Regional stratigraphy, elemental chemostratigraphy, and organic richness of the Niobrara Member of the Mancos Shale, Piceance Basin, Colorado

Aya El Attar and Matthew J. Pranter

ABSTRACT

The elemental chemostratigraphy of the Upper Cretaceous Niobrara Member of the Mancos Shale shows that six chemostratigraphic zones can be identified in the Piceance Basin, Colorado, based on geochemical data. Chemostratigraphic correlations of nine wells spaced 20 mi (~32 km) apart closely match lithostratigraphic correlations made using gamma-ray and deep-resistivity wireline logs. Lithologic interpretations made from wireline logs indicate that the Niobrara Member and equivalent strata consist primarily of interbedded calcareous shale and shaley limestone facies that increase in thickness to the northwest in the basin. The geochemical data suggest that during deposition of the Niobrara Member, anoxia and calcium enrichment increased to the east of the basin, whereas terrestrial input and clay enrichment increased to the northwest. Element crossplots suggest that a large part of the silicon is detrital and that the Niobrara Member becomes an increasingly more clastic than carbonate system to the west and northwest.

The Δlog R–derived total organic carbon (TOC) calculated using a sonic-resistivity overlay analysis technique shows that the Niobrara Member comprises organic-rich and organic-poor deposits. Average TOC values range between 1 wt. % (in organic-poor deposits) and 2.37 wt. % (in organic-rich deposits), with higher TOC values recorded in the southern and eastern parts of the basin. Relative-rock brittleness estimates from element and TOC data show the stratigraphic variability of alternating ductile (TOC rich, Ca and Si/Al poor) and brittle (TOC poor, Ca and Si/Al rich) intervals for the Niobrara Member.

ACKNOWLEDGMENTS

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INTRODUCTION

The Upper Cretaceous Niobrara Formation and its stratigraphic equivalents (e.g., Niobrara Member of the Mancos Shale) produce both oil and gas in the Rocky Mountain region. Hydrocarbon production from chalks, marls, and marine shales of the Niobrara Formation and correlative parts of the Mancos Shale occurs in the Powder River, Denver, North Park, Sand Wash, San Juan, and Piceance basins. In 2009, the success of the horizontally drilled EOG Resources 2-01H Jake discovery well marked the beginning of an ongoing exploitation of these low-permeability oil reservoirs in the Denver Basin in northeastern Colorado (Durham, 2012). In 2012, the WPX Energy 701-4 HN1 Williams GM discovery well produced at an initial rate of 16 million ft³ (4.53 × 10⁵ m³) of gas per day choked back substantially (to restrict flow) (Durham, 2013), suggesting that the Niobrara Member gas play has the potential to be economically viable in the Piceance Basin in northwestern Colorado. Unconventional shale gas resource plays are self-sourced systems, having generally low matrix permeability and continuous accumulations of biogenic or thermogenic gas.

The Niobrara Formation and equivalent rocks in Colorado have been studied by several authors (e.g., Kauffman, 1977; Clayton and Swetland, 1980; Rice, 1984a, b; Barlow and Kauffman, 1985; Pollastro and Martinez, 1985; Precht and Pollastro, 1985; Molenaar and Wilson, 1990; Nuccio and Barker, 1990; Kauffman and Caldwell, 1993). However, published accounts detailing the hydrocarbon source-rock potential of the Niobrara Member and equivalent parts of the Mancos Shale are sparse, especially in northwestern Colorado (e.g., Vincelette and Foster, 1992; Longman et al., 1998; Landon et al., 2001; Fisher, 2007; Kuzniak, 2009; Rogers, 2012). Longman et al. (1998) showed that the organic-rich marine shales provide the main hydrocarbon source rocks of the Niobrara Member, and Vincelette and Foster (1992) tied major hydrocarbon production from the Niobrara Member in northwestern Colorado to the presence of post-Laramide fracturing in the calcareous shales and marls. A comprehensive understanding of the stratigraphic and geographic relationships, as well as the origin and distribution of lithologies of source and reservoir rocks within the Niobrara, is essential for providing a framework for predicting the occurrence and distribution of hydrocarbon accumulations.

Seismic and petrophysical data are commonly used to develop lithostratigraphic and seismic stratigraphic frameworks. These data allow interwell correlations to be made; however, they sometimes lack the necessary resolution for detailed stratigraphic analysis (Pearce et al., 2005). The fine-grained, organic-rich, and seemingly homogenous nature of shale sequences has stimulated the search for new techniques that allow an improved understanding of reservoir stratigraphy. Consequently, chemical
Figure 1. Map of Piceance Basin showing Mancos Shale outcrops, major Mancos Shale oil and gas fields, and wells used for this study. The x-ray fluorescence (XRF) analyzed cuttings from wells labeled A through I are listed in Table 1. Wells labeled 1–6 are listed in Table 3 and have measured total organic carbon (TOC) values from cuttings and calculated TOC values based on well logs (Δlog R-derived TOC). Modified from Hoak and Klawitter (1997) and Pranter et al. (2009). Mancos Shale oil and gas fields are from Kirschbaum (2003). Hwy. = highway.
data and chemical stratigraphy (or chemostratigraphy) have become useful aids for stratigraphic correlation. Chemostratigraphic zonation relies upon the characterization of a sedimentary interval in terms of its major- and trace-element concentrations, whereas chemostratigraphic correlations refer to the extension of this characterization from one wellbore section to another (Ratcliffe et al., 2007; Pearce et al., 2008). To date, several authors have tested and reported the applicability of this technique in frontier and mature basins across the world (e.g., Ehrenberg and Siring, 1992; Racey et al., 1995; Pearce et al., 1999, 2005; Ratcliffe et al., 2004, 2007; Rowe et al., 2009; Wright and Ratcliffe, 2010; Wright et al., 2010). For example, Pearce et al. (2008) showed how a blind test of chemostratigraphic correlations compared well with lithofacies correlations made from outcrop-measured sections of the Green River Formation, whereas Wright and Ratcliffe (2010) used chemostratigraphy as a means to infer bulk mineralogy and to model organic content using the Haynesville and Eagle Ford Formations’ shale gas plays as case studies.

In this study, an approach to chemostratigraphy is used for stratigraphic correlation of the Niobrara Member interval in the Piceance Basin. A subsurface lithostratigraphic framework was established using gamma-ray and deep-induction resistivity logs from 251 wells. After identifying key surfaces and correlating mappable intervals within the Niobrara Member, subdivisions were compared with previous work on the lower Mancos Shale on the Douglas Creek arch (Fisher, 2007; Kuzniak, 2009) and in the Piceance Basin (Rogers, 2012), as well as with the study by Vincelette and Foster (1992) in northwestern Colorado. Elemental data were acquired from a total of 960 drill-cutting samples (total footage of 15,430 ft [4,703 m]) from nine wells across the basin using the Thermo Scientific Niton® XL3t 950 x-ray fluorescence (XRF) portable handheld analyzer (Figure 1; Table 1). Direct measurements and analysis of cores of the Niobrara Member in the Piceance Basin were not possible because of the lack of publicly available cores. The handheld XRF has been shown to generate elemental data that are replicable using more conventional techniques, such as inductively coupled plasma mass spectrometry, wavelength dispersive XRF, and inductively coupled plasma optical emission spectrometry (Rowe et al., 2012). Additionally, workers have successfully built chemostratigraphic profiles using handheld XRF from core, outcrop, and cuttings analyses (Nance and Rowe, 2015; Turner et al., 2015). Average well spacing is approximately 20 mi (~32 km), and vertical sample spacing is 10, 20, or 30 ft (~3, 6, or 9 m). The geochemical data allowed

### Table 1. Well Name, API Number, Operator, and Geographic Location for the Nine Wells Labeled A through I in Figure 1 (Wells of X-Ray Fluorescence Analyzed Cuttings)

<table>
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<th>Section</th>
<th>Township</th>
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the subdivision of the Niobrara Member into chemostratigraphic zones based on changes in elemental composition. Interwell correlations were made, and by generating element maps for each unit, stratigraphic and lateral changes of key elements were investigated.

In addition to the Niobrara Member chemostratigraphy, this study uses a petrophysical approach to evaluate the stratigraphic variation and lateral distribution of organic-rich intervals within the Niobrara Member. Total organic carbon (TOC) describes the organic matter concentration (in wt. % of organic carbon) in sedimentary rocks and is used to assess the quality of hydrocarbon source rocks. The Δlog R technique (Passey et al., 1990), a porosity-resistivity overlay analysis, was applied in this study to identify organic-rich intervals and calculate TOC in 68 wells. The technique yields profiles of TOC at the combined resolution of the logging tools of approximately 3 ft (1 m) (Passey et al., 1990). Profiles produced by this method were used to evaluate the stratigraphic changes of source-rock richness, and data of this resolution have not been previously reported for the Niobrara Member of the Mancos Shale interval in this area.

Together, the chemostratigraphic and petrophysical techniques allow a better understanding of the source- and reservoir-rock potential of the Niobrara Member. The results of this study establish a database from which correlations can be made for the Niobrara Member in the Piceance Basin. Additionally, implications of the changes in elemental composition and organic richness are investigated; changes in the depositional environment (e.g., oxygenation level and terrestrial input) of the Niobrara Member are interpreted; and a qualitative approach to interpreting relative changes in rock brittleness, which would aid in assessing variations in potential reservoir quality, is discussed. Moreover, this study provides direction and insight for further chemostratigraphic study and petrophysical interpretations of this interval.

**TECTONIC AND STRATIGRAPHIC SETTING**

**Geologic History**

During the Late Cretaceous, an epeiric seaway, the Western Interior seaway, covered the central part of North America from the Gulf of Mexico to northern Canada (Kauffman, 1977; Kauffman and Caldwell, 1993). The seaway inundated an asymmetric foreland basin, the Western Interior Basin, which resulted in the deposition of widespread marine sediments (Figure 2) (Longman et al., 1998). The process of mountain building from the tectonically active Sevier orogenic belt to the west supplied coarse siliciclastic sediments to the western part of the

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Figure 2. Cross section of Cretaceous strata deposited in eastern Utah and western Colorado. Niobrara Member of Mancos Shale study interval is shown with red bar. From Cole and Pranter (2008), modified from Dyman et al. (1994). Cen. = Cenomanian; CO = Colorado; Con. = Coniacian; Cr. = creek; Equiv. = equivalent; Fk. = fork; Fm. = formation; Ls. = limestone; Mbr. = member; Riv. = river; Sh. = shale; Ss. = sandstone; Tng. = tongue; UT = Utah.
seaway. Eastward-flowing currents transported finer-grained siliciclastic silts and muds onto the low relief eastern part of the seaway (Longman et al., 1998; Finn and Johnson, 2005). Across the western part of the foreland basin, a “complex pattern of intertonguing marine and nonmarine” sediments was deposited (Finn and Johnson, 2005, p. 3). Westward-thinning tongues of marine shale and siltstone characterize the marine deposits, whereas eastward-thinning clastic wedges of sandstone, siltstone, shale, and coal are representative of the non-marine deposits (Figure 2) (Dyman et al., 1994; Finn and Johnson, 2005; Cole and Pranter, 2008). On the eastern shelf of the seaway, where the influx of siliciclastic sediments was restricted and conditions were favorable for carbonate deposition, a variety of carbonate sediments (many rich in coccolith debris and planktonic foraminifers) accumulated (Roberts and Kirschbaum, 1995; Longman et al., 1998; Finn and Johnson, 2005). The Niobrara Formation (as named in the eastern part of the seaway), which is part of a sequence of “thick Upper Cretaceous marine shales that blanket the entire Western Interior of North America” (Johnson, 2003, p. 6) was deposited during a time of major marine transgression.

During the Laramide orogeny, a period of mountain building in western North America that started in the Late Cretaceous (ca. 70 Ma) and ended in the Eocene (ca. 55 to 40 Ma), a series of north-trending uplifts and intermontane structural basins formed. In the United States, these basins occur primarily in the central Rocky Mountains from Colorado and Utah to Montana. The area presently occupied by the Piceance Basin was partitioned during Laramide tectonism from the larger preexisting Western Interior foreland basin (Willis, 1999; Johnson and Flores, 2003; DeCelles, 2004).

The Piceance Basin is a highly asymmetrical northwest-trending structural depression located entirely in northwestern Colorado and is part of the Colorado Plateau physiographic province. The basin is bounded by the Rangely anticline and Axial arch to the north; the Grand Hogback monocline to the east; the Gunnison uplift, the Elk Mountains, and the Sawatch uplift to the south and southeast; the Uncompahgre uplift to the southwest; and the Douglas Creek arch to the west (Figure 1) (Johnson, 1989).

Review of Niobrara Stratigraphy and Lithology

The Niobrara Formation was first described by Meek and Hayden (1861) for exposures near the mouth of the Niobrara River in Nebraska. Longman et al. (1998) thoroughly reviewed the various published descriptions of the Niobrara stratigraphy in the Western Interior seaway of the Rocky Mountain region. In the eastern part of the seaway, the Niobrara Formation is formally divided into two members: the lower Fort Hays Limestone Member and the overlying Smoky Hill Member (e.g., in Kansas and in the Denver Basin in eastern Colorado) (Landon et al., 2001). These stratigraphic intervals were correlated northward and westward from the Denver Basin. In the western part of the seaway (that includes the Piceance Basin), stratigraphic correlations become difficult “due to the disappearance of distinctive log markers and the relatively uniform log character in the thick shaly section of the Mancos” (Longman et al., 1998, p. 138).

In the westernmost part of the Piceance Basin, primarily at Rangely, production from fractured Cretaceous shales has been referred to as Mancos production (Vincelette and Foster, 1992). However, log correlations indicate that most of this production is from the “lower third of the Mancos, which is the Niobrara Formation equivalent and has a lithology typical of the Niobrara Formation in areas farther east” (Vincelette and Foster, 1992, p. 233). In the southern Piceance Basin, the Niobrara Member is underlain by the Montezuma Valley and Juana Lopez Members of the Mancos Shale (Figure 3). This nomenclature conforms with usage by Merewether et al. (2006), Ball et al. (2009), and E. R. Gustason (2013, personal communication). Over the extent of the basin, a consistent and distinctive well-log marker below the Niobrara Member corresponds to the Juana Lopez Member of the Mancos Shale. The Niobrara Member is overlain by the Prairie Canyon Member (Cole et al., 1997). To the west of the Piceance Basin, the Niobrara Member is likely equivalent to the Blue Gate Shale (Johnson, 2003; Rogers, 2012). The Niobrara Member is considered to be Coniacian to Campanian in age (Scott and Cobban, 1964), and Ball et al. (2009) show that the base of the formation corresponds to the inoceramid biozone of Cremnoceramus erectus.
The Niobrara Formation and stratigraphically equivalent strata contain a spectrum of lithologies ranging from limestone and chalks to marls and less calcareous shales (Longman et al., 1998). In the eastern part of the seaway, typical Niobrara Formation lithologies are chalks and limestone (Finn and Johnson, 2005). A gradual westward decrease in chalk and other carbonate components characterizes the lithology variation of the Niobrara Formation as it grades into the Niobrara Member of the Mancos Shale (Longman et al., 1998). This is considered to be the result of a closer proximity to the Sevier thrust belt to the west, which constitutes the primary detrital source (Longman et al., 1998). In the western part of the seaway that includes the study area, a typical Niobrara Member calcareous (limestone and chalk) facies grades laterally into calcareous shale (marl) and weakly into noncalcareous shale of the Mancos Shale. However, “the limits of the calcareous facies of the Niobrara [Formation] are not well mapped” (Finn and Johnson, 2005, p. 6).

**METHODOLOGY**

**Chemostratigraphic Analysis**

Whole-rock elemental data were acquired using a Thermo Scientific Niton® XL3t 950 XRF portable handheld analyzer for 40 elements: 8 major elements (Al, Si, Ti, Fe, Mn, Ca, Mg, and K) and 32 minor and trace elements (Ag, As, Au, Ba, Bi, Cd, Cl, Co, Cr, Cs, Cu, Hg, Mo, Nb, Ni, P, Pb, Pd, Pb, S, Sb, Sc, Se, Sn, Sr, Te, Th, U, V, W, Zn, and Zr). For the mining analysis mode (used to detect metals), counting times were 30 sec each on the low- and main-energy filters and 45 sec on the light-filter setting (105 sec total counting time); for the soils analysis mode (used to detect elements typically associated with soils), counting times were 45, 35, and 30 sec respectively on the low-, main-, and high-filter settings (110 sec total counting time). Elements Ti to U were analyzed using the low-, main-, and high-filter settings, and the light-filter setting was used to analyze Mg to S. Measurements in the mining mode were recorded in weight percent, and those in the soils mode were recorded in parts per million. Calibration of the handheld analyzer was performed in house at Niton using a proprietary patented algorithm. Repeated analyses on reference standard samples with known elemental composition (obtained by Niton) were performed for accuracy and resulted in correlations with $R^2$ greater than 0.90.

**Total Organic Carbon and ∆Log R Technique**

Several well-log techniques have been developed for identifying and calculating the TOC of subsurface strata. The method termed “∆log $R$” of Passey et al. (1990) uses the well-log curve separation resulting from the overlay of properly scaled porosity and resistivity logs to determine TOC. When plotted on the same log track, the porosity and resistivity curves parallel each other and can be overlain in a nonsource rock. For hydrocarbon-bearing (reservoir) or organic-rich nonreservoir intervals, a separation between the two curves, ∆log $R$, occurs. A gamma-ray log can be used to differentiate between lithologies and to
eliminate reservoir sections from the analysis. In an immature source rock, the \( \Delta \log R \) separation is primarily caused by the porosity curve responding to the low-density organic matter. However, in a mature source rock, the separation results from the additional response of the resistivity log to the presence of hydrocarbons (Passey et al., 1990) (Figure 4). Three curves (sonic, bulk density, and neutron porosity) produce a response that can mimic an increase in porosity, but the use of a sonic-resistivity combination is recommended, because it is shown to be more accurate than the density-resistivity and neutron-resistivity combinations (Passey et al., 1990).

The TOC content in mature source rocks is calculated using the \( \Delta \log R \) separation (measured in logarithmic resistivity cycles) and by applying the maturity factor level of organic metamorphism (LOM). Two empirical equations are used to quantify TOC:

\[
\Delta \log R = \log_{10}(R/R_{\text{baseline}}) + 0.02 \times (\Delta t - \Delta t_{\text{baseline}}) \tag{1}
\]

\[
\text{TOC} = (\Delta \log R) \times 10^{(2.297 - 0.1688 \times \text{LOM})} \tag{2}
\]

The variable \( R \) is the measured deep resistivity value in ohm meters, and \( \Delta t \) is the measured transit time in microseconds per foot. The variables \( R_{\text{baseline}} \) and \( \Delta t_{\text{baseline}} \) are the respective resistivity and transit-time values when the curves are overlain (baselined) in a nonsource rock.

Differential transit time, or sonic, and deep-induction resistivity logs were used (as recommended by Passey et al., 1990) to solve for TOC in 68 wells (Figure 1).

The first step in applying the \( \Delta \log R \) technique is to adjust the sonic and resistivity logs such that their relative scaling is \(-100 \, \mu \text{s/ft} (-328 \, \mu \text{s/m})\) per two logarithmic resistivity cycles. The two curves are then overlain and baselined over a fine-grained, nonsource interval. A baseline condition is identified when the two log profiles directly track each other over a considerable depth range (e.g., 400 ft [122 m]) (Passey et al., 1990). Once the baseline is established, organic-rich zones are identified by (1) the separation and (2) nonparallelism of the two curves (Figure 4). A TOC profile is then constructed, first by quantifying the \( \Delta \log R \) separation (equation 1) and then by calculating the TOC (equation 2) when the maturity factor (LOM) is determined.

The thermal maturity indicator LOM “describes how far the thermal metamorphism of sedimented organic matter has progressed during subsurface burial” (Hood et al., 1975, p. 986). It is a linear scale used for numerically correlating different indicators of organic metamorphism, such as coal rank, carbonization of structured organic matter, and vitrinite reflectance (\%R\text{\textsubscript{o}}).

Thermal maturity data used in this study are from average \%R\text{\textsubscript{o}} values (\( N = 81 \) samples from 18 wells, at sample frequencies ranging between <100 ft [<31 m] and 970 ft [296 m]) for the Niobrara Member interval converted to LOM using a rearranged Leclaire and Hursan’s (2010) formula (Cardneaux, 2012). To determine LOM values at each well to use for TOC calculations, known LOM values from 18 wells were used to map the LOM distribution across the study area and assign values for wells at which no published maturity data were available.

In addition, because baselining the transit-time and resistivity curves considers the baselined interval as zero TOC, background TOC must be added back to the TOC calculated from equation 2 (Passey et al., 1990). The average TOC in shales worldwide generally exceeds 0.8 wt. % (Tissot and Welte, 1984),
and 1 wt. % TOC is used in this study to account for
this background TOC. Because the Δlog R technique
can yield high anomalous Δlog R separation values
(not related to an increase in both resistivity and sonic
values), a resistivity-sonic log crossplot was used to
qualitatively eliminate potentially anomalous TOC
from the analysis and account for sections that cause a
separation resulting from an increase in both the
porosity and resistivity values. By using a lower TOC
cutoff value of 1 wt. %, only TOC values associated
with both high resistivity and high sonic values are
kept in the analysis (M. Connolly, 2013, personal
communication). Data points that are interpreted not
to cause the proper Δlog R separation are therefore
removed from the analysis by setting lower values of
ILD (=10 ohm m) and Δt (=80 μs/ft [262 μs/m]). To
declare intervals based on these selected cutoffs,
TOC flags are used, and only those intervals that have
ILD and Δt values higher than the cutoff values are
considered to yield “real” TOC values. The remaining
intervals are considered to only have a background
TOC of 1 wt. % (M. Connolly, 2013, personal commu-
ication). Figure 5 provides an example of the applica-
tion of the Δlog R technique for the PRE Resources
2-20 South Baxter Pass Unit well in Garfield County,
Colorado.

SUBSURFACE STRATIGRAPHY

The subsurface stratigraphy of the Niobrara Member
of the Mancos Shale in northwestern Colorado has
been previously described by Vincelette and Foster
(1992), Longman et al. (1998), Fisher (2007), Kuzniak
(2009), and Rogers (2012), although subdivisions of
the Niobrara Member in the Piceance Basin remain
as informal nomenclature. In this study, eight litho-
stratigraphic units are defined and correlated across
much of the basin, based on changes in gamma-ray
and deep-resistivity logs (Figure 6). These units are
termed from the base to the top (oldest to youngest)
of the Niobrara Member as Niobrara 1 to 8. The
Niobrara Member ranges in thickness between less
than 750 ft (228.6 m) in the southeast to more than
1700 ft (518.16 m) in the northwest of the Piceance
Basin. In general, all Niobrara Member lithostrato-
graphic units thicken to the northwest (Figure 7).

The base of the Niobrara Member as defined in
this study is a laterally consistent surface across the
Piceance Basin that marks a shift on the gamma-ray
curve with higher values recorded in the under-
lying units, reflecting a change in lithology from
shale-dominated deposits (below) to carbonate-
enriched deposits (above). Where the gamma-ray
character change was less readily identifiable, the
base of the Niobrara Member was picked at an
increase in deep resistivity values (from lower values
below to higher values above). Within the Niobrara
Member, the key surfaces (“markers”) that were used
for stratigraphic correlation correspond to sharp
shifts on the gamma-ray curve, from lower values
below to higher values above. The character of the
gamma-ray log was more extensively used for cor-
relating key surfaces, whereas the deep-resistivity
log proved less helpful over large areal extents. All
stratigraphic markers are generally consistent across
the study area, although log characters of the tops
of lithostratigraphic units Niobrara 1, Niobrara 3,
and Niobrara 7 appear to be more readily identi-
fiable across the entire study area. The “Niobrara
hot shale” marker (top of Niobrara 7) is regionally
very consistent and was used to identify the Niobrara
Member within the lower Mancos Shale, and the high
gamma-ray values recorded at this surface can be
attributed to the presence of a regionally organic-
rich interval. The top of the Niobrara Member is
picked in this study at the first decrease of a highly
resistive marker, which is interpreted to correspond
to the top of the calcareous lithology (Haskett, 1959;
Vincelette and Foster, 1992; Finn and Johnson, 2005;
Rogers, 2012).

Based on interpretations made from well-log
characteristics, all units appear to be similar in
terms of lithologic composition (noncalcareous, cal-
careous, and very calcareous shale), varying pri-
marily in shale and carbonate content and organic
richness.

ELEMENTAL CHEMOSTRATIGRAPHY

Chemostratigraphic Zonation

Chemostratigraphic zonation is defined as the sub-
division of sedimentary intervals based on changes in
inorganic geochemical composition (Ratcliffe et al.,
2004; Pearce et al., 2005; Rowe et al., 2009). In this
study, abundance profiles (or geochemical logs) of
**Figure 5.** The $\Delta \log R$ technique (Passey et al., 1990) applied to PRE Resources 2-20 South Baxter Pass Unit (API no. 05-045-05112) well in western Garfield county (see Figure 1 for well location). The first log track shows the overlay of the sonic and the resistivity logs. The logs are properly scaled and baselined over a nonsource interval. A part of the interval over which the baseline was established is shown with a black bar in the first track. The gray filling highlights the $(\Delta \log R)$ separation between the two curves. The second log track shows the $\Delta \log R$ curve. The third and fourth log tracks show the initial total organic carbon (TOC) and the TOC + 1 curves, respectively, as they both compare with TOC data points (from US Geological Survey Core Library data files). The TOC flag log track highlights intervals over which the $\Delta \log R$ separation is likely resulting from the increase in both the measured transit time ($\Delta t$) and the deep induction log (resistivity) curve (ILD) values. The final TOC curve is the curve yielded after potentially anomalous TOC is removed from the analysis. Mbr. = member.

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<td>5</td>
<td>0</td>
<td>Final TOC</td>
</tr>
<tr>
<td>(ILD)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ILD)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Delta t$: Measured transit time (usec/ft)
ILD: Deep Induction Log (resistivity) curve
DLGR: $\Delta \log R$ curve calculated from equation (1)
TOCi: Initial TOC calculated from equation (2)
TOC-1: TOC curve yielded after adding 1 wt.% to TOCi
Final TOC: Final TOC curve yielded after qualitatively eliminating anomalous TOC from the analysis.
Figure 6. Type log for the Niobrara Member in the Piceance Basin. Eight lithostratigraphic units are identified. Location of well is shown in Figure 1 (labeled C). $\Delta t$ = measured transit time ($\mu$s/ft); GR = gamma ray; ILD = deep-induction resistivity; PEF = photoelectric factor.
elemental data are plotted versus depth. Elemental data are expressed as absolute concentrations (ppm or wt. %) or as a ratio of one element to another. Analytical data from the ratio plots highlight compositional changes associated with mineralogy (Pearce et al., 2008), and normalizing the data against Al values compensates for changes in geochemistry that can be attributed to grain-sized variations (Pearce et al., 2008). The subdivision of a sedimentary interval into chemostratigraphic zones was established on the basis of the changing morphology (log motifs) of the geochemical logs.

Figure 7. Cross sections (A) AA' and (B) BB' flattened on top of the “Niobrara hot shale” marker. Spacing between wells is equal and not representative of actual distances. Numbers at log tops correspond to well API numbers. Mbr. = member.
Figure 7. Continued.
The XRF data were acquired for 40 elements from well cuttings. However, many element concentrations fell below the quantification limits of the instrument (Ag, Au, Bi, Cd, Cl, Co, Hg, Mg, Nb, Ni, Pb, Pd, Sb, Se, Sn, U, and W), and only certain detected elements (with measurement error < 20%) were used to develop geochemical fingerprints for each zone. These elements, referred to as chemostratigraphic index elements, are selected on the basis of their systematic variation as they relate to stratigraphy. From well data, distinctive trends can be recognized, because changes in elemental composition with depth are directly related to stratigraphy (Ratcliffe et al., 2007).

The Black Hills Plateau Production 1-15 Kathryn Young well (sec. 15 T10S R95W; having cuttings sampling interval of 10 ft [3 m] over complete Niobrara Member) is used as the chemostratigraphic reference well for the Niobrara Member in the Piceance Basin. Key geochemical profiles of 10 index elements and element ratios were used to independently define 6 chemostratigraphic zones within the Niobrara Member interval (Figure 8). The chemostratigraphic zones are designated stratigraphically upward as CN1 to CN6. Representative elements and element ratios used for geochemical zonation are Ca, Si, Si/Al, Al, Fe, K/Al, Mo, Cr + V, Ti, and Zr.

Overall, four calcium-enriched zones are identified (CN1, CN2, CN4, and CN6) (Figure 8). In general, Ca and Si geochemical logs show opposite trends, and this observation is most apparent in well A (Figure 1). The Si, Al, Fe, Ti, and Zr logs generally track each other, although some exceptions exist locally. Similarly, curves of Si/Al and K/Al closely track each other.

Chemostratigraphic zone CN1 is the first calcium-enriched zone and begins with high values of Ca (up to 12 wt. % in well A) that gradually decrease upward. The base of this zone (base of Niobrara Member) is marked by higher Si/Al and K/Al values. Overall, curves of Si/Al and K/Al show an increasing-upward trend, whereas values of Si, Fe, Mo, Cr + V, Ti, and Zr slightly increase upward. The Al values remain relatively constant in most wells. The top of this zone is characterized by an abrupt decrease in Si and Ti values and an increase in Si/Al and K/Al values.

Chemostratigraphic zone CN2 is the second calcium-enriched zone. Overall, values of Si/Al and K/Al slightly increase upward, and this change is most pronounced in well E. Values of Fe slightly decrease upward, whereas curves of Ti and Zr show an increase in the lower half of this zone followed by lower values. Within zones CN1 and CN2, values of Mo and Cr + V are among the lowest across the Niobrara Member. The top of this zone is defined by lower Si/Al, K/Al, and Fe values and higher Al values.

Chemostratigraphic zone CN3 is characterized by lower Ca values. The Si, Ti, Fe, and Zr log curves show similar, slightly upward-decreasing trends in five wells (wells B, E, G, H, and I) and a constant trend in wells A, C, and F. The Si/Al and K/Al curves show a slight decrease in most wells, with exceptions occurring within two wells (wells G and H). Within this interval, Mo and Cr + V curves display laterally persistent peaks of higher values. In most wells, the top of this zone is defined by an increase in Ca, Si, and Al values and a decrease in ratios Si/Al and K/Al.

Chemostratigraphic zone CN4 is the third calcium-enriched zone, with its base defined by a shift to higher Ca, Si/Al, Mo, and Cr + V values. Overall, Ca values gradually increase upward, although local constant trends are noted (e.g., wells B and H). Curves of Si/Al, K/Al, Mo, and Cr + V show an upward-increasing trend, with exceptions occurring in wells A, F, and I that show and upward decrease in Cr + V values. The Al and Zr values appear to decrease over this interval, whereas Fe and Ti curves show a uniform character. The top of this zone is characterized by a decrease in Si/Al and K/Al and an increase in Fe and Al values.

Chemostratigraphic zone CN5 is one of the most geochemically distinctive zones within the study interval, displaying pronounced changes in log character. Overall, this interval has lower Ca values than the underlying zone. The Si, Al, Mo, Cr + V, and Ti values increase upward within most wells, whereas ratios Si/Al and K/Al decrease upward. The Zr and Fe values show a slightly upward-increasing trend. The top of this zone is characterized by a shift to higher Si/Al and K/Al values.

Chemostratigraphic zone CN6 is the fourth calcium-enriched zone. Zone CN6, along with zone CN5, is an easily identifiable geochemical zone across the nine wells, with its top (corresponding to the top of the Niobrara Member) defined by a marked decrease in Ca values. In general, Si/Al and K/Al decrease upward, whereas Al and Fe values slightly increase upward in most wells. The Zr and Ti values slightly decrease upward, although some constant trends are noted locally. Zone CN6 displays the highest Mo values...
Figure 8. Geochemical profiles for chemostratigraphic reference well Black Hills Plateau Production 1-15 Kathlyn Young (sec. 15 T10S R95W) as correlated to gamma-ray (GR) and deep-induction resistivity (ILD) logs from nearby well Black Hills Plateau Production 1-5 Swetland (sec. 5 T11S R95W). Six chemostratigraphic zones (CN1 to CN6) are identified from the geochemical logs. Well locations are shown in Figure 1. Al = aluminum; Cr+V = chromium + vanadium; Fe = iron; K = potassium; Mbr. = member; Mo = molybdenum; Si = silicon; Ti = titanium; Zr = zirconium.
recorded from the study interval, with Mo curves showing a slight decrease at the upper half of the zone.

Chemostratigraphic Correlations

The correlation of the six chemostratigraphic zones between wells was accomplished through the visual identification of significant trends. Although several compositional changes are consistent between the nine wells, many trends are not recognized within all wells, particularly when using lower-resolution datasets (e.g., 30-ft [9-m] sampling interval). To the north, interwell correlations are more difficult, and chemostratigraphic zones are more poorly defined, with the geochemical differences between wells becoming more marked. Important geochemical differences that were recognized between wells are significant changes in Ca content; although four Ca-enriched zones are identified to the south and to the east of the study area, these defined cycles of Carenrichment are not laterally continuous features, suggesting that they are localized trends. Curves of Si/Al and K/Al appear to have the most laterally consistent trends and were the most useful in identifying correlative features over large distances.

In siliciclastic sequences, the primary control on whole-rock geochemistry is lithology (Ratcliffe et al., 2007), and lateral changes of geochemical features can be attributed to (1) changes in detrital mineralogy and provenance composition, (2) changes in depositional environment and facies, and (3) diagenesis (Pearce et al., 2005).

Comparisons of chemostratigraphic and lithostratigraphic correlations show that four marker horizons identified on the geochemical logs correspond to marker beds picked using gamma-ray and resistivity logs (Figures 6, 8). The tops of chemostratigraphic zones CN1, CN2, CN3, and CN5 closely match the tops of lithostratigraphic units Niobrara 1, Niobrara 3, Niobrara 4, and Niobrara 6, respectively. Discrepancies involve the tops of chemostratigraphic zones CN2 and CN3 that were picked below the tops of Niobrara 3 and 4 within two wells (E and G wells) and the top of CN5 that was picked above Niobrara 6 within well H. These discrepancies may be accounted for by the relatively lower resolution sampling intervals.

Lateral Variation of Elements

Average values of element concentrations and element ratios vary laterally for the six chemostratigraphic zones of the Niobrara Member. Limited data toward the east–central part of the basin make the constructed element contour maps less reliable over this area where no well control exists (Figures 9–12). Average Ca maps (Figure 9) indicate that Ca enrichment increased eastward, with the lowest values observed to the north and west. Chemostratigraphic zones CN1 and CN4 display the most dramatic lateral changes of average Ca concentrations, whereas CN6 exhibits the highest degree of homogeneity of Ca enrichment. Similarly, average Mo maps (Figure 10) show a consistent gradual enrichment eastward, with chemostratigraphic zones CN4, CN5, and CN6 recording the highest Mo values. The Cr + V maps also show an eastward trend. Average Al (Figure 11), Si, and Ti + K maps display similar trends, with values of Si and Ti + K significantly increasing to the northwest in all six chemostratigraphic zones. Zones CN1 through CN4 exhibit the highest degree of Si enrichment, whereas zones CN1 through CN5 show the highest Ti + K values. The Si/Al ratio maps (Figure 12) display an eastward-increasing trend, with the lowest values to the northwest and moderate-to-high values westward. The K/Al maps show a consistent trend within all six chemostratigraphic zones: average K/Al ratio values increase to the northwest, with the most pronounced lateral variation exhibited within chemostratigraphic zone CN2.

Controls on Element Distribution and Abundance

Element ratios and element crossplots highlight possible controls on element distribution and abundance, as well as element–mineral affinities (Pearce et al., 2005). In siliciclastic sediments, the Si/Al ratio can be used as a proxy for the amount of quartz versus aluminosilicates (clays) (Ratcliffe et al., 2007). Laterally, the Si/Al ratio map (Figure 12) demonstrates that the relative amount of quartz versus clay increases to the east within all chemostratigraphic zones. Peaks of Si/Al on geochemical profiles suggest more silica input into the system from sources other than clays. Figure 8 indicates that the Niobrara
Member comprises at least four intervals of increased Si/Al (upper half of chemostratigraphic zone CN1, zone CN2, base of zone CN4, and zone CN6). To evaluate whether the excess silica in the Niobrara Member is of detrital or biogenic origin, crossplots of Si with Al were used (Tribovillard et al., 2006). As shown in Figure 13, Si exhibits a linear relationship with Al, suggesting that a large part of the Si is detrital and resides within the clay fraction. This correlation increases consistently westward and northward, with the highest $R^2$ recorded in well H ($R^2 = 0.87$). The lowest $R^2$ values are observed in the eastern part of the basin (well A, $R^2 = 0.56$), suggesting that in that area Si is more likely to be found in other compounds such as detrital or biogenic quartz.

Element Si exhibits a moderate-to-weak inverse correlation with Ca that is highest in the southeastern

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**Figure 9.** Average calcium (Ca) (wt. %) maps for the six chemostratigraphic zones of the Niobrara Member of the Mancos Shale. Stratigraphically upward, these zones are CN1 to CN6. Overall, Ca values increase to the east of the Piceance Basin. XRF = x-ray fluorescence.
part of the basin (well A, $R^2 = 0.53$) (Figure 14). The $R^2$ values significantly and gradually decrease westward and northward, with the lowest value recorded in well H ($R^2 = 0.05$). This relationship suggests that in the Piceance Basin, the Niobrara Member is not a strictly bimodal carbonate and siliciclastic system but instead contains a mixture of clastic and carbonate deposits. Unlike descriptions of the Niobrara Member equivalent in the eastern and central parts of the Western Interior seaway (e.g., in the Denver Basin) where informal subdivisions are based on varying proportions of carbonate and clastic minerals (Dean and Arthur, 1998), gradually decreasing $R^2$ values indicate that the Niobrara Member becomes increasingly mixed to the west and to the north of the study area.

Levels of K/Al may indicate the relative abundance of the clay minerals illite (or mica) and kaolinite, because K is generally abundant in illite, and Al

Figure 10. Average molybdenum (Mo) (parts per million) maps for the six chemostratigraphic zones of the Niobrara Member of the Mancos Shale. Stratigraphically upward, these zones are CN1 to CN6. Overall, Mo values increase to the east of the Piceance Basin, suggesting that during deposition of the Niobrara Member, anoxia increased to the east. XRF = x-ray fluorescence.
is abundant in kaolinite (Pearce et al., 2005). Increasing values of K/Al thus reflect increasing illite levels versus kaolinite levels. Stratigraphically, higher K/Al values are recorded within Ca-enriched chemostratigraphic zones (CN1, CN2, CN4, and CN6), suggesting higher relative illite versus kaolinite levels compared with other intervals (Figure 8). The K/Al maps show that higher relative illite versus kaolinite levels are recorded to the northwest of the study area within all six chemostratigraphic zones.

**Interpretation of Changes in Paleoredox Conditions**

High organic carbon concentrations are typically associated with sediments deposited in anoxic
bottom-water conditions (Wright and Ratcliffe, 2010). The use of elemental geochemistry in sediments as a proxy for paleoredox conditions is a well-documented application (e.g., Tribovillard et al., 2006, 2008; Turgeon and Brumsack, 2006; Jenkyns, 2010). Trace-metal concentrations and element ratios involving Mo, Cr, V, Ni, and Zn are geochemical proxies used as paleo-oxygenation indicators. This study uses variations in Mo, Cr, and V concentrations to identify zones deposited during low-oxygenation levels.

In sedimentary rocks, the presence of Mo is generally associated with authigenic enrichment under anoxic conditions. In oxic-water columns, Mo is highly stable in suspension and forms molybdate oxyanion (MoO$_4^{-2}$) but adsorbs into humic substances, Mn-oxoydroxides, or Fe-sulfides in anoxic environments.

Figure 12. Average silicon/aluminum (Si/Al) maps for the six chemostratigraphic zones of the Niobrara Member of the Mancos Shale. Stratigraphically upward, these zones are CN1 to CN6. Overall, Si/Al values increase to the east of the Piceance Basin, demonstrating that the relative amount of quartz versus clay increases to the east. XRF = x-ray fluorescence.
Berrang and Grill, 1974; Magyar et al., 1993; Morse and Luther, 1999; Algeo and Lyons, 2006). Under reducing conditions, Cr substitutes for Al within clays, and V bonds with organic matter (Jones and Manning, 1994; Rimmer, 2004; Mackenzie, 2005). Therefore, an increase in the sum Cr + V marks a reduction in the availability of oxygen in the system (Mackenzie, 2005).

Stratigraphic (depth) profiles of Mo suggest that more anoxic conditions existed during deposition of the upper zones (CN4, CN5, and CN6), whereas higher oxygenation levels were present during deposition of the stratigraphically lower zones (CN1 through CN3) (Figure 8). Average Mo maps show that during deposition of the Niobrara Member, anoxia increased to the east (Figure 10).

Figure 13. Variation of aluminum (Al) content (wt. %) as a function of silicon (Si) content (wt. %) for all Niobrara Member samples within nine wells (A–I). Elements Al and Si show a moderate-to-strong linear relationship, suggesting that a large part of the Si is detrital and resides without the clay fraction. See Figure 1 and Table 1 for well locations and names.
Interpretation of Changes in Terrestrial Input

In addition to bottom-water redox conditions, terrestrial input controls the amount of organic matter preserved in shales (Tribovillard et al., 2006, 2008; Turgeon and Brumsack, 2006; Negri et al., 2009; Jenkyns, 2010), and changes in terrestrial input can be interpreted from major and trace-element data.

Element Al is detrital and commonly used as a proxy for clay, because it is scarce in seawater and is generally not affected by biologic or diagenetic processes (Orians and Bruland, 1986; Brumsack, 2006).

Figure 14. Variation of silicon (Si) content (wt. %) as a function of calcium (Ca) content (wt. %) for all Niobrara Member samples within nine wells (A–I). Elements Ca and Si show a moderate-to-weak inverse relationship. The $R^2$ values decrease to the west and to the north of the study area, suggesting that the Niobrara Member becomes an increasingly mixed, more clastic than carbonate system. See Figure 1 and Table 1 for well locations and names.
Similarly, Ti and Zr have very low seawater concentrations and are not involved in biologic cycling (Li, 1982), with Ti being usually associated with Ti oxides and Zr with zircon. Therefore, peaks of Al, Ti, and Zr on geochemical logs indicate detrital input into the system (Piper and Calvert, 2009).

Stratigraphically, two to three pulses of increased terrestrial input within the Niobrara Member are identified (Figure 8): CN1 transitioning to CN2, CN3 (locally), and CN4 transitioning to CN5. Laterally, the highest level of detrital elements is recorded to the northwest of the study area, reflecting a closer proximity to the detrital source (Figure 11).

Figure 15. Contour map of level of organic metamorphism (LOM) for the Niobrara Member of the Mancos Shale. The LOM values for control wells were obtained using vitrinite reflectance data (from US Geological Survey Core Library data files) converted to LOM using the formula of Lecompte and Hursan (2010). Thermal maturity of the Niobrara Member increases toward the center of the Piceance Basin.
Figure 16. The $\Delta \log R$-derived total organic carbon (TOC) curves’ cross sections (A) CC and (B) DD flattened on the top of the Niobrara Member (top chemostratigraphic zone CN6). Space between wells is equal and not representative of actual distances. Numbers at log tops correspond to well API numbers. The TOC values are only calibrated for the Niobrara Member interval. The highest TOC values are recorded in chemostratigraphic zones CN5, CN6, and base of CN2. Zones CN4 and CN5 show higher TOC values to the northeast. On the logs, TOC values increase to the right. Mbr. = member.
Figure 16. Continued.
Geochemical plots of Ca, Al, Ti, and Zr show that the chemostratigraphic zonation of the Niobrara Member corresponds to shifts in depositional systems (Figure 8). Chemostratigraphic zones CN1 and CN2 contain higher Ca content than the overlying zone CN3, and within these zones, where Ca values appear to decrease, terrestrial input can be seen to increase. The base of chemostratigraphic zone CN3 marks a shift from a carbonate depositional system to a siliciclastic depositional system. Terrestrial input increases through chemostratigraphic zone CN3 before shifting to lower values at the base of the Ca-enriched chemostratigraphic zone CN4 (carbonate depositional system). Within chemostratigraphic

Table 2. Statistical Summary of ΔLog R–Derived Total Organic Carbon for Each Chemostratigraphic Zone (CN1 to CN6) of the Niobrara Member of the Mancos Shale

<table>
<thead>
<tr>
<th>Chemostratigraphic Zone</th>
<th>Min TOC (wt. %)</th>
<th>Mean TOC (wt. %)</th>
<th>Max TOC (wt. %)</th>
<th>Std TOC (wt. %)</th>
</tr>
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<tbody>
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<td>Garfield County (N = 16)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<tr>
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</tr>
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</tr>
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<tr>
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</tr>
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</tr>
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</tr>
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</table>

The minimum calculated TOC value is constant (=1 wt. % TOC) because baselining the transit-time and resistivity curves considers the baselined interval as “zero TOC,” and therefore the background TOC (of 1 wt. %) was added back to the calculated value.

Abbreviations: Max = maximum; Min = minimum; N = number of wells; Std = standard deviation; TOC = total organic carbon.

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Figure 17. Average Δlog R–derived total organic carbon (TOC) maps for the six chemostratigraphic zones of the Niobrara Member of the Mancos Shale. Stratigraphically upward, these zones are CN1 to CN6. Yellow discs on maps are well control locations. Chemostratigraphic zones CN2, CN5, and CN6 show increasing TOC values to the southern and eastern parts of the basin, whereas zones CN4 and CN5 show a local increase to the northeast.
zone CN5, terrestrial input is seen to increase again, reflecting a second shift to a siliclastic depositional system and coinciding with a lower Ca content. The base of chemostratigraphic zone CN6 marks a shift to a carbonate depositional system with Al, Ti, and Zr shifting to lower values and slightly decreasing upward. Moreover, comparison of Al, Ti, and Zr with Mo logs suggests that when terrestrial input was highest, bottom-water conditions were at their least reducing.

STRATIGRAPHIC AND GEOGRAPHIC DISTRIBUTION OF ORGANIC MATTER

Thermal Maturity

This study uses average \( \%R_o \) data converted to LOM for TOC calculations. The \( \%R_o \) data were selected instead of \( T_{\text{max}} \) because they are typically more representative of thermal maturity, particularly in highly mature samples (D. Thul, 2013, personal communication).

The LOM changes within the Niobrara Member in the study area are depicted in Figure 15. Contours of LOM indicate that maturation of the Niobrara Member exceeds values of 7.5 LOM (corresponding to 0.5 \( \%R_o \)) over much of the Piceance Basin. Thermal maturity increases to the northeast, attaining the highest values (LOM = 11, corresponding to 1.2 \( \%R_o \)) within the center of the Piceance Basin, suggesting that the Niobrara Member (lower Mancos Shale) has passed through the oil window and is presently within the gas generation window (Kirschbaum, 2003).

Organic Richness

Two cross sections (CC’ and DD’) using TOC profiles produced from applying the \( \Delta \log R \) technique are presented in Figure 16. Two important features of the \( \Delta \log R \)-derived TOC profiles for the Niobrara Member interval are (1) the vertical variation in TOC and (2) the apparent similarity in vertical TOC distribution among the investigated wells. Three main intervals of higher TOC values are identified: chemostratigraphic zone CN6, chemostratigraphic zone CN5, and the lower third of chemostratigraphic zone CN2. Estimated TOC values are relatively low through most of chemostratigraphic zones CN1, CN3, and CN4. The highest average TOC value is recorded in Mesa County within chemostratigraphic zone CN6 (2.37 wt. %), whereas the lowest (1 wt. %) is recorded in both Moffat and Mesa counties (chemostratigraphic zones CN2 and CN3, respectively) (Table 2). For the entire study area, the highest average TOC value is recorded within chemostratigraphic zone CN6 (1.46 wt. %), and the lowest is within chemostratigraphic zone CN1 (1.08 wt. %). Cross section DD’ (Figure 16) shows that chemostratigraphic zones CN4 and CN5 exhibit locally high TOC values to the north and to the northeast of the study area.

Average \( \Delta \log R \)-derived TOC maps for the six chemostratigraphic zones of the Niobrara
Member (Figure 17) show that TOC values generally increase from 1 to 3 wt. % to the south and to the east within chemostratigraphic zones CN2, CN5, and CN6. Zones CN4 and CN5 also display a local increase to the northeast, whereas zones CN1 and CN3 show relatively lower values across the basin.

Many areas recording anoxic bottom-water conditions appear to correspond to areas of higher TOC values. For example, chemostratigraphic zones CN3, CN4, and CN5 display relatively higher TOC values to the north and northeast of the basin, whereas chemostratigraphic zone CN2 shows increased TOC to the southeast (Figure 16). These areas also exhibit higher Mo levels (Figure 10). The Mo maps also suggest relatively less anoxic conditions within chemostratigraphic zones CN1 and CN3, which appear to correspond to lower overall TOC values in these zones compared with CN5 and CN6. Other areas (such as the northeast area at CN6, southeast area at CN4, and southeast area at CN1) exhibit a negative correlation between TOC and Mo that could be explained by a lack of TOC and chemostratigraphic well control toward the eastern part of the basin.

**Calibration and Accuracy of Total Organic Carbon Calculations**

The mean absolute error (MAE; measured in wt. %) is provided to show how close the Δlog R–derived TOC values are to measured TOC values from cutting samples. Wells of higher maturity (LOM = 8.92 and LOM = 9.36) exhibit lower MAE (and thus higher accuracy) compared with wells of lower maturity (LOM < 8) (Table 3).

As detailed in Passey et al. (1990), anomalous sonic or resistivity log responses not associated with source intervals may result in inaccurate TOC calculations. Although a qualitative method was used to remove potentially anomalous TOC values (associated with anomalous sonic or resistivity values) from the analysis, this method may underestimate TOC over some organic-rich intervals, because only background TOC (1 wt. %) is accounted for. The underestimation of Δlog R–derived TOC (as compared with core data) in lithologically complex formations (e.g., the Haynesville Formation) has been observed in other studies (Hammes et al., 2009). The multimineral method of Eastwood and Hammes (2011) uses an optimized solver model by achieving log-computed estimates of lithology to solve for TOC. The TOC estimates using this method yield TOC values of improved reliability in the Bossier and Haynesville shales (Eastwood and Hammes, 2011), and this method could provide improved calculation of TOC estimates from wireline logs for the Niobrara Member.

The estimation of the maturity parameter (LOM) is another factor potentially contributing to the discrepancy between measured and log-derived TOC values. Although LOM values were obtained from the conversion of Ro data in 18 wells, a margin of error may be present when estimating LOM within other wells. However, if the value of LOM is not properly estimated, “absolute TOC values will be somewhat in error, but the vertical variability in TOC will be correctly represented” (Passey et al., 1990, p. 1779).

In addition, because little is known about the cuttings data (e.g., hole quality, possible high-grading), uncertainty may arise regarding the quality of the comparison between cuttings- and Δlog R–derived data.

**Qualitative Interpretation of Relative Rock Brittleness**

Production from shale-gas reservoirs typically requires fracture stimulation, and wells are typically drilled horizontally in the most brittle rock. Brittle rocks are generally silica or carbonate enriched, whereas ductile rocks are considered to be clay–mineral and organic (TOC) rich (Slatt and Abousleiman, 2011).

As previously discussed, chemostratigraphic zones CN1, CN2, CN4, and CN6 are Ca-enriched and are associated with a relatively high quartz/clay ratio (with CN1, CN2, and CN4 being TOC poor). These zones can be interpreted to be relatively brittle. Chemostratigraphic zone CN5 (organic rich) and CN3 have lower Ca and Si/Al values and higher Al values. These zones can be interpreted to be more ductile. These interpretations suggest that within the Niobrara Member, rocks occur as alternating brittle
and ductile intervals. Brittle intervals are suggested to be better targets for horizontal wells, because they are considered better stimulated by artificial fracturing and appear to be occurring in stratigraphic proximity to organic-rich zones.

**CONCLUSIONS**

Elemental chemostratigraphy based on changes in major and trace elements and element ratios is used to subdivide the Niobrara Member of the Mancos Shale into six chemostratigraphic zones (CN1 to CN6). Chemostratigraphic correlations from nine wells show that four markers identified on the geochemical logs correspond to markers used for lithostratigraphic correlations, which highlights the potential of chemostratigraphy as an independent tool for stratigraphic correlations.

The geochemical data were also used to infer stratigraphic and lateral changes in the depositional environment of the Niobrara Member. Trace elements Mo, Cr, and V indicate that, during deposition of the Niobrara Member, more anoxic conditions were present to the east of the study area and that lower oxygenation levels existed during deposition of the stratigraphically upper intervals. Elements Ti, Si, K, and Al show the occurrence of two to three pulses of increased terrestrial input from a source area to the northwest. The geochemical logs suggest that when terrestrial input was increasing, bottom-water conditions were at their least reducing.

Crossplots of Si versus Al show a positive relationship indicating that the quartz in the Niobrara Member is dominantly detrital in origin, whereas crossplots of Si and Ca show that the Niobrara Member gradually moves away from its bimodal (clastic/carbonate) character identified in the eastern and central parts of the Western Interior Seaway.

The TOC calculated for 68 wells using a sonic-resistivity overlay analysis technique (Δlog R) and calibrated to measurements from published TOC data show that TOC varies laterally and stratigraphically throughout the study area. The TOC values tend to be highest to the south and east of the study area, and TOC profiles identify three organically rich intervals within the Niobrara Member. The Δlog R technique of Passey et al. (1990) shows reasonable results when compared with measured TOC data. The LOM maps (from %R_o data conversions) show that the Niobrara Member is more thermally mature within the east–central parts of the basin, where LOM values are as high as 11 (corresponding to 1.2 %R_o).

Interpretations of relative changes in rock brittleness made using geochemical data coupled with TOC profiles show that the Niobrara Member is composed of alternating brittle and ductile rocks. Organic (TOC) and clay–mineral-rich intervals are considered mechanically ductile, whereas more Si/Al (quartz/clay)– and Ca-enriched rocks are considered mechanically brittle.

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