LINKS BETWEEN GEOCHEMISTRY, TOTAL ORGANIC CARBON, MAGNETIC PROPERTIES AND ANISOTROPY IN SHALE CORE SAMPLES FROM THE HORN RIVER GROUP, BRITISH COLUMBIA, CANADA

[1]Vivian T. Ebufegha and [1,2]David K. Potter

[1]Department of Physics, and [2]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Trondheim, Norway, 27-30 August 2018

ABSTRACT

Geochemical analyses of shale core samples from the Muskwa, Otter Park and Evie formations of the Horn River Group were undertaken using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and total organic carbon (TOC) was determined via combustion analysis. The results were compared with bulk volume magnetic susceptibility and anisotropy of magnetic susceptibility (AMS) measurements on the same samples. Strong positive correlations were observed between the bulk volume magnetic susceptibility and the weight percent of each of the following metallic oxides: Fe_2O_3, Al_2O_3, K_2O and MnO. Furthermore, strong positive correlations between Al_2O_3 and Fe_2O_3 and between K_2O and Fe_2O_3 indicated that paramagnetic clays (especially illite), and not ferrimagnetic minerals like magnetite, are the main source of iron in the Horn River Group shales. In contrast, strong negative correlations were observed between bulk volume magnetic susceptibility and TOC, and between bulk volume susceptibility and SiO_2 (i.e., magnetic susceptibility decreased as TOC and quartz content increased). The correlation between TOC and bulk volume magnetic susceptibility has not, to our knowledge, been reported in any other studies. Higher TOC and quartz concentrations in the Upper Muskwa and Evie formations are responsible for their lower bulk volume magnetic susceptibilities. The study suggests that in these shale samples bulk magnetic susceptibility measurements can be used as a proxy to rapidly and non-destructively estimate TOC content and metallic oxide content.

Significantly, a strong positive correlation was also found between TOC and anisotropy of magnetic susceptibility (AMS). This unexpected relationship has not been reported in any previous studies. The data suggested that organic matter content controls the preferred orientation of other key matrix minerals in the shales, especially paramagnetic clays such as illite. Further independent support for this came from thin section analysis of the samples. The relationship between AMS measurements and TOC can potentially be used to estimate TOC content, as well as providing insights into the controls on anisotropy.

INTRODUCTION

Shales are a heterogeneous mix of diamagnetic, paramagnetic, and ferrimagnetic minerals, as well as organic matter. However, the general consensus of previous studies is that the concentration of paramagnetic clay minerals such as illite and chlorite control both bulk magnetic susceptibility and AMS [1-3]. As paramagnetic clay content increases, bulk magnetic susceptibility and AMS would normally be expected to increase. We have previously shown how rapid probe bulk magnetic susceptibility measurements on slabbed core can characterize variations in the mineral content of the different shale intervals in the Horn River Group [4]. The main aims of the present study were to extend previous work to:

- Compare the magnetic results with geochemical data to understand the mineralogical controls on the magnetic susceptibility, and in turn evaluate whether magnetic susceptibility can be used to rapidly, non-destructively and cost effectively estimate mineral content.
- Compare the magnetic data with TOC to evaluate the effect of organic matter, and also to see whether the magnetic measurements could be used to rapidly estimate TOC.
- Compare AMS with paramagnetic clay content and TOC in order to evaluate the controls on anisotropy in the shales. Anisotropy in shales is rarely taken into account, but can be a potentially important parameter (for example, it can influence the efficiency in which different shales can be hydraulically fractured, and it can be a factor in determining the effectiveness of different shales as potential seals).

SAMPLES AND METHODS

Bulk volume magnetic susceptibility

Magnetic susceptibility measurements of slabbed core from the Imperial Komie well of the Horn River Group in British Columbia, Canada, were undertaken using a Bartington MS2E probe surface scanning sensor connected to an MS2 meter, which provided a digital readout of the volume magnetic susceptibility. No additional sample preparation was required for the measurements of magnetic susceptibility as the cut faces of the slabbed core samples were suitable measurement surfaces. The probe sensor applies a weak magnetic field (80 Am^{-1}) to the sample and detects the resulting magnetization produced. The magnetic susceptibility is the magnetization divided by the applied field. The applied magnetic field of the probe sensor interrogates an area of about 3.8 x 10.5 mm and penetrates just a few mm into the core. The raw magnetic susceptibility values represent a reading on the core minus a background (in air) reading. Each reading (background or slabbed core reading) took around 1.5 seconds. We were able to use the less sensitive scale due to the relatively large signal in the shales, and this allowed a faster measurement time compared to using the sensitive scale (where measurement times are of the order of 15 seconds). Volume magnetic susceptibility measurements were taken every 0.25m on a 182m section of the Horn River Group slabbed core from the Imperial Komie well.

Anisotropy of magnetic susceptibility (AMS)

Anisotropy of magnetic susceptibility (AMS) was determined for fifty-seven 2.2cm × 2.2cm × 2.2cm cubic Horn River Group samples: 10 from the Muskwa, 19 from the Upper Otter Park, 20 from the Lower Otter Park and 9 from the Evie. Core samples too fissile to cut into cubes, were first impregnated with an adhesive of weakly diamagnetic sodium silicate (Na_2SiO_3) before cutting under a jet of propylene glycol. Magnetic susceptibility was measured in 18 directions for each of the samples using a Bartington MS2B sensor connected to an MS2 meter. From the 18 directional susceptibilities, the AMS tensor and its ellipsoid were computed. The AMS ellipsoid for each sample consists of three orthogonal principal axes, $k_1 \geq k_2 \geq k_3$, which are the maximum, intermediate, and minimum magnetic susceptibilities. The eigenvalues of the AMS tensor are the magnitudes of these principal susceptibilities and the eigenvectors of the tensor describe the directions of the principal axes. Using the principal magnitudes, the percent anisotropy of magnetic susceptibility for each sample was calculated as follows:

$$\% \text{ AMS} = 100\,[(k_1 - k_3)/k_2] \qquad (1)$$

Geochemical composition

For representative samples from the Muskwa, Otter Park and Evie formations, oxide concentrations were determined at Acme Analytical Laboratories using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This is a type of mass spectrometry that can detect extremely low concentrations, and has greater sensitivity, speed and precision compared to atomic absorption spectroscopy. The sample is ionized with inductively coupled plasma, and then a mass spectrometer is used to separate and quantify the ions [5]. Total organic carbon (TOC) was determined at Weatherford Laboratories using LECO combustion. The process involves treating ground up samples with hydrochloric acid to remove inorganic carbon (like carbonates), and then combusting the dried samples in an oxygen-rich atmosphere. The mass of CO_2 released during the combustion of organic matter (organic carbon) is converted to percent total organic carbon (TOC) based on the dry sample weight [6,7].

RESULTS AND DISCUSSION

Correlations between Geochemistry, TOC and Volume Magnetic Susceptibility

Figures 1(a)-(d) are crossplots demonstrating strong correlations between the volume magnetic susceptibility and the content of the metallic oxides Fe_2O_3, Al_2O_3, K_2O and MnO from the geochemical analyses. Moreover, **Figures 1(e)-(f)** show strong positive correlations between Al_2O_3 and Fe_2O_3 and between K_2O and Fe_2O_3 and indicated that paramagnetic clays (mainly illite), and not ferrimagnetic minerals like magnetite, are the main source of iron in the Horn River Group shales. Higher concentrations of these oxides in the Lower Muskwa and Otter Park resulted in higher bulk magnetic susceptibilities compared to the Upper Muskwa and Evie formations.

In contrast, **Figures 2 (a)** and **(b)** show that TOC and quartz content are negatively correlated with bulk magnetic susceptibility. As the TOC and quartz content increases the volume magnetic susceptibility decreases. This suggests that the high magnetic susceptibility shales are more clay rich and the low susceptibility shales are richer in organic matter and quartz.

Correlations between Anisotropy of Magnetic Susceptibility (AMS) and TOC

It has normally been assumed that increasing clay content also correlates with increasing anisotropy of magnetic susceptibility (AMS) [1-3]. However, **Figure 2(c)** shows that this is not the case in the Horn River Group shales. In fact the largest % AMS is seen in the Evie samples that have the lowest illite content, whilst samples with much higher illite content (about 30-95%) show a lower AMS with no discernible trend. Significantly, however, strong correlations are observed between TOC and AMS. **Figure 2(d)** shows a crossplot of TOC and a magnetic susceptibility anisotropy parameter (the ratio of bedding parallel to bedding perpendicular magnetic susceptibility determined from the Bartington MS2E probe) in the Otter Park formation. Since organic matter only makes up a small portion of the total composition in the shales studied (TOC is between 0.46wt % and 6.85wt %), a likely explanation for the correlation would be that organic matter richness influences the extent of the preferred orientation of other matrix minerals, especially clays. Although no work showing the effect of organic matter on the AMS of shales or mudrocks was found, reference [8] reported that the presence of organic matter may enhance the preferred orientation of clay minerals in the mudrock matrix. References [9] and [10] suggest that organic carbon acts to minimize clay flocculation, allowing for better alignment of individually dispersed clay platelets. Thin section micrographs of some of our Otter Park samples (**Figures 3(a)-(d)**) lend some support to this view. **Figures 3(a) and (b)** show thin sections perpendicular to bedding where anisotropy is clearly evident. At higher magnification, **Figures 3(c) and (d)** show long, dark, thin stringers of organic material which appear to influence the overall alignment of the matrix minerals present.

Figure 4 is a composite plot through the Muskwa, Otter Park and Evie formations comparing three normalized parameters with depth: % AMS, wireline gamma ray and % TOC. In this plot the % AMS was determined from 18 directional susceptibilities on each of the cubic samples as described in the **Samples and Methods** section above. **Figure 4** shows that the % AMS has quite a similar profile to the % TOC (middle profile). This adds further support to the suggestion that TOC is a control on the AMS. The % AMS and % TOC profiles also correlate well with the gamma ray (left and right profiles). The gamma ray to a large extent reflects the organic content in these shales, due to uranium adsorbed by organic matter. Higher gamma ray readings in the Upper Muskwa and Evie provided further evidence of increased TOC in these formations.

CONCLUSIONS

1. Strong negative correlations were observed between bulk volume magnetic susceptibility and total organic carbon (TOC), and between bulk volume magnetic

susceptibility and SiO_2 (i.e., magnetic susceptibility decreased as TOC and quartz content increased). Strong positive correlations were observed between the bulk volume magnetic susceptibility and the weight percent of each of the following metallic oxides: Fe_2O_3, Al_2O_3, K_2O and MnO. The study suggests that in these shale samples bulk magnetic susceptibility measurements can be used as a proxy to rapidly and non-destructively estimate TOC content and metallic oxide content.

2. Significantly, a strong positive correlation was also found between TOC and anisotropy of magnetic susceptibility (AMS). This unexpected relationship has not been reported in any previous studies. The data suggested that organic matter content controls the preferred orientation of other key matrix minerals in the shales, especially paramagnetic clays such as illite. Further independent support for this came from thin section analysis of the samples.

3. Strong positive correlations between Al_2O_3 and Fe_2O_3 and between K_2O and Fe_2O_3 indicated that paramagnetic clays (especially illite), and not ferrimagnetic minerals like magnetite, are the main source of iron in the Horn River Group shales.

ACKNOWLEDGEMENTS
The support of an NSERC Discovery Grant to DKP is gratefully acknowledged.

REFERENCES

1. Jackson, M., Sprowl, D., and Ellwood, B., 1989. Anisotropies of partial anhysteretic remanence and susceptibility in compacted black shales: Grain size and composition dependent magnetic fabric. *Geophysical Research Letters*, **16**, 1063-1066.
2. Hirt, A. M., Evans, K. F., and Engelder, T., 1995. Correlation between magnetic anisotropy and fabric for Devonian shales on the Appalachian Plateau. *Tectonophysics*, **247**, 121-132.
3. Parés, J. M., 2004. How deformed are weakly deformed mudrocks? Insights from magnetic anisotropy. *Geological Society, London, Special Publication*, **238**, 191-203.
4. Ebufegha, V. T. and Potter, D. K., 2014. A comparison of quantitative techniques for determining the 3D anisotropy of shale samples: application to Horn River Basin shales, British Columbia, Canada. In *Proceedings of the 2014 International Symposium of the Society of Core Analysts, 8-11 September 2014*, Avignon, France. Paper SCA2014-011 (12 pages).
5. Beauchemin, D., 2017. Inductively coupled plasma mass spectrometry methods. In *Encyclopedia of Spectroscopy and Spectrometry (3rd Edition)*, 236-245.
6. Spencer, A. M., 1993. Generation, accumulation and production of Europe's hydrocarbons III. *Special Pub. European Assoc. Pet. Geoscientists*, No. 3, p. 101.
7. Schumacher, B. A., 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments. *US. Environmental Protection Agency*, NCEA-C- 1282 EMASC-00.
8. Odom, I. E., 1964. Fabric and clay mineralogy of some argillaceous sediments immediately overlying coal beds in Illinois. *Geol Soc America, Special paper*, **76**, p. 124.

9. Moon, C. F., and Hurst, C. W., 1984. Fabric of muds and shales: an overview. In: Stow, D. A. V., and Piper, D. J. W. (eds.), Fine grained sediments: deep-water processes and facies. Blackwell Scientific, Palo Alto, CA, p. 579-593.
10. Hounslow, M. W., 1985. Magnetic fabric arising from paramagnetic phyllosilicate minerals in mud rocks. *Journal of the Geological Society of London*, **142**, 995-1006.
11. Ebufegha, V. and Potter, D. K., 2016. Quantifying shale mineralogy and anisotropy from low temperature magnetic susceptibility measurements. In *Proceedings of the 2016 International Symposium of the Society of Core Analysts, 21-26 August 2016,* Snowmass, Colorado, USA. Paper SCA2016-033 (12 pages).

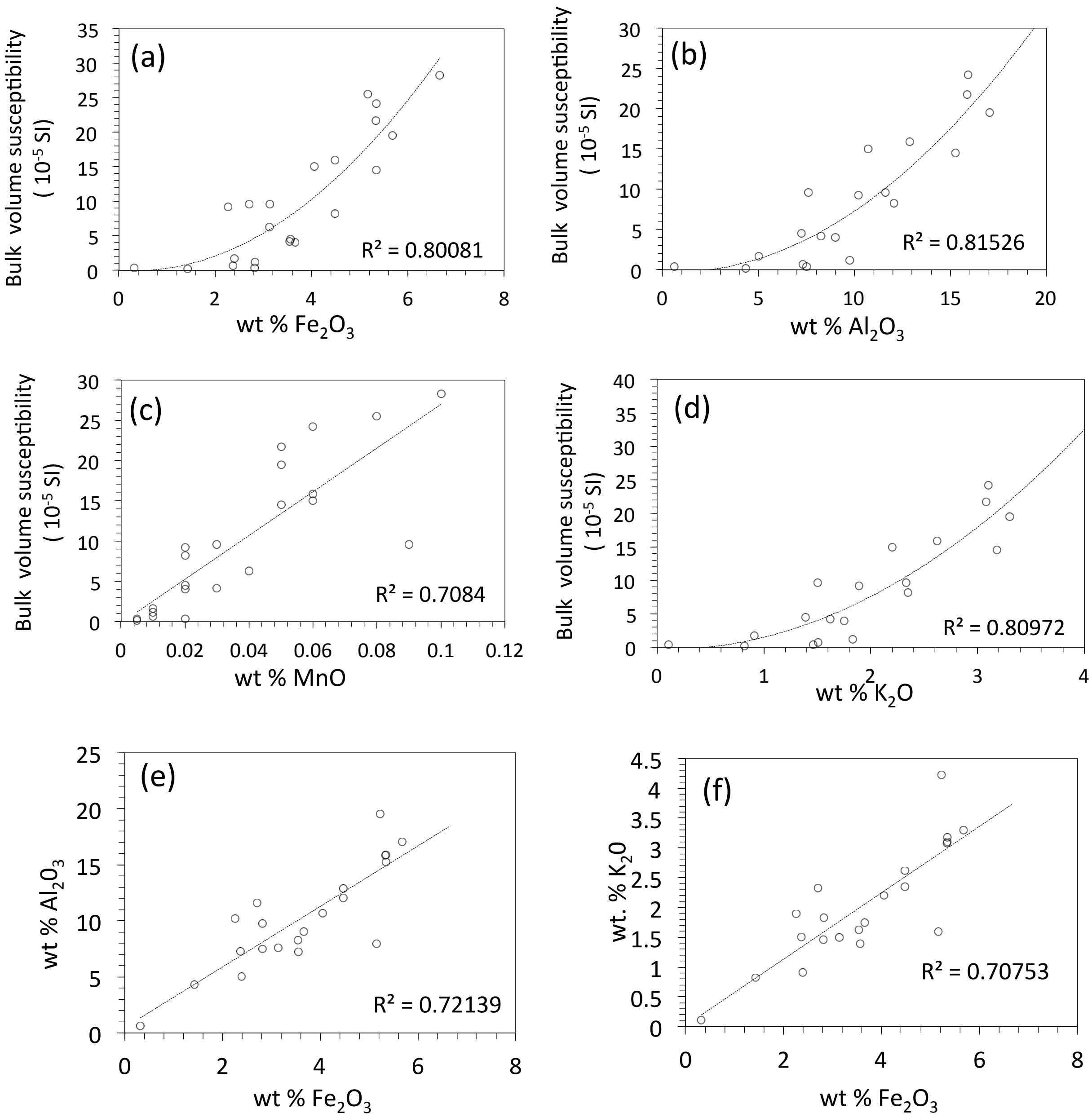

Figure 1. (a)-(d): Relationships between geochemical composition of various metallic oxides and bulk volume magnetic susceptibility. **(e)-(f):** Relationships between iron oxide concentration and aluminium oxide and potassium oxide concentrations indicate that clays are the primary source of iron in the Horn River Group.

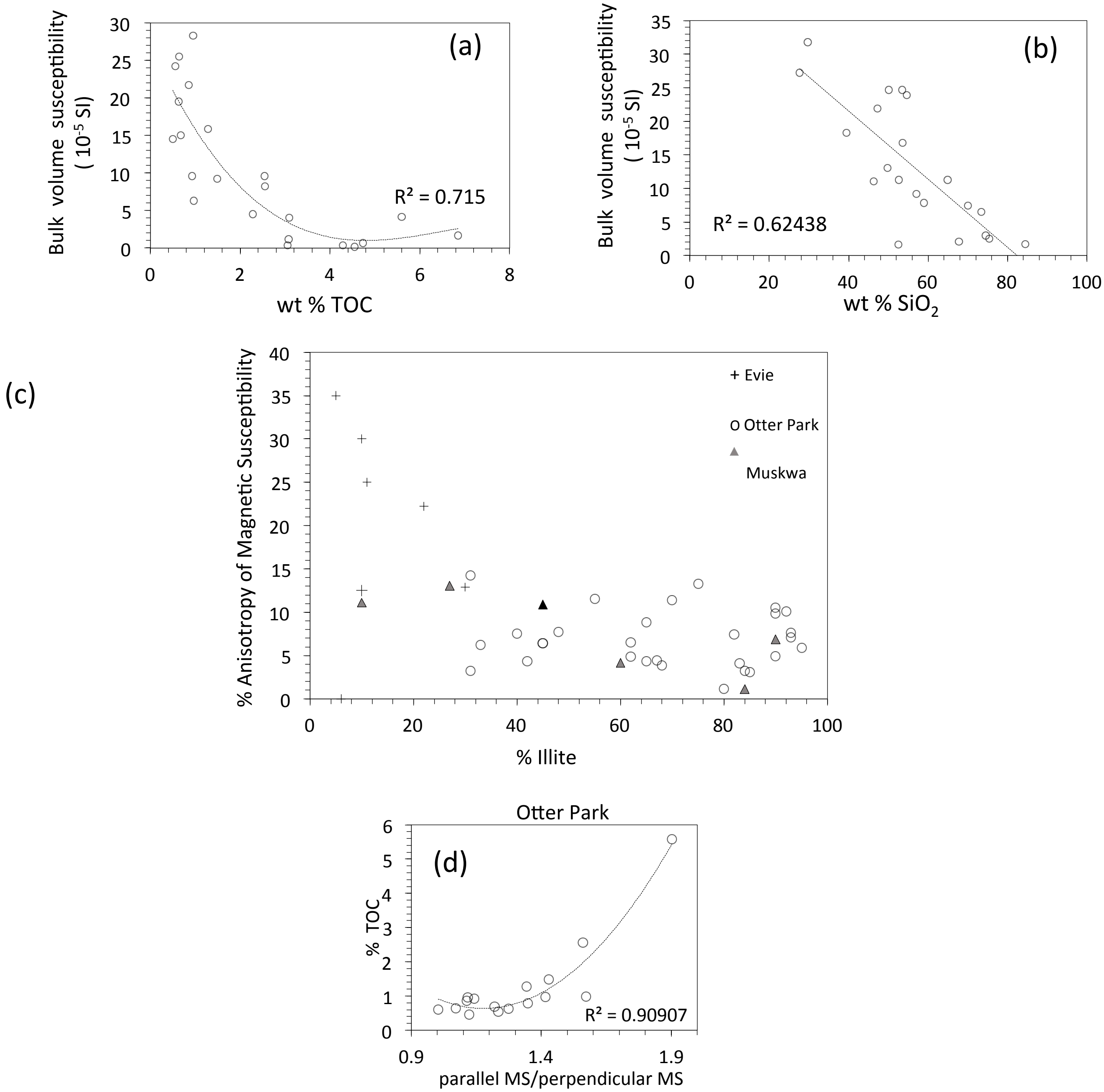

Figure 2. Relationships between **(a)** weight % TOC and bulk volume magnetic susceptibility, **(b)** weight % SiO_2 and bulk volume magnetic susceptibility, **(c)** % illite determined from low temperature magnetic susceptibility measurements (using the methodology in reference [11]), and **(d)** % TOC and the ratio of parallel to perpendicular volume magnetic susceptibility in the Otter Park formation.

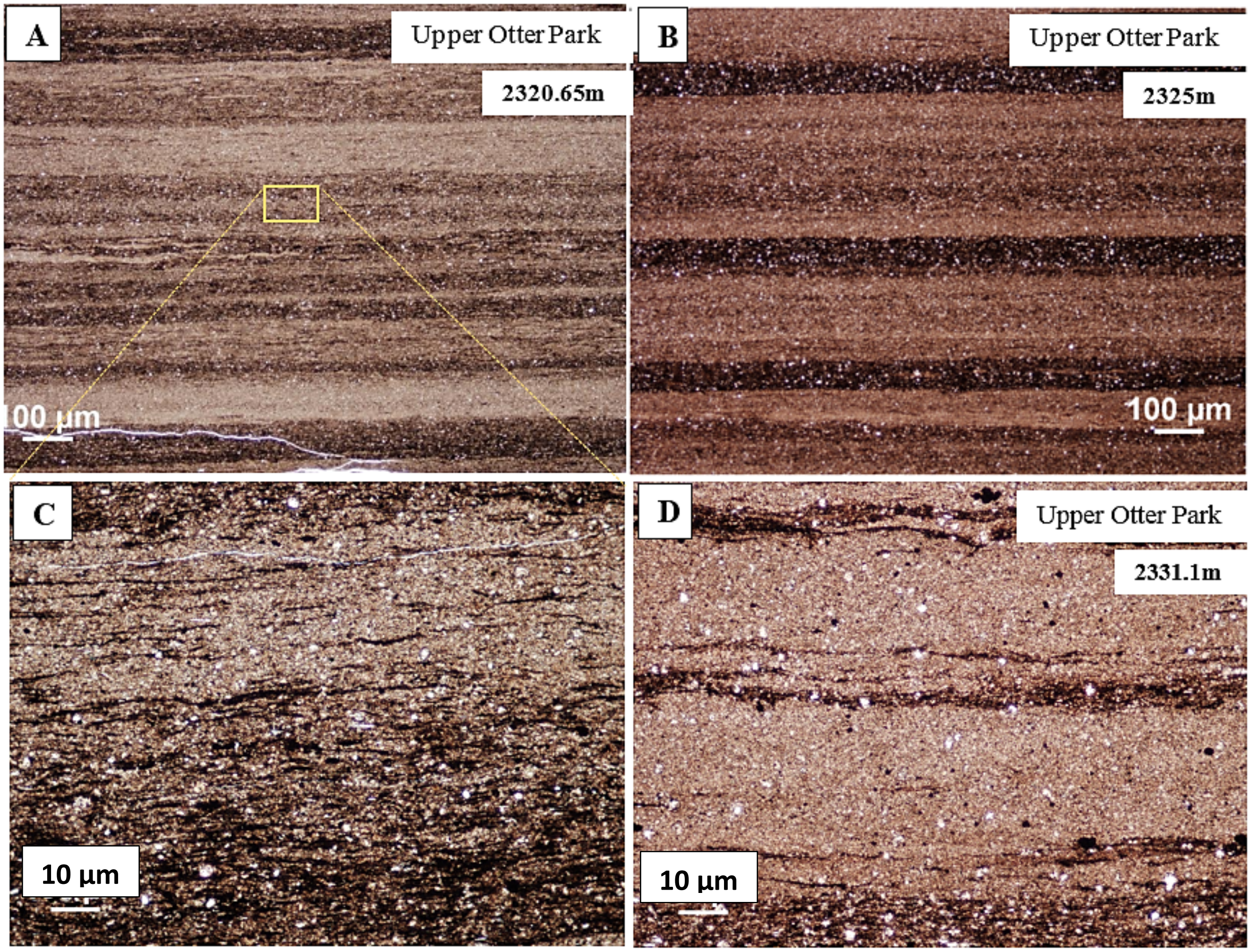

Figure 3. (A)-(D): Thin section images of Upper Otter Park samples taken under plane polarized light. Image **(C)** is a magnification of the rectangle enclosed area in (A). It shows bedding parallel, long, thin organic matter stringers, which appear to influence the overall anisotropy of the matrix minerals. (D) is another high magnification image showing long, thin organic matter stringers.

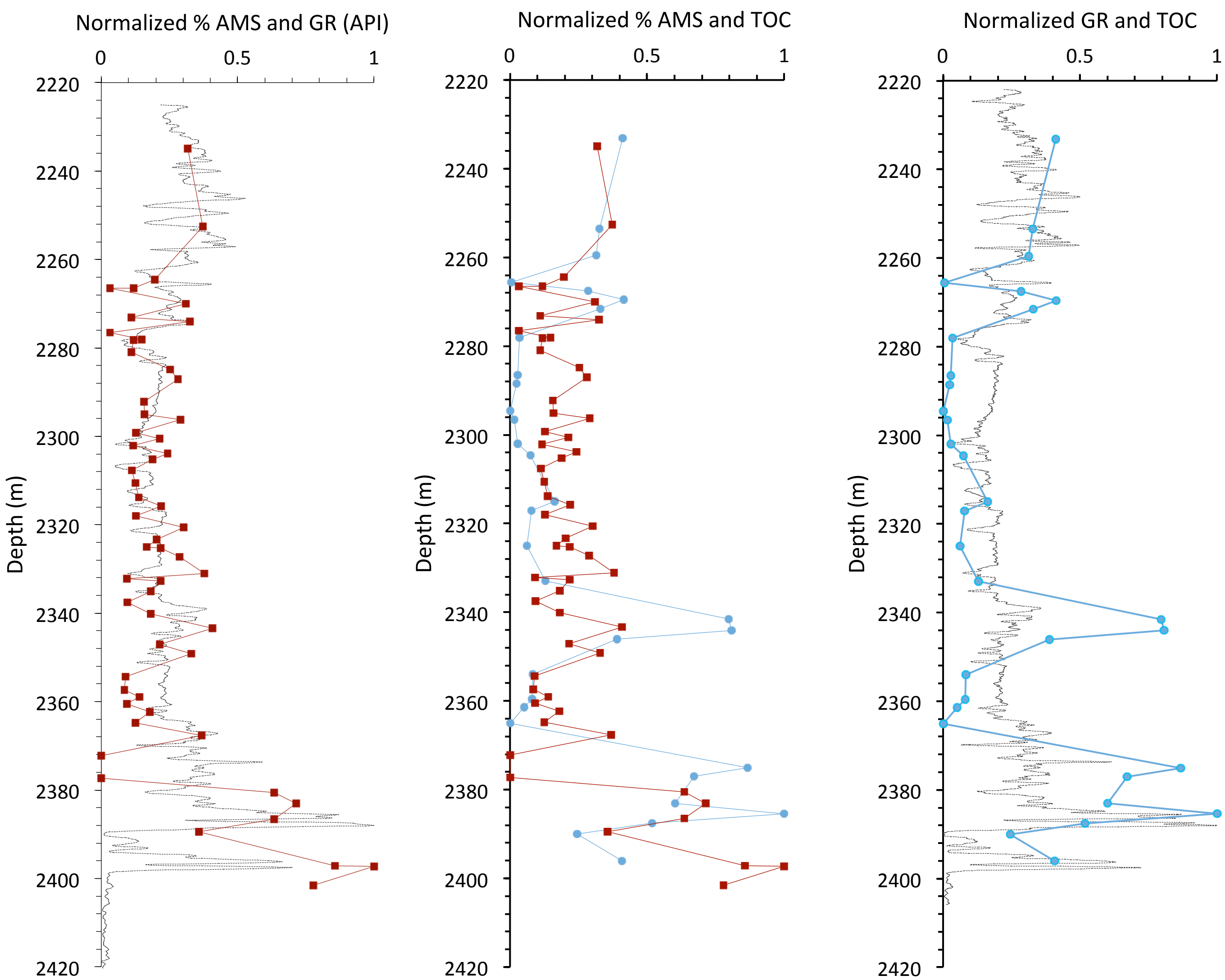

Figure 4. Profiles with depth through the Muskwa (top of section to 2275 m), Otter Park (2275-2363 m) and Evie (below 2363 m) formations. The profiles compare normalized % AMS (anisotropy of magnetic susceptibility, brown curve and square symbols), normalized % TOC (total organic carbon, blue curve), and normalized wireline gamma ray (black dashed curve).