Facies differentiation in fine grained sediments using inorganic whole-rock elemental data within the Ferron Sandstone Member, Notom delta complex, south-central Utah.

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Abstract:

The whole rock inorganic geochemical composition of 210 samples from fine grained lithologies of the Ferron Sandstone Member, and over and underlying Tununk and Bluegate Shale members of the Mancos Formation have been determined. Changes in the whole rock geochemistry are used to define a six- fold chemostratigraphic correlation framework between seven measured sections over an approximately 25km dip-oriented transect of the Notom Delta Complex in South-central Utah.

The key elements used to define the chemostratigraphic framework are Al2O3, Na2O, MgO, K2O, Rb, V, TiO2 and Nb, and are shown to indicate that the geological factors controlling the geochemical variations within each chemostratigraphic unit are primarily controlled by changes in related changing feldspar abundances, changing clay mineral species and periodic volcanogenic influences.

When the chemostratigraphic correlation is placed against detailed facies descriptions and sequence stratigraphic interpretations, it is apparent that the major changes in whole rock geochemistry are related to changes in depositional facies, rather than to any chronostratigraphic surfaces. The whole rock geochemistry clearly differentiates mudstones deposited in marine conditions from those deposited in fluvial environments and highlights the presence of fluvially derived mudstones within demonstrably marine deltaic depositional environments. Their presence is attributed to episodic fluvial flooding events that result in deposition of hyperpycnites, which have been previously documented within the Ferron Sandstone Member.

Introduction:
Background

Although a significant proportion of deltaic successions are mudstone-dominated), these fine grained lithologies have received little attention compared to the coarser grained lithologies. In this study, the mudstone lithologies in the Notom Delta Complex of south central Utah are used to primarily determine the efficacy of inorganic whole-rock elemental analysis as a means to characterize fine-grained facies within sequences that comprise pro-delta to shoreface to fluvial mudstones and silty-mudstones.

The Notom Delta Complex crops out in south central Utah and forms part of the Ferron Sandstone Member of the Mancos Shale Formation. In this area, the Ferron Sandstone Member is overlain by the Bluegate Shale Member and underlain by Tununk Shale Member (Fielding, 2010). The Cretaceous-aged (Turonian) Ferron Sandstone Member (Mancos Shale Formation) has been studied since the early 20th century and, although this member has been previously interpreted as shallow or shelfal marine in many early studies (Ryer 2004, Ryer and Anderson 2004), it is now interpreted as a series of fluvial-deltaic successions (Ryer 2004). Figure 1 shows an outcrop map for the Ferron Sandstone Member, while on Figure 2 a palaeo-geographic reconstruction of Ferron Sandstone Member deposition is shown, where five easterly prograding deltas are identified on the western margin of the Cretaceous interior seaway (Bhattacharya and Tye, 2004).

Extensive studies have been done on the Ferron Sandstone Member of the Mancos Formation, especially in the Last Chance Delta complex, where detailed sequence stratigraphic correlations have been made (Garrison and van den Bergh, 2004). However, until recently (Fielding, 2010, Li, 2010, Li *in press* and Zhu, 2010) little work has been published on the Ferron Sandstone as it crops out in the Notom Delta Complex area (Figure 1).

In a regional sense, the Ferron Sandstone Member was deposited as a series of sand-rich clastic wedges along the western margin of the Cretaceous Interior Seaway during the Turonian (Ryer and Anderson, 2004). The seaway connected the Northern Boreal Sea with the Gulf of Mexico, and Notom Delta complex, is just one of many delta

complexes which were deposited throughout the Cretaceous along the this margin (Figure 2). The Ferron Sandstone Member itself comprises of three clastic wedges: the Vernal, Last Chance, and Notom delta complexes (Garrison and van den Bergh, 2004).The Cretaceous Interior Seaway was a relatively shallow, elongate body of water that occupied much of the North American Mid-Continent during the early and mid Cretaceous. The seaway connected to the Tethyan Ocean in the south and the Arctic Ocean in the north (Krystinik and Dejarnett, 1995). Deltaic systems are thought to provide the dominant sediment input on the western margin of the interior seaway, with ancient deltas such as the Vernal, Last Chance and Notom (Figure 2), and delta systems which supplied Wall Creek Member of the Frontier Formation (Huff and Nummedal (1990), Winn (1991) and Keumsek et al. (2007)) and Cardium Formation (Walker (1983), Bergman and Walker (1987) and Vossler and Pemberton (1989)) all active during this time. Slingerland et al. (1996) has suggested that long shore drift processes operated from north to south along the western margin of the seaway, and as a result it is possible that mud plumes (MacEachen et al. (2005), Liu et al. (1999), Hoyal et al. (1999) and Syvitski et al. (2005)) originating from deltas to the north of the Notom delta system may provide an additional source of fine grained sediment within the marine mudstone facies of the Ferron Sandstone Member.

Inorganic whole rock geochemical data have been used to define stratigraphic correlations in the petroleum industry for over a decade now (Ratcliffe et al., 2010 and references cited therein) The stratigraphic technique of chemostratigraphy relies upon recognizing changes in element concentrations through time and using those to model changes in geological features, such as paleoclimate (Pearce et al., 2005a, Ratcliffe et al., 2010) and provenance (Ratcliffe et al., 2007, Ratcliffe et al., 2006, Wright et al., 2010). Published accounts using this approach are largely on fluvial successions, where stratigraphic correlation using traditional techniques are often problematic (e.g. Pearce et al., 2005a, Ratcliffe et al., 2004, Ratcliffe et al., 2010, Wright et al., 2010 and Hildred et al., 2010). Typically, because these studies are done on sequences with complex stratigraphies, using subsurface samples, commonly drilled cuttings. As a result there is no confident means to validate the proposed chemostratigraphic correlations, or to fully

comprehend the relationship between chemostratigraphy, sequence stratigraphy and facies.

Here, selected sections (Figure 1) within the correlation framework published by Zhu, (2010) have been sampled for whole-rock geochemical analyses. Not only can these sampled sections be confidently placed within a sequence stratigraphic framework, but walk out correlations between the sections have been done to confirm the proposed correlations and detailed facies analysis has been done in the field by Zhu, (2010). Therefore, the geochemical dataset acquire here provides a perfect opportunity to test chemostratigraphic correlations in a prograding delta complex and to understand how chemostratigraphic correlation relates to sequence stratigraphy, facies variations and chronostratigraphy.

Typically, published works, such as those referenced above, use visual (logs), graphical (binary and ternary) and multivariate statistical approaches to interpret and present whole-rock geochemical data (Ratcliffe et al., 2010, Svendsen et al., 2006). Here, the same approaches as previously published authors are broadly followed. By adopting this approach, the work presented here demonstrates that in the case of the Ferron Sandstone Member as documented within the Notom Delta Complex, the primary control on changes in geochemistry are environmental lithofacies, with clear changes between pro-delta, shoreface and fluvial depositional environments.

Although there is a broad agreement between the chemostratigraphic and sequence stratigraphic correlations presented in Enclosure A. There does not appear to be a clear relationship between the detailed sequence stratigraphically defined time correlative surfaces and chemostratigraphic boundaries. However, sample spacing is somewhat coarse to definitively conclude that there is no relationship and higher resolution sampling of both sandstones and claystones would perhaps better allow integration of whole rock geochemical data and sequence stratigraphy.

Sampling Methodology

For this study, silty-mudstone samples were collected from seven measured sections (Figure 1). These sections were selected at an approximately 3-4km spacing along the dip section of the Notom Delta Complex out crop belt, as shown on Figure 1.

The sections selected for chemostratigraphic analysis had been previously logged and integrated into a detailed sequence stratigraphic framework for the area (Zhu, 2010). Therefore it was possible to select the intervals to be sampled based on lithological descriptions and facies assignment of Zhu, (2010). Sampling and analysis in this study focused on the silty mudstone lithologies, as the underlying aim of this work was the better understand mudstone facies in fluvio-deltaic sequences. Currently no data for sandstone lithologies has been acquired in this area.

Initially, sampling was attempted at an average of 6m intervals through each measured section. However, due to poor exposure in some areas (Figure 1) the sampling interval could not be uniform, with some areas clearly more densely sampled than others. Figure 1 shows the location of the study area and sections analyzed along with the position of sampled material.

In many areas, especially in lower parts of the sections, comprising pre-delta mudstones, the desired rock material was highly weathered. In order to select a representative sample, trenches were dug at the sampling point to expose the clean rock surface.

Analytical Methodology

In this study, whole-rock inorganic elemental analysis was carried out on approximately 210 field samples, which, prior to analysis had been cleaned of any obvious surface contamination, disaggregated and ground to a fine powder.

Whole-rock inorganic geochemical data were acquired for all samples using inductively coupled plasma optical emission (ICP-OES) and mass spectrometry (ICP-MS), following a Li-metaborate fusion procedure (Jarvis and Jarvis 1992). The sample preparation and analytical procedures used in this study are the same as those detailed in Pearce et al. (1999) and Jarvis and Jarvis (1995).

These preparation and analytical methods provide data for 10 major elements (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO,MnO, CaO, Na_2O, K_2O, P_2O_5), 25 trace elements (Ba, Be, Co, Cr, Cs,Cu, Ga, Hf, Mo, Nb, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Tl, Th, U, V, W, Y, Zn,and Zr) and 14 rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho,Dy, Er, Tm, Yb, and Lu). Precision error for the major-element data is generally better than 2%, and is

around 3% for the data for high abundance trace elements derived by ICP-OES (Ba, Cr, Sc, Sr, Zn, and Zr). The lower abundance trace elements are determined from the ICP-MS analysis and data are generally less precise, with precision error in the order of 5%. Accuracy error is less than 1% for majors and between 3 to 7 ppm for trace elements, depending on abundance. Expanded uncertainty values (95% confidence), which incorporate all likely errors within a statistical framework derived from 11 batches of 5 certified reference materials (CRMs), each prepared in duplicate, are typically 5–7% (relative) for major elements and 7–12% (relative) for trace elements. The ICP OES and MS facility that produced the data presented here was granted laboratory quality system accreditation to ISO 17025:2005, which is equivalent to the ISO 9000 series but focused on laboratory total quality systems.

Previous authors using whole rock geochemical data for stratigraphic definitions have also used mineralogical data obtained by X-ray diffraction to help understand which factors control geochemical changes (Pearce et al. (2005a), Ratcliffe et al. (2004), Ratcliffe et al. (2006), and Ellwood et al. (2008). The approach of these authors is adopted here and a sub-set of 30 samples from sections 9 and 2 (Figure 1) were analyzed via XRD (X-ray diffraction) analysis. Data for these XRD analyses are shown on Table 1.

Results
Whole rock geochemical Characterization of the Ferron Sandstone Member:
The geochemical data acquired from silty-mudstone lithologies in this study show significant vertical variations within the seven analyzed sections shown on Enclosure A, which has allowed the study intervals to be divided into six locally correlative chemostratigraphic or "Chem Units".

Although whole-rock geochemical data was acquired for 50 elements in this study, not all elements are useful when building a chemostratigraphic framework. Typically, as demonstrated by Ratcliffe et al., (2010) and Hildred et al., (2010), in chemostratigraphic studies between 6 to12 elements are selected as "key elements". These key elements are

selected after the entire dataset has been appraised and by consideration of both lateral and temporal changes in concentration. On Figure 2, key element ratios (Mg/Al, Na/Al, Ti/Nb, K/Rb and EFV) used here have been plotted for each silty-mudstone sample from the seven measured sections studied (Figure 1). Once a series of key elements have been selected from the dataset, it is then possible to create a series of elemental ratios, which are designed to best show the geochemical variation between units and to relate changes in mineral compositions and relationships, and environment of deposition.

Samples on Figure 2 are plotted in relative stratigraphic order (Table 2) such that all samples assigned to Chem Unit 1 are plotted together, all samples assigned to Chem Unit 2 plot together, etc to form composite geochemical logs (*sensu* Ratcliffe et al., 2004 and Wright et al., 2010). Within each Chem Unit on Figure 2, no stratigraphic order is implied. Except within Chem Unit 4, where the sequence stratigraphic correlation developed by Zhu, (2010) has allowed for a better understanding of the lateral changes in stratigraphy through this interval (Table 2).

Both the chemical logs (Figure 3) and the graphical plots (Figure 4) clearly demonstrate that each Chem Unit can be systematically differentiated from all others across the study area and these changes are described below:

Chem Unit 1 is characterized by low TiO_2/Nb values compared to overlying samples and generally higher Na_2O/Al_2O_3 values compared to Chem Unit 2.

Chem Unit 2 is characterized by higher TiO_2/Nb values compared Chem Unit 1, lower MgO/Al_2O_3 values than Chem Unit 4 and higher Na_2O/Al_2O_3 values than Chem Unit 5. Chem Unit 2 has generally higher K_2O/Rb values than Chem Unit 3.

Chem Unit 3 is chemically transitional between Chem Units 2 and 4. It is characterized by generally lower and upward decreasing K_2O/Rb values coupled with lower Na_2O/Al_2O_3 values compared to Chem Unit 2. Chem Unit 3 also has lower MgO/Al_2O_3 values than Chem Unit 4.

Chem Unit 4 is characterized by higher MgO/Al_2O_3 values than Chem Units 1-3 and higher Na_2O/Al_2O_3 values than Chem Unit 5.

Chem Unit 5 is characterized by lower Na_2O/Al_2O_3 values and generally lower MgO/Al_2O_3 values compared to overlying and underlying units.

Chem Unit 6 is characterized by higher Na_2O/Al_2O_3 and MgO/Al_2O_3 values than Chem Unit 5. Additionally these samples show higher EFV (enrichment factor of Vanadium), (Tribovillard et al, 2006) values than the underlying Ferron Sandstone sequences, suggesting that they were deposited under more anoxic conditions at the sediment water interface (Figure 3).

Observed relationship between "Chem" Units and facies:
In each of the seven sections analyzed there are clear vertical changes in whole rock geochemistry and the changes are consistent between the sections, allowing the construction of a 6-fold chemostratigraphic correlation between the seven sections (Enclosure A).

However, when this correlation framework is viewed in the context of a larger high-resolution sequence stratigraphic interpretation over the same area (Zhu, 2010) (Enclosure A), it becomes apparent the most marked geochemical changes in each section are largely coincident with major changes in depositional facies, as described by Zhu, (2010).

Zhu (2010) established a compex, high-resolution sequence stratigraphic framework of the Ferron Notom Deltaic Complex, comprising six depositional sequences, 18 parasequence sets, and 43 parasequences. Each sequence (Enclosure A) is thought to represent approximately 100,000 years, with each parasequence set was deposited over about 34,000 years, and each parasequence representing about 14,000 years of deposition (Zhu, 2010). For the purposes of this study a more simplistic view is

taken, with depositional elements defined by Zhu (2010) being grouped into four broad facies, which are discussed below in the context of their geochemical signatures:

Facies 1 = Pro-Delta Mudstones, with occasional bentonites horizons.
All samples assigned to Chem Unit 1 and Chem Unit 2 are from this facies assignment (Figure 5). The silty claystones of this facies are differentiated from those of Facies 2-4 by higher K/Rb values.

Facies 2 = Shoreface mudstone-sandstone lithologies, with occasionally river dominated sandstones.
All samples from Chem Unit 3 and Chem Unit 4 are from this facies assignment (Figure 5). Both Chem Units 3 and 4 have lower K/Rb values compared to Facies 1 and higher Na/Al values compared to Facies 3. As shown on Enclosure A, Chem Unit 3 is a relatively thin unit, which is transitional between Chem Units 2 and 4. The majority of samples within Facies 2 are assigned to Chem Unit 4, which is chemically characterized by high Mg/Al values, however samples assigned to Chem Unit 3 have low Mg/Al values more typical of Facies 1.

Facies 3 = Fluvial Mudstones-Sandstones with occasional estuarine facies.
Samples from facies 3 are all assigned to Chem Unit 5 (Figure 5), and were all from sediment deposited under predominantly fluvial conditions. These samples are characterized by having lower Na/Al values compared to all other samples analyzed in this study.

Facies 4 = Marine Mudstones of the overlying Bluegate Shale Member of the Mancos Formation. Samples from this facies group are all assigned to Chem Unit 6 (Figure 5). This unit is characterized by high EFV values compared to the underlying Ferron Sandstone Member.

Elemental Ratios and their probable mineralogical controls

A total of 50 elements have been determined as part of the study, but as discussed above, only a limited number of key element ratios are sufficient to geochemically characterize the Ferron Sandstone Member. Although Chemostratigraphy is the zonation of rocks based on changes in their whole-rock geochemistry *sensu strict*, a chemostratigraphic zonation based on geochemical changes that reflect diagenetic factors is as equally valid as a zonation that reflects changes in provenance, palaeoclimate or redox conditions. However, once a chemostratigraphic zonation is extended geographically, so as to establish a chemostratigraphic correlation framework (Enclosure A), an understanding of the factors governing the zonation is required in order place a geological interpretation on the geochemical data, and additionally to help understand how chemostratigraphic correlations can be integrated with other correlation techniques, such as sequence stratigraphy.

The primary control on whole rock geochemistry is sediment mineralogy. Therefore, in order to fully understand the relationship between geochemistry and mineralogy, elements and element ratios should be compared against mineralogical data acquired using methodologies such x-ray diffraction, petrography or heavy mineralogy. In the case of this study a subset of samples from sections 9 and 2 were analysed using X-ray diffraction and their mineralogy determined (Table 1, Figure 6). This work carried out on the same rock sample as the geochemical analysis, thereby ensuring the two datasets can be compared. The key elements used in this study are Al, Na, Mg, K, Rb, V, Ti and Nb, and the likely mineralogical affinities and controls on these elements are discussed below:

Aluminum

The close relationship of Al to total clay content is demonstrated on Figure 7a.

Magnesium

Mg abundances in sediments are commonly controlled be either clay minerals, such as chlorite, or dolomite. Chlorite is a very minor component of the Ferron Sandstone Member (only 2 samples have chlorite concentrations over 1%, with both of these samples occurring within Chem Unit 5) and therefore it is unlikely that chlorite is a major

control on Mg abundances in these sequences. On Figure 7b Mg values are plotted against dolomite abundances, and it is apparent that in mudstones that have high Mg values, dolomite values are also high. Furthermore, it is clear that the samples with high Mg values are restricted to Chem Unit 4. Samples assigned to Chem Units 1-3 and Chem Unit 5 show no discernable relationship between MgO and dolomite values.

Sodium

Na in silty mudstones is typically associated commonly with a number of different minerals, such as clay minerals, plagioclase feldspars and halite. On Figure 7c plagioclase concentrations are plotted against a Na/Al ratio. Although a clear linear relationship is not seen, there does appear to be a broad relationship, which indicates that as the Na/Al values increase so do the plagioclase values. More significantly perhaps, samples assigned to Chem Unit 5 are characterized by very low Na/Al values. On Figure 6 it is also clear that these samples have very low or no recorded plagioclase. Therefore, it is evident that broadly Na is related to the plagioclase feldspar contents in this dataset. It is noted however, that at a more detailed level, there may be more complex secondary controls on Na distribution.

Potassium and Rubidium

In silty mudstone lithologies K is commonly associated with clay minerals, such as illite and K-feldspar. In the Ferron Sandstone Member K_2O abundances show no relationship with clay minerals, but do show a positive linear relationship with K-feldspar abundances (Figure Xd), strongly suggesting that the primary control on changes in K_2O concentrations in these samples is K-feldspar abundance. Rb, like K_2O can similarly be associated with both feldspars and clay minerals. On Figure 7e a binary diagram is plotted for K_2O and Rb values and it is clear that a strongly linear relationship exists between these elements, implying that changes in Rb values are also controlled by K-feldspar abundances. Furthermore on Figure 7f, when the Chem Unit assignments for each sample are shown on a K_2O vs. Rb binary plot, it is clear that samples from Chem units 1 and 2 from a parallel linear trend to that observed for samples assigned to Chem Units 3-5. As these trends are parallel it is suggested that between Chem Unit 2 and

Chem Unit 3a, a subtle change in the K-feldspar composition occurs, with the older sequences being more relatively enriched in K2O and younger sequences being relatively enriched in Rb.

Vanadium

V can have many probably mineralogical affinities in sedimentary rocks however, work by authors such as Tribovillard et al., (2006) have shown that in certain circumstances this element may be used to estimate the relative degree of anoxia at the sediment/water interface at the time of deposition. In this study, the relationship between V concentrations and sediment chemistry is best shown by plotting the values of V in the sample relative to a standard marine shale value. This variable is calculated from the formula: EFV(enrichment factor of Vandium) = V/Al_{sample} / $V/Al_{average\ shale.}$ Average shale values are those used by Tribovillard *et al.,* (2006). Where anoxic or disoxic bottom waters prevail, V tends to be concentrated in the sediment via cation exchange with the seawater (Turgen and Brumsack, 2006, Tribovillard et al., 2006, Tribovillard et al., 2008, Negri et al., 2009, Jenkyns, 2010). EFV values of less than 1, are though to be typical of oxic bottom water conditions, where EVF values are over 1, bottom water may be interpreted as disoxic to anoxic (Tribovillard et al., 2006).

Titanium and Niobium

Both Ti and Nb can be present in clay minerals, such as illite, and Ti-oxide heavy mineral, such as rutile. In this study, however, the exact mineralogical controls on both TiO2 and Nb are not clearly understood with the current dataset. Neither Ti or Nb show a relationship in illite abundances or clay minerals in general. Therefore it is assumed that these elements may be controlled by the distribution of fine-grained heavy minerals such as Ti-oxides. Often, (Wright et al, 2010, Ratcliffe et al, 2006) changes in Ti vs. Nb ratios may be related to changes in sediment provenance or changes in the amount and type of volcanic material introduced in a sedimentary system. It is noted that several laterally extensive bentonites have been identified and correlated in the Ferron Sandstone Member (Li., 2010 and Zhu, 2010), and as such it is suggested that changes in the relative abundances of Ti vs. Nb may be controlled by the amount and type of volcanogenically

detritus. However further mineralogical analysis would be required in order to confirm this suggestion.

Based on the discussion above, the probable mineralogical and therefore geological significance of the key ratios utilized in this study are defined as follows:

- MgO/Al_2O_3 = Relative dolomite abundance.
- Na_2O/Al_2O_3 = Relative plagioclase feldspar abundance.
- TiO_2/Nb = Relative abundance of clay-sized Ti-rich volcanogenically derived material verses rutile (or illite).
- K_2O/Rb = Interplay between K-feldspar abundances.
- EFV (enrichment factor of vanadium) = relative bottom water anoxia at the time of deposition.

Discussion:

By combining the geochemical changes used to define the Chem Units with the interpreted mineralogy and facies group each unit has been assigned to, the following interpretations can be made:

FACIES 1:

Chem Unit 1/Chem Unit 2 = upward increase in Ti-rich volcanic material and decrease in plagioclase feldspar content. It is suggested that is there is no discernable lithological difference between these units and that the Chem Unit1/ Chem Unit 2 boundary displays a genuine change in sediment provenance and in a chemical sense it is suggested that the top of Chem Unit 1 marks the base of the Ferron Sandstone Member. Chem Unit 1 is therefore thought to be equivalent to the underlying Tunnok Shale Member.

Chem Unit 2/Chem Unit 3 = at the top of Chem Unit 2 K-feldspar contents (modeled by the K/Rb ratio) are seen to decrease. Chem Unit 3 is transitional between Chem Unit 2 and Chem Unit 4, and as such during the deposition of this unit K-feldspar content shows an upward decrease and the amount of dolomite (Mg/Al values) increase. This change is geochemistry is consistent with the gradational change in facies from pro-delta

mudstones within Facies 1 and the delta-front and shoreface sequences seen within Facies 2.

FACIES 2:

Chem Unit 3 = A transitional unit between Chem Units 2 and 4. From the top of Chem Unit 2 to the base of Chem Unit 4 K-feldspar decreases and dolomite contents increase.

Chem Unit 4 = the boundary between Chem Unit 3 and Chem Unit 4 is characterized by an increase in dolomite, resulting in higher Mg/Al values within Chem Unit 4. As the majority of samples within Facies 2 are assigned to this unit, the chemical characteristics of Chem Unit 4 are thought to best represent Facies 2. It is suggested that the change in depositional facies from a pro-delta setting, to more proximal, delta-front and shoreface sequences promoted the dolomitization of samples assigned to Chem Unit 4. At present it not known whether dolomitization of these samples was enhanced by the presence of an Mg-rich clay mineral such as Chlorite (two samples from Chem Unit 4 contain the only significant amounts of Chlorite recorded in this study (Figure 6)) or is purely a result of deposition in sea water, as is document in carbonate systems.

FACIES 3:

All samples assigned to Facies 3 fall within Chem Unit 5 and display significantly reduced plagioclase abundances, compared to samples deposited under marine conditions. Dolomite, a characteristic of Facies 2 samples, is also absent in samples deposited in Facies 3. It is suggested that the changes seen in both geochemical and mineralogical datasets between fluvial and marine mudstones in this study may be driven primarily by changes in facies, rather than changes in sediment provenance. It is suggested that dearly diagenesis of sediments deposited in marine conditions may have resulted in the albitization of feldspar. However, detailed petrographic work would be needed in order to fully test this hypothesis.

FACIES 4:

The base of Facies 4 (Chem Unit 6) is identified as the top of the Ferron Sandstone Member (Enclosure A), with the overlying mudstones being assigned to the Bluegate Member of the Mancos Formation. Upward increases in both plagioclase and chlorite contents at the base of Chem Unit 6 also indicate that a major change in depositional environment took place at this time. In addition, an increase in EFV values (greater than 1) indicates that these sediments, unlike those from the underlying from the Ferron Sandstone Member, were deposited in a depositional environment where anoxic to disoxic conditions prevailed at the sediment/water interface (Tribouvillard., 2006).

Based on the discussions above, it is clear that although a chemostratigraphic correlation can be produced for the Ferron Sandstone Member (Enclosure A), on the scale of this study changes in geochemistry are co-incident with major changes in depositional facies, therefore, on a regional scale the chemostratigraphic boundaries will be highly diachronous.

The only exception to this is the boundary between Chem Unit 1 and Chem Unit 2, where both chemical units are deposited within the same facies group (Facies 1), but where a marked change in geochemistry, independent of depositional environment takes place. It is suggested that the increase in Ti/Nb values that occurs at this boundary is related to a change in the type and/or amount of volcanogenically derived clay minerals in the system at the time of deposition and as such marks a change in source composition independent of facies. Therefore, within this facies group the chemostratigraphic boundary will have some chronostratigraphic significance and if the same change in provenance can be recognized it may be possible to define approximately chronostratigraphic markers based on changing geochemistry.

Generally, samples from marine Facies 1, 2 & 4 have higher MgO/Al_2O_3 and Na_2O/Al_2O_3 values than samples from Facies 3 (Chem Unit 5), as shown on the chemical logs (**Figure 2**) and binary plots (**Figure 3**). However, 4 samples within Chem Unit 4, have values of MgO/Al_2O_3 and Na_2O/Al_2O_3 that are similar to those of Chem Unit 5 (Figure 8). Chem Unit 5 is a fluvially deposited sequence, while Chem Unit 4 represents

a marine shoreface and deltaic environment. Therefore, the four highlighted samples within Chem Unit 4 may represent mudstones that have a fluvial chemical signature within a marine shoreface setting. One interpretation of this feature is that the Chem Unit 4 mudstones with a "fluvial" geochemical signature have been introduced into the delta-front environment by hyperpycnal flow during periods of river flooding. Therefore, the geochemical data in this study have the potential to identify hyperpycnites, which have been separately document in this area of the Ferron Sandstone (Bhattacharya and MacEachern, 2009).

Previously authors such as Ratcliffe et al., (2010) and Wright et al., (2010) have used Na values and Na/Al ratios as a proxy for changing plagioclase contents and by extension changes in sediment provenance in fluvio-deltaic depositional environments. However, evidence from this dataset argues strongly that more caution is needed before inferring changes in source material from elemental or mineralogical datasets alone. Although data from this study does not categorically disprove the concept that changes in plagioclase content may suggest a change in provenance, it certainly suggest a strong facies control, which must be taken into account when making interpretations from bulk inorganic date in dynamic sedimentary environments.

Conclusions:

Within fluvio-deltaic sequences of the Ferron Sandstone Member (as documented within the Notom Delta Complex) six "Chem Units" can be recognized and correlated between the analyzed sections, based on changes in K_2O/Rb, Na_2O/Al_2O_3, $MgO/Al_2O_3,$ TiO_2/Nb and EFV ratio values. The geological factors controlling the geochemical variations within each chemostratigraphic unit are thought to primarily be related to changes in depositional facies, with secondary influences related changing K-feldspar abundances, changing clay mineral species and periodic volcanogenic influences.

The discussion above displays the importance of fully understanding the mineralogical controls on whole-rock geochemistry and integrating chemostratigraphic

studies with facies models. Failure to take these aspects into account, especially when translating chemostratigraphic techniques to sub-surface studies can result in spurious stratigraphic correlations and resulting mineralogical and geological interpretations.

Additionally, the inorganic geochemical signature of mudstone samples from fluvial sequences shows a significant difference to that seen from mudstone samples analyzed from deltaic sequences. This is the most notable change in geochemistry throughout the study intervals and it is suggested that this may be due to the albitization of feldspars in sediments deposited in dominantly marine conditions.

By enabling the clear differentiation of marine and fluvial mudstones this work has highlighted the presence of fluvially derived mudstones within demonstrably marine deltaic depositional environments (**Figure 8**). Their presence could tentatively be attributed to episodic fluvial flooding events that result in deposition of hyperpycnites. Within these Ferron delta-front sections thin (cm scale) hyperpycnite beds have been identified (photo and/or descriptions). It is suggested that where samples in this study have a "fluvial" geochemical signature within a demonstrably marine sequence, proportionally more hyperpycnite beds have been sampled. This hypothesis may be tested by more detailed (cm-scale) sampling of shore face mudstones within the Ferron Sandstone Member.

Comparisons between the resulting chemostratigraphic correlation and sequence stratigraphic correlations show broadly similar features, with the chemostratigraphic correlation showing changes in geochemical data at approximately the same position as changes in lithostratigraphy and depositional facies. However, there does not appear to be a clear relationship between the detailed sequence stratigraphically defined time correlative surfaces shown on Enclosure A and chemostratigraphic units defined herein (Enclosure A). This may be a result of the paucity of samples within these intervals (primarily Chem Unit 4), and it is suggested that a higher resolution sampling program would be needed to better understand how bulk geochemical data may be integrated with high resolution sequence stratigraphic correlations.

References:

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Figure Captions:

Enclosure A: Key element ratios plotted for seven measured sections and shown in relation to sequence stratigraphic correlation produced for the Ferron Sandstone Member in this area (Zhu, 2010).

Figure 1: Shows study area and the location of measured sections sampled in this study. The location of all sampled material is also numbered on each section.

Figure 2:.Map showing mid-Cretaceous paleogeographic reconstruction of delta systems flowing into the western margin of the Cretaceous interior seaway (Bhattacharya and Tye, 2004)

Figure 3: Key element ratios for all samples, all sections plotted in relative stratigraphic order. The measured section displayed on the figure is a schematic placed to give a sense of the sedimentology through each composite Chem Unit.

Figure 4: Binary differentiation of Chem Units 1-5.

Figure 5: Schematic measured siction showing the relationship between "Chem Units" and "Facies" groups.

Figure 6: Log plotted for XRD (X-ray diffraction) data in relative stratigraphic order (Table 2).

Figure 7: Element to mineral and element to element binary plots showing the potential relationships between geochemical data and mineralogy for key elements in the study.

Figure 8: Binary plot showing samples which plot with a chemical signature indicative of fluvial depositional facies in this study. Samples highlighted in red show a chemical signature which suggests they are deposited under fluvial conditions, but are located within predominantly marine depositional facies.

Table 1 – XRD (X-Ray Diffraction) data

Table 2 – All samples selected for elemental analysis shown in approximate relative stratigraphic order.
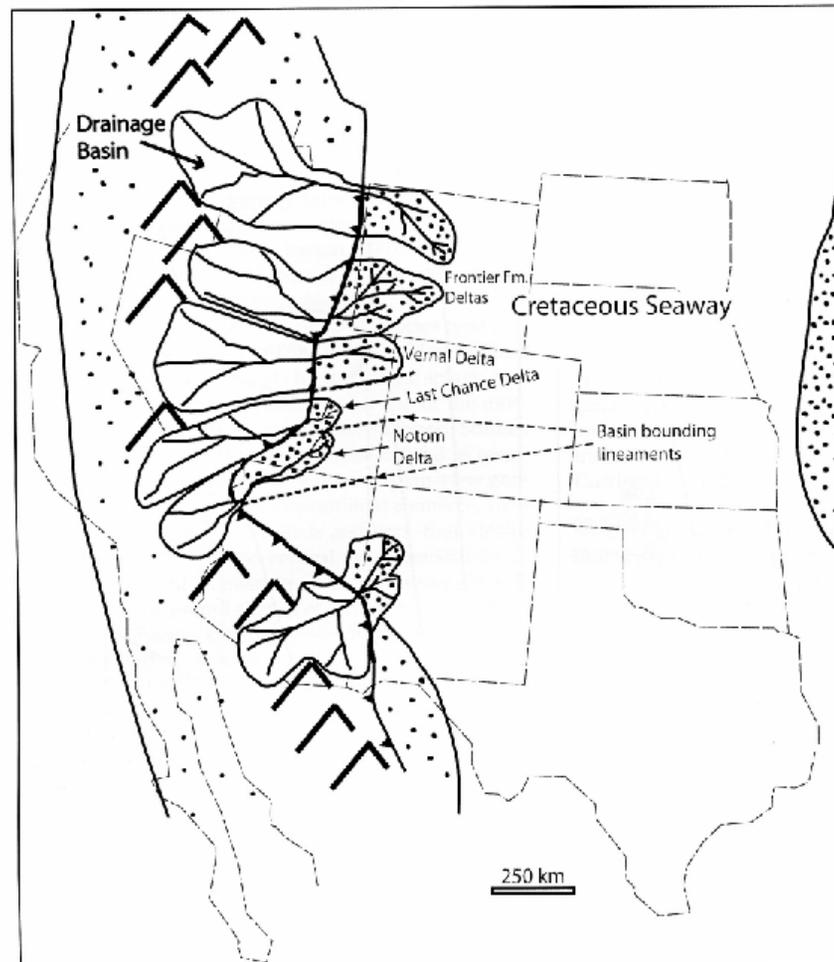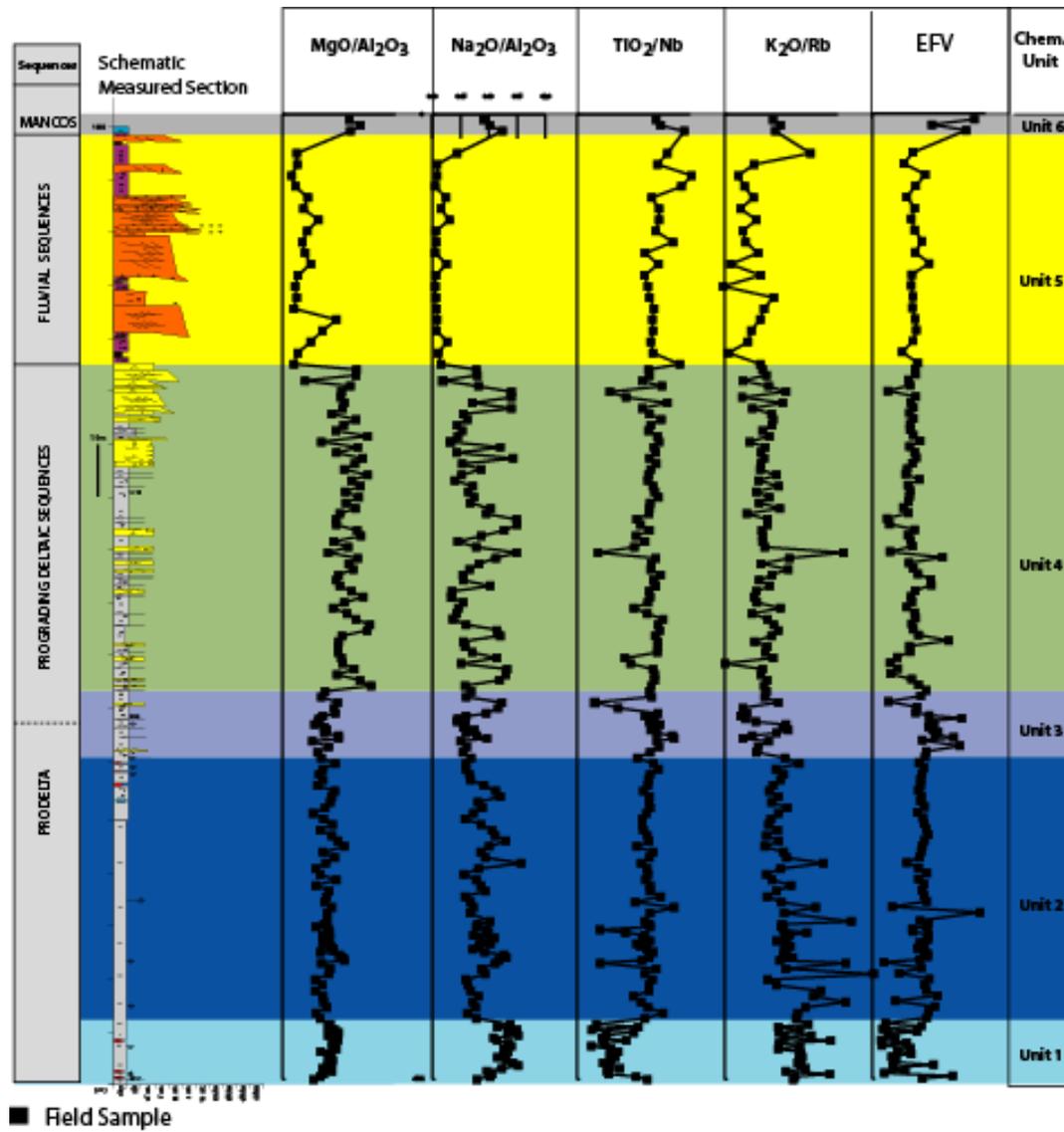
Figure 1

Figure 2
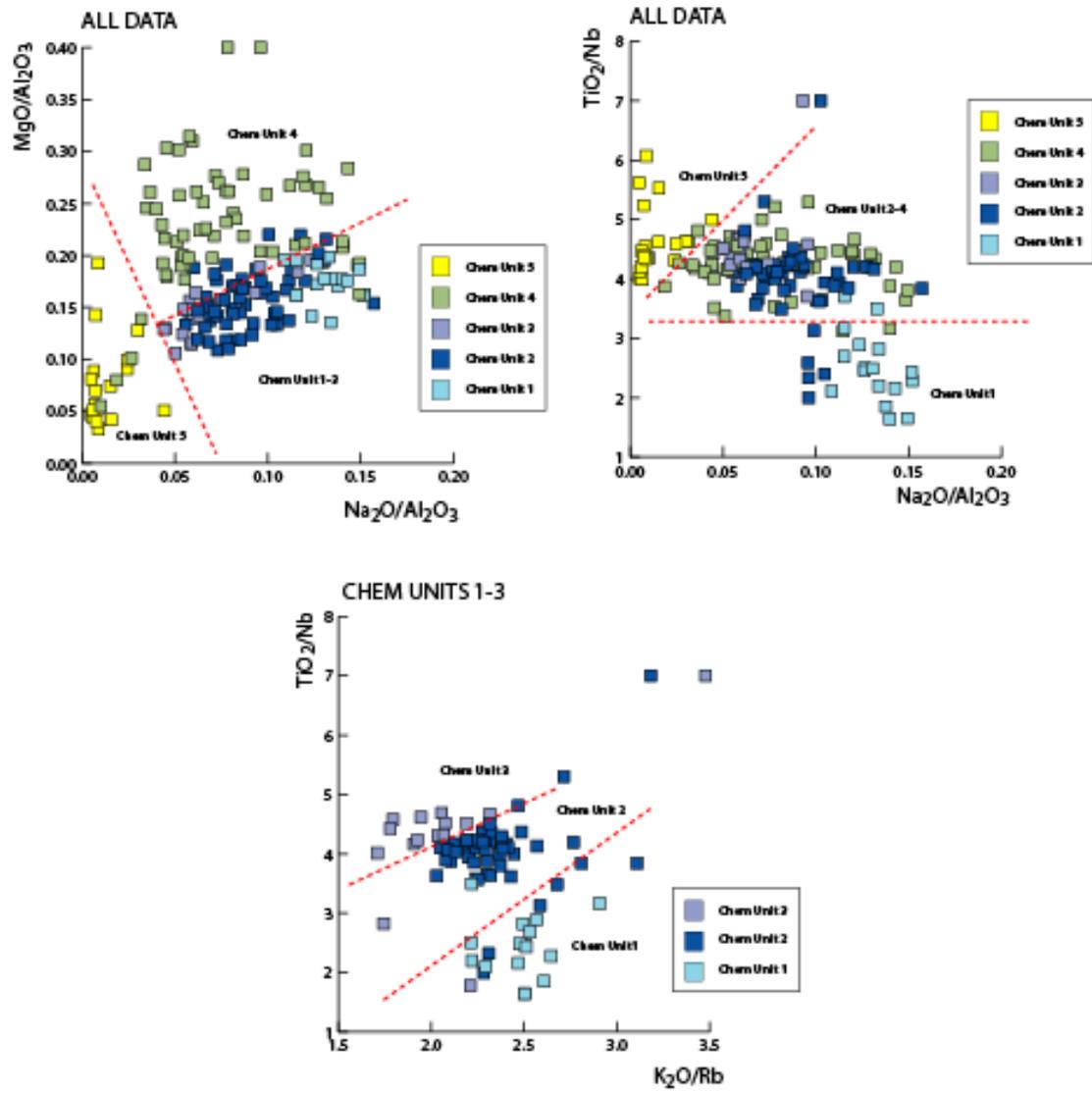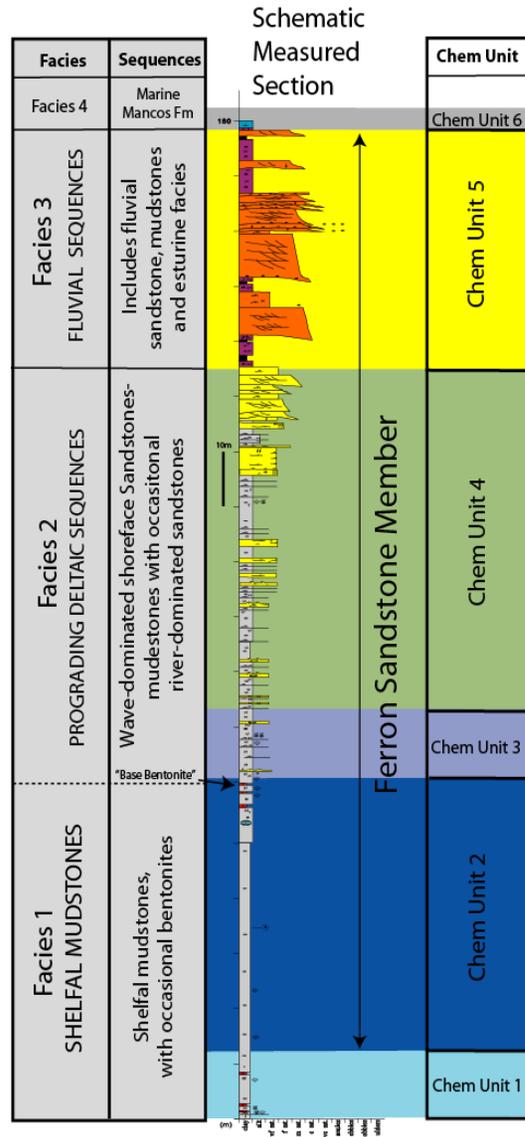
Figure 3

Figure 4

Facies	Sequences
Facies 4	Marine Mancos Fm
Facies 3 FLUVIAL SEQUENCES	Includes fluvial sandstone, mudstones and esturine facies
Facies 2 PROGRADING DELTAIC SEQUENCES	Wave-dominated shoreface Sandstones-mudestones with occasitonal river-dominated sandstones
Facies 1 SHELFAL MUDSTONES	Shelfal mudstones, with occasional bentonites

Schematic Measured Section

Chem Unit

Chem Unit 6

Chem Unit 5

Chem Unit 4

Chem Unit 3
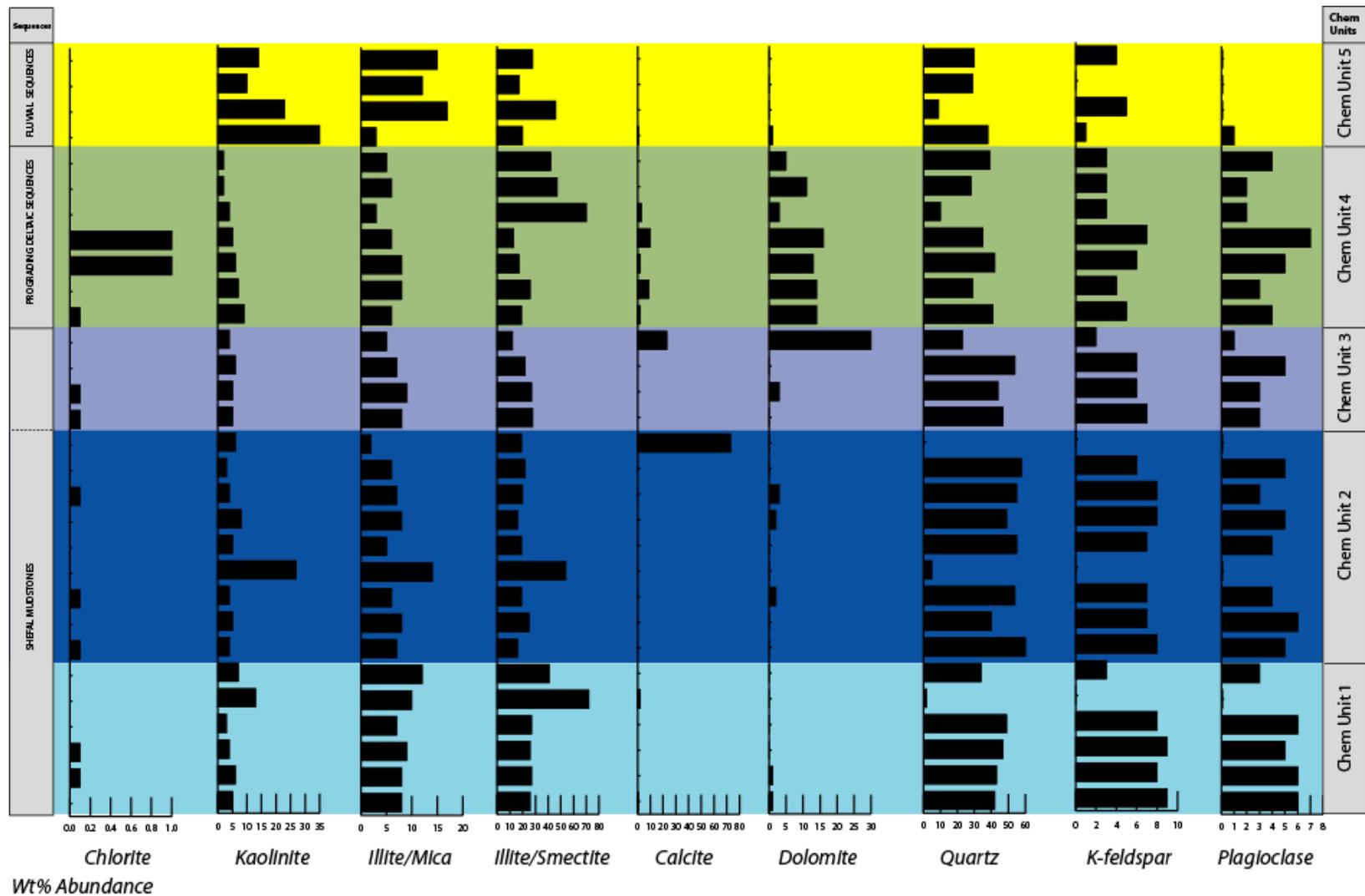
Chem Unit 2

Chem Unit 1

Ferron Sandstone Member

"Base Bentonite"

180

10m

Figure 5

Figure 6

Figure 7

Figure 8