High-resolution chemostratigraphy and bulk mineralogical characterization of the Wilcox: A complimentary new multi-disciplinary approach to enhanced stratigraphic correlation

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Summary

Presented within this study is an example of high resolution chemostratigraphic zonation of the Wilcox Group. Elemental data from Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) and Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) has been used to chemostratigraphically evaluate the Wilcox Group interval. The geochemical data has been integrated with palynological data (Cornick et al. 2023) and x-ray diffraction mineralogical data to develop a multi-disciplinary approach to stratigraphic zonations and correlations.

Introduction

The stratigraphic correlation of the Wilcox Group is challenging, with strong reliance on calcareous fossils, which invariably results in a low-resolution stratigraphy – especially within the thick sand-prone sections. In recent years, palynology has proven an effective tool for correlating the Wilcox Group (Cornick et al. 2023) and the addition of integrated chemostratigraphy would greatly improve confidence, and complement the zonation.

Elemental chemostratigraphy, and x-ray diffraction (XRD), have been used on the Wilcox Group, but little to no integration of these results have been previously undertaken. This study utilizes chemostratigraphy, integrated with available palynological data, to produce a robust zonation for the Wilcox Group. Targeted XRD samples have been utilized to aid the mineralogical interpretation of the elemental data.

Methods

A total of three hundred and seventy-seven cutting samples from two study wells have been analysed for whole rock geochemistry. Within this study, these wells are referred to as “Well A” and “Well B”. In addition, sixty-one samples have been selected from these wells for mineralogical analysis by XRD.

Elemental chemostratigraphy focuses on stratigraphic changes in whole rock, inorganic, geochemistry. The elemental data used within this study is acquired from the analysis of sample by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

Within this study two penetrations of the Wilcox Group have been selected. Based on the samples appearance when examined under binocular microscope the samples were sieved with 7grams of sample selected from the 1mm sieve fraction.

The samples are prepared for analysis using the lithium borate fusion method advocated by Jarvis and Jarvis (1992a &1992b). Following preparation, the samples are analysed on a Thermo ICAP 7200 Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) and a Thermo ICAP RQICPMS Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) to obtain data for 50 elements, including major, trace and rare earth elements (REEs).

The precision of the geochemical data acquired by the ICP-OES and ICP-MS is determined using the replication of standard reference material (SRM) which are analysed during the analysis of the samples. Consistent analysis of SRM ensures that instrument drift can be corrected for.

Following analysis an assessment of the samples’ representativity is key; samples that are representative of the depths from which they are taken can have a higher level of confidence attached to the interpretation. This is achieved by a comparison of a synthetic gamma ray, calculated from the elemental K, O, Th and U data, compared to the traditional gamma ray (GR). Provided there is a match between these two profiles the cutting samples can be inferred to be representative and of good quality. If there is no match between the GR and calculated gamma ray the representivity of the sample must be checked, and if needed, the sample is omitted if no representative lithology is identified.

Representative samples which are selected XRD analysis were disaggregated gently using a pestle and mortar. A 2grams split of this material was then ‘microionised’ using a McCrone Microionising Mill to obtain an x-ray diffraction powder with a mean particle diameter of between 5-10µm. Samples were then dried overnight at 80°C, then re-crushed to a fine powder and backpacked into an aluminum cavity mount, producing a randomly orientated sample for presentation to the x-ray beam.

Samples were then analysed on the PANalytical X’pert3 diffractometer instrument with a copper anode tube. Samples were analysed between 4.5° and 75° 2Θ (theta) at a step size
of 0.013 and nominal time per step of 0.2s (continuous scanning mode) using x-ray radiation from a copper anode at 40kV, 40mA.

Identification of unknown minerals was achieved by using X-Ray Mineral Services Ltd “Traces” and “Search-Match” software to compare the x-ray diffraction pattern from the unknown sample with the International Centre for Diffraction Data PDF-4 Minerals database containing reference patterns for more than 157,000 phases.

Mineralogical Characterization

Eighty-one samples from across the two study wells have been analysed for whole rock mineralogy (XRD) to mineralogically characterize the bulk mineral changes within the Wilcox Group.

XRD data shows the quartz is broadly consistent across the study interval, with values ranging from 32 to 65%; its distribution predominantly a function of lithology, with fine grained intervals, denoted by higher GR values, corresponding to lower quartz abundance. Conversely, the higher GR intervals are characterized by higher overall abundance in total clay minerals.

From the whole rock XRD four clay species have been recognized: illite(+mica), illite-smectite, kaolinite, and chlorite. Illite(+mica) is the most dominant clay, with abundances up to 25% recorded; the highest values recorded correspond to the Selndian. Illite-smectite is generally low throughout the study interval, typically 1-5%. However, within the latest Ypresian values significantly increase, up to 41.3%. Chlorite is the next most abundant clay identified, up to 10% recorded. Chlorite abundance is reduced in the late Ypresian; most samples report zero chlorite abundance. Kaolinite abundances are typically consistent across the study interval; however, zero abundances are also identified within the late Ypresian – like the chlorite distribution.

Plagioclase and K-feldspar are both identified as framework grains; plagioclase is the dominant feldspar, values up to 20%. K-feldspar abundances are up to 8% within the samples. Plagioclase abundance appears lower within the Selndian, but also decreases upwards through the Ypresian. K-feldspar abundance appears relatively consistent but is absent from the latest Ypresian.

Calcite is primarily associated with the Ypresian aged stratigraphy and increases upwards through this interval. The highest values are recorded towards the top of the Ypresian and associated with limestone occurrence. Dolomite occurs independently of calcite and is associated with the Ypresian; values typically range from 1 to 2%.

Element to mineral affinities

Elements are known to have multiple mineralogical affinities, for example Si is commonly attributed to quartz abundance, however, it is also known to associate with other siliciclastic minerals, such as feldspars, micas, and clay minerals. However, certain assumptions are required, and the strongest element-to-mineral affinity is utilized. The two methods for determining these associations are either statistical testing, in the form of principal component analysis (PCA) or direct comparison of the elemental data to a mineralogical technique, such as XRD or petrography.

As discussed, the changes in elemental concentrations within the study interval primarily reflect changes in the abundance of minerals. However, the changes in the mineralogical abundances may be the result of changes in provenance, climate, environment of deposition, or diageneis. Of these provenance and climate have the most widespread correlation potential.

A total of fifteen key element ratios have been selected to best characterize chemostratigraphic zones within the Wilcox Group.

Chemostatigraphic Zonation

Using the key element ratios, six chemostratigraphic sequences have been characterized across the study interval through the Wilcox Group (Figure 2); these have then been subdivided into a total of sixteen chemostratigraphic packages, which are as follows:

- MS1-S1, the lowermost sequence characterised here, typically corresponds to a sandstone interval with, a low degree of weathering (shown by the weathering indices), and abundant K feldspar. MS1-S1 is subdivided into two chemostratigraphic packages.
- MS1-S2 is a predominantly claystone interval punctuated by several sandstones. A high chemical alteration index value is recorded at the base of this sequence and the clays within this sequence are inferred to be marine composition. MS1-S2 is further divided into three chemostratigraphic packages,
- MS1-S3 is a sand prone sequence with a higher abundance of phosphatic minerals and feldspar content than the over and underlying stratigraphy.
- MS1-S4 is a claystone prone section with sand intervals increasing in frequency towards the top of the section. This sequence is characterized by an abundance of mafic provenance indicators at the base, with upward increasing chlorite abundance, with the maximum values
Chem stratigraphy of the Wilcox Group encountered at the sequence top. The claystones within this sequence are also characterized by high chemical alteration index values. MS1-S4 is subdivided into five chemostratigraphic packages.

- MS1-S5 is defined as a coarsening up sequence, with a high indication of marine clays towards the base, possibly reflecting the occurrence of a maximum flooding surface. Phosphate decreases upwards through the sequence, and is inverse to the grain size proxies, suggesting the phosphate is associated with the finer-grained fractions. Indicators suggesting the presence of siliceous ooze are shown to increase to a maximum at the top of this sequence. MS1-S5 is subdivided into four chemostratigraphic packages.
- MS1-S6 is the uppermost chemostratigraphic sequence recognized within this study and is characterized by the occurrence of calcium, indicating a shift to from clastic to carbonate lithology.

A direct comparison to the biostratigraphy of Cornick et al. (2023) is also shown within Figure 2. Overall, there is a reasonable degree of consistency between the two stratigraphic techniques within only minor variation. In addition, the dinocyst palaeoenvironmental group is also plotted alongside the geochemistry further demonstrating the high level of consistency between the biostratigraphy and chemostratigraphy techniques.

The elemental data suggests that a provenance control is active within geochemistry. Provenance analysis of sandstone within the section has been carried out by Pearce et al., (2023c).

Conclusions

Following this high resolution chemostratigraphic study on the Wilcox Group the following conclusions have been identified:

- Elemental chemostratigraphic data from ICP-OES/MS analysis has been used to characterize the interval of the Wilcox Group. A total of six chemostratigraphic sequences, which are further subdivided into sixteen chemostratigraphic packages.
- The elements used to characterise the stratigraphy at chemostratigraphic package level are primarily associated with climate and

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<th>Well A</th>
<th>ChemGR</th>
<th>Quartz</th>
<th>K Feldspar</th>
<th>Plagioclase</th>
<th>Illite/Mica</th>
<th>Chlorite</th>
<th>Kaolinite</th>
<th>Illite/Smectite</th>
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Figure 1: Mineralogical characterization of the Wilcox Group
provenance. To further test this provenance analysis has been carried out on selected sandstone samples (see Pearce et al. 2023c).

- The comparison of chemostratigraphy to biostratigraphy of Cornick et al. (2023) shows reasonable correlation between the chemostratigraphy zonation and the biostratigraphic framework. In addition, the assemblages show strong affinity for the established chemostratigraphic sequences (see Figure 2).

- Mineralogical data shows the plagioclase is the dominant feldspar. Illite/mica is the dominant clay, followed by chlorite. Illite/smectite is only recorded within the upper part of the study well.

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