

Nanoscale imaging of the Woodford Shale,  
Oklahoma, USA: Organic matter preservation  
as clay-organic nanocomposites

Thesis submitted in accordance with the requirements of the University of  
Adelaide for an Honours Degree in Geology

Samuel Alex Fraser  
November 2012



THE UNIVERSITY  
*of* ADELAIDE

**TITLE**

Nanoscale imaging of the Woodford Shale, Oklahoma, USA: Organic matter preservation as clay-organic nanocomposites

**RUNNING TITLE**

Nanoscale imaging of the Woodford Shale, Oklahoma, USA

**ABSTRACT**

Regional and within well variability in hydrocarbon production from organic carbon-rich shales has demonstrated that these unconventional reservoirs are complex and require an in-depth understanding of geological factors to make successful predictions. Variability is apparent in porosity and permeability, mechanical properties governing fracture susceptibility for enhanced hydrocarbon release, and concentrations of organic carbon (OC). The economically successful, though variable Woodford Shale, Oklahoma, USA, shows a  $R^2 = 0.72$  correlation between mineral surface area (MSA) and total organic carbon (TOC) consistent with a mineral surface preservative effect on OC extending across a range of samples from multiple cores and with TOC values of <0.5% to 18%. The TOC and MSA data illustrates the systematic stratigraphic co-variant relationship between TOC and MSA showing steps of up to 15% TOC that are matched by similar shifts in MSA. Transmission electron microscope (TEM) imaging performed on ~80 nanometre thick ultramicrotomed thin sections independently confirms quantitative geochemical clay-OC associations at the nanoscopic scale of interaction. Energy Dispersive Spectrometry (EDS) spot analyses reveal that organic carbon is entirely constrained to nanoscale clay laminae within the sample. Grey zones encapsulated by clay aggregates appear homogeneous at low magnifications and are similar to discrete organic matter particles commonly interpreted in recent studies. However, high resolution inspection resolves these zones in to laminated clay particles occurring at tens of nanometres. TEM micrographs of later stage submicron-scale quartz grain growth may also explain how the opposing mechanisms of hydrocarbon leaching and entrapment can co-exist for over 300 million years and provide an insight into shale brittleness, known to increase fracture susceptibility. Determining key modes of how OC is preserved during deposition and early diagenesis in proven gas-shales, such as the Woodford Shale encompasses a more holistic approach to enhancing the prediction of prospective hydrocarbon resources in frontier basins.

**Keywords**

Organic matter preservation, clay minerals, quartz grain diagenesis, shale, gas storage, TEM, FIB, EGME, TOC variability.

**TABLE OF CONTENTS**

Title.....	3
Running title .....	3
Abstract.....	3
List of Figures and Tables .....	5
Introduction .....	9
Geological Background .....	13
Methods .....	16
Sample Collection .....	16
Geochemical Analysis .....	17
Mineralogy .....	18
Petrography.....	18
Results .....	19
Lithological Observations .....	19
Mineralogical Identification .....	25
Geochemical Analysis .....	27
Multi-scale Petrography of the Woodford Shale .....	30
Nanoscale imaging from TEM .....	33
micron-scale Quartz Grain Diagenesis and Hydrocarbon Entrapment .....	37
Discussion.....	39
Clay Mineral Controls on Organic Matter Preservation.....	39
Quartz Diagenesis and Hydrocarbon Entrapment .....	46
Conclusions .....	48
Acknowledgments .....	50
References .....	50
Appendix A: Methods .....	54
Ethylene Glycol Monoethyl Ether - Mineral Surface Area.....	54
GC-MS Thermal Maturity .....	56
Appendix B: Results.....	57
Geochemical Data Summary .....	57
GC-MS MPI Thermal Maturity .....	61

## LIST OF FIGURES AND TABLES

Figure 1 Three-dimensional schematic showing an example of an organic molecule, in this case - bacteriohopanetetrol, adsorbed onto the interlayer surface site of a clay platelet. Blue dashes (-) illustrate the negative charge at the clay mineral surface resulting from the electron interactions of the aluminium-silicon-oxygen tetrahedral atomic structure. Included are illustrations of the characteristic sodium ions ( $\text{Na}^+$ ) and water ( $\text{H}_2\text{O}$ ) molecules occupying the expandable clay interlayer site – in this case, a montmorillonite clay platelet 18 angstroms ( $\text{\AA}$ , 1.8 nanometres) thick. (Note; X and Y scale of platelet is reduced for the purpose of illustration clarity). .....	11
Figure 2 USA states superimposed on a palaeographic map showing the region of Woodford Shale deposition (south-south-eastern margin of Laurentia) during the Late Devonian (365 Ma). Colour coded regions show the Permian (green), Anadarko (purple), Ardmore (orange) and Arkoma (red) basins wherein the Woodford Shale (yellow) is presently preserved. Modified from Blakey (2008) .....	13
Figure 3 Stratigraphic chart of the Woodford Shale and binding strata in various basins throughout Oklahoma, USA. Adapted from Cardott & Chaplin (1993) and Comer (1991) .....	15
Figure 4 Map of Oklahoma and Counties, USA showing locations of the East Fitts. ...	17
Figure 5 Core lithology log illustrating the lithological variances in the East Fitts (EF) and Chitwood-Harris (CH) cores. CH displays three distinct lithological zones - phosphatic nodular shale with intermittent siliceous lenses (lower), minor level 2 bioturbated massive shale (middle), and extensively bioturbated (level 2-4) siltstone (upper). EF displays variable lithologies consisting of laminated shales, interbedded siliceous silty shales, and phosphatic nodular shales. Intermittent level 2-3 bioturbation is constrained exclusively to the middle zone. Note that level 1 bioturbation is not bioturbation interpreted. MSA and TOC data matched to depth illustrate the association of bioturbation intensity with poor TOC-MSA correlations. ....	22
Figure 6 Digital Photographs of slab-cut core samples showing varying intensities of bioturbation referring to photo locations in Figure 3, and categorised following the Ichnofabric Index by Droser & Bottjer (1993) (Table 2). White arrows mark various examples of trace fossils (burrows), and black arrows indicate density current ripple marks and wavy beds. a) East Fitts (EF) core sample (1,041.7 m) showing a typical sample of very finely laminated shale with very fine pyritised laminae ( $\leq 1$ mm thick), and does not feature any bioturbation (level 1). b) (EF) Example of density ripple marks (black arrows) and level 2 bioturbation. c) (EF) shows level 2-3 bioturbation featuring overlapping burrows. d) (CH) Example of level 4 bioturbation featuring numerous burrow overlap and extensive laminae disruption. e) (CH) Example of level 3 bioturbation with overlapping burrows and moderate sediment disruption. f) (CH) An example of nodular and siliceous lens growth and consequential laminae displacement. ....	24
Figure 7 Bulk powder mineralogy X-ray diffractogram of representative Woodford Shale samples from the East Fitts (EF) and Chitwood-Harris (CH) cores, and the Arbuckle outcrop (AO). Quartz (qz) peaks are dominant throughout all samples, as are	

phyllosilicate minerals matched phengite, clinocllore (chamosite), and muscovite interpreted in bulk XRD were categorised as either chlorite (chl) and illite (ill) based on comparisons with clay fraction XRD results. All samples showed varying peak intensities of dolomite (dol), pyrite (py), and also alkali and plagioclase feldspars matching multiple types of related mineral species (i.e. albite and anorthoclase). Note, diffractograms have been shifted proportionally above one another and all scaled equally for the purpose of clarity for the average peak intensity. .... 25

Figure 8 Clay mineral fraction X-ray diffractograms of a typical East Fitts core sample (EF-3422.4) (a) used to determine the phyllosilicate mineral types following the USGS Clay Mineral Flow Diagram by Poppe (2001). Results indicate the presence of chlorite (chl) which was not observed in Chitwood-Harris samples. Illite (ill) was detected in strong abundance (high counts) in all samples. Note, diffractograms are shifted upwards and separated for figure clarity. b) A zoomed section showing authigenic quartz peak ratios from an X-ray diffractogram of a typical Woodford Shale samples (EF-3422.4). A ratio of intensity diffraction peaks  $I_{100}$  and  $I_{101}$  and corresponding count values (188 and 646) are used to determine secondary quartz of phase (Table 4). .... 26

Figure 9 Total organic carbon (TOC) and  $\text{CaCO}_3$  corrected mineral surface area (MSA) plotted against calcium carbonate ( $\text{CaCO}_3$ ) corrected TOC% for the Chitwood-Harris and East Fitts core samples, and the Arbuckle outcrop samples. Linear regression shows strong positive correlations with  $R^2 = 0.82$  (East Fitts) and  $R^2 = 0.95$  (Chitwood-Harris). The moderate  $R^2 = 0.58$  correlation (Arbuckle outcrop) is possibly due to outcrop weathering effects resulting in OC loss (detailed in discussion), and samples plotting as high TOC to MSA have abnormally high fossil concentrations possibly containing remnant OM not associated with clays. Bioturbated samples are plotted separately ( $R^2 = 29$ ) displaying loss of OC and homogenization of MSA through sediment ingestion and OM digestion by organisms..... 28

Figure 10 Organic carbon (OC) and calcium carbonate ( $\text{CaCO}_3$ ) corrected MSA plotted against  $\text{CaCO}_3$  corrected TOC% for the Chitwood-Harris and East Fitts cores according to depth (metres). TOC and MSA with depth illustrates the co-variant relationship of TOC% with MSA on a sample to sample basis that remains in phase. Exceptions to this relationship are two zones (4,539.3 – 4,544.9 m and 4,545.8 - 4,548.8 m) in the Chitwood-Harris core which correspond to varying intensities of bioturbation (level 2-4). This results in both irrigation of sediment, and OM digestion and degradation, leading to significantly reduced OM loading onto minerals and homogenisation of MSA variability prior to burial. The East Fitts core displayed intermittent level 2-3 bioturbation, constrained to the intermediate section (1,037-1,039m) where TOC and MSA do not scale together. .... 29

Figure 11 Photomicrographs of optical thin sections (30  $\mu\text{m}$  thick) examined under reflected and transmission optical light. a) A typical Arbuckle outcrop (AO) sample showing an amorphous clay matrix hosting quartz grains (grey to off-white specs) (10-80  $\mu\text{m}$  in size) and brighter pyrite grains (py) of similar size. b) A rare carbonate fossiliferous AO sample hosting abundant calcareous shell fragments and intact shells (sh) of multiple species. c) East Fitts (EF) sample showing laminae of varying composition (some quartz dominant and some clay dominant). Clay dominant interval hosts pyritised tasmanite (py tas) cyst fossils (three examples indicated) constrained to <1 cm intervals and not always present in other samples. d) EF sample showing laminae displacive pyrite aggregate growth which occur intermittently but are common throughout the Woodford samples. e) Chitwood-Harris (CH) from 4,554 m depth (level

3 bioturbated zone) showing burrowing and disturbance of laminae, and pyrite aggregates (py). f) CH sample from 4,552 m depth showing abundant siliceous radiolaria (rad) fossils (two examples indicated) preserved in an amorphous clay matrix with some radiolaria fossils occasionally hosting pyretic cores (py rad). ..... 32

Figure 12 Scanning Electron Microscope (SEM) images of polished thin sections and polished blocks. a) Back scatter electron (BSE) image shows a squashed organic-rich (darker proportion) tasmanite cyst (~200  $\mu\text{m}$  in length) with a microcrystalline core (light proportion) preserved within a clay-quartz matrix. b) Secondary electron image of a squashed tasmanite cyst (~120  $\mu\text{m}$  in length) preserved within a clay-quartz matrix. Organic-rich fossils are either constrained to mm scale zones, sparsely distributed or not present in some samples. .... 33

Figure 13: TEM photomicrograph of an ultra-thin section from the East Fitts core (sample EF-3422.4). Organic carbon (OC) is hosted exclusively within clay layers where it forms a clay-organic nanocomposite (cl+C). Clay layers are planar to shale laminae 300 – 900 nm thick) separated by diagenetic quartz labelled 'diaQz'. Note; dolomite (dol) grain at top left, and quartz grains (qz). 'SA' marks locations of elemental spot analysis by Energy Dispersive Spectroscopy (EDS) shown in Figure 14. Dark zones result from sample thickening or pyrite grains (py) (darkening resulting from a higher density contrast). Resin ceases at the edge of the sample indicating a lack of penetration into the sample.  $\text{OsO}_4$  also did not penetrate into the sample, as it was not detected by EDS spot analysis. Spot analysis on resin showed minute counts of carbon compared to that carbon detected within clay layers. Dashed squares labelled a) and d) outline areas of zoomed in photomicrographs featured in Figure 15. .... 35

Figure 14 Examples of energy dispersive spectroscopy (EDS) spot analyses (SA) at spot size 5 (100 nm) and 6 (80 nm) performed throughout the East Fitts 3422.4 sample (see Figure 13 for locations). Peaks in silicon (Si), aluminium (Al), iron (Fe), potassium (K) and carbon (C) (a, b, c,) confirm the presence of clay-organic nanocomposites in Figure 13. d) shows a different aluminosilicate mineral hosting C. e) has been interpreted as dolomite (peaks in Mg, Si, Fe, Ca and C as carbonate), consistent with XRD analysis of the sample. f) shows peaks in Si interpreted as diagenetic quartz and lacks C above minute background levels. All copper (Cu) peaks are resultant from the copper sample holder. .... 36

Figure 15 Zoomed in TEM micrographs of the East Fitts ultra-thin (~80 nm) section shown in Figure 13. Image labels (a) and (d) correspond with dashed squares outlined in Figure 13 and labelled in the top left hand corner. Image a) shows a clay-organic carbon (cl + C) domain hosting what appears as a homogeneous grey area resembling an organic matter blob ~90 nm thick. Dashed squares outline zoomed in images with indicative image labels (i.e. b and c). Higher resolution images (b) and (c) reveal clay lattice fringes (atomic aluminosilicate lattice structures) dispersed within the grey matrix. Darker zones represent thicker (denser) clay layering typically stacked in lens shapes parallel to the depositional laminae. d) shows the interface of a dolomite (Dol) grain and diagenetic quartz (diaSi) nano-layer. .... 37

Figure 16 TEM micrograph of a FIB milled thin foil from the Chitwood-Harris core at 4,546 m depth. Micron-scale quartz grains (qz) exhibiting polyhedral grain shape and systematic displacement of clay particles, indicative of in situ quartz grain growth. White arrows indicate quartz growth direction causing displacement of clay particles (clay lattice fringe orientation) illustrated by green lines. These lattice orientations were determined at higher magnifications throughout the sample. Included in this image is a

## Nanoscale imaging of the Woodford Shale, Oklahoma, USA

hypothetical zone of hydrocarbon entrapment (orange polygon) where upon quartz grain growth may enclose nanometre to micron-scale zones in a three-dimensional environment, thus trapping hydrocarbons during thermal maturation. .... 38