

PS Geochemistry of the Mancos Shale as Shown by the Fees Federal 2-6-8-101 Well, Mesa County, CO*

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Abstract

A detailed geochemical analysis (calibrated x-ray fluorescence) of the Late Cretaceous Mancos Shale was conducted on 176 cuttings samples (total interval = 4,730 ft.) collected from the Fees Federal 2-6-8-101 well (API 05-045-07432). Major elements (>2% on an oxide basis) evaluated included Si, Al, Ca, Mg, Fe, and K and minor elements (<2% on an oxide basis) examined include Ti, Mn, Na, S, and P. Trace elements (ppm concentration) investigated include Se, Ni, Co, V, Cr, and Mo. The samples were also analyzed by calcimeter for total carbonate and by ignition loss at 400 °C for total organic carbon and water. Numerous vertical trends and discontinuities are present in the data. Some significant observations are: silicon (as SiO₂ is about 65% in the lower Mancos (Mowry through Monument Valley members), drops to 40.6% at the base of the Niobrara (Ft. Hays), then generally increases to about 75% through the Niobrara, Prairie Canyon, Sharon Springs, Castlegate, and Buck Tongue members. Calcium, as CaO, is less than 4% in the lower Mancos, increases rapidly to a high of 18.5% in the basal Niobrara (Ft. Hays), then decreases irregularly to the top of the formation. Aluminum (as Al₂O₃), the other major cation, stays between 11% and 15% throughout the Mancos, suggesting that there was a fairly constant influx of clay minerals during deposition. The 'MINLITH' program was used to calculate a normative mineralogy for the cuttings samples. These values allow the identification of zones that are less clay rich and hence more amenable to potential hydraulic fracturing. Another interesting result involves selenium, which creates water-quality issues when the Mancos is weathered. The data show that selenium is primarily concentrated in the lower half of the Mancos. The redox indicators, Ni/Co, V/Cr, V/(V+Ni), and Mo/Al, suggest that a 200-foot-thick interval in the Niobrara was deposited under more reducing conditions than the rest of the formation.

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Geochemistry of the Mancos Shale as shown by the Fees Federal 2-6-8-101 well, Mesa County, CO

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Abstract

The geochemistry of cuttings from the Mancos Shale interval in the Fees Federal 2-6-8-101 well show some very pronounced trends and discontinuities. For example, SiO₂ is about 55% at the base of the Mancos, drops close to 40% at the base of the Niobrara, then gradually increases to about 75% at the top of the formation. Calcium, as CaO, is less than 4% near the base of the formation, increases rapidly to a high of over 12%, then decreases irregularly to the top of the formation. Aluminum, as Al₂O₃, stays between 11 and 15% throughout the formation. These trends suggest that there was a fairly constant influx of clay into the basin whereas quartz and calcite varied.

Trace element indicators of redox conditions (Ni/Co, V/Cr, V/(Vr+Ni) and Mo/Al) gave inconsistent results, but overall indicated that the upper part of the Niobrara interval was deposited under dysoxic conditions. The element Se is an environmental problem in the Mancos Shale outcrop belt in Colorado and Utah. Our results indicate that Se is concentrated in the upper part of the Niobrara and lowermost Prairie Canyon intervals in the shale.

A normative mineralogy for the Mancos Shale was calculated using the program MINLITH. Overall, the results are similar to those obtained by earlier by XRD (Cole & Hood, 2014) but feldspar is underestimated.

Location

The well studied is located in western Mesa County, CO, near the western edge of the Piceance Basin. As part of our study, we have also been collecting data on other Mancos Shale penetrations in the area. These are shown in Figure 1. A schematic cross-section showing the location of the well in context of the Upper Cretaceous formations is shown in Figure 2.

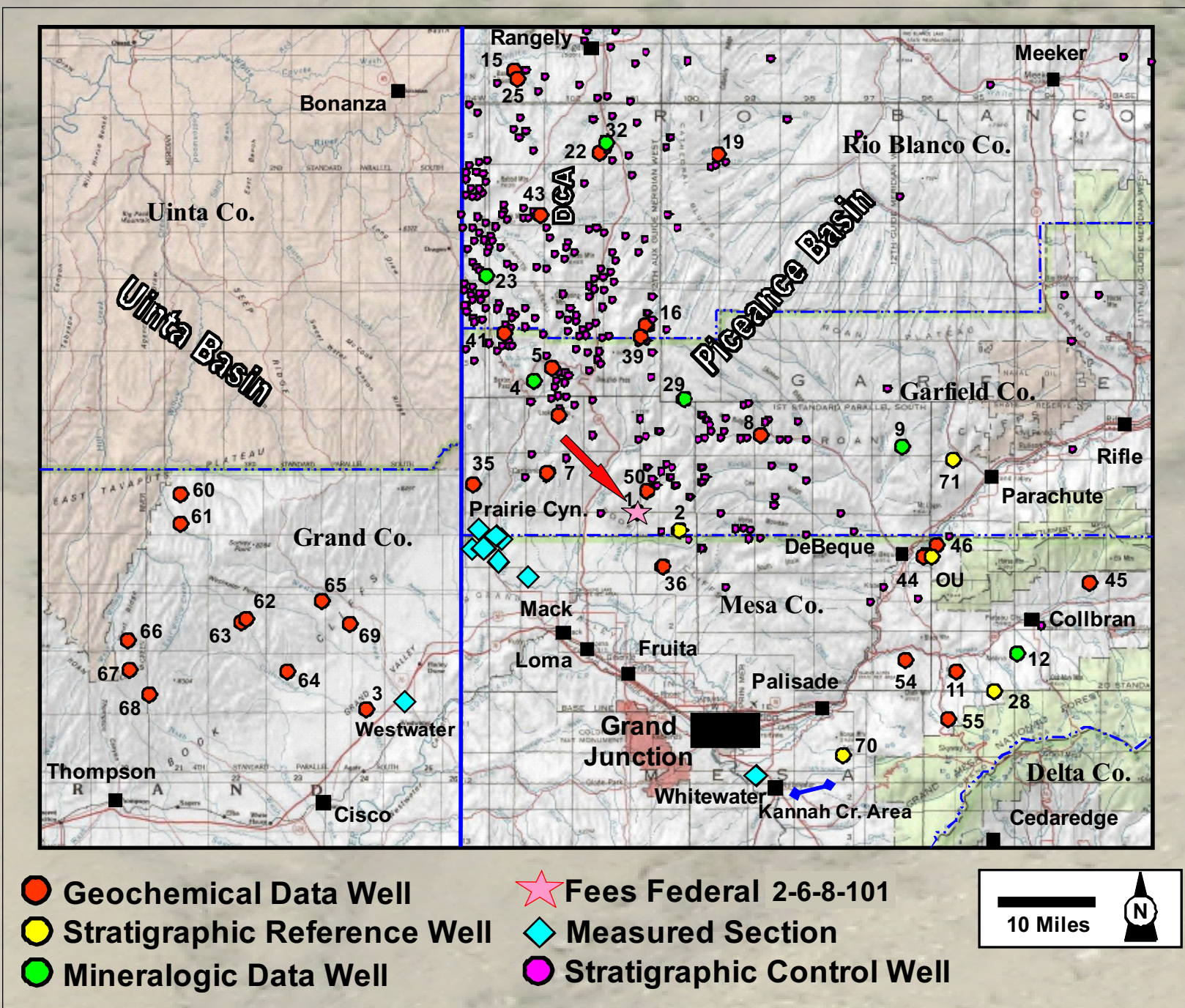


Fig. 1. Location map of the Fees Federal 2-6-8-101 well plus public domain data in the CMU database.

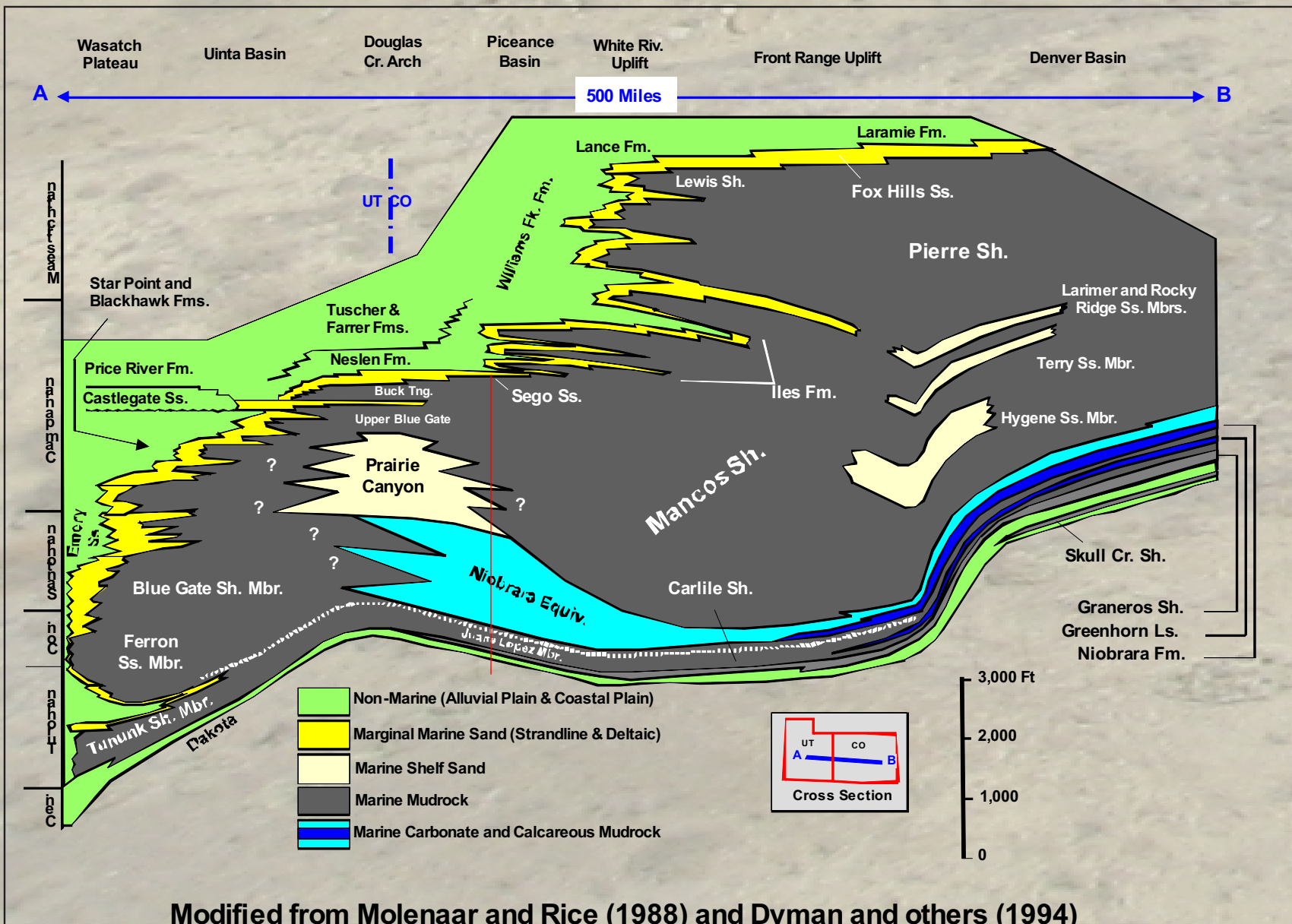


Fig. 2. Schematic cross-section of Upper Cretaceous formations in CO and UT showing the position of the Fees Federal 2-5-8-101 well.

Purpose

The Mancos Shale in western Colorado is a 4700 ft. thick uniform-appearing gray shale. Using fossils and/or gamma ray logs, it can be divided into sections that are equivalent to distinct formations that occur east of the Rocky Mountains. Our purpose in this investigation was to see if it could be similarly divided based on chemostratigraphy. We also wanted to identify redox conditions on the seafloor and to determine the stratigraphic source of the selenium that pollutes western Colorado water.

Method of analysis.

The sample set consisted of bags of air-drilled cuttings, collected at 30-foot intervals from 310 to 4200 feet and 10-foot intervals thereafter to the base of the Mancos Shale at 4700 feet. A few samples were missing. Major elements were determined with a Bruker Tracer III-sd x-ray fluorescence instrument, run with the detector under vacuum to improve detection of low energy radiation. Carbon dioxide was determined using a calcimeter. Water (H₂O+) plus organic carbon were determined by loss on ignition(LOI) at 400° C and H₂O- was determined by LOI at 1200° C. All elemental analyses except sulfur were converted to weight percent oxide. The results of the analyses are shown in Figure 3. Gaps in the data represent missing samples. Quality of the data is indicated by closeness of the sum to 100 percent (Table 1).

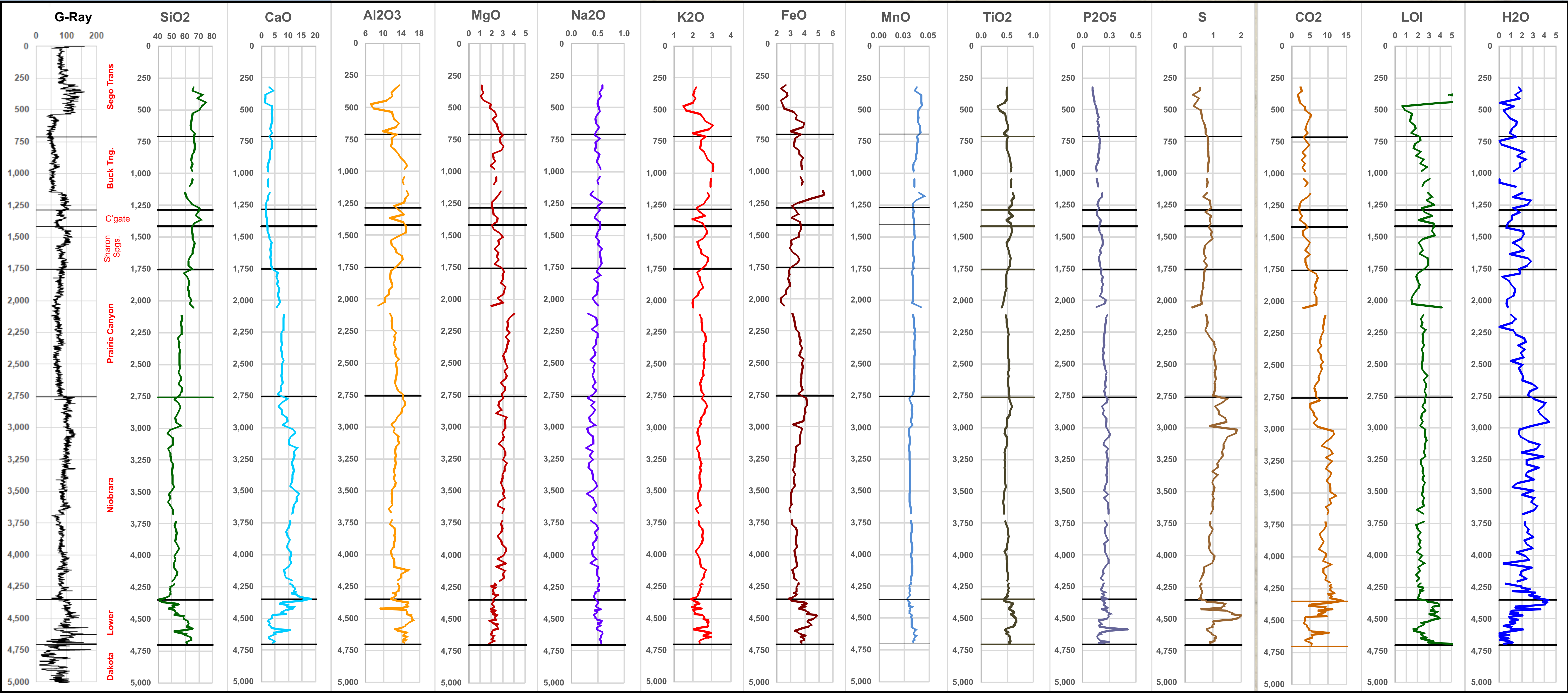


Fig. 3. Results of the chemical analyses of Mancos Shale from the Fees Federal 2-6-8-101 well.

Table 1. Deviation of analytical results from 100 percent.

Deviation	Less than 1%	1% to 2%	2% to 3%	3% to 4%	Greater than 4%
Percent	57.1%	32.6%	8%	0.6%	1.7%

Discussion

Previous work showed that the most abundant minerals in the Mancos Shale in this well are quartz, clay minerals and calcite (Cole and Hood, 2014). Because most clay minerals typically contain less than 50% SiO₂, any excursion of SiO₂ above this amount likely represents the mineral quartz. SiO₂ is high at the base of the Mancos, drops to about 50% through the Niobrara, and increases slowly toward the top. CaO shows the inverse of the SiO₂ trend, beginning low, increasing to 10-12% through the Niobrara and then gradually decreasing upward. The only calcium-bearing minerals identified by Cole and Hood (2013) were calcite and minor dolomite, so the CaO content mainly represents the mineral calcite. The CO₂ trend mimics the CaO trend, reinforcing the suggestion that CaO largely represents calcite (Fig. 4). The Al₂O₃ content with few exceptions, varies only between 12 and 15%, suggesting that there was a rather uniform influx of clay into the basin during Mancos Shale deposition. This shows up very well in a triangular plot of SiO₂-Al₂O₃-CaO (Fig. 5). The ratio of SiO₂ to Al₂O₃ remains nearly constant, but the amount of CaO varies, suggesting that there was a rather uniform influx of aluminum and silica-bearing minerals into the basin with the largest variation being the amount of calcite incorporated into the sediment. The LOI₄₀₀ data compared to organic carbon analyses suggests that a significant part of the loss is organic carbon (Fig. 6), but this is based on only a few samples for which we have carbon analyses.

The only section of the Mancos Shale that is somewhat distinctive on a chemostratigraphic basis is the Niobrara section, which is relatively richer in calcite. The distinct fromations that are recognized in eastern Colorado are only very slightly different chemically in the western Piceance basin.

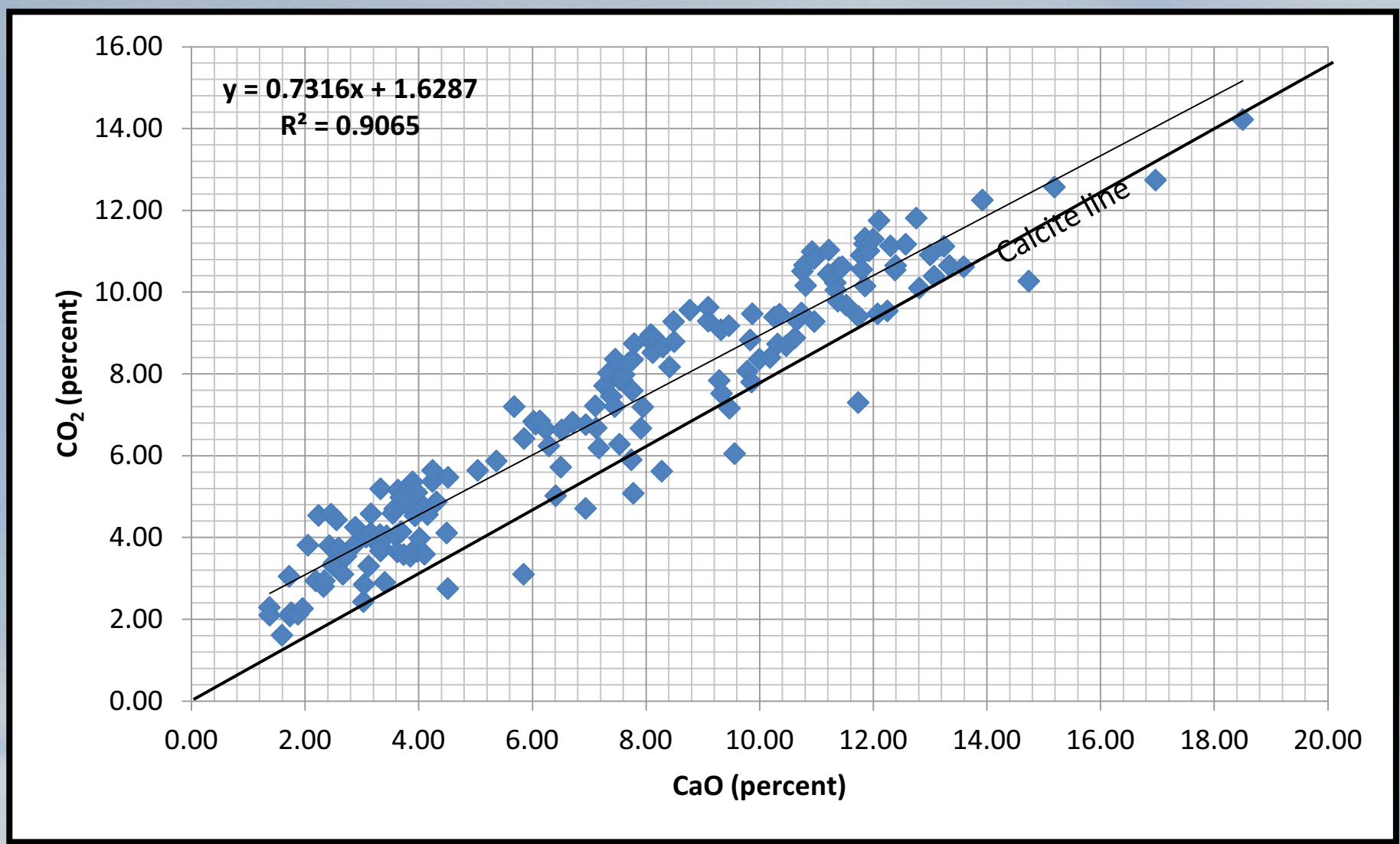


Fig. 4. The CaO-CO₂ relationship in the Fees Federal 2-6-8-101 well. Most samples contain CO₂ in excess of that needed for calcite and probably contain the mineral dolomite.

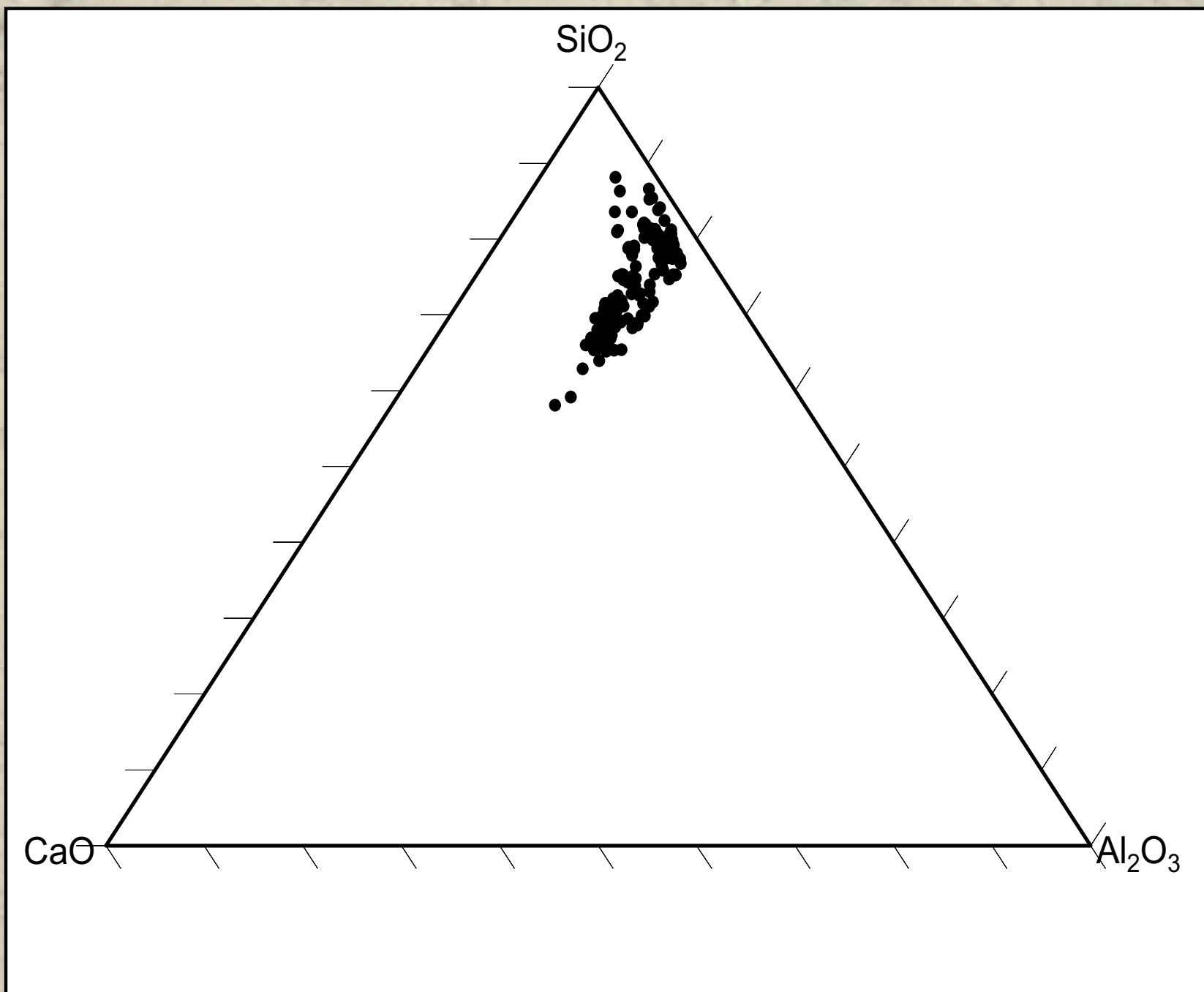


Fig. 5. The relationship among SiO₂, Al₂O₃ and CaO. The ratio of Al₂O₃ to SiO₂ is fairly constant but the amount of CaO varies much more. This suggests that the composition of clastic muds entering the basin remained fairly uniform over much of the time of deposition but the amount of calcite deposited changed much more.

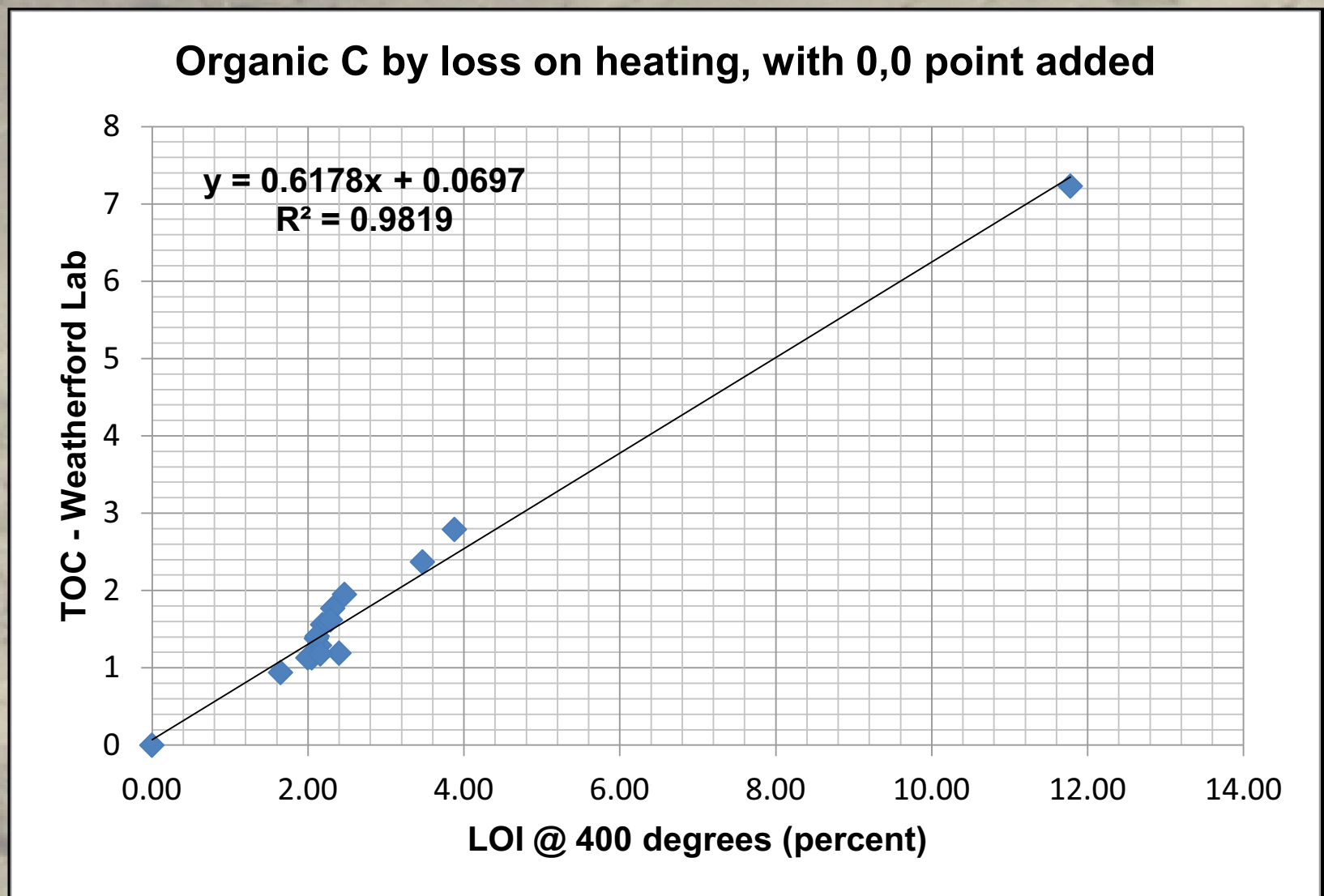


Fig. 6. The relationship between loss on ignition at 400° C and organic carbon. There is a very good correlation between the two variables although this is based on a limited number of samples. The results indicate that about 60 percent of the LOI₄₀₀ is due to loss of organic carbon.

Geochemistry of the Mancos Shale as shown by the Fees Federal 2-6-8-101 well, Mesa County, CO, part 2

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Redox conditions on the Mancos Sea floor.

Several investigators have suggested various trace element ratios as redox indicators. Jones and Manning (1994) used the Ni/Co and V/Cr ratios as indicators. Hatch and Leventhal (1992) used the ratio of V/(V+Ni) an indicator. Lyons, et al. (2003) observed higher Mo/Al values in anoxic marine sediments.

Figure 7 shows the boundaries that these investigators considered appropriate for the various redox conditions. Lyons et al. (2003) did not suggest a lower boundary for dysoxic conditions, but we put one on the graph to be consistent with the V/Cr and V/(V+Ni) results. Note that the results of Ni/Co are inconsistent with the other redox indicators. The other three redox proxies are consistent in indicating that the upper half of the Niobrara section was deposited under dysoxic conditions. This is the interval in the Mancos Shale that should have the greatest potential for organic carbon accumulation and therefore the greatest potential for hydrocarbon production.

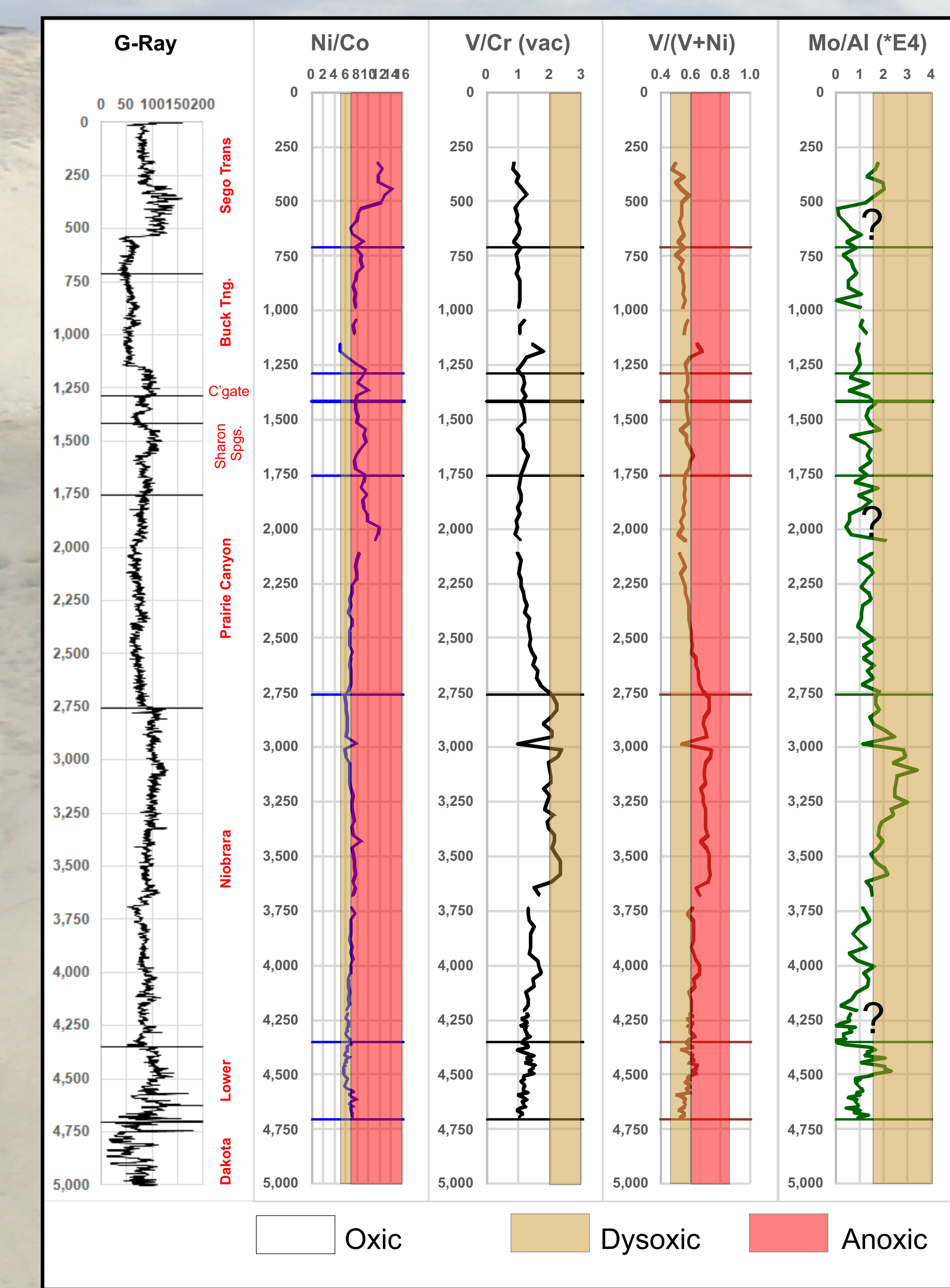


Fig. 7. Various trace element redox indicators in the Mancos Shale.

The Selenium Problem

Studies identified excessive selenium concentrations soils and water in the Green River basin in Utah (Stephens et al., 1988) and in the Colorado and Gunnison river basins in western Colorado in 1987-1988 (Butler, et al., 1996). Apodaca (1988) showed that ground water from the Mancos Shale had the poorest water quality of any rock unit examined, with 22 percent of the samples exceeding the EPA standard of 50 micrograms/L of selenium. Butler et al. (1996) found selenium concentrations as high as 1,300 micrograms/L in shallow wells. The maximum selenium concentrations in surface waters were 600 micrograms/L in the Uncompahgre Valley and 380 micrograms/L in the Grand Valley. Sixty-four percent of their Gunnison River samples and 50% of the Colorado River samples exceeded the EPA standard of 5 micrograms/L, thought to be necessary to protect aquatic life. Morrison et al. (2011,2012) examined water from springs and seeps originating in the Mancos Shale and found the water to be highly saline, with 8 of 51 locations exceeding 1,000 micrograms/L of selenium. Recognizing the pollution potential of the Mancos Shale, we examined the vertical distribution of the shale as part of our investigation.

Selenium results. Selenium is present in most samples of Mancos Shale in the Federal 2-6-8-101 well (Fig. 8). The concentration of selenium varies from 0 to 11.3 ppm with an arithmetic mean value of 2.4 ppm. There is a definite vertical zonation of selenium in the well. From the top down to about 2400 feet, the amount of selenium is less than 3 ppm. Beginning at a depth of 2400 feet, near the top of the Niobrara, the amount of selenium increases to about 9 ppm, with two values reaching 10 or above. Then, at a depth of about 3750 feet the concentration drops sharply and by 3800 feet selenium is back to 3 ppm or less. There are two higher values at depth of 4405 and 4535 feet, but these reach only slightly more than 4 ppm. These data suggest that efforts to remediate selenium pollution in water should be concentrated on that portion of the outcrop belt that corresponds to the high selenium zone shown in the drill hole. It also suggests that well cutting derived from this zone should be handled carefully and not be allowed to weather on the surface, as this would probably liberate some of the selenium.

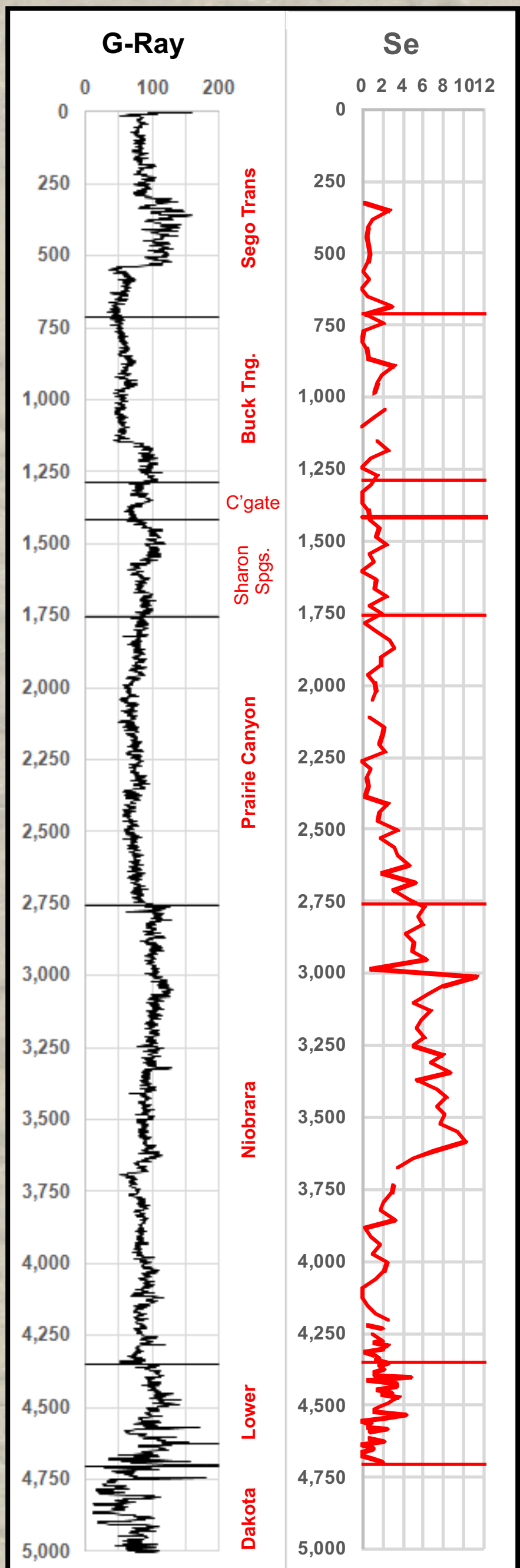


Fig. 8. Vertical distribution of Se in the Fees Federal 2-6-8-101 well. Se values are generally low except in the lower third of the Prairie Canyon and the upper half of the Niobrara.

Calculation of mineralogy using the MINLITH computer program

MINLITH is an Excel spreadsheet algorithm that calculates a simplified mineralogy of a sedimentary rock from a chemical analysis, somewhat like a CIPW norm in igneous rocks (Rosen, et al., 2004). Although we have not yet done a detailed comparison between the MINLITH results and those obtained by other methods, we believe that the results are a reasonable approximation of the Mancos Shale mineralogy, with the exception of feldspars. Our earlier work on the mineralogy of the shale by XRD indicated that a small amount of potassium feldspar is present but the MINLITH algorithm allots the potassium to illite (including mica).

The MINLITH code is freely available the publishers of Computers and Geosciences at: <https://www.iamg.org/index.php/publisher/articleview/frmArticleID/117>

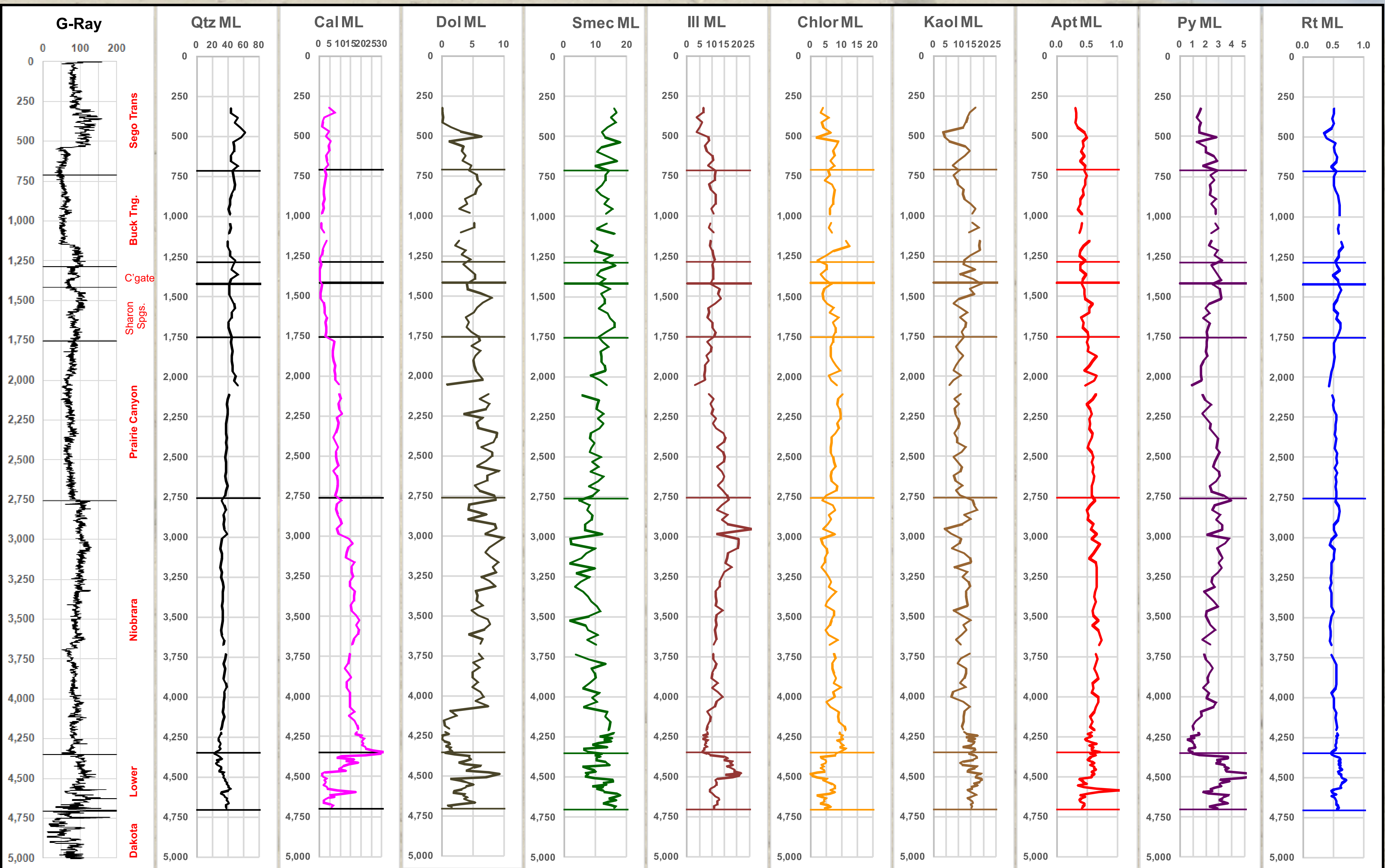


Fig. 9. Results of the MINLITH calculations of mineralogy of the Mancos Shale.

There are several things that can be seen in the MINLITH calculation of mineralogy. Quartz is lowest at the base of the Niobrara section then gradually increases to the top of the Mancos. Calcite shows the opposite trend, being highest at the base of the Niobrara section and gradually decreasing upwards. Among the clay minerals, smectite decreases from the base of the Mancos to about the middle of the Niobrara, then gradually increases upward. Illite is greatest near the top of the Niobrara but otherwise remains fairly constant throughout the section.

These mineralogical trends are similar to those we obtained earlier by x-ray diffraction (Cole and Hood, 2014), but were obtained much more easily.

Acknowledgements

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