevelen diagram (Tissot and Welte, 1978) showing data from both the Sharon Springs and Niobrara. Values for thermal maturity ($T_{\text{max}}$ values) are shown next to the plotted values. The general trend in the hydrogen index (HI) and the oxygen index (OI) with increasing maturity follows that expected for type II (marine) organic matter (Tissot and Welte, 1978). There is one notable difference
Modified van Krevelen Diagram

Figure 6-26. Modified van Krevelen diagram (Tissot and Welte, 1978) with $T_{\text{max}}$ values (see Chapter 3). Data from Gautier et al. (1984), Rice (1984), and this study.
between the Sharon Springs and the Niobrara samples. At a low level of maturity (e.g., 
\( T_{\text{max}} = 404^\circ \text{C} \)), Sharon Springs samples have a much lower OI than those of the Niobrara 
at a comparable level of maturity.

The higher OI of the immature Niobrara could be caused by pyrolytic generation of 
carbon dioxide from residual carbonate in the samples (Katz, 1983; Peters, 1986). This 
seems unlikely, however, as more mature Niobrara samples show no increase in the OI 
compared to equally mature Sharon Springs samples. The lower OI of the Sharon 
Springs could also reflect original differences in OM composition, namely the presence of 
more terrigenous OM (oxygen-rich OM) in the Niobrara samples. However, visual 
kerogen analyses presented in Rice (1984) indicate that the opposite may be the case. 
Alternatively, the lower OI of the Sharon Springs samples may reflect a greater degree of 
early diagenesis in the Sharon Springs. Early diagenesis results in the breaking of C=O 
bonds and the lowering of the OI index (Tissot and Welte, 1978). As the immature 
(\( T_{\text{max}} = 404^\circ \text{C} \)) Sharon Springs samples are from a thin, lower Sharon Springs section, 
they may have been subject to a greater degree of early, near-surface diagenesis than the 
more rapidly buried Niobrara sediments.

OC-rich parts of the Sharon Springs contain abundant organic platelets that are 
arranged parallel to bedding (Schultz et al., 1980). In uncompacted limestone concretions 
these retain an original spheroidal to oblate shape and they are interpreted to be fecal 
pellets (Parrish and Gautier, 1993). The abundance of these pellets and the fact that they 
apparently account for most of the OM in many Sharon Springs sections (Parrish and 
Gautier, 1993) raises some interesting possibilities.

The fecal pellets range from in size from 100 \( \text{mm} \) to a few 100 \( \text{mm} \), consistent 
with a zooplanktonic origin (Parrish and Gautier, 1993). Pellets of this size have settling 
velocities of approximately 50 to 200 m/d (Angel, 1989), equivalent to those for fine
quartz sand (Blatt et al., 1972). Though equivalent entrainment velocities are likely to be different, it is clear that currents could selectively winnow a mixture of clays and fecal pellets. The fact that the peloidal facies of the Sharon Springs occurs in thin, condensed sections, suggests that this facies might result from winnowing of the sediments by periodic slow bottom currents. Winnowing in similar condensed sections has been proposed for the OC-rich Peterborough Member of the Oxford Clay (Macquaker, 1994). Variation in the concentration of pellets produces bedding layers in the OC-rich Sharon Springs (Parrish and Gautier, 1993). These layered variations are consistent with current winnowing.

Bottom-water currents strong enough to erode and winnow Sharon Springs sediments were probably produced by rare storm events of short duration. These events were followed by long periods of relative bottom-water quiescence during which anoxia-dysoxia could be re-established. In areas of slow sedimentation, cessation of Sharon Springs deposition at any given locality probably resulted from the more frequent impingement of oxygen-carrying currents at the bottom. Gill et al. (1972), for example, cited evidence of bottom currents near the top of the Sharon Springs in the phosphatic facies. This transitional facies (from the OC-rich Sharon Springs to more normal marine shales) is probably a product of slow sedimentation as suggested by Gill et al. (1972) in a zone with fluctuating oxygenation as suggested by Parrish and Gautier (1993). In these localities, the transition from OC-rich Sharon Springs to overlying OC-poor shales is abrupt.

In other areas (i.e., along the Front Range), increased rates of sedimentation progressively diluted the OC-rich facies. The upper contact of the Sharon Springs in these areas is gradational, often over many tens of meters and the phosphatic facies is unlikely to be developed.
SUMMARY AND CONCLUSIONS

The Sharon Springs Member of the Pierre Shale is a very distinctive, OC-rich shale that is readily recognized in outcrop and in the subsurface. The Ardmore Bentonite zone provides a convenient chronostratigraphic horizon that can be used to divide the Sharon Springs into an upper and lower unit. Cross sections of the Sharon Springs and isopach maps of the two units provide a stratigraphic framework in which controls on Sharon Springs sedimentation and OC content can be assessed. Important conclusions are summarized below.

1. The Sharon Springs facies is not present where sedimentation rates are high—to the southwest (lower Sharon Springs) and west (upper Sharon Springs). This resulted from clastic dilution.

2. Water depths were probably only 100-150 m.

2. Paleobathymetry was important in controlling the distribution of the Sharon Springs. Shoal areas could be exposed to bottom currents and/or an oxygenated water column. For example:

(a) Shoal areas limited sedimentation rates and eventually exposed large areas to erosion as sea level fell during lower Sharon Spring deposition.

(b) At times, shoal areas produced by syndepositional tectonics, extended above the normal level of the dysoxic/anoxic bottom water. In these areas the Sharon Springs facies did not develop.
(c) Sea level rise beginning in *Baculites obtusi* time resulted in the westward expansion of the Sharon Springs facies.

(d) Subsequent sea level fall, probably beginning in *Baculites mclearni* time, reduced the areal extent of the Sharon Springs as deeper water areas shrank in extent.

3. The estimates of paleoproductivity shown in Figures 6.22-23 are reasonable in light of evidence that productivity was at least moderate, if not high. But the estimates do not support a long term migration of paleoproductivity to the east, nor do they provide strong evidence for or against upwelling in the study area.

4. Sections most characteristic of the Sharon Springs appear to be condensed sections with slow and intermittent sedimentation. In these sections, the OM seems to be dominated by fecal pellets which may have been winnowed by periodic bottom currents.
CHAPTER 7
SUMMARY AND CONCLUSIONS

STUDY SYNOPSIS

Cretaceous organic-carbon (OC) rich strata, including the Niobrara Formation and Sharon Springs Member of the Pierre Shale, in the Western Interior are among the most studied rocks in the world. As pointed out in Chapter 1, however, they have remained problematical with respect to their origin. Previous studies have tended to focus attention on only one or a few key outcrops or cores. I felt that a fruitful approach to understanding the origin of OC enrichment in the Niobrara and Sharon Springs would be to examine this enrichment within a three-dimensional framework. This was possible because of the abundance of geophysical well logs in the region (the region is a significant petroleum province, so tens of thousands of well have been drilled into and through the Cretaceous section). These logs provided a wealth of stratigraphic and compositional data on the studied units. Key to the success of this approach was the recognition that (1) there are numerous widely correlatable chronostratigraphic horizons in both units, but particularly in the Niobrara, and (2) that OC contents can be estimated with a degree of accuracy from geophysical well logs.

Chapter 2 established the chronostratigraphic framework for the Niobrara portion of the study. Numerous, regionally correlative chronostratigraphic horizons were recognized in the Niobrara. These help establish the important influence of climatic variations on Niobrara deposition. Thickness patterns revealed the role that tectonics, paleobathymetry, and sediment flux (paleoproductivity and terrigenous input) played in producing the Niobrara section.
In Chapter 3, a previously published method of estimating OC content from geophysical well logs was adapted specifically to the Niobrara and Sharon Springs. A way to predict and then take into account variable levels of organic maturity was demonstrated. The method developed in Chapter 3 was then applied in Chapters 5 and 6.

The close association of organic carbon and authigenic uranium was documented in Chapter 4. Data from a wide variety of marine settings were used to demonstrate the two key controls on the $U_A/OC$ ratio—sedimentation rate and bottom-water oxygenation. Examples of how this ratio might be applied to assessing ancient bottom-water oxygenation were presented and then applied to the Niobrara and Sharon Springs in Chapters 5 and 6, respectively.

The results of the first three chapters were applied to the Niobrara in Chapter 5. The chronostratigraphic framework established in Chapter 2, was combined with log estimates of OC, to produce a three-dimensional picture of OC distribution. Temporal and regional changes in OC content, OC fluxes, and estimated paleoproductivities could then be examined and their possible significance concerning the origin of OC enrichment in the Niobrara addressed.

The regional stratigraphy of the Sharon Springs was outlined in Chapter 6. The pattern of Sharon Springs deposition was addressed in detail and revealed. Then an approach similar to that used in Chapter 5 was applied to the Sharon Springs to assess the possible origin of OC enrichment in this unit.

**CONCLUSIONS AND FINAL DISCUSSION**

This study indicates that both the Niobrara and Sharon Springs were deposited in a shallower, more dynamic environment that most previous studies have suggested. Long-term, stable stratification of a deep-water seaway was unlikely during deposition of either
unit. Paleoproductivities were probably moderate to high. The limited, episodic, bioturbation in the Niobrara indicates that the bottom-water was seldom fully oxic, however. In the Sharon Springs, the near total absence of bioturbation and benthonic organisms are evidence that the bottom-water was anoxic. In the absence of a long-term, stably, stratified water column, it is likely that the moderate-to-high paleoproductivities were responsible for depleting the bottom-water oxygen.

The model that can best account for the pattern of OC enrichment and bottom-water dysoxia to anoxia in the Niobrara and Sharon Springs is a seasonal one that has been outlined by Tyson and Pearson (1991). They suggested that a seasonal thermocline probably developed in at least some epieric seas and argue that periods of seasonal stratification would result in oxygen depletion of the near-bottom water. (Seasonal precipitation and runoff could enhance this stratification). Stratification would disappear in the late fall to winter, and mixing of the water column could occur. As a result, the surface-water nutrient content would be renewed, and a spring bloom of phytoplankton would be promoted. Oxygen would be transported to the bottom, but the high OC flux to the bottom would quite rapidly consume the available oxygen, not giving benthic organisms time to become re-established (Tyson and Pearson, 1991). It would be especially hard for benthic organisms to become re-established across a large body of water like the WIS.

Tyson and Pearson (1991) also link this seasonal model to Milankovitch cyclicity by noting that these cycles could have controlled the existence and time span of the seasonal thermocline. Periods of warm climate would have been characterized by seasonally longer stratification and shorter periods of water-column mixing, resulting in greater bottom water anoxia. The opposite would be true for periods of cooler climate.

The Tyson and Pearson (1991) model seems to fit the Niobrara and Sharon Springs quite well. For example, as discussed in Chapter 5 the Niobrara chalk/marl cycles are
attributed to productivity cycles, not dilution cycles. Under the Tyson and Pearson (1991) model, the chalks would have formed during cooler periods of climate when seasonal stratification was shorter. The longer period of vertical mixing would have enhanced the productivity compared to periods of warmer climate, but OC preservation rates (i.e., burial efficiency) would have been reduced by the increased oxygen flux to the bottom and at times the periodic recolonization of the bottom by benthic organisms. This fits with the evidence presented in Chapter 5.

A long term secular trend towards increased OC is noted for Niobrara stratigraphic sequence (see Figs. 5.4-5). This trend culminates in the very OC-rich Sharon Springs. In this sense, the Niobrara and Sharon Springs represent a stratigraphic continuum, and their lithologic distinction (carbonate versus clastic) is based on the gradual reduction in the carbonate content that occurs in the uppermost Niobrara and lowermost Sharon Springs. The reason for this transition has not been well explained, but a secular trend towards higher OC contents may reflect a long-term trend towards warmer climate as implied by Tyson and Pearson (1991).

This multifaceted study has demonstrated that subsurface geophysical well logs can be used in a variety of ways to study the three-dimensional distribution of OC-rich strata. This has important implications well beyond this study, as geophysical well logs are common in many, if not most, basins where OC-rich rocks have been described.
APPENDIX A

WELLS USED IN THIS STUDY

List 1

This list includes wells for which log copies were made. Most of these include both the Sharon Springs and Niobrara sections. Wells are arranged in inverse numerical order beginning with range, then township, then section.

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239 Benton Oil & Gas Co. #20-1 Weld County  
240 Sun Expl. & Prod. Co. #1 Cervi Interstate  
241 Energy Minerals Corp. #7 Anne State  
242 Energy Minerals Corp. #1 Krause  
243 Wenner Petr. #1 Alkire Brothers  
244 Clark Energy Corp. #18-1 Clark-Bashor  
245 Dakota Energy & Resources #1-3 Weitzel  
246 Sun Expl. & Prod. Co. #1 Ulibarri  
247 Dome Petroleum #1-6 Hill  
248 High Summit Oil & Gas Inc. #36-3 State  
249 Energy Mineral Corp. #1 Bree  
250 Excelsior Oil Corp. #1 Alice G. May  
251 Petroleum Energy Corp. #G Rauth  
252 Energy Minerals Corp. #1 Nicola  
253 Petcon Assoc. LTD. #6 Wirth  
254 Energy Minerals Corp. #1 Christianson  
255 Frank H. Walsh #16-1 Morgan State  
256 Benson Mineral Group #26-13 Club  
257 Petro Lewis Corp. #2-26 Spence  
258 Union Oil Of Cal. #13-A24 Nichols Adena Un.  
259 Champlin Pet et al #3 G. Glenn  
260 Nerouch Company #1-10 Toedliti  
261 Ensearch Expl. Inc. #1-14 State Of Colorado  
262 Diversified Oper. Corp. #3-1 Doc Wenninger  
263 Union Oil Of Cal. #3F Glenn  
264 E. P. Operating #1-23 Federal  
265 Marathon Oil Co. #1-32 Avalo  
266 Intermountain Oil Co. #1-12 Jack Cody  
267 Sundance Oil Company #1-18 Pederson  
268 Marshall R. Young #13-7 Peterson  
269 Stream Inc. et al #1 Rasmussen  
270 Mizel Petro. Resource Inc. #11-9 Griffith  
271 Tenneco Oil Co. #1 Pomerooy  
272 Phillips Petr. Co. #2A Thorton  
273 Bruce D. Brooks #1 Valero-State  
274 Century Oil & Gas Corp. #1 Weatherill  
275 Hunt Oil Company #1-33 D. Brunikhart

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277 Churchill Energy Inc. #2-A-5 Horn
278 Sun Expl. & Prod. Co. #1 Sed F. Roelle
279 Holly Resources #44-36X State
280 Sun Expl. & Prod. Co. #1 M. Segelke
281 Hunt Oil Co. #1-28 D. Schmidt
282 Sundance Oil Company #1-36 State-Croissant
283 Burro Oil Co. #1 Le Blanc
284 Kilroy Company Of Texas, Inc. #1 Roper
285 Cougar Petroleum #1 Prud-Homme
286 Lewis & Clark #6-15 Arco-Sindt
287 Shepler & Thomas #1 Ward Curry
288 Sunray D-X Oil Co. #1 Resler
289 American Petrofina Co, oof Texas #1 McNish
290 Arco Oil & Gas Co. #1 Ouija
291 Robert R. Bamey et al #2 Rickie A. Wool Trust
292 William E. Carl & Hawn Bros.#1 Lorna D. Walker
293 Cougar Petr. Corp. #1 Roberts
294 CSG Exploration Co. #1-14 Morrison
295 Viersen & Cockran #1 Peters
296 J. M. Huber #36-1 Riley State
297 J. M. Huber #1-Petlenfein
298 Mormac Oil & Gas Co. #2-23X Koenig
299 Stelbar Oil Corp. 1-1 Pratt
300 Intercontinental Energy Corp. #1 State
301 J-W Operating Co. #14-13 McConnell
302 Kansas-Nebraska Natural Gas Co. #1-33 Powell
303 Southland Royalty Co. #1-36 State
304 J-W Operating Co. #1 Joseph Brophy
305 J-W Operating Co. #3-20 Mekelburg
306 Kansas-Nebraska Natural Gas Co. #1-7 Korf
307 Kansas-Nebraska Natural Gas Co. #1-33 Cillins
308 Midlands Gas Corp. #1-33 Woolery/Roundtree
309 CSG Expl. Co. #1-29 Schlachter
310 Murfin #2-9 Ferguson
311 Mesa Petroleum #5-29 Eckley Federal
312 S.D. Johnson #1 William Pyle
313 Mesa Petroleum #1-5 Federal
314 Viersen & Cockran #1 Deich
315 Amoco Production Co. #1 Hagemann
316 Murfin #1-Pope

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**Kansas**

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397 Sohio Petroleum Co. #2-8 Lee  SE NE  2-8N-37W
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422 J. C. Anderson #7-14 Snover  NW SE  14-29N-21W
423 D.G. Hamilton #1 Hock  C SE NE  27-10N-21W
424 J. C. Anderson #16-19 J. C. Anderson Dick  NE NE  19-31N-19W
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426 H.L. Hunt #1 Synder  NE NE  8-24N-18W
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462 Davis Oil Co. #1 Canvassback Federal
463 Exxon Company U.S.A. #1 Jackson Young
464 Conoco Inc. #43-1 Ellis
465 L.R. Company #1-6 Johnson
466 Milestone Petroleum #12-34 Federal
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496 Unioil #1 North Hereford       SE SW  11-12N-62W
497 Bennett Petroleum Corp. #6-10 Garrelts NW SE  6-22N-61W
498 Samuel Gary Oil Producers #9-1 Swope SW NE NE  9-34N-60W
499 Gary #17-8 Lohr                 SE NE  17-33N-60W
500 Union Oil of California #1 Rauner C NE NW  31-14N-60W
Well List 2

This list includes additional wells for which log copies were made.

Note: filing and indexing of wells at the Herold Geological Research Center, Denver, is done by location, not name, so location is the key criteria in designating wells.

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## APPENDIX B

### WELL LOCATION INDEX FOR CROSS SECTIONS A-A'—H-H'

Locations by section, Township, Range. Asterisks indicate wells also listed in Appendix A.

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73 2-31N-57W
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75 NE NE 9-34N-60W*
76 SE SE 34-35N-60W
77 SE SW 19-36N-63W*
78 NE SW 5-36N-63W
79 NE NE 23-37N-64W
80 NE SE 6-37N-64W*
81 NW SE 21-38N-64W
82 NE NE 7-38N-64W
83 SW NE SW 8-39N-64W
84 SE SW 15-42N-64W
85 SW SE NE 23-44N-64W
86 SW SE 5-45N-65W*
87 NE NE 31-46N-66W
88 NE NE 28-47N-66W
89 SE SE 26-48N-67W*
90 NE NW 6-49N-67W

B-B'

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4 SW SW 13-14S-50W*
5 SE NW 1-14S-50W*
6 SW NW 34-13S-50W*
7 SE SE 25-13S-50W
8 SE SE 14-13S-50W*
9 NW NW 7-13S-50W*
10 C NW NE 5-13S-50W*
11 SW SW 32-12S-50W*
12 SW NE NE 24-12S-50W*
13 NW 29-11S-50W*

14 NE NW 20-11S-50W*
15 NE NW 11-9S-50W*
16 NE NE 4-8S-49W*
17 NW NE 34-7S-50W*
18 SE NE 10-6S-52W*
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C-C'

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APPENDIX C
DETAILED STRATIGRAPHIC CROSS SECTIONS

The subsurface (gamma-ray) cross sections on the next two pages provide additional evidence for some features discussed in the body of the paper.

Figure A-1. (p. 361) This cross section uses 13 wells spanning a 635 km distance from Pueblo, Colorado, to north-central Nebraska, to demonstrate the regional continuity of individual zones (to the limits of well log resolution) within the lower chalk member of the Niobrara. The subdivisions shown on this cross section are the one used to divide the lower chalk into three individual units. Cycles in the lower chalk may be a result of Milankovitch cyclicity.

Figure A-2. (p. 362) This cross section is an enlarged part of cross section F-F', located in northeastern Colorado. This section illustrates the lateral continuity of beds in the upper three fourths of the Niobrara, but it also illustrates that disconformities are common. (1) In well 20 the upper portion of the upper chalk is truncated. (2) The upper marl unit 3 is completely missing in well 22 and note that it is partially truncated in well 21. (3) In wells 20 and 21 there is a disconformity near the top of upper marl unit 1. (4) The upper chalk is partially truncated in well 24, and it is overlain by a thin, condensed section of lower chalk that is itself bounded by a disconformity at its top.
Figure A-1. Lower chalk cross section T-T' (figure explained on previous page).
Figure A-2. Enlarged portion of Niobrara cross section F-F' (see Chapter 2—figure explained on previous page).
APPENDIX D
Derivation of Log TOC Equations: CARBOLOG® Method

In the Carbolog method the inverse square root of the rock resistivity ($1/R_t^{1/2}$) is plotted against the inverse sonic velocity ($\Delta T$) of the rock. Each individual rock component will plot separately as a specific point or pole on this graph. The matrix and water poles define a line, as does the matrix and shale poles. Data that plots to the right of these lines (larger $\Delta T$ values) reflect the presence of organic matter. If the $\Delta T$ of the organic matter is known or can be determined (by calibration), then the amount of organic matter (OM) can be quantified. See Carpentier et. al. (1991) for details.

![Graph showing the relationship between $1/R_t^{1/2}$ and $\Delta T$ with poles for water, clay, matrix, and organic matter]
The quadratic equation for line $S$ on the previous page is:

$$x=my+b$$

(this form is used so that the intercept is on the $x$-axis, corresponding to a key input value, $\Delta T_m$):

where $m=(\Delta T_w-\Delta T_m)/(I_Rw-0)$ and $b=\Delta T_m$

if we assume a specific point $(A,B)$ corresponding to possible log values in an OM-rich rock, the distance, $z$, (parallel to the $x$-axis) will be equal to:

$$z=A-(mB+b)$$

Then the volume percentage of OM will be:

$$VOM\%=100\frac{z}{(\Delta T_m-\Delta T_m)}$$

or substituting:

$$VOM\%=100\frac{(A-mB-b)}{(\Delta T_m-\Delta T_m)}$$

a shale correction can be added in which the slope, $M$, is a function of both water and shale contents (in practice this did not prove to be of values in estimating OC in the Niobrara), so that:
\[ M = ((m_S - m)(Sh\%/100)) + m \]

or substituting:

\[ VOM\% = 100(A - ((m_S - m)(Sh\%/100) + m)B - b)/\Delta T_{om} - \Delta T_m \]

we can also make the conversion from Vol. \% OM to Wt. \% OC:

\[ Wt. \% OC = l/f(\partial_{om}/\partial r)VOM \]

by combining equations:

\[ Wt. \% OC = 1/l(f(\partial_{om}/\partial r))100(A - ((m_S - m)(Sh\%/100) + m)B - b)/\Delta T_{om} - \Delta T_m \]

(This is wt. \% OC based on the wet bulk density)

Where:

- **OC** = organic carbon
- **f** = organic matter/organic carbon conversion factor\(^1\)
- **\(\partial_{om}\)** = density of organic matter\(^2\)
- **\(\partial r\)** = density of the rock\(^3\)
- **\(\Delta T_{om}\)** = inverse sonic velocity (transit time) of the OM (ms/ft)\(^4\)
- **\(\Delta T_m\)** = transit time of the matrix\(^5\)
- **\(\Delta T_w\)** = transit time of the formation water\(^6\)
- **\(\Delta T_s\)** = transit time of shale\(^7\)
- **\(1/R_w = 1/(R_w)^{1/2}\)** where **\(R_w\)** = formation water resistivity\(^8\)
- **\(1/R_s = 1/(R_s)^{1/2}\)** where **\(R_s\)** = resistivity of formation shale\(^9\)
- **A** = transit of the formation (\(\mu s/ft\))\(^{10}\)
\[ B = \frac{1}{(R_t)^{1/2}} \text{ where } R_t = \text{resistivity of the formation}^{11} \]

\[ \text{Sh\%} = \text{percentage of shale in formation (limestone sections)}^{12} \]

Notes:
1. Depends on type and maturity of the OM: ranges from about 1.12 to 1.57 (Tissot and Welte, 1978). Generally is not known, but can be estimated from pyrolysis data.
2. Usually 1.05 to 1.15 g/cm\(^3\). Generally is not known so is estimated and then calibrated to produce an acceptable value.
3. Read from density log.
4. Varies. Value is obtained by calibration using measured OC contents.
5. Fixed value depending on rock matrix (e.g., 47.5 \(\mu\)s/ft. for limestone).
6. Value varies slightly with salinity, temperature, and pressure; but usually can be taken to be about 189 \(\mu\)s/ft.
7. Estimated from sonic log values through shale sections with little or no organic matter.
8. Formation water resistivities can be calculated from the logs, taken from catalogues of formation water resistivities, taken from DST’s, or determined from the CARBOLOG plot.
9. Read from resistivity log through shale section.
10. Read from sonic log.
11. Read from deep resistivity curve on induction log or equivalent.
12. Estimated from corrected gamma ray log or from neutron-density log.
APPENDIX E
CALIBRATION OF ORGANIC-MATTER PARAMETERS

The three OM parameters used in the Carbolog method are the conversion factor (f), the transit time of the OM (ΔT_{om}) and the density of the OM (δ_{om}). As shown in the main body of this paper, f can be estimated from pyrolysis data. This leaves two variables in the Carbolog equation that can be covaried to give the same result. At this point the values for ΔT_{om} and δ_{om} are not unique, however, the actual values for these parameters can be independently estimated. The following two equations should closely reflect the actual values of ΔT and formation density (δ) recorded by the sonic and density logs, respectively:

1. ΔT = (ΔT_{ma} V_{ma}) + (ΔT_{sh} V_{sh}) + (ΔT_{w} V_{w}) + (ΔT_{om} V_{om}) + (ΔT_{pyr} V_{pyr})
2. δ = (δ_{ma} V_{ma}) + (δ_{sh} V_{sh}) + (δ_{w} V_{w}) + (δ_{om} V_{om}) + (δ_{pyr} V_{pyr})

Values for some of these terms are fixed and known, others are subject to estimation using other log combinations (e.g. V_{sh} and V_{om}), and others are uncertain. Porosity, for example, is generally quite readily calculated using sonic, neutron, and/or density logs; however, in OC-rich rocks porosity will tend be over-estimated as OM effects these logs in the same way as porosity. To eliminate the porosity term, equations 1 and 2 can be rearranged and solved for V_{w} (porosity):

1a. V_{w} = ΔT - ((47.5 V_{ma}) - (55.5 V_{sh}) - (ΔT_{om} V_{om}) - (45 V_{pyr}))/189
2a. V_{w} = δ - ((2.71 V_{ma}) - (2.65 V_{sh}) - (δ_{om} V_{om}) - (5 V_{pyr}))/1.0
These two equations can then be combined to eliminate the $V_w$ (porosity) term and then solved for $V_{ma}$:

$$3. \ V_{ma} = 189 \ (\partial - (2.65 \ V_{sh}) - (\partial_{om} V_{sh}) - (5 \ V_{pyr})) + 1.1 \ ((55.5 \ V_{sh}) - (\Delta T_{om} V_{om}) - (45 \ V_{pyr})) / 459.94$$

Now it is possible to calculate $V_w$:

$$4. \ V_w = 1 - V_{ma} - V_{sh} - V_{sh} - V_{pyr}$$

Values for all volume terms have now been estimated. These values (averages over the entire interval to be calibrated) along with the values for $\partial_{om}$ and $\Delta T_{om}$ (used in the Carbolog equation) are substituted into equations 1 and 2 above. The values for $\Delta T$ and $\partial$ should be close to the average values obtained from the logs themselves. If they are not, values for $\Delta T_{om}$ and $\partial_{om}$ used in the Carbolog method can be adjusted until the log and calculated values more closely match. This produces unique values for both $\partial_{om}$ and $\Delta T_{om}$. If necessary, the value for the formation water resistivity can be changed within the accuracy limits imposed by the method of its calculation.

Definition of terms:

$\Delta T$ = transit time of the formation (read from sonic log),

$\Delta T_{ma}$ = transit time of matrix (47.5 $\mu$s/ft for calcite),

$\Delta T_{sh}$ = transit time of shale (55.5 $\mu$s/ft - an ave. for clay minerals and quartz in the Niobrara?),

$\Delta T_w$ = transit time of water (189 $\mu$s/ft)

$\Delta T_{om}$ = transit time of OM (varies from about 165 to 500 $\mu$s/ft)

$\Delta T_{pyr}$ = transit time of pyrite (about 45 $\mu$s/ft)*
\[ \rho = \text{density of the formation (read from density log)}, \]
\[ \rho_{\text{ma}} = \text{density of matrix (2.71 g/cm}^3 \text{ for calcite)}, \]
\[ \rho_{\text{sh}} = \text{density of shale (2.65 g/cm}^3 \text{ - an ave. for clay minerals and quartz in the Niobrara?)}, \]
\[ \rho_{w} = \text{density of water (1.0 g/cm}^3 \text{)} \]
\[ \rho_{\text{om}} = \text{density of OM (varies from about 1.05 to 1.15 g/cm}^3 \text{)} \]
\[ \rho_{\text{pyr}} = \text{density of pyrite (5.0 g/cm}^3 \text{)} \]

and where

\[ V_{\text{ma}} = \text{volume percentage of matrix in the rock} \]
\[ V_{\text{sh}} = \text{volume percentage of shale (estimated from CGR log or Neutron-Density combination)} \]
\[ V_{w} = \text{volume percentage of water} \]
\[ V_{\text{om}} = \text{volume percentage of OM} \]
\[ V_{\text{pyr}} = \text{volume percentage of pyrite} \]

[*Pyrite is included in the equations above, because it affects the logs in exactly the opposite sense as OM (its conductive and has a short interval transit time). As a practical matter, its effect on calculations of OC-content from logs is limited, as its volumetric abundance is usually very small (0.5-1.5%). It is not considered in the CARBOLOG equations, but it is included in the calibration equations to enhance their accuracy. Its abundance cannot be estimated from well logs, however, there is a strong positive correlation between OC and pyrite. Data from Zelt (1985) indicates that pyrite (wt. %) equals about 0.4 times OC (wt. %). That relationship is used to provide a loose estimate of the possible pyrite in the calibration equations.]*
APPENDIX F
TOC AND ROCK-EVAL DATA

Niobrara

Golden Buckeye #2 Gill Land Co., Weld Co., CO 22-6N-64W

These data are from composite core samples over two foot intervals (see Chapter 3)

All depths are in feet. All samples were analyzed by DGSI, The Woodlands, TX

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### Nebraska Outcrop - Upper Marl, Franklin Co., 8-1N-15W

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Sharon Springs

Sharon Springs samples are all from composite well cuttings over the intervals indicated.

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APPENDIX G
NOTES ON $U_A/OC$ RATIOS vs. SED. RATE CHART

GENERAL NOTES
Sedimentation rates are corrected to a common porosity of 60% (WBD=1.69 g/cm$^3$ on limestone porosity basis). Uranium values are corrected to authigenic uranium values by assuming a 2 ppm uranium value for syngenetic uranium associated with 100% clay, unless otherwise noted.


ANTARCTICA, Kerguelen Plateau; SUBANTARCTICA, SE Indian Ocean; CAPE BASIN-(Recent-Pleistocene). Data are from Rosenthal et al. (1995a). Data are grouped by glacial stages (1-6). Oxic water is present in all locations in recent. Authors suggested that lower oxygenation levels and greater productivity were likely at the subantarctic site during the Pleistocene.


ARABIAN SEA-(PLEISTOCENE). Data are from Sarkar et al. (1993). Authors suggested that near-anoxic conditions prevailed in the deep Arabian Sea in the last glacial stage (Stages 2, 3, and 4). They based this conclusion on geochemical considerations including the high level of U precipitation with no significant change in the sedimentation rate during this period.
BLACK SEA-1, 2, 3.—(Recent). These correspond to Units 1, 2, and 3 of Ross et al. (1970) and Units A, C, and D of Calvert et al. (1987). U/OC data are from Rona and Joensu (1974). U values are reported on a carbonate free basis, but have been converted to a whole-sediment basis by multiplying them by the detrital (carbonate free) to whole-sediment ratio. Sedimentation rates are taken from Calvert et al. (1987). Bottom water is anoxic in recent (unit 1), but probably was not during deposition of earlier units (Calvert et al., 1987).

CALIFORNIA BORDERLAND BASINS: SANTA BARBARA, CATALINA, EAST CORTEZ, AND TANNER.—(Recent). Data are from Kalil (1976). Three ppm is used for the allogenic uranium component to account for Kalil's conclusion that some U is associated with terrestrial OM. O₂ content is below 0.1 ml/l in the deep Santa Barbara basin, higher in other basins.

CALIFORNIA SHELF, (Recent). Data are from Klinkhammer and Palmer (1991). Lower sedimentation rate is authors' estimate for site M (Jahnke et al., 1990) at a depth of 3780 m. High sedimentation rate is value is for site J (Jahnke et al., 1990) at a depth of 790 m in the oxygen minimum zone. (O₂=0.13 ml/l). Sedimentation-rate estimate is upper end of estimates for this area by Schwalbach and Gorsline (1985).

EXMOUTH PLATEAU, NW Australia—(Jurassic). Data are from ODP site 766 (Shipboard Scientific Party, 1990). Uranium content is from gamma-ray spectra log.

GALICIA MARGIN, Portugal—(Upper Cretaceous, Cenomanian-Turonian). Data are from the OC-enriched Cenomanian–Turonian Boundary Event (CTBE) (Shipboard Scientific Party, 1986; Thurov et al., 1988). Sedimentation rate from authors' estimate and consistent with Schlanger et al.'s (1987) estimate of one Ma for the CTBE given the 2.5 meter thickness (Thurov et al., 1988) of the interval in this area.
GULF OF CALIFORNIA BASINS: SAL SI PUEDES, CARMEN, FARALLON, GUAYMAS, AND PESCADERO-(Recent). Data from Kaliil (1976). Kaliil's (1976) sedimentation-rate estimates are based in part on correlation of U-concentration curves from core to core and are roughly tied to the estimates based on 14C analyses of Van Andel (1964), but these estimates are problematical. Estimates for the well studied Guaymas Basin, for example, vary widely from 20 to over 500 cm/ka depending on location (Van Andel, 1964; Calvert, 1966; Soutar et al. 1981; Aubry et al., 1982). Standardization of sedimentation rates was hampered by lack of bulk density/porosity data, though porosities of about 80% are typical for the few few 10's of meters in the Guaymas Basin (Shipboard Scientific Party, 1982). Bottom water oxygenation levels vary with basin depth.

KIMMERIDGE CLAY, North Sea-(Jurassic-Cretaceous). Data are from Miller (1990). Sedimentation rates are mean values from those given. Some may be too low, as they may include depositional hiatuses. Following the author, one ppm is used for the allogenic uranium component. In the past this unit has typically been interpreted as deposited under anoxic conditions (e.g., Miller, 1990), but recent work (Bertrand and Lallier-Vergès, 1993; Tribovillard, 1994) indicates that deposition occurred under more oxic conditions.

MEDITERRANEAN-(Pleistocene). Data are from Mangini and Dominik (1979) on Pleistocene sapropels. Though often cited as deposited in a stratified basin under anoxic conditions, Calvert (1983) has interpreted these as being the result of high productivity.

MONTEREY FORMATION, Santa Maria Basin-(Miocene). Data from several sources. U/OC data from three wells are from Durham (1987) and Leventhal (1989). Data are mostly from a single well (12 of 16 samples) with a sedimentation rate estimate from McCory et al. (1995). Data are also taken from Piper and Isaacs (1995) on Naples Beach (Santa Barbara-Ventura Basin) and Lions Head (Santa Maria Basin) outcrops.
NW ATLANTIC MARGIN, New Jersey-(Miocene). Data are from ODP site 903
(Shipboard Scientific Party, 1994). Uranium values taken from gamma-ray
spectra log.

OMAN-(Pleistocene). Data are from ODP site 723 in an upwelling zone (Shipboard

PACIFIC-CENTRAL-(Recent). U/OC data for deep-sea, red clays are from Baturin
(1973). Sedimentation rate is a mean value for deep-sea clays from Stow and
Piper (1984). Data are not site specific, but relative uniformity of deep sea
sedimentation is assumed. Because red clays include eolian dust, a portion of the
uranium is allogetic, furthermore, some U-enrichment can be due to proximity to
oceanic basalts, particularly near ocean ridges (Stow and Piper, 1984).

PACIFIC-NORTH-(Recent). Data from Klinkhammer and Palmer (1991) for
MANOP site S (Kadko et al., 1981), in a deep water oxic setting. Sediment is a
siliceous ooze.

PERU-(Pleistocene and Miocene). Data are from ODP site 825 (Shipboard Scientific
Party, 1988) below the OMZ (5070m). Uranium data from gamma-ray spectra
log. Sedimentation-rate estimates are subject to error due to slumping and
depositional hiatuses.

PETTAQUAMSCUTT RIVER, Rhode Island-(Recent). Data on this silled estuary
consist of TOC and U data on two cores (1 and 6) from Mo et al. (1973). The
authors report a 15 to 68 cm/ka range in estimated sedimentation rates and use 25
cm/ka for core 1 from the lower basin. The upper end of the sedimentation-rate
range was applied to core 6 from the upper basin as it is close to where the river
enters the estuary. Bottom water is anoxic, but is periodically flushed.

SAANICH INLET, Vancouver-(Recent). Data for this silled fjord are from Anderson
et al. (1989b). U/OC ratio taken from graphic data originally presented by
Kolodny and Kaplan (1973). Bottom water is anoxic with brief seasonal flushing.
## APPENDIX H

### WELLS USED TO ESTIMATE NIOBRARA OC CONTENT

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APPENDIX I
DERIVATION OF PALEOPRODUCTIVITY EQUATION

The Betzer et al. (1984) equation is:

(1) \( OC \text{ flux} = 0.409 \times \text{productivity}^{1.4} \times \text{depth}^{-0.63} \)

where productivity is \( \text{gC/m}^2/\text{a} \)

OC flux (\( OC_f \)) is \( \text{gC/m}^2/\text{a} \)

and depth is in meters

The Henrichs and Reeburgh (1987) equation is:

(2) \( \text{Burial efficiency (BE)} = \frac{\text{LSAR}^{0.4}}{2.1} \)

where \( \text{LSAR} \) is the linear sedimentation rate in \( \text{cm/a} \)

and BE = preserved OC flux (\( OC_{AR} \))/OC flux to bottom = (\( OC_{AR}/OC_f \))

These two equations can be combined and solved for paleoproducivity (PP)
as follows:

Equation 2 is:

(3) \( \text{BE} = \frac{OC_{AR} (\text{gC/m}^2/\text{a})}{OC_f (\text{gC/m}^2/\text{a})} = \frac{\text{LSAR (cm/a)^0.4}}{2.1} \)

Substituting (1) for \( OC_f \):

(4) \( \frac{OC_{AR} (\text{gC/m}^2/\text{a})}{(0.409 \times \text{PP} (\text{gC/m}^2/\text{a})^{1.4} \times \text{depth(m)}^{-0.63})} = \frac{\text{LSAR (cm/a)^0.4}}{2.1} \)

and rearranging:

(5) \( \text{PP (gC/m}^2/\text{a}) = \left(\frac{(5.13 \times OC_{AR} (\text{gC/m}^2/\text{a}) \times \text{depth (m)}^{-0.63}) \times \text{LSAR (cm/a)^0.4}}{2.1}\right)^{0.71} \)

As \( OC_{ARs} \) are generally reported in \( \text{gC/cm}^2/\text{ka} \) and \( \text{LSARs} \) in \( \text{(cm/ka)} \),
the equation is written:

\( \text{PP} = \left(\frac{(51.3 \times OC_{AR} (\text{gC/cm}^2/\text{ka}) \times (\text{LSAR (cm}^2/\text{ka}) \times 0.001)^{0.4} \times \text{depth}^{-0.63}}{2.1}\right)^{0.71} \)
### APPENDIX J

**WELLS USED TO ESTIMATE SHARON SPRINGS OC CONTENT**

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<td>18 Exxon Co. U.S.A. #1 Iler Olsen</td>
<td>SE NW</td>
<td>8-19N-55W</td>
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<tr>
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<td>NW SW</td>
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<td>NW NE</td>
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<td>21 Amoco Prod. Co. #1 Pueppka</td>
<td>C SW SE</td>
<td>18-18N-35W</td>
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<td>22 Sohio Petroleum Co. #19-16 Trout</td>
<td>SE SE</td>
<td>19-8N-35W</td>
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<td>C SW NE</td>
<td>34-35N-24W</td>
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<td>24 H.L. Hunt #1 Synder</td>
<td>NE NE</td>
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<td></td>
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<td>25 Buckhorn Petroleum #1-22 Bennett</td>
<td>NE NE</td>
<td>12-98N-73W</td>
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