

# Application of inorganic whole-rock geochemistry to shale resource plays: an example from the Eagle Ford Shale Formation, Texas.

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## ABSTRACT

Shale resource plays continue to be the most actively explored and developed hydrocarbon plays in North America. However, despite the intense activity surrounding the shale plays, understanding the controls on reservoir quality and successfully exploiting shale formations remains challenging. Using examples primarily from the Eagle Ford Formation, this paper demonstrates how inorganic whole-rock geochemical data can be used to help with the development of shale plays. Elemental data are used to provide regional stratigraphic correlations and provide sufficiently high resolution characterization to enable horizontal well-bores to be related back to pilot holes. The same elemental data used for chemostratigraphy can also be used to model mineralogy and total organic carbon, determine paleoredox facies and provide information on the formation brittleness, all valuable information in the exploitation of shale resource plays. The methodologies demonstrated here in the Eagle Ford Shale Formation have been used extensively in other North American shale plays and are readily applicable to any of the newly emerging shale gas resource play around the World.

## INTRODUCTION

Over the past few years shale resource plays have become increasingly important hydrocarbon targets. In the USA, formations such as the Marcellus Formation, the Haynesville Formation and the Eagle Ford Formation have become major hydrocarbon exploration targets, with over 270 rigs active in the Eagle Ford Formation in April 2012. However, the fine grained, macro-scale homogeneity of many shale plays currently being exploited has negated some of the more traditional approaches to reservoir characterization and stratigraphic correlation, resulting in the search for new methodologies that enable better understanding of shale reservoirs. Here, the application and potential of one approach is demonstrated, namely the application of inorganic whole-rock geochemical data to shale resource plays. Inorganic whole-rock data from the Eagle Ford Formation are used to create a regional chemostratigraphic correlation framework, model bulk mineralogy, model total organic carbon (TOC) data, better understand paleoredox conditions and provide information on relative rock brittleness, which are all aspects that are key to understanding shale reservoirs.

Inorganic whole-rock geochemical data have been used to define stratigraphic correlations in the petroleum industry for over a decade

(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 with respect to geological events, such as paleoclimate (Pearce et al. 2005, Ratcliffe et al. 2010) and provenance (Ratcliffe et al. 2007, 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. 2005, Ratcliffe et al. 2006, Ratcliffe et al. 2010, Wright et al. 2010, Hildred et al. 2010). Over the same decade, inorganic whole-rock geochemical datasets have routinely been acquired from organic-rich mudrocks, the data typically being used to help elucidate paleoredox conditions during oceanic anoxic events (e.g. Tribovillard et al. 2006, Turgen and Brumsack 2006, Tribovillard et al. 2008, Negri et al. 2009, Jenkyns 2010). Here, approaches of the chemostratigraphic workers and the oceanic anoxic event workers are combined and pragmatically applied to shale gas plays.

## METHODOLOGY AND DATASET

The Eagle Ford Formation is a dark grey, calcareous, locally organic-rich mudstone of Cenomanian – Turonian age between the Cenomanian-age Buda Formation and the Coniacian-Santonian-age Austin Chalk Formation (Figure 1). The study area, in south Texas, forms a narrow strip that extends from La Salle County in the SW to Lavaca County in the NE, a distance of >150 miles (241 km) (Figure 2). Over this distance, the Eagle Ford Shale Formation varies in thickness from approximately 75ft to 300ft (23 to 91 m).

For this paper, over 500 samples from 11 wells have been analysed using inductively coupled plasma optical emission (ICP-OES) and mass spectrometry (ICP-MS), following a Li-metaborate fusion procedure (Jarvis and Jarvis 1995). These preparation and analytical methods provide data for 10 major elements, 25 trace elements and 14 rare-earth elements. Precision error for the major-element data is generally better than 2%, and is around 3% for the high abundance trace-element data derived by ICP-OES (Ba, Cr, Sc, Sr, Zn and Zr). The remaining trace elements are determined from the ICP-MS and data are generally less precise, with precision error in the order of 5%.

## APPLICATIONS

### Regional stratigraphic characterization and correlation

Developing stratigraphic frameworks is the key to the exploration for and exploitation of any hydrocarbon-bearing basin. In shale plays, the more traditional methods to stratigraphic correlations used by the petroleum industry are often limited. Commonly, the restricted basin

whether the chemostratigraphic correlations produced can be viewed as chronostratigraphic, lithostratigraphic or sequence stratigraphic. For example a correlation based upon modeling the kaolinite/illite ratio in a fluvial setting as described by Ratcliffe et al. (2010), and shown by those authors to be climate-related, can be considered to be broadly chronostratigraphic, whereas Hildred et al. (2010) demonstrated the homotaxial nature of two valley systems using changes in provenance-related elements and element ratios. The elemental composition of individual minerals is relatively well understood, however, it is being able to disentangle the bulk and trace mineral controls on the elemental geochemistry acquired from a bulk sample that is the challenge to the chemostratigrapher. One pragmatic approach is the use of direct comparison between elemental data and mineralogical data (e.g. Pearce et al. 2005) or when mineralogical data are not available by using multivariate statistical analysis (e.g. Ratcliffe et al. 2010, Wright et al. 2010). Using both of these approaches on numerous sections through the Eagle Ford Formation, it can be demonstrated that changes in the key element and element ratios displayed on Figure 3, and their interpretation are:

$CaO/Al_2O_3$  = changes in relative proportion of carbonate and clay mineral content

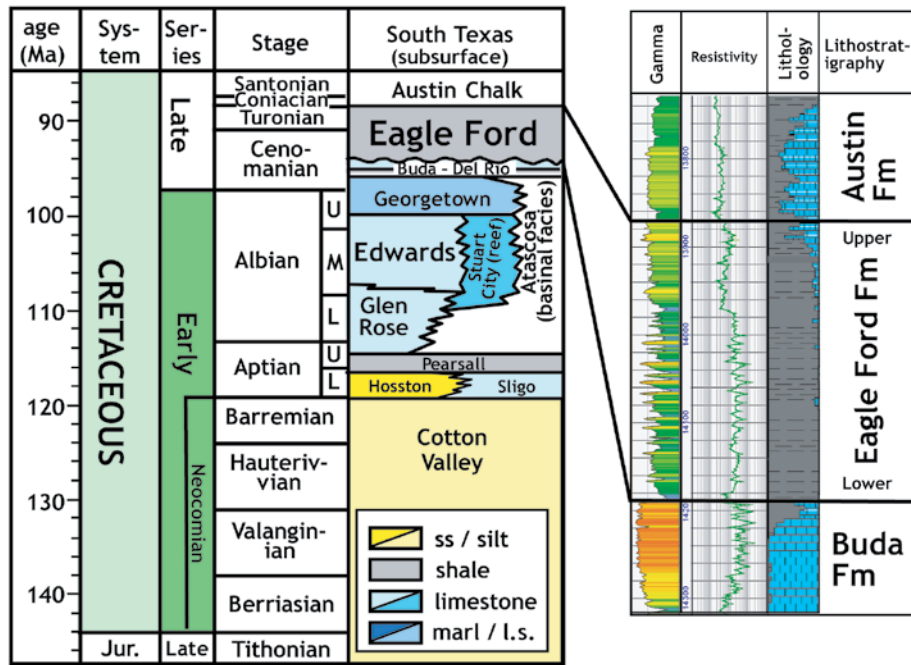


Figure 1: Stratigraphic column and type log for Eagle Ford Formation.

nature of their accumulation can limit the use of biostratigraphy and palynomorphs are often thermally degraded. Log correlations are hampered by high, but erratic U values that reflect a mixture of detrital input and authigenic enrichment from sea water. Furthermore, the apparent macro-scale homogeneity of the mudrocks precludes the recognition of sedimentary facies that can be used for stratigraphic correlations, particularly when the only samples available are cuttings.

Figure 3 displays the geochemical characterization of the Del Rio, Buda, Eagle Ford and Austin formations in Friedrichs #1 well and Figure 4 the extension of that characterization into 4 of the 11 wells in the study. The Eagle Ford Formation is divisible into a chemically defined upper and lower Eagle Ford, which is primarily based on an upward decrease in U values at the lower/upper Eagle Ford boundary (Figure 3). Furthermore, both the Lower and Upper Eagle Ford can be subdivided into 3 geochemical units, based on changing values of  $P_2O_5$ , Th/U,  $Na_2O/Al_2O_3$  and U. The formation top is readily geochemically defined by a decrease in the values of U and an increase in  $TiO_2/Nb$ ,  $Na_2O/Al_2O_3$  and  $CaO/Al_2O_3$  values. It is also noted that in many wells in this study the boundary between the Eagle Ford and Austin formations is not expressed as a sharp change in chemical composition, but more as a gradational change, which is shown as a chemical “transition” on Figures 3 and 4.

When dealing with basin-wide chemostratigraphic correlations, it is imperative to understand the mineralogical and therefore geological controls on the elements and element ratios used to define the zonation (e.g., Wright et al. 2010). It is essential to do so in order to ascertain

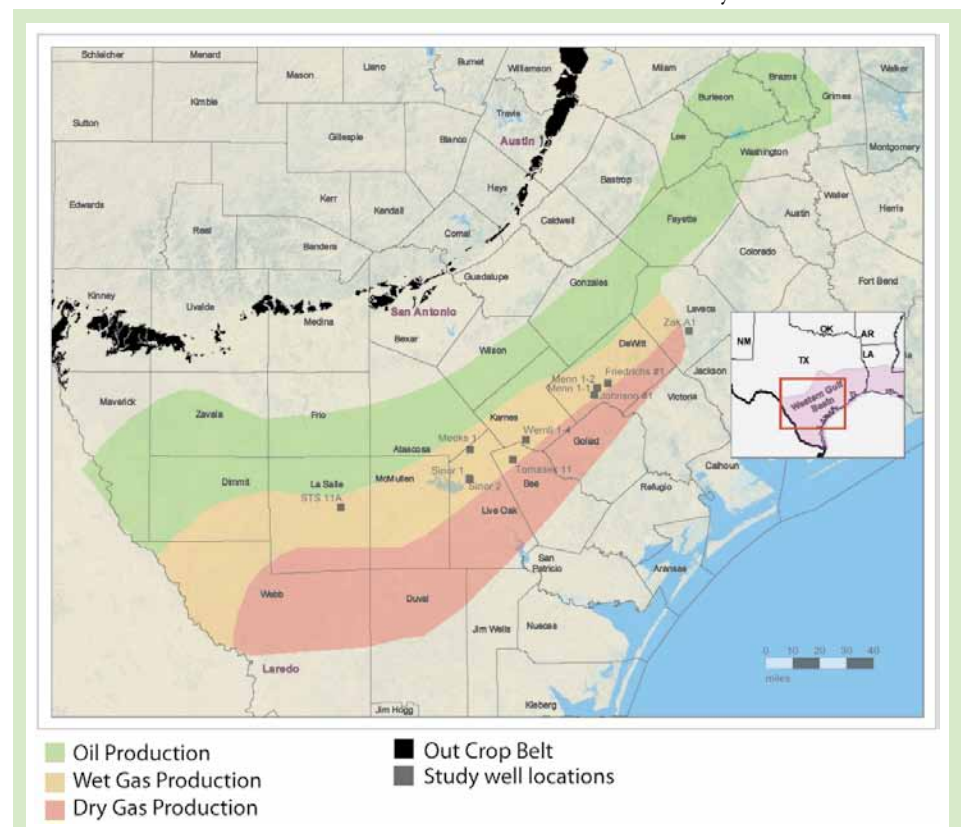
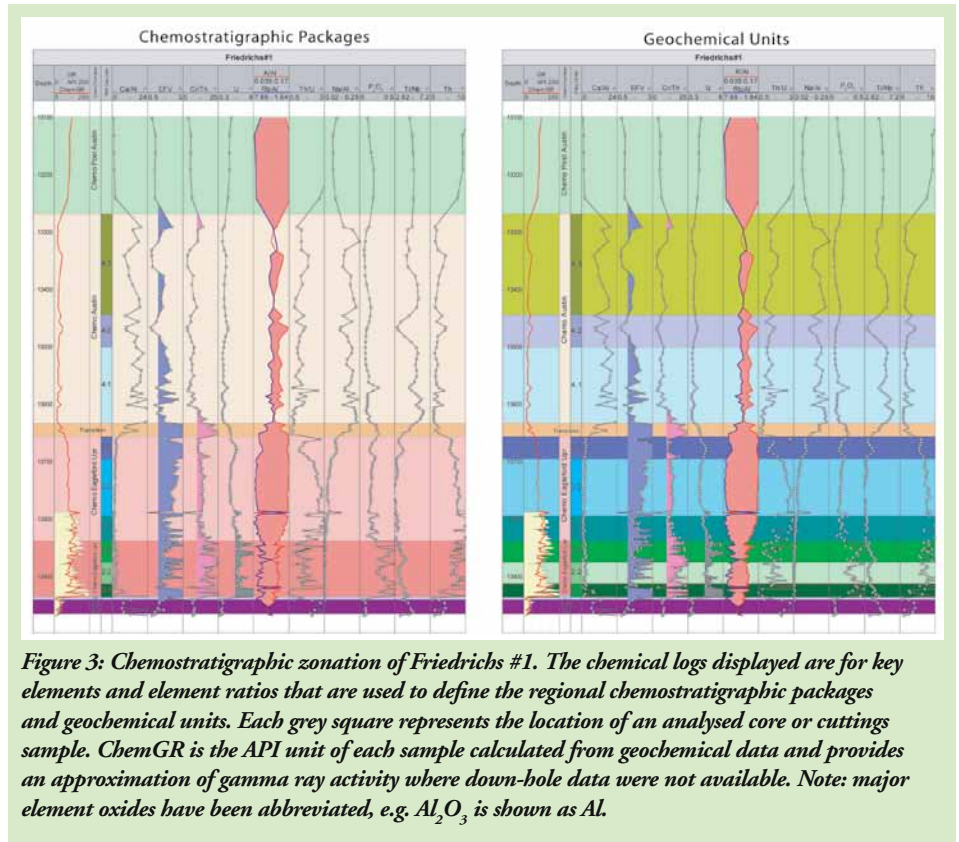


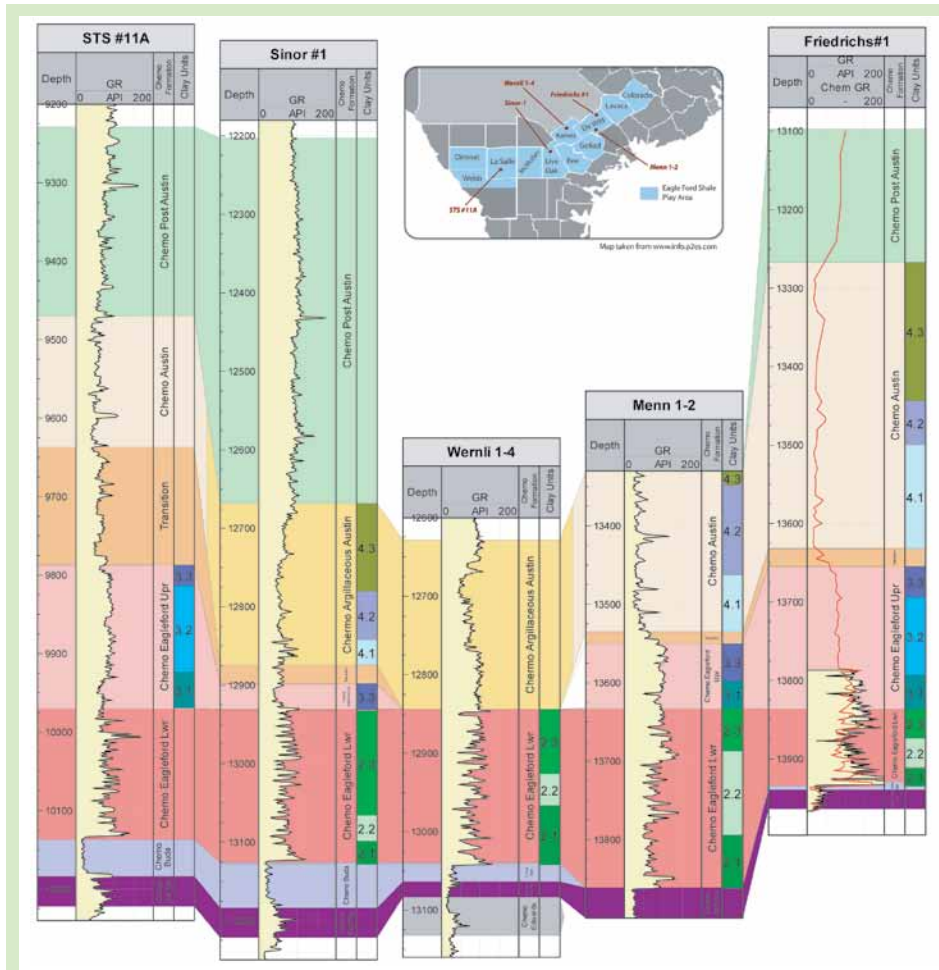
Figure 2: Location map for the Eagle Ford wells in the study.

- $P_2O_5$  = changes in biogenic apatite, which relate to surface productivity
- V Enrichment factor (EFV) = changes in oxygenation of bottom waters
- U = changes in total organic carbon contents (TOC)
- Th/U = amount of clastic input vs. organic content
- $Na_2O/Al_2O_3$  = amount of plagioclase feldspar present
- $TiO_2/Nb$  = changes in composition of clastic material entering the basin
- $K_2O/Al_2O_3$  (and  $Rb/Al_2O_3$ ) = changes in the percentage of clay mineral species
- Cr/Th = changes in oxygenation of bottom waters vs. clastic material entering the basin
- Th = amount of clastic input. Where values exceed 20 ppm, Th can be related to volcanogenic material

Many of the geochemical patterns show distinct stratigraphic variations. For example,  $P_2O_5$  and Cr/Th are higher in the lower Eagle Ford chemo unit relative to the upper



*Figure 3: Chemostratigraphic zonation of Friedrichs #1. The chemical logs displayed are for key elements and element ratios that are used to define the regional chemostratigraphic packages and geochemical units. Each grey square represents the location of an analysed core or cuttings sample. ChemGR is the API unit of each sample calculated from geochemical data and provides an approximation of gamma ray activity where down-hole data were not available. Note: major element oxides have been abbreviated, e.g.  $Al_2O_3$  is shown as Al.*



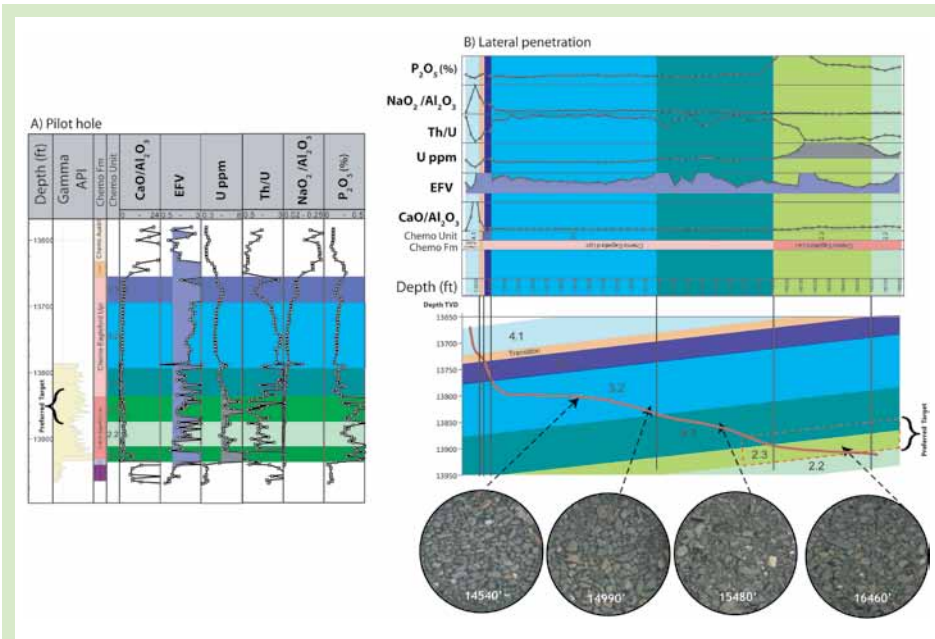
*Figure 4: Chemostratigraphic correlation summary of the Eagle Ford Formation and the overlying Austin Formation in selected wells*

Eagle Ford chemo unit, illustrating greater surface productivity and lower bottom water oxygenation during lower Eagle Ford deposition. Differences in clastic influx and organic accumulation between the Eagle Ford and Austin chalk are also indicated by temporal  $CaO/Al_2O_3$  and  $TiO_2/Nb$  ratios.

## HIGH-RESOLUTION STRATIGRAPHIC CHARACTERIZATION FOR AID WITH GEOSTEERING

The need for high-resolution stratigraphic frameworks is exacerbated in shale plays by the increased use of horizontal drilling in their exploitation. Typically, the horizontal leg of a well will be several thousand feet in length, with the aim of remaining in a thin stratigraphic horizon over as much of that distance as possible.

Key to working in lateral wells is identifying element and element ratios that change at the top and base of the target zone. The ideal target zone for lateral wells through the Eagle Ford Formation in the Friedrichs area is shown in Figure 5A and it is broadly coincident with unit 2.3. Regionally, the top of the Eagle Ford lithostratigraphic unit is coincident with the top of chemo unit 3.3, and the top of the Lower Eagle Ford lithostratigraphic unit is the top of chemo unit 2.3 (upper portion of the



**Figure 5: Relating a lateral well back to the pilot hole using selected chemical logs. 5A) High resolution zonation of Friedrichs #1 pilot hole, with the target zone for the lateral well indicated. 5B) Data obtained from cuttings samples in the Friedrichs lateral well, with an interpretation of the geochemical units through which the lateral travelled.**

target zone), where there is a marked down-hole increase in  $P_2O_5$  and U values and decrease in Th/U values. From the top of chemo unit 2.3 to its base the  $P_2O_5$  and U values remain

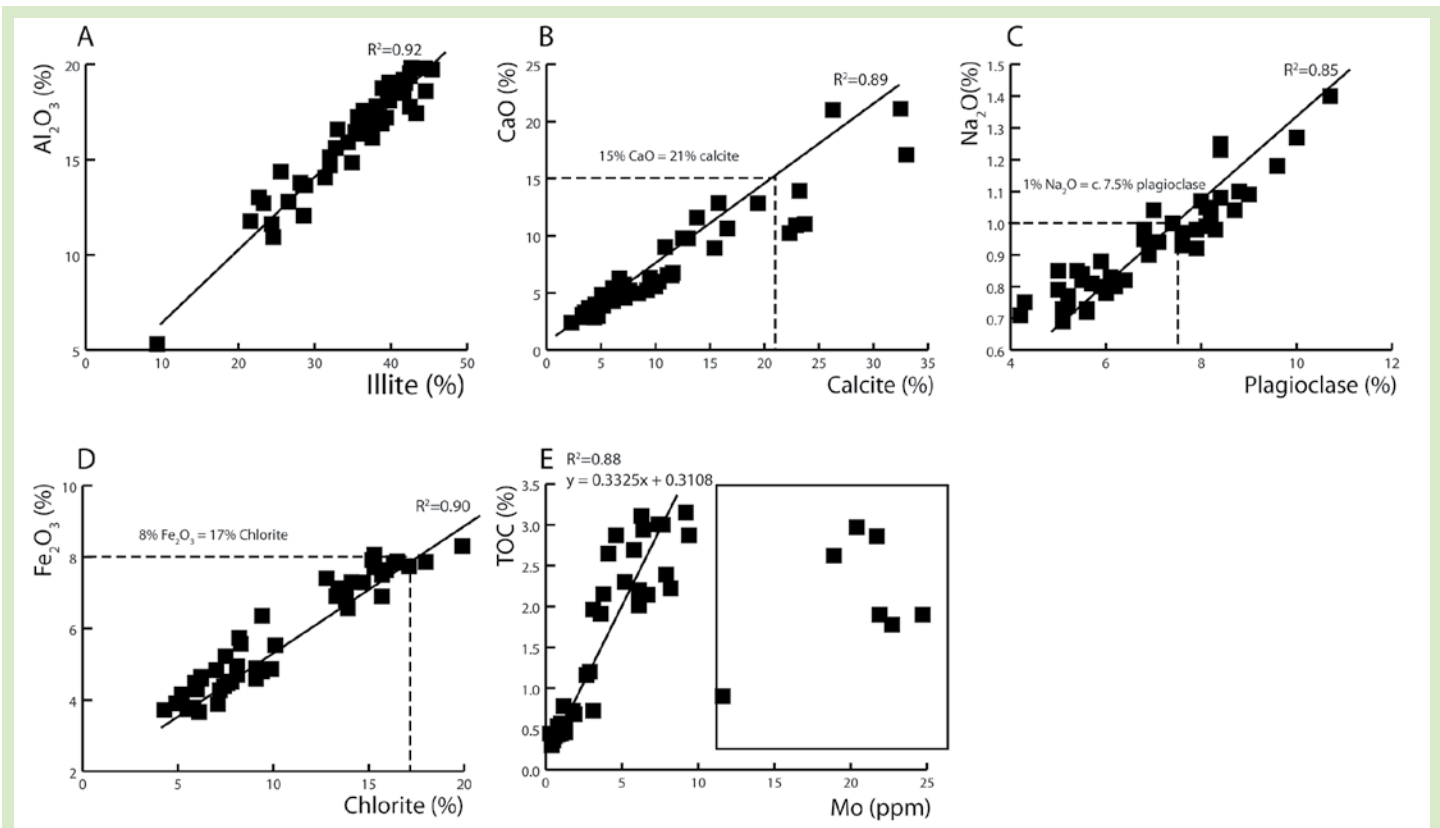
high (Figure 5), with a drop in U values and increases in Th/U and EFV ratios marking the boundary between chemo units 2.3/2.2. This chemo unit boundary is coincident with the

base of the preferred zone for horizontal wells. Therefore, from the pilot well, a target zone for lateral wells (chemo unit 2.3) can be defined using chemostratigraphy.

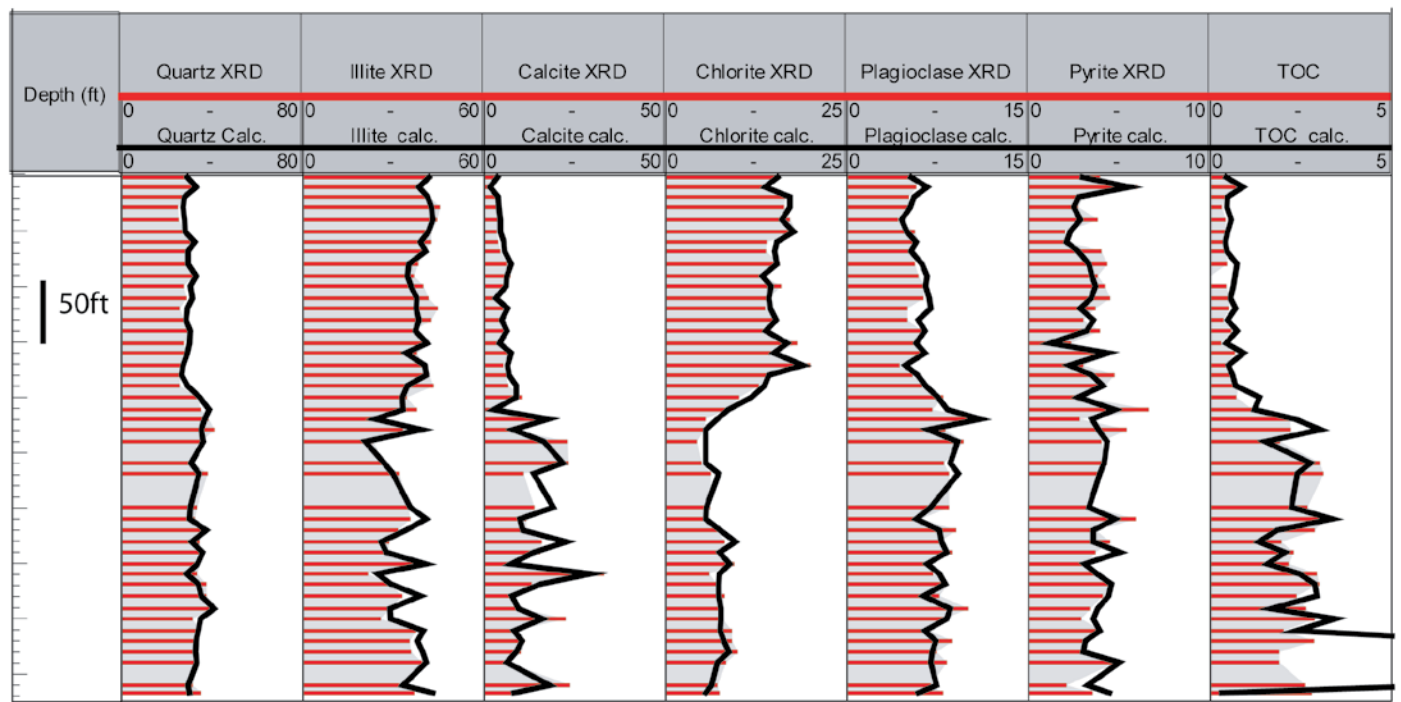
Figure 5B has the same ratios as used in Figure 5A plotted for the Friedrichs #1 lateral. While drilling the horizontal section immediately beyond the heel of the well (c. 14000' measured depth (MD)), field technicians monitoring the data suggested that the well-bore was above chemo unit 3.3 (top Eagle Ford Formation) and therefore needed deepening. Throughout the Upper Eagle Ford Formation  $P_2O_5$  and U values remain low, however as the well deepens toward the target zone an increase in  $P_2O_5$  and U values occurs and subsequent drop in Th/U values clearly defines the top of chemo unit 2.3, indicating that the target zone is penetrated. Furthermore, near the toe of the well a drop in U values is observed suggesting that chemo unit 2.3 has been penetrated and that the last 200 ft of this lateral sits just below the target zone.

## MINERAL AND TOC MODELLING

Reservoir quality in shale resource plays is



**Figure 6: A-D) Comparison of selected element concentration and mineral abundance. E) Comparison of Mo concentration and TOC. Mineral abundances have been determined by XRD measurements. In all cases elemental data, mineralogical data and TOC data are from the same sample, but not the same, homogenised powder, which will result in some scatter.  $R^2$  values and regression equations are displayed.**



**Figure 7:** A comparison of mineralogy calculated from elemental data using ChemMin™ and mineralogy obtained by XRD. The right-hand column is a comparison of TOC calculated from a linear regression equation and TOC measured in the sample. Note that this example is from the Haynesville Formation, not the Eagle Ford Formation.

dependent on numerous factors, all of which revolve around mineralogy and TOC values. Mineralogically, the Eagle Ford Formation is relatively simple, comprising quartz (av. 13%), calcite (av. 50%) and clay minerals (av. 27% illite, illite/smectite, kaolinite and chlorite), with lesser amounts of pyrite, apatite and plagioclase feldspar. TOC values are typically between 1% and 7%. Each of these mineral phases and the TOC contents are readily modelled from the same elemental dataset used to define chemostratigraphic correlation framework.

Figure 6 demonstrates the close association of major element concentrations and mineralogy. From those cross-plots it is evident that aspects of mineralogy can be modelled using the regression line equations displayed. Several public domain programs take this simple modeling further and use changes in geochemistry to provide semi quantitative mineralogical data (Paktunc 2001, Rosen et al. 2004). Proprietary software is also used by wireline logging companies to transform elemental data gathered from down-hole geochemical logging tools into mineralogical data. Figure 7 compares the bulk mineralogy calculated from whole rock geochemical data acquired by ICP analysis against mineralogical data acquired from x-ray diffraction (XRD).

In this case, the bulk mineralogical data were calculated using Chemostrat's in-house software program, ChemMin™ and the samples used for this are from the Haynesville Formation, not the Eagle Ford Formation.

Semi quantitative TOC values can be calculated from trace element geochemistry by calculating a linear regression equation between selected trace elements and measured TOC (Figure 6E). Provided the relationship between trace elements and TOC has a regression coefficient of over 0.8, it can be used to model TOC values where TOC measurements have not been made. The results of this approach are displayed in the right hand column of Figure 7.

## PALEOREDOX

Understanding paleoredox conditions is of paramount importance to shale gas exploration, since high TOC values are only typically found in sediments deposited where bottom conditions were anoxic or euxinic. Oceanic anoxic events have long been recognized and studied (Schlanger and Jenkyns 1976) and in recent years, much has been written on the use of elemental geochemistry in sediments and water columns as a proxy for depositional redox conditions (e.g., Tribovillard et al. 2006, Turgen and Brumsack 2006, Tribovillard et al. 2008, Negri et al. 2009, Jenkyns, 2010). The

key to using major and trace element changes to understand paleoredox in ancient sequences is understanding the geological controls on each of the elements. Principal components analysis provides a quick and effective way to detangle the influences of terrigenous input, carbonate production and authigenic enrichment from sea water on major and trace elements (Ratcliffe et al. 2012). Typically redox-sensitive elements, such as V, Cr and U provide a means to determine the degree of anoxia during deposition. Vertical and lateral changes in elements associated with authigenic enrichment within the Eagle Ford Formation (Figure 3) provide a means to understand temporal and geographic changes in paleoredox conditions, therefore providing important data regarding likely hydrocarbon productivity. For example, in Figure 3, Cr/Th and EFV values are generally high throughout the Eagle Ford Formation relative to over and underlying sequences; however, it is also clear that within the Eagle Ford Formation there are significant fluctuations of these ratios. This implies that although bottom water conditions tended to be anoxic during deposition, there is considerable high-resolution variability in paleoredox conditions throughout the deposition of the Eagle Ford Formation.

## RELATIVE ROCK BRITTLENESS

Another important feature of shale gas production is the “fracability” of the formations being drilled. This is controlled by the inorganic and organic mineralogy of the sediments and the rock fabrics. Since the whole rock geochemical data is directly linked to mineralogy and, as discussed above and demonstrated on Figure 7, the bulk mineralogy can be used to calculate mineralogy and TOC, it is possible to calculate a relative brittleness (R<sub>Bi</sub>) value for each sample analysed for chemostratigraphy. Simplistically, Al<sub>2</sub>O<sub>3</sub> is primarily controlled by clay content, which increases ductility; SiO<sub>2</sub> relates to silica, which increases brittleness, particularly if present as biogenic quartz; and CaO is present as calcite, which can potentially increase brittleness. While R<sub>Bi</sub> does not provide a quantitative value of brittleness such as a Young’s Modulus calculation, it does provide a rapid and visual indication of relative brittleness within the formation. This measure can be rapidly determined from core samples, where it can be calibrated against physical data, such as a scratch-test before being calculated from cutting samples, thereby enabling R<sub>Bi</sub> to be calculated in lateral wells. This information can then be used to better understand which sections in a lateral well will be most likely to respond well to fracturing.

## CONCLUSIONS

Until relatively recently, the prime purpose of obtaining whole rock inorganic geochemical data for the petroleum industry has been for stratigraphic purposes. However, with increased exploration in shale resource plays, it is rapidly becoming apparent that the same dataset obtained to help refine stratigraphic correlations can be used to;

- Determine bulk mineralogy semi-quantitatively
- Determine TOC semi-quantitatively
- Understand temporal and lateral variation in paleoredox conditions
- Determine relative changes in rock brittleness
- Determine stages in a lateral well that may be unsuitable for frac-ing, thereby reducing the number of frac-jobs carried out.
- Understand how changes in mineralogical composition along a lateral may be used to design better completion treatment programs for a given area.

While the calculations of mineralogy, TOC and rock brittleness are not as accurate as direct measurements of those parameters, the results described here can all be achieved rapidly and at no extra cost from the same ICP-derived data used for chemostratigraphy. Furthermore, the applications for the Eagle Ford Formation can readily be applied to any shale resource play.

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