Exploring links between thermal maturity and electrical properties of organic-rich shales

Claudio Delle Piane
CSIRO Energy, Deep Earth Imaging
26 Dick Perry Avenue
Kensington 6151 WA
Claudio.dellepiane@csiro.au

Matthew Josh
CSIRO Energy
26 Dick Perry Avenue
Kensington 6151 WA
Matthew.josh@csiro.au

Julien Bourdet
CSIRO Energy
26 Dick Perry Avenue
Kensington 6151 WA
Julien.bourdet@csiro.au

David N. Dewhurst
CSIRO Energy
26 Dick Perry Avenue
Kensington 6151 WA
David.dewhurst@csiro.au

M. Ben Clennell
CSIRO Energy
26 Dick Perry Avenue
Kensington 6151 WA
Ben.Clennell@csiro.au

SUMMARY

Electrical resistivity is widely used as an effective proxy for detection of organic matter and hydrocarbons in shales. Recently, with more organic-rich shales being studied, it has been noted that resistivity follows a non-linear evolution with thermal maturity, influenced by the changes in conductivity of the liquid and solid phases and their distribution within the rocks.

At the high end of thermal maturities relevant for hydrocarbon exploration, the sediments undergo chemical and structural reorganization involving loss of hydrogen and oxygen and aromatization of the organic component leading to a dramatic decrease in the overall electrical resistivity. This influence, especially at thermal maturities consistent with and beyond the gas generation window is not accounted for in petrophysical log interpretation and the petrophysical properties of over-mature shales are poorly documented in the literature.

We show examples of hydrocarbon prospective shales characterized by low electrical resistivity of the organic-rich sections and explore the mechanisms that influence resistivity. By integrating petrophysical, petrological, and nanoanalytical observations we show that the anomalous resistivity is related to a conductive, connected network of partially graphitised bitumen and not to commonly assumed conductive accessory minerals such as pyrite. This interpretation is verified in several case studies on prospective organic-rich shales that have been exposed to high thermal maturation induced by either deep burial conditions (Appalachian Basin, USA; Sichuan Basin, China), or by contact metamorphism (Beetaloo Sub-basin, Australia).

Key words: Organic rich shale, thermal maturity, petrophysics, resistivity.

INTRODUCTION

Electrical properties have been widely used as a proxy to detect of organic matter and hydrocarbons in shales from wireline logs. Up to thermal maturities within the oil window, the so-called delta-log R method (Passey *et al*. 1990) is commonly used to estimate organic richness of potential source rocks from the sonic and the resistivity wireline log curves.

Recently, studies of organic-rich shales from North American Basins, Argentina and China demonstrated a complex evolution of electrical resistivity with thermal maturity in organic-rich shales (Clennell *et al.* 2017; Cumella *et al.* 2018; Ortiz *et al.* 2018). At the practical level, this anomalous petrophysical signature complicates calculations of gas saturation and gas-in-place.

Here we elucidate the factors contributing to extremely low resistivity observed in intervals organic-rich sections of hydrocarbon prospective shale formations. We draw examples from i) the over mature sections of the Marcellus and Longmaxi Shale (Appalachian and Sichuan Basins, respectively) that have been affected by deep burial and subsequent uplift; and ii) organic-rich Velkerri Formation from the Beetaloo Sub-basin locally affected by rapid heating induced by emplacement of a dolerite intrusion.

Despite the difference in age and geological settings, these examples indicate that the dominant cause of low-resistivity is the presence of variably graphitised secondary organic matter providing an interconnected high-conductivity network.

METHOD AND RESULTS

Aiming to identify the causes of the resistivity reduction, we studied the petrophysical response of the intervals of interest at the well scale and sampled core material to assess the physical response under controlled laboratory conditions. These investigations were complemented by analyses designed to document the abundance, distribution, and physical state of mineral and organic rock components.

The Middle Devonian Marcellus Shale, Appalachian Basin (USA) has become one of the most prolific gas producing plays in the USA. Previous work has established that in the north eastern part of Pennsylvania, deep burial and high temperatures have led to extreme levels of maturity (e.g. Laughrey et al., 2011). Wireline logs from a well in this overmature area identified a hot zone (high gamma ray) with TOC between 3 and 7 wt% and ultra-low resistivity (~0.2 ohm.m). Organic and inorganic indicators used to derive the maximum palaeotemperature witnessed by the sediment converge to indicate values above 250°C (Delle Piane et al., 2018). High resolution electron microscopy shows that organic matter in the Marcellus Shale is highly connected through the rock. The organic matter type is predominantly pyrobitumen, converted from liquid hydrocarbons that had been generated earlier and migrated through the original pore system. At the nanoscale, this secondary organic material comprises clusters of short-range ordered carbon characterised by basal spacings consistent with that of graphite (Fig. 1A).

The upper Ordovician Wufeng shale and lower Silurian Longmaxi shale are part of a prospective marine shale system located in the south-eastern part of the Sichuan Basin, southern China. Burial history simulation shows that the Wufeng-Longmaxi shale was buried to depth greater than 6000 m in the Early-Middle Cretaceous before being uplifted during the Late Cretaceous (Jin *et al.* 2015). Previous studies reported low resistivity (< 2 ohm.m) in organic-rich (TOC > 3 wt%) sections of this highly mature shale from downhole logs acquired in several exploration blocks and low resistivity of dry samples in the laboratory (Yuman *et al*. 2014).

Our analysis of organic and inorganic temperature proxies suggest that the sediment was exposed to temperatures exceeding 270°C. Similar to the Marcellus Shale case, high resolution electron microscopy shows the organic matter identified as pore-filling, pyrobitumen is percolating and has nano-structural characteristics of turbostratic carbon organized in stacked basal structural units with interlayer distance of ca. 3.4 nm (e.g. Daniels et al., 2007) (Fig. 1B).

The Proterozoic (~1.43 Ga) Velkerri Formation (McArthur Basin, Northern Territory) is believed to host one of the world's oldest petroleum systems. Drilling and production tests demonstrated the encouraging potential of this unconventional gas resource and current efforts are aimed at better defining the extent of the gas and liquid-rich portions of this shale play. Intrusion of the ca. 1.3 Ga Derim Derim Dolerite within the Velkerri Formation represents an important heat source locally affecting thermal maturity of the organic-rich shale and its petrophysical properties.

Wells intersecting the organic-rich sections of the Velkerri Fm. intruded by dolerite sills are mostly clustered in the north-western part of the basin and show distinct evidence of the interaction between magmatic and organic-rich shales. This manifests as a pair of Low Resistivity Zones (LRZs) that appear to be symmetrical around the top and the bottom of the sill (Fig 2A). The thickness of the LRZs is defined as the distance between the top and bottom contacts to the sill and the depth where resistivity returns to baseline values typical of the unaltered host rock (cfr. Spacapan et al., 2020) and is comparable to the sill's half thickness. LRZ thickness provides an estimate of the volume of rock affected by thermal metamorphism around the intrusion. Geochemically, this volume is rich in organic carbon (up to 10% wt TOC) but has lost any generative potential as evidenced by the low HI values recorded during pyrolysis. The consistent symmetry of the LRZs across the contact aureole of several wells suggest that heat transport mainly occurred via conduction with little hydrothermal fluid flow associated with the dolerite emplacement.

Continuous hyperspectral logging of the cores on either sides of the dolerite sill and electron microscopy analyses indicate that mineralogy of the shale is affected by the intrusion over a scale of only a few cm. In these thin zones, concentration of pyrite, chlorite and albite seem to exceed the values typically measured in sections of the shale further away from the dolerite contacts. Optical reflectance measurements and Raman spectroscopy-based investigation of the organic matter in the shale samples collected at increasing distance from the dolerite contacts were used to estimate the maximum temperature affecting the shale and this is plotted as a function of distance from the dolerite contact in Fig 2B. Maximum estimated temperature shows a power law decay with distance from the sill contact and rapidly falls below the graphitization temperature at a distance consistent with the thickness of the LRZ.

Electrical properties were measured using a parallel plate cell on dry samples and are plotted in Fig. 2B as electrical resistivity measured at a frequency of 10 kHz. Samples from within the LRZs show low resistivity values comparable to those measured downhole, increasing as a function of distance from the dolerite contact.

CONCLUSIONS

We investigated the nature of low resistivity zones identified in organic-rich shale formations of different age and geographical location by integrating downhole data, petrology and petrophysical analyses from cores. Our analysis indicates that the low resistivity signal in these formations is consistently attributable to thermal alteration be it through prolonged deep burial or localised, transient heating associated with emplacement of a magmatic intrusion.

Where total organic content is high enough to be volumetrically connected (ca. > 2 wt%) and maximum temperatures experienced by the sediments exceed 260 °C, the presence of partly graphitised carbonaceous material provides highly conductive macroscopic pathways. This connectivity and transformation of pyrobitumen to proto-graphite results in low to extremely low resistivity.

ACKNOWLEDGMENTS

Wireline log and Hylogger data from wells in the Beetaloo Sub-basin discussed in this study are available through the Northern Territory Geoscience Exploration and Mining Information System.

This research is supported by the CSIRO Deep Earth Imaging Future Science Platform and formerly by the SHARC2 joint industry project sponsored by BG Group, Sinopec, Saudi Aramco, and BP. We thank William Rickard (Curtin University) and Martin Saunders (University of Western Australia) for their help with electron microscopy and sample preparation.

REFERENCES

Clennell, M.B., Matthew, J., Esteban, L., Piane, C.D. and Dewhurst, D.N., 2017, September. Petrophysical characterization at the extremes and across three continents: contrasting examples from Utica, Marcellus, Longmaxi and Roseneath-Murteree resource shales. In Unconventional Resources Technology Conference, Austin, Texas, 24-26 July 2017 (pp. 3746-3765). Society of Exploration Geophysicists, American Association of Petroleum Geologists, Society of Petroleum Engineers.

Cumella, S., Byrnes, A. and Sonnenfeld, M., 2018, September. Investigation of the Shale Electrical Resistivity Reversal Commonly Observed at the Wet-to Dry-Gas Transition. In Unconventional Resources Technology Conference, Houston, Texas, 23-25 July 2018 (pp. 2222-2240). Society of Exploration Geophysicists, American Association of Petroleum Geologists, Society of Petroleum Engineers.

Daniels, H., Brydson, R., Rand, B. and Brown, A., 2007. Investigating carbonization and graphitization using electron energy loss spectroscopy (EELS) in the transmission electron microscope (TEM). Philosophical Magazine, 87(27), pp.4073-4092.

Delle Piane, C., et al., 2018. Organic matter network in post-mature Marcellus Shale: Effects on petrophysical properties. AAPG Bulletin, 102(11), pp.2305-2332.

Jin, Z., Li, M., Hu, Z., Gao, B., Nie, H., Zhao, J., 2015. Shorten the Learning Curve Through Technological Innovation: A Case Study of the Fuling Shale Gas Discovery in Sichuan Basin, SW China, in: Unconventional Resources Technology Conference. SPE, AAPG, SEG, San Antonio, Texas, USA, pp. 1–13. https://doi.org/10.15530/urtec-2015-2152994

Laughrey, C. D., T. E. Ruble, H. Lemmens, J. Kostelnik, A. R. Butcher, G. Walker, and W. Knowles, 2011, Black shale diagenesis: Insights from integrated high-definition analyses of post-mature Marcellus Formation rocks, northeastern Pennsylvania: AAPG Search and Discovery article 110150

Ortiz, A.C., Bernhardt, C., Tomassini, F.G., Cumella, S., Saldungaray, P. and Mosse, L., 2018, September. Causes of Resistivity Reversal in the Vaca Muerta Formation, Argentina. In Unconventional Resources Technology Conference, Houston, Texas, 23-25 July 2018 (pp. 3679-3698). Society of Exploration Geophysicists, American Association of Petroleum Geologists, Society of Petroleum Engineers.

Passey, Q. R., S. Creaney, J. B. Kulla, F. J. Moretti, and J. D. Stroud, 1990, A practical model for organic richness from porosity and resistivity logs: AAPG Bulletin, 74, no. 12, 1777–1794.

Spacapan, J.B., et al., 2020. Low resistivity zones at contacts of igneous intrusions emplaced in organic-rich formations and their implications on fluid flow and petroleum systems: A case study in the northern Neuquén Basin, Argentina. Basin Research, 32(1), pp.3-24.

Yuman, W.A.N.G., et al. 2014. Electric property evidences of the carbonification of organic matters in marine shales and its geologic significance: A case study of the Lower Cambrian Qiongzhusi Shale in the southern Sichuan Basin. Natural Gas Industry, 34(8), pp.1-7.

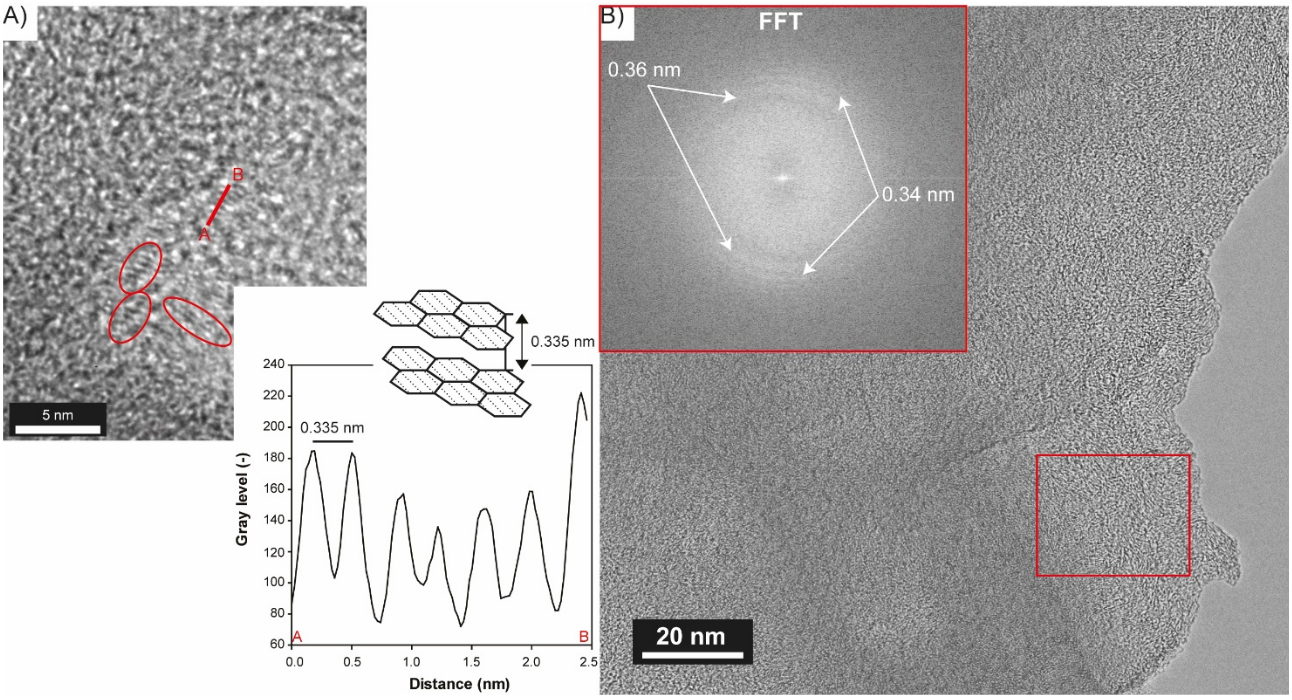

Figure 1. High resolution transmission electron images of portions of secondary organic matter from the Marcellus (A) and Longmaxi (B) shales. A) TEM image of a portion of migrated bitumen with clusters of short-range ordered structural units (red ovals). Characteristic interlayer spacing of these units is shown in the A-B profile and is consistent with that of graphite (i.e. 0.335 nm). B) TEM image and Fast Fourier Transform (FFT) image (inset) of the area in the red box from of a portion of migrated bitumen. The FFT image shows the presence of diffuse reflections indicating randomly oriented, crystalline ordered domains with interlayer spacings of 0.34 and 0.36 nm characteristic of turbostratic carbon.

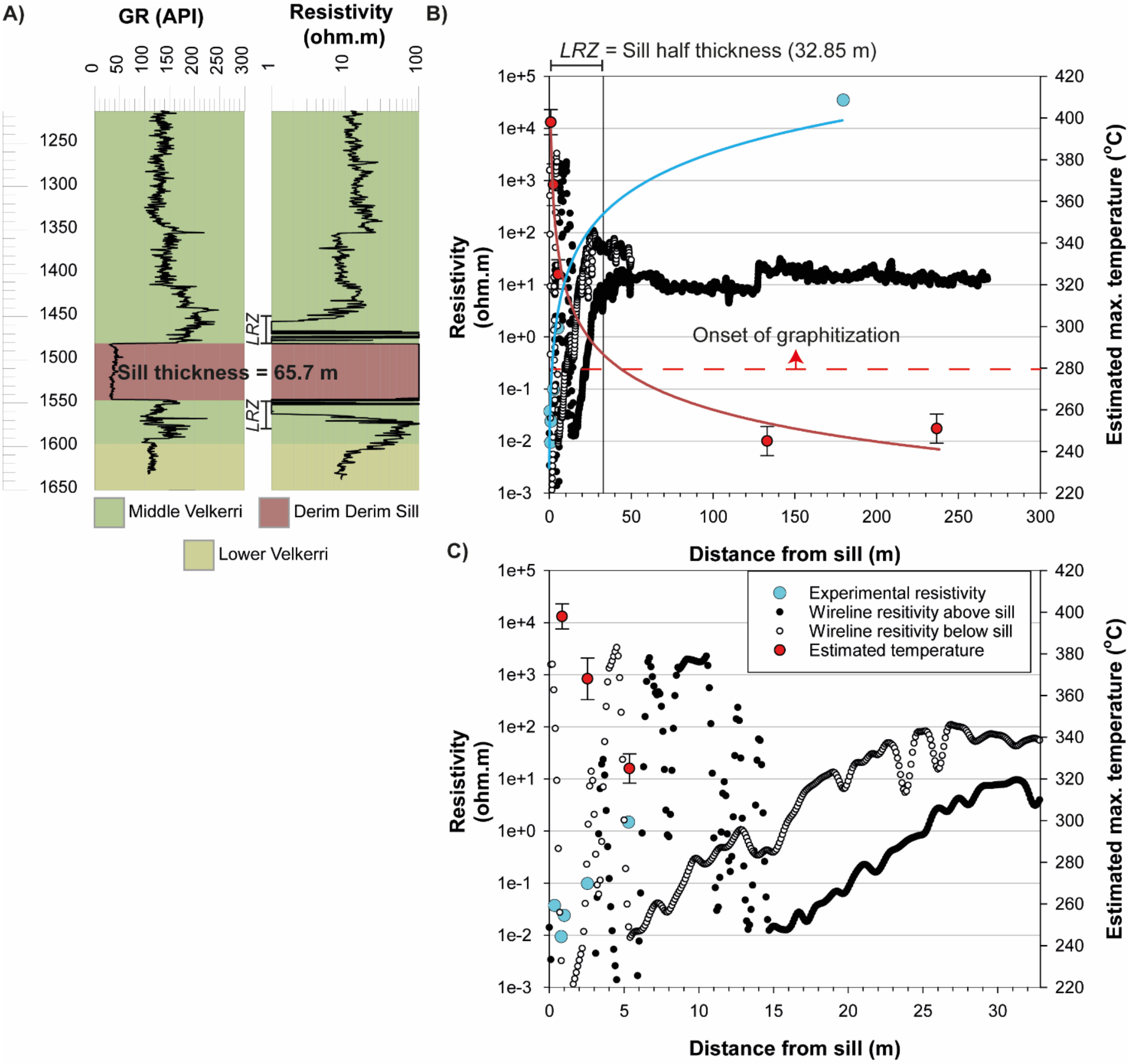

Figure 2. A) Gamma ray (GR) and electrical resistivity logs from well Tarlee S3 drilled in the NW part of the Beetaloo Sub-basin. The organic-rich portion of the middle Velkerri Fm. is intruded by a 65.7m doleritic sill. B) wireline resistivity plotted as a function of distance from the top and bottom of the dolerite sill: anomalously low values are recorded within a low resistivity zone (LRZ), beyond a distance comparable to the half thickness of the sill, resistivity values are back to normal range. Also shown are experimentally determined values of resistivity and Raman-based estimated maximum temperatures experienced by the sediment. Red line = power law fit to the estimated temperature data (R^2 = 0.9768); Cyan line = power law fit to the laboratory measured resistivity data (R^2 = 0.9347). C) Enlarged view of the data within the LRZ thickness.