

# SUCCESS, PITFALLS AND LIMITATIONS IN THE CHEMOSTRATIGRAPHIC ANALYSIS OF BRINE-RICH CORES: THREE FORKS FORMATION, NORTH DAKOTA

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## ABSTRACT

The Three Forks Formation (Devonian, Williston Basin, ND) is difficult to analyze for facies-scale chemostratigraphic variability due to the overwhelming concentrations of brines emanating from the rock which coat the surface of the core. The brine coating impacts the surface-sensitive X-ray fluorescence (XRF) analysis typically undertaken by 1) creating a layer that attenuates X-ray energies from the low-energy emitters (e.g., Mg, Al, Si, and P, S, K, and Ca), and 2) impacting the inter-element corrections established for non-brine-bearing mudrocks. Tremendous care was taken to wash and immediately analyze a cored Three Forks succession for the purposes of removing/minimizing brine contributions, and consequently, develop a high-quality chemostratigraphic record of change from the economically important succession of strata.

The rocks were soaked with water and rinsed multiple times before scanning for major and trace elements. It was observed that brine would quickly build up on the surface of the rocks, thus the rocks were scanned under incipient dryness, and an evaluation of the brine contamination was made by monitoring the chlorine peak on the X-ray fluorescence software. Raw counts data for the chlorine were evaluated, and samples were reanalyzed until deemed “clean” of chlorine or the overwhelming inter-element effects of chlorine. The chemostratigraphic results reveal that significant stratigraphic variations in %Al (clay proxy), %Mg (dolomite proxy), %S (sulfate proxy), and Si/Th (quartz/clay proxy) occur and can be used to break up the succession. Trace element signatures (Sr, Ba, Mn), and elemental ratios also help refine the traceability of the stratigraphic record by defining marker horizons/zones. The chemostratigraphic evaluation will focus on understanding stratigraphic variations in the distribution of clay-dolomite-sulfate-quartz, and developing a chemofacies model with the potential to use across large portions of the Williston Basin.

## INTRODUCTION

The Williston Basin (North Dakota, Montana, and southern Canada) initially developed as

an inter-cratonic sag during the Cambrian, but evolved throughout the Phanerozoic Eon (Figure 1). Strata of the Three Forks Formation were interpreted to represent deposition in sabkha, tidal flat, and shallow marine environments that were intermittently connected to the Panthalassic Ocean [1-5]. The Three Forks Formation was deposited conformably above the Late Devonian Birdbear Formation, and lays unconformably below the Devonian-Mississippian-aged Bakken Formation, Williston Basin, North America (Figure 2). The spatial extent of the Three Forks and related units is shown in Figure 1B.

The purposes of the study are to demonstrate 1) common analytical pitfalls associated with a brine-laden succession of rock, and 2) how bulk elemental chemostratigraphy can be utilized to develop an understanding of stratal subdivisions and the changes in paleoenvironments that they represent. Most importantly, the development of a highly-resolved (facies-scale) chemostratigraphic/chemofacies framework for any stratigraphic succession creates a structure upon which other, less resolving analyses can be tied and interpreted. For instance, the linkages between strata and the parameters that govern production (e.g., porosity, permeability) may be further interpreted in the context of changing chemofacies, which are a function of facies-specific differences in mineralogy, depositional conditions, and diagenesis.

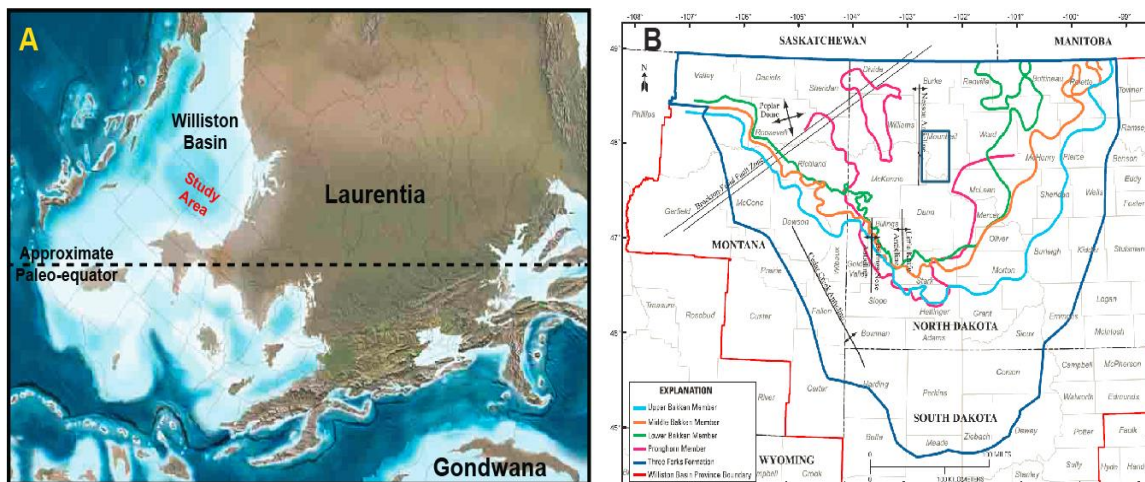


Figure 1: A) Paleogeographic map of Late Devonian North America (Laurentia), with the Williston Basin located on the western edge of the continent, at tropical to subtropical latitudes [6]. B) Lateral extent of the Three Forks Formation (dark blue boundary) in the context of overlying related units of Late Devonian and earliest Mississippian age [7]. The dark blue rectangle in southwestern Mountrail County, ND, marks the general location of the study core.

Linkages between the chemostratigraphic framework and productivity parameters are not explored for the presented core, as the study of the core by the operator is ongoing. However, recent work on the Three Forks suggests that a direct linkage between mineralogy (mainly dolomite) and porosity is lacking, and instead, porosity development is more tightly linked with changes in maturity across the basin. Maximum porosities are reported to be ~12%-15% [8-9], but another recent work presented limited data on facies-

specific samples that showed a range of 1.2 to 8.0% porosity and broad permeability range of 11 to 2585nD [10].

## **METHODS**

A 257-foot thick succession of Three Forks was cored in southwestern Mountrail County, North Dakota, USA. The lower Three Forks contact with the Birdbear Formation was estimated to be 2 feet below the bottom of the core, and the upper Three Forks contact with the Bakken was recovered, providing an almost complete record of Three Forks deposition. The exact core name and location is not provided, as they are proprietary; however, the detailed geochemical workflow is defined.

### **Geochemistry: Energy-Dispersive X-ray Fluorescence (ED-XRF)**

ED-XRF spectra were generated using Bruker Tracer IV spectrometers. Two instruments were used--one for major element analysis plus Ba, V, and Cr, the second for trace element analysis. The major elements were analyzed at 15kV and 35 $\mu$ A with a helium flow system (DeWitt Systems) that enhanced the X-ray signal of low-energy emitters, like Mg and Al. Trace elements were analyzed at 40kV and 11 $\mu$ A using a Ti-Al energy filter. Prior to analysis the slabbed core face was pre-scrubbed with a wet rag, and labeled every three inches with small Avery labels (#5412). Immediately before major element analysis, the sample was dunked in warm tap water and scrubbed multiple times with a hard plastic brush, then dried. Major element analysis was undertaken for 60 seconds; however, if the accumulation of each raw X-ray spectrum indicated an abundance of chlorine (denoted by an energy peak immediately to the left of the Rh-L $\alpha$  peak), then the analysis was stopped, the sample was re-scrubbed and re-dried, and reanalyzed until the chlorine peak was absent or barely above baseline.

Before trace element analysis the core slab face was dunked and lightly scrubbed with a wet towel, then dried and analyzed. It was deemed imperative that the major element analysis occur before trace analysis in order to confirm that the original brine film was removed, but it was also important for trace analysis to quickly follow major element analysis so that minimal brine accumulation occurred on the surface of the cleaned sample. A total of 1016 major and trace analyses were undertaken in the Three Forks, accompanied by 14 analyses of the overlying lowermost Bakken (Pronghorn Mbr). Raw x-ray spectra were subsequently calibrated using a suite of reference materials [11-12]

### **Hierarchical Cluster Analysis (HCA), Elemental Characteristics of Clusters, and Chemofacies Assignment**

In data mining, hierarchical clustering is a method of sample grouping which seeks to build a hierarchy of sample groups usually presented in terms of a sample dendrogram, demonstrating sample ranking by similarity. In order to decide which sample groups (*clusters*) should be combined (for agglomerative), or where a cluster should be split (for divisive), a measure of dissimilarity between sets of observations is required [12-16]. This

measure is achieved by use of an appropriate metric (a measure of distance between pairs of observations). The primary goal of HCA is to partition a multivariate data set into meaningful groups--in the present case these groups may be considered *chemofacies*. The primary outcome of HCA is a number of clusters that maximize the sample similarity within each cluster and maximize the sample differences between clusters. In a vertical succession characterized by discrete lithologies, the inter-cluster differences are well-defined; however, in many mudstone lithologies, the inter-cluster differences are smeared because the lithologies fall along a spectrum of geochemical composition (e.g., limestone--muddy limestone--limey mudstone--mudstone).

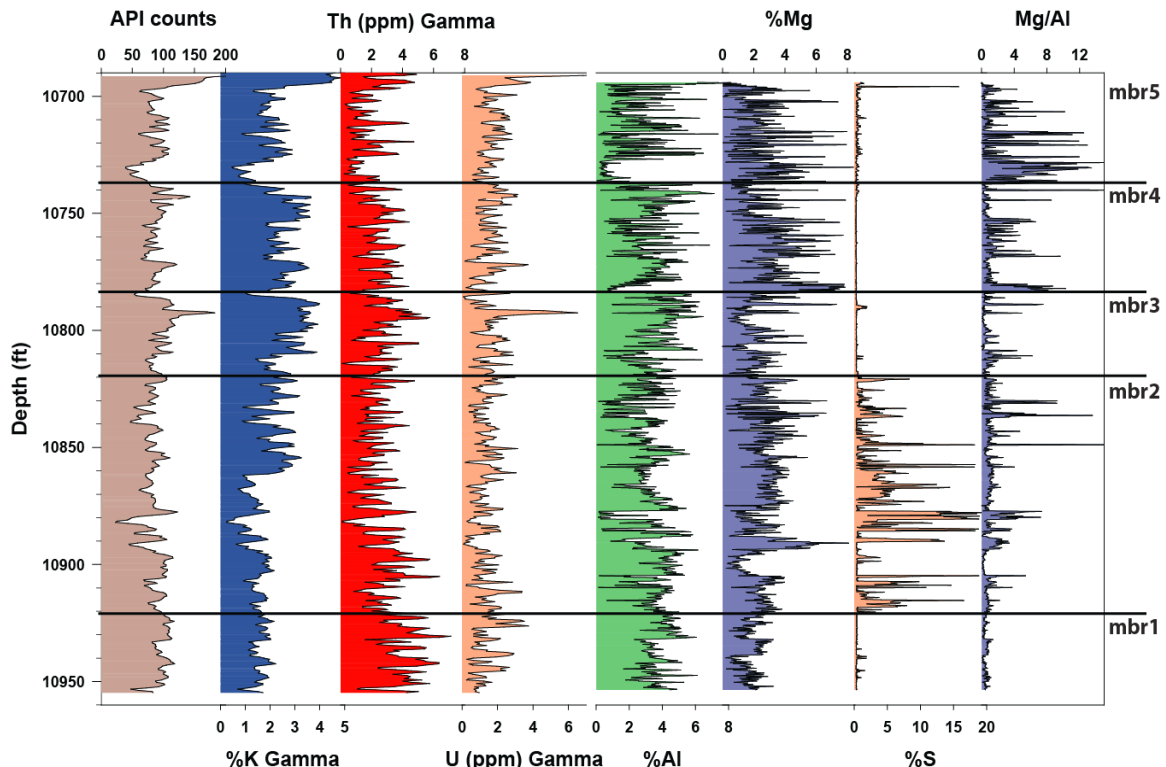


Figure 2: Spectral gamma ray logs (API, %K, Th, U) and bulk elemental (%Al, %Mg, %S, Mg/Al) chemostratigraphic results for the well and the study core, respectively. The %Al is used as a proxy for clay content. The %Mg is used as a proxy for dolomite content. Calcium cannot be used as effectively as a dolomite proxy because intervals of calcite- and anhydrite-bearing strata occur within the Three Forks succession. The %S content is used as an anhydrite proxy. Finally, the Mg/Al ratio can largely be used as a dolomite/clay proxy, as these two minerals dominate the bulk mineralogy of the Three Forks Formation. Subdivision of the Three Forks succession, using “member” terminology, is based on the initial occurrence of anhydrite (mbr1-mbr-2) near the bottom of the succession (~10,920 ft), the large-scale decrease in anhydrite content (mbr2-mbr3) around 10,820 ft, the abrupt increase in dolomite (mbr-3-mbr-4) at ~10,780 ft, and another abrupt increase in dolomite (mbr4-mbr5) at ~10,738 ft. The hiatus between the upper Three Forks and the overlying Pronghorn/Lower Bakken is marked by a one-inch-thick pyrite-rich interval characterized by sulfur values >15% and arsenic values >3,000 ppm.

## RESULTS

Large-scale changes in the geochemical characteristics of the Three Forks Formation are observed in Figure 2. The dominant mineral components of the sedimentary succession are

detritals (clay and quartz), dolomite, and anhydrite, which are proxied by %Al and %Si, %Mg, and %S, respectively. Pulses of anhydrite and dolomite reflect the oscillatory nature of the depositional system. Furthermore, changes in the trace element composition (Zr/Ti, Sr, Ba) and the Fe/Ti demonstrate additional signatures that help subdivide the succession (Figure 3). The HCA and elemental ranking within each cluster (specifics not shown) lead to the generation of eleven chemofacies assignments whose nomenclature were affirmed through evaluation of their location in bi-plots of key major elements (Figure 4A-C). For instance, chemofacies samples termed “quartz-arenaceous Dolomite” fall along the high-%Si/low-%Al trend, while the “Dominant Detrital” chemofacies samples plot in the high-%Si/high-%Al region of the graph (Figure 4A). Similarly, samples belonging to the “Anhydrite” chemofacies plot in the high-%Ca/high-%S region of Figure 4C.

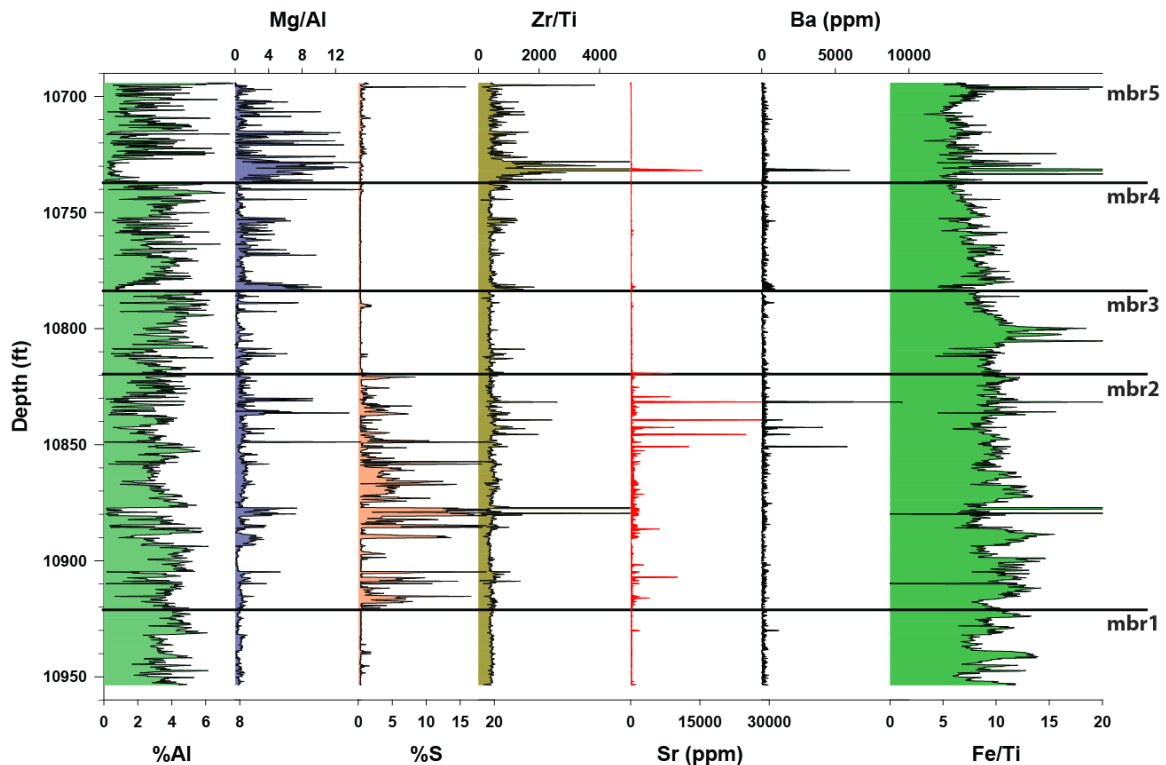


Figure 3: Additional chemostratigraphic signatures defined in the context of the clay-, dolomite-, and anhydrite-defined members. The Zr/Ti ratio reveals abrupt changes in detrital characteristics throughout mbr2, at the base and in the middle of mbr4, and throughout mbr5. This ratio may indicate changes in relative grain size, as Ti is often associated with clays, and Zr with zircons. The Sr and Ba records define abrupt, large-scale changes in their content increase upward throughout mbr2, and a single punctuated interval near the base of mbr5. It is possible that the Sr is a signature of Sr enrichment in dolomite and or calcite, but it could also exist in the anhydrite, strontianite, and/or celestine phase. The Ba content is most-likely preserved in barite, but may inhabit a carbonate phase. The significance of the shift in Fe/Ti in the middle of mbr3 is uncertain, however, it signals a protracted decrease in the iron content to the basin relative to other detrital content, as proxied by Ti. The same signature is observed with Al in the denominator.

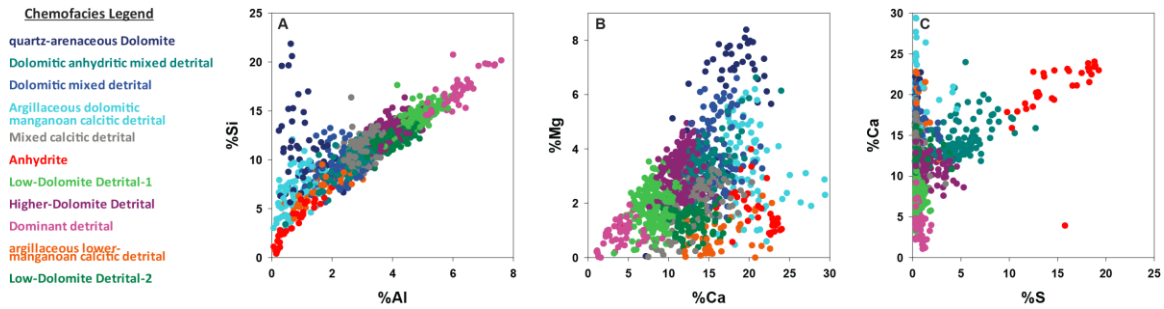


Figure 4: Bi-plots of elements color-coded by chemofacies assignment. A) %Al vs %Si, indicating %clay vs. %silica (clay and quartz) variability. B) %Ca vs. %Mg, largely a function of anhydrite and dolomite variability. C) %S vs. %Ca, demonstrating anhydrite-rich trend (red and dark cyan samples).

The stratigraphic expression of the eleven chemofacies defined through HCA and elemental ranking within each cluster are demonstrated (Figure 5A) in the context of proxies for dolomite and anhydrite (Figure 5B). A well-defined evolution from detrital, low-dolomite deposition, to higher dolomite and ultimately higher anhydrite deposition, culminating in maximum anhydrite deposition at ~10, 880 feet is observed. The overlying succession reveals a complex oscillation between dolomite-rich and dolomite-poor strata, culminating in detrital-rich strata deposition immediately below the overlying Pronghorn unit. Starting from the bottom of Figure 5, the overall evolution of chemofacies can be viewed as tracing the progression of the system from detrital to dolomitic/detrital, to dolomitic-anhydritic, and ultimately to a system that oscillated between dolomite-rich and -poor deposition. Further investigation will be focused on better defining the evolving nature of the depositional system and the potential forcing mechanisms (climate, sea level, connectivity to the global ocean) that shaped its evolution.

## CONCLUSION

Using a rigorous, labor-intensive approach that relies on interpretation of raw X-ray spectral lines, brine-laden drill core can be cleaned sufficiently to generate a high-quality chemostratigraphic record from the Three Forks Formation. Major elemental trends (Mg, Al, S) define previously-characterized members/units, and potentially provide additional resolution for further refinement. For instance, the upper Three Forks (above anhydrite) is characterized by more dolomite-mudstone cycles than previously defined. Spikes in Sr, Ba, Zr, and other trace elements may be correlated locally or across large parts of the Williston Basin. Chemofacies analysis (grouping of elemental information) may provide a more complex but useful way of defining facies heterogeneity in the Three Forks, and is particularly useful when coupled with traditional core description and lithofacies assignments. Chemofacies trends may indicate the need for refinement of the paleoenvironmental model, which has traditionally been described as evaporitic to nearshore deposition, dominated by sabkha-like depositional conditions.

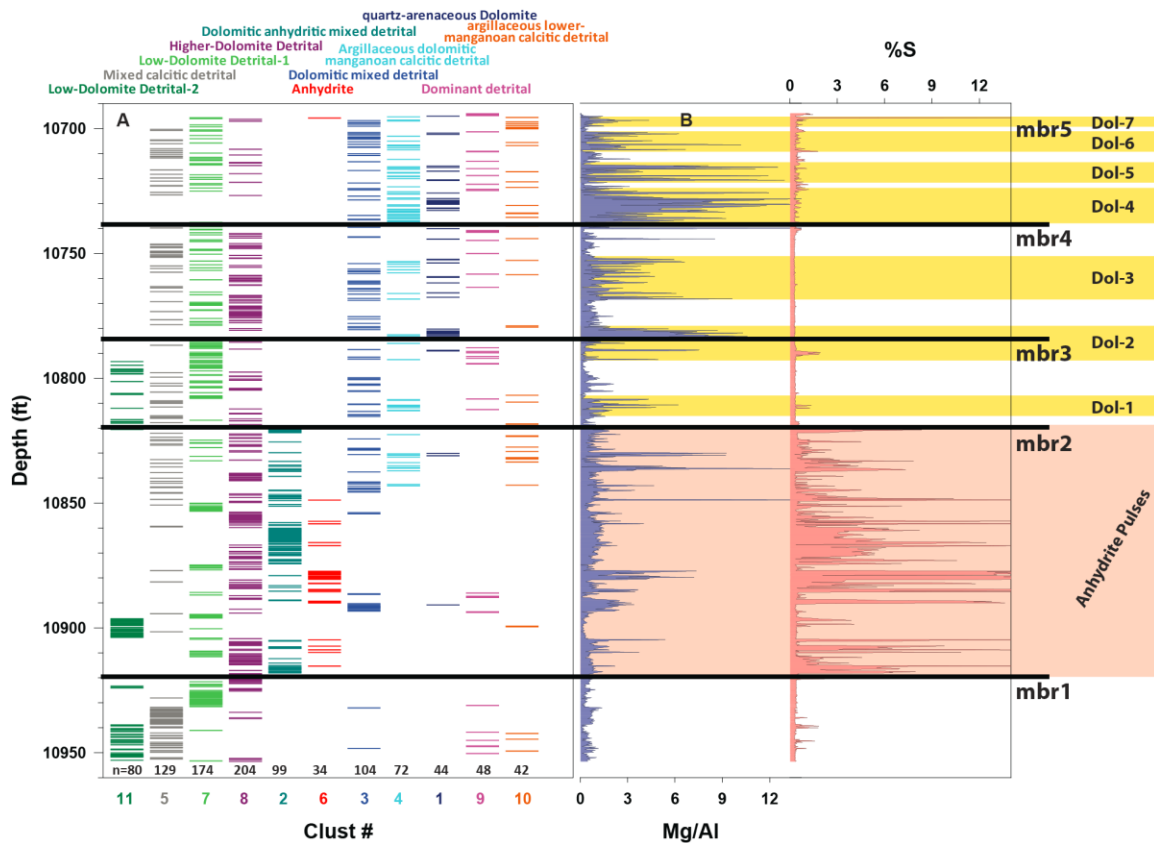


Figure 5: A) Stratigraphic display of chemofacies assignments derived from HCA and evaluation of elemental characteristics defined in HCA. B) Chemofacies in “A” are defined in the context of major mineralogical shifts in the dolomite/clay (Mg/Al) proxy, and anhydrite (%S) proxy. Note dominance of “Dolomitic anhydritic mixed detrital” and “Anhydrite” chemofacies assignments in mbr2 (pink shading). Also note multiple dolomite-rich zones (Dol-1 through Dol-7) in the upper Three Forks (yellow shading).

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