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PS The Effects and Distribution of Moisture in Gas Shale Reservoir Systems*

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Abstract

The moisture content is an important component within the gas shale reservoir system as the amount and distribution of water can have adverse effects on the volume of sorbed and free gas, relative permeability/diffusivity and solution gas may be a measurable contributor to total gas in place. The variation in the effects of moisture content depends on the mineralogy, maturity, kerogen type, and pore size distribution. To understand these variations a suite of organic-rich shales from northeastern British Columbia have been analysed. Analysis includes organic geochemistry, mineralogy, methane sorption capacity, water adsorption isotherms and surface area analysis.

Devonian, Jurassic and Cretaceous shales from northeastern British Columbia have moisture contents ranging from 0.5 to 15% and methane capacities between 0.1 to 3.5 cc/g at 6 MPa. Maturity ranges from immature to overmature and TOC contents range from 0.5 to 17 wt%. When moisture content of a shale is varied, a trend of decreasing methane capacity with increasing moisture content is observed. However, when comparing a suite of moisture-equilibrated shales, there is no correlation between moisture content and the methane sorption capacity. Shales can have both high and low sorption capacities with high moisture content. Some general trends are observed; the Cretaceous and Devonian shales show methane capacity increases with moisture content while the opposite trend is found for the Jurassic shale. These differences are due to the variation of the amount and distribution of the water within the different shales. Water isotherms identify the range of pore sizes that contain hydrophilic sorption sites. Hydrophilic sorption sites are concentrated within the micro- and mesoporosity as a positive trend occurs between the moisture content and micro- and mesoporous surface area. The pore size distribution, in turn, is controlled by mineralogy, maturity, kerogen type and mineralogy. For example, the mineralogy affects the moisture content with clay-rich shale sorbing more water than quartz-rich shales.

Identifying the controls and distribution of inherent moisture in gas shale reservoir systems provides an understanding of water sensitivity and aids the overall evaluation of the reservoir with respect to one of the controlling factors of sorbed methane capacities.

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Discussion and Summary

Methane sorption capacities of organic rich shales are not controlled by their moisture contents but the proportion of hydrophobic to hydrophilic sorption sites. Shales that contain a high proportion of hydrophobic sorption sites will be able to sorb a greater volume of methane compared to shales that have lower proportion of hydrophobic sorption sites. Shales that have high methane sorption capacities can have either high or low moisture contents. The 10 samples that have been investigated are shown in the summary figure (Figure 16). The percentages shown in Figure 16 are the increases in methane capacity from moisture equilibrated ("wet") to dry conditions. The greatest increases in the methane capacity from wet to dry conditions are from the clay rich shales as the hydrophilic sorption sites (negatively charged surfaces) become available for methane sorption when dried.

Hydrophilic sorption sites are located within pore structures that are composed of either: a) clays or b) organic matter that contains oxygen functional (aliphatic) groups (Figures 17A-C). Maturity would have an effect on the distribution of hydrophilic and hydrophobic sorption sites (Figures 17A & B). Higher maturity sample would have a greater proportion of hydrophobic to hydrophilic sorption sites and this would decrease the moisture content and increase the methane capacity. The lower maturity Cretaceous shale may contain greater amount of oxygen functional groups and increase the amount of sorption sites available water but to methane when dried. More research is needed to determine the significance of aliphatic rich TOC to methane capacity of organic rich shales.

The distribution of hydrophobic and hydrophilic sorption sites throughout the pore network would play a major role in the effect moisture would have on the methane capacity with regard to blocking pore throats. In the two scenarios in Figures 17B & C, the methane capacity would be significantly reduced if the pore throat is hydrophilic and narrow enough that adsorption of water molecules would block access to the potential methane sorption (hydrophobic) sites. Methane that is produced within the pore body will not be able to move through the pore system as liquid water is harder to remove from pores as pressure decreases (shown by the water isotherms in Figure 11). If the pore throat is hydrophobic then water will not condense in the throat and both water and methane molecules can move through the pore network.

The moisture content can play a significant role in the methane capacity of an organic rich shale as well as, depending on the hydrophobic and hydrophilic sorption site distribution within the pore network, effect the flow of gas from the matrix to the wellbore.

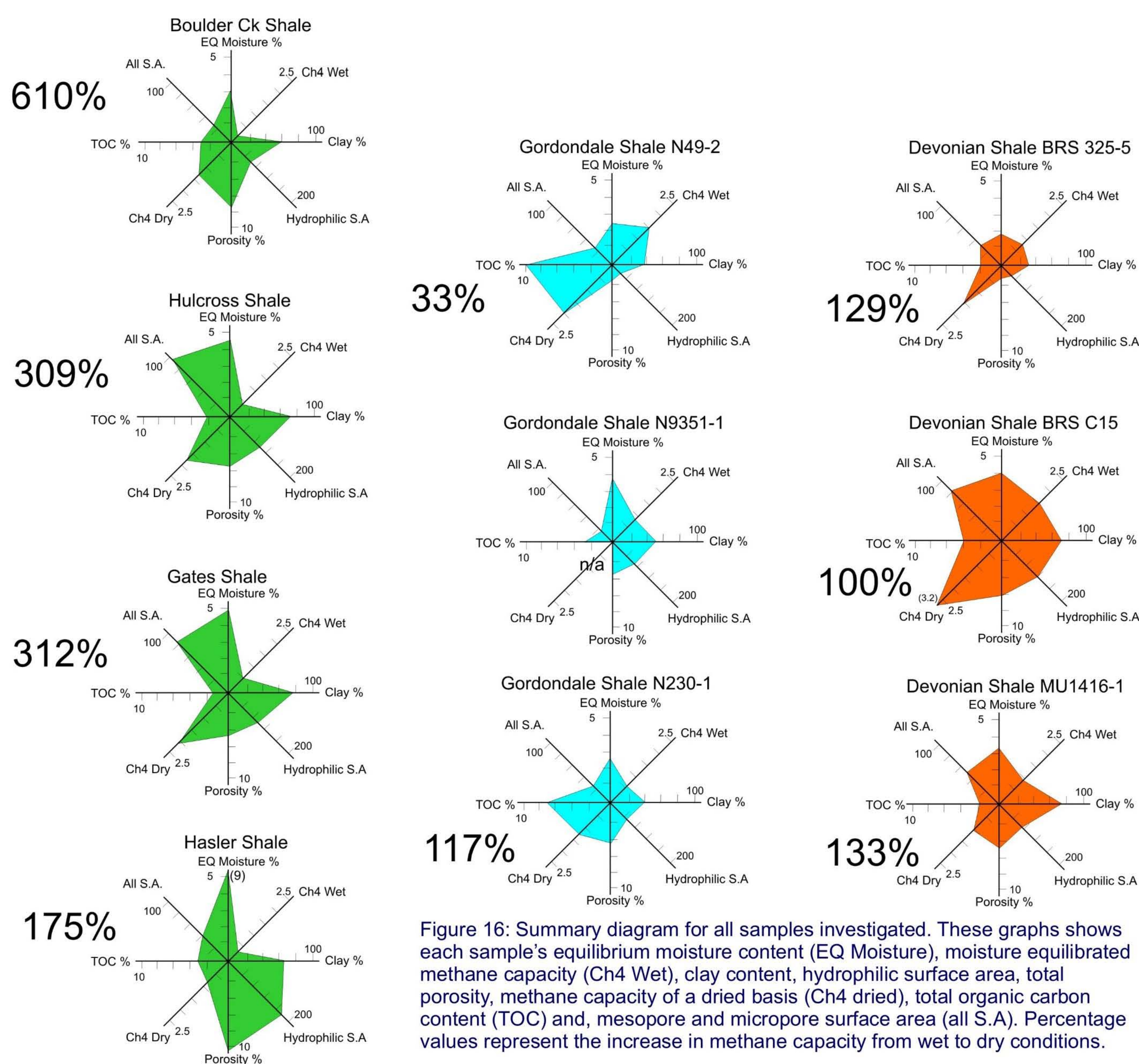


Figure 16: Summary diagram for all samples investigated. These graphs shows each sample's equilibrium moisture content (EQ Moisture), moisture equilibrated methane capacity (Ch4 Wet), clay content, hydrophilic surface area, total porosity, methane capacity of a dried basis (Ch4 Dry), total organic carbon content (TOC) and, mesopore and micropore surface area (all S.A.). Percentage values represent the increase in methane capacity from wet to dry conditions.

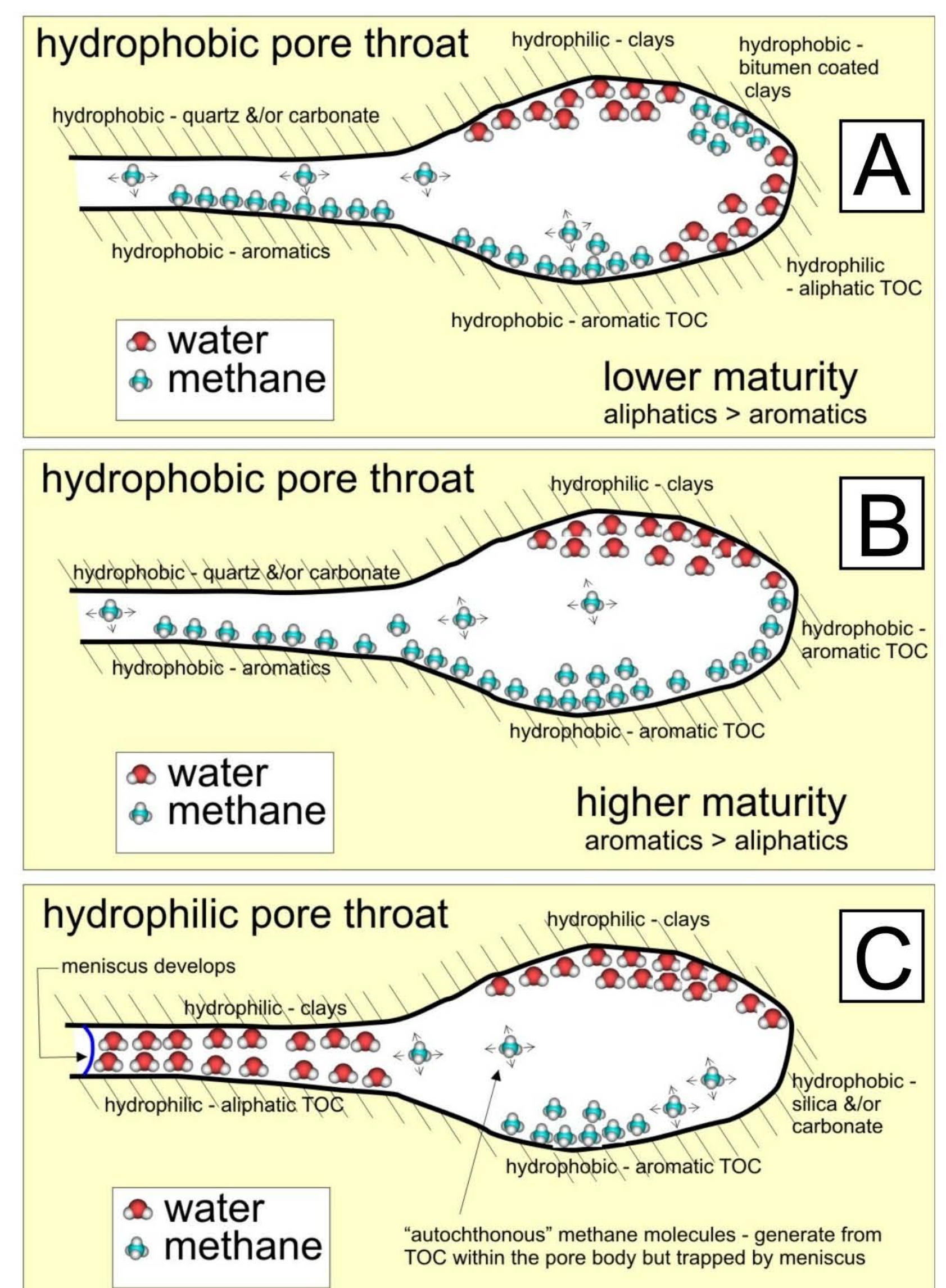


Figure 17: Schematic pore model for the hydrophilic and hydrophobic sorption sites within an organic rich gas shale. Although methane is generated in local pores, if pore throats are hydrophilic, water may block pore networks that allow gas to flow through the matrix of the reservoir. As shown in Figure 11 there is a lag between the removal of water from a meniscus and the decrease in pressure (hysteresis effect).

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Abstract

The moisture content is an important component within the gas shale reservoir system as the amount and distribution of water can have adverse effects on the volume of sorbed and free gas, relative permeability/diffusivity and solution gas may be a measurable contributor to total gas in place. The variation in the effects of moisture content depends on the mineralogy, maturity, kerogen type, and pore size distribution. To understand these variations a suite of organic-rich shales from northeastern British Columbia have been analysed. Analysis includes organic geochemistry, mineralogy, methane sorption capacity, water adsorption isotherms and surface area analysis. Devonian, Jurassic and Cretaceous shales from northeastern British Columbia have moisture contents ranging from 0.5 to 15% and methane capacities between 0.1 to 3.5 cc/g at 6 MPa. Maturity ranges from immature to overmature and TOC contents range from 0.5 to 17 wt%. When moisture content of a shale is varied, a trend of decreasing methane capacity with increasing moisture content is observed. However, when comparing a suite of moisture-equilibrated shales, there is no correlation between moisture content and the methane sorption capacity. Shales can have both high and low sorption capacities with high moisture content. Some general trends are observed; the Cretaceous and Devonian shales show methane capacity increases with moisture content while the opposite trend is found for the Jurassic shale. These differences are due to the variation of the amount and distribution of the water within the different shales. Water isotherms identify the range of pore sizes that contain hydrophilic sorption sites. Hydrophilic sorption sites are concentrated within the micro- and mesoporosity as a positive trend occurs between the moisture content and micro- and mesoporous surface area. The pore size distribution, in turn, is controlled by mineralogy, maturity, kerogen type and mineralogy. For example, the mineralogy affects the moisture content with clay-rich shale sorbing more water than quartz-rich shales.

Identifying the controls and distribution of inherent moisture in gas shale reservoir systems provides an understanding of water sensitivity and aids the overall evaluation of the reservoir with respect to one of the controlling factors of sorbed methane capacities.

Statement of the Problem & hypotheses

The internal surface area of a shale controls both the methane capacity and the moisture content. Although moisture content has a negative impact on the methane capacity in samples when the moisture content is varied (Figure 1), the correlation between moisture content and methane capacity for a suite of samples can be poor and in fact, a positive trend can be seen between moisture content and methane capacity for the Lower Cretaceous Buckinghorse shale (Figure 2), a negative trend for the Jurassic Gordondale shale (Figure 3) and no correlation for the Devonian shales (Figure 4). The observations above indicate surface area within a shale is a combination of hydrophilic and hydrophobic sorption sites where methane is adsorbing onto hydrophobic sites in moisture equilibrated samples and sorbing onto both hydrophobic and hydrophilic sorption sites in dried samples (Figure 1). Shales that contain a greater proportion of hydrophobic sorption sites will sorb more methane regardless of the moisture content (i.e. Figure 2).

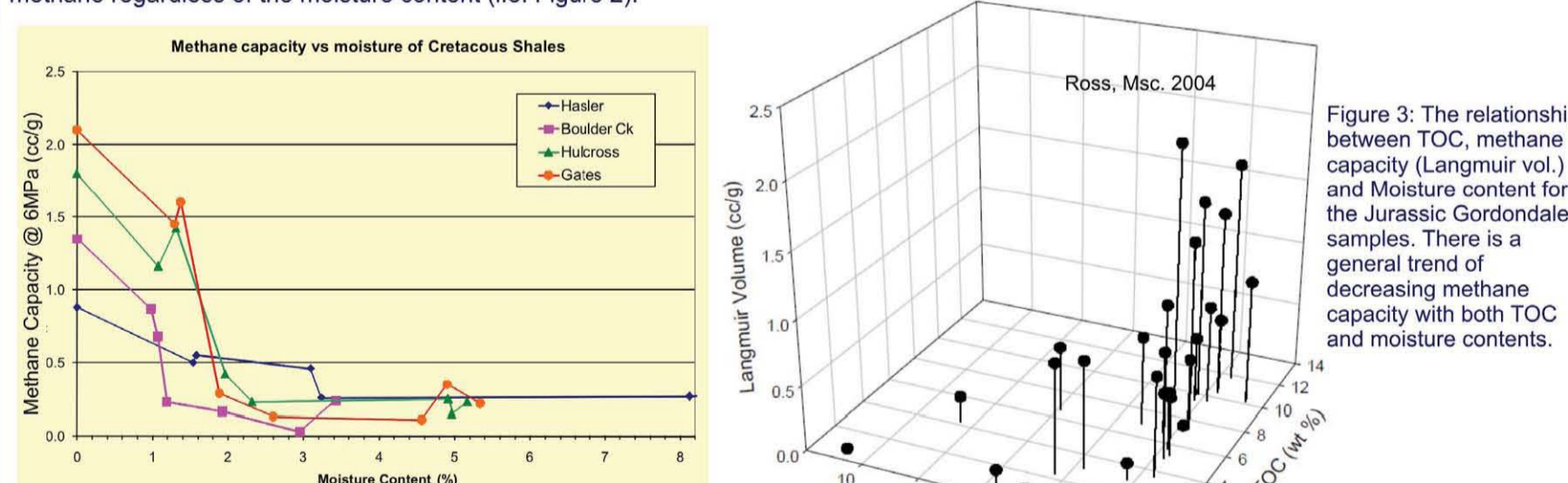


Figure 1: Increasing the moisture content of Cretaceous illite-rich shales has a negative impact on the methane capacity. There is a limit to the impact moisture has on the methane capacity and increasing moisture past this limit does not affect the capacity.

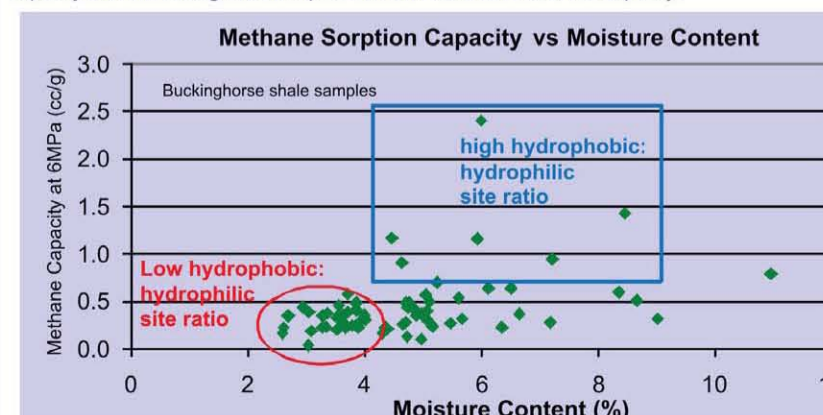


Figure 2: No correlation exists between moisture content and methane capacity for Cretaceous Buckinghorse shales, however there is a subtle positive trend. High methane capacities are found with both high and low moisture-equilibrated samples.

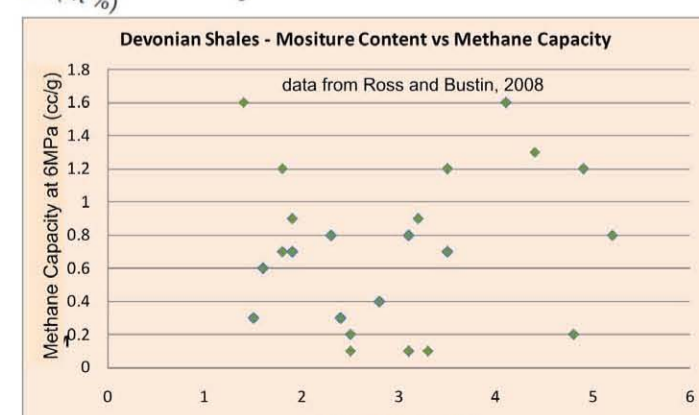


Figure 4: No correlation exists between moisture content and methane capacity for the Devonian shale sample suite.

Devonian, Jurassic and Cretaceous Shale Reservoir Characteristics

	Devonian Shale*	Jurassic Shale ^	Cretaceous Shale **
Moisture Content (%)	1.3 - 6	0.6 - 8.5	1.5 - 11
TOC (wt%)	< 6	< 12	< 17
Maturity	1.6 - 4.5	< 1.2	0.46 - 1.42
Porosity (%)	4 - 7 (clay rich) 0.6 - 2 (qtz rich)	0.5 - 4.2	0.7 - 22
Micropore Vol.	0.2 - 1.4 cc/100g	0.2 - 1 cc/100g	0.5 - 1.9 cc/100g
Mesopore S.A.	6 - 45 m ² /g	0.04 - 9 m ² /g	1.5 - 53 m ² /g
Methane Sorption Capacity at 6 MPa	0.1 - 2 cc/g	0.05 to 2.0 cc/g	0.03 - 1.9 cc/g
GIP (bcf/section)	60 - 600	1 to 31	< 340

* Ross and Bustin 2008; ^ Ross and Bustin, 2007; ** Chalmers and Bustin, 2008

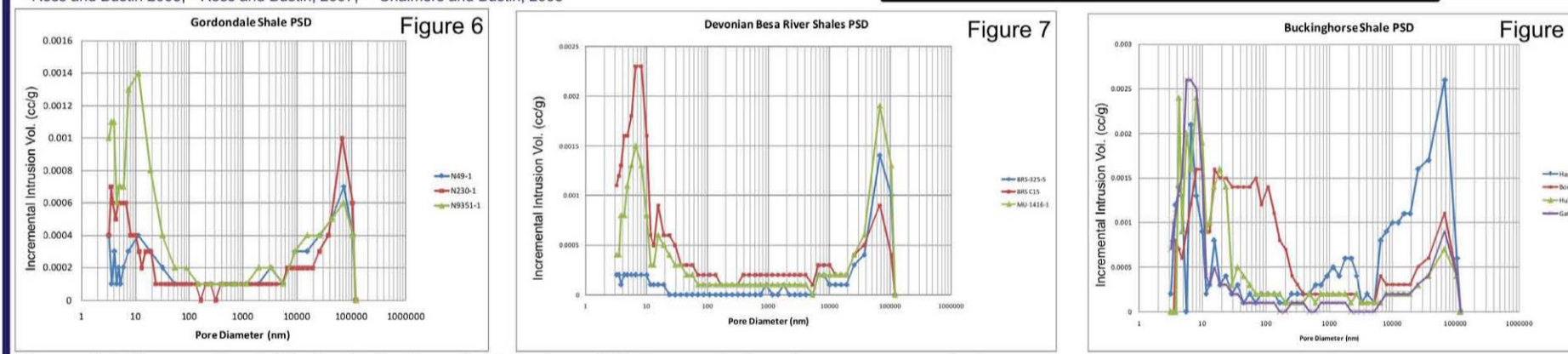


Figure 5: Ternary plot of the mineralogy of all 10 samples analysed. All but two samples from the Jurassic Gordondale shale are quartz and clay rich. The Gordondale samples are calcareous shales. The dominant clay in these samples is illite. Figure 6-8: The pore size distribution for the Jurassic, Devonian and Cretaceous shales using mercury porosimetry. The table above summarises the reservoir characteristics of the three shale reservoirs from northeastern British Columbia. The ternary diagram (Figure 5) illustrates the mineralogy and the pore size distribution (PSD) is shown for the ten samples analysed (Figures 6-8). Majority of samples are rich in clay (illite) and quartz with two Jurassic samples (N49-2 and N230-1) having near equal portions of quartz, clay and carbonate. The pore size distribution illustrates that a high proportion of pores are found in either the finer mesopore size fraction or in the 10-100µm macropore size fraction. Results from mercury porosimetry has a detection limit of 3 nm and a significant amount of pores are within the micropore size fraction which is not measured by this analysis. Mineralogy (and diagenesis) has a large impact on the PSD which is illustrated by the quartz rich Devonian BRS 325-5 sample lacks mesopores (Figures 5 & 7) compared to the illite rich BRS-325-5 and MU1416-1 samples.

Differential Thermogravimetric Analysis of Selected Shale Samples

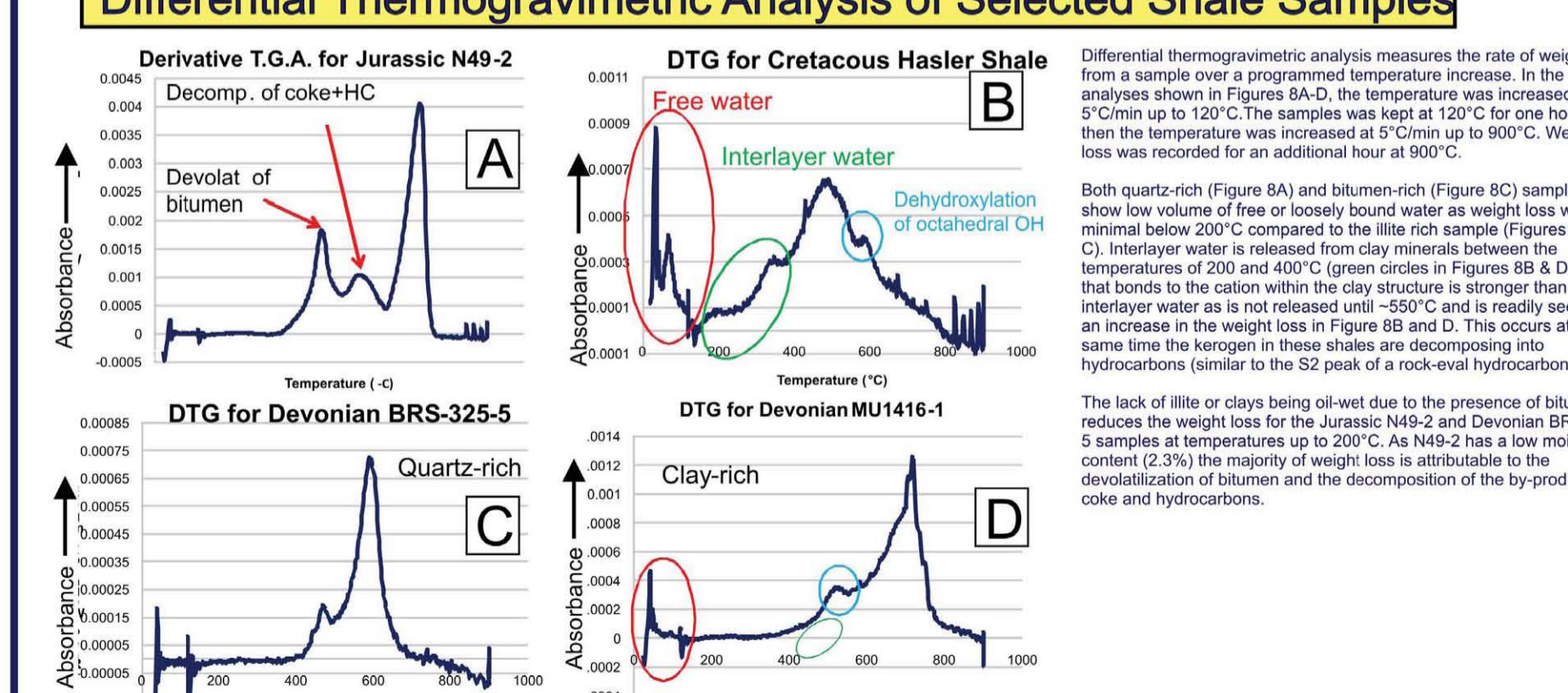


Figure 7: Differential thermogravimetric analyses of a selection of analysed samples. Differential thermogravimetric analysis measures the rate of weight loss from a sample over a programmed temperature increase. In the analyses shown in Figures 8A-D, the temperature was increased at 5°C/min up to 120°C. The samples were kept at 120°C for one hour and then the temperature was increased at 5°C/min up to 900°C. Weight loss was recorded for an additional hour at 900°C. Both quartz-rich (Figure 8A) and bitumen-rich (Figure 8C) samples show low volume of free or loosely bound water as weight loss was minimal below 200°C compared to the illite rich sample (Figures 8B & C). Interlayer water is released from clay minerals between the temperatures of 200 and 400°C (green circles in Figures 8B & D). Water that bonds to the cation within the clay structure is stronger than interlayer water as is not released until ~550°C and is readily seen as an increase in the weight loss in Figure 8B and D. This occurs at the same time the kerogen in these shales is decomposing into hydrocarbons (similar to the S2 peak of a rock-eval hydrocarbon trace). The lack of illite or clays being oil-wet due to the presence of bitumen reduces the weight loss for the Jurassic N49-2 and Devonian BRS-325-5 samples at temperatures up to 200°C. As N49-2 has a low moisture content (2.3%) the majority of weight loss is attributable to the devolatilization of bitumen and the decomposition of the by-product coke and hydrocarbons.

FT-IR Spectroscopy of Selected Shale Samples

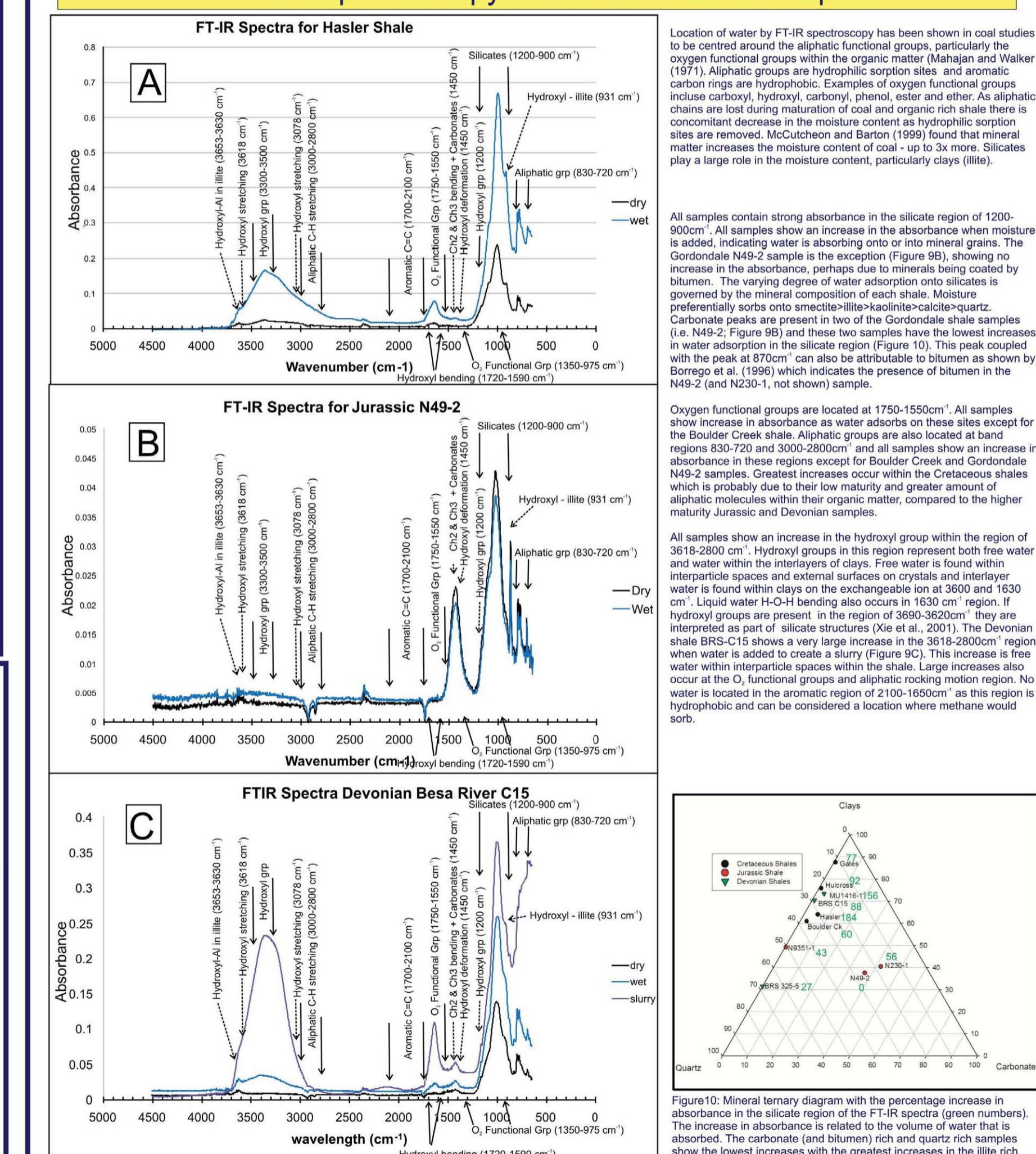


Figure 9: FT-IR spectra from a selection of analysed samples. Interpretations of spectra are from Lis et al. (2005), Xie et al. (2001), Post & Borer (2002), Mu & Malhotra (1991), Esmee et al. (2008), Giovanela et al. (2004), Petersen et al. (2008) and Borrego et al. (1996).

Water Vapour Isotherms of Selected Shale Samples

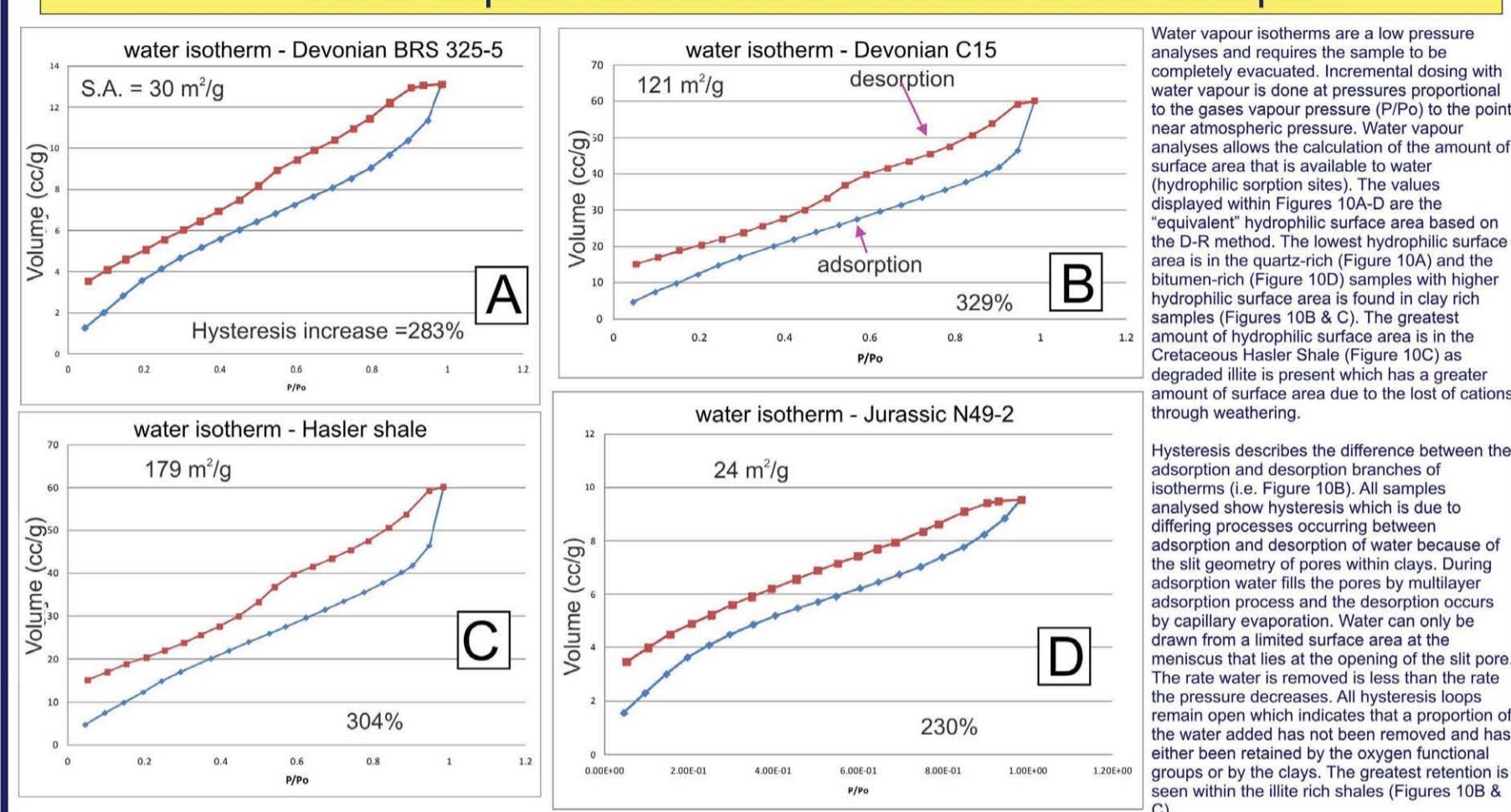


Figure 10: Water vapour isotherms for a selection of analysed samples, showing the difference between quartz, bitumen, and illite rich samples. S.A. = hydrophilic surface area and hysteresis increase is the percent increase from the initial adsorption volume of water to the final desorption volume. Water vapour isotherms are a low pressure analyses and requires the sample to be completely evacuated. Incremental dosing with water vapour is done at pressures proportional to the gases vapour pressure (P/P0) to the point near atmospheric pressure. Water vapour analyses allows the calculation of the amount of surface area that is available to water (hydrophilic sorption sites). The values displayed within Figures 10A-D are the "equivalent" hydrophilic surface area based on the D-R method. The lowest hydrophilic surface area is in the quartz-rich (Figure 10A) and the bitumen-rich (Figure 10D) samples with higher hydrophilic surface area is found in clay rich samples (Figures 10B & C). The greatest amount of hydrophilic surface area is in the Cretaceous Hasler shale (Figure 10C) as degraded illite is present which has a greater amount of surface area due to the lost of cations through weathering. Hysteresis describes the difference between the adsorption and desorption branches of isotherms (i.e. Figure 10B). All samples analysed show hysteresis which is due to differing processes occurring between adsorption and desorption of water because of the slit geometry of pores within clays. During adsorption water fills the pores by multilayer adsorption process and the desorption occurs by capillary evaporation. Water can only be drawn from a limited surface area at the meniscus that lies at the opening of the slit pore. The rate water is removed is less than the rate the pressure decreases. All hysteresis loops remain open which indicates that a proportion of the water added has not been removed and has either been retained by the oxygen functional groups or by the clays. The greatest retention is seen within the illite rich shales (Figures 10B & C).

Cross-Plots

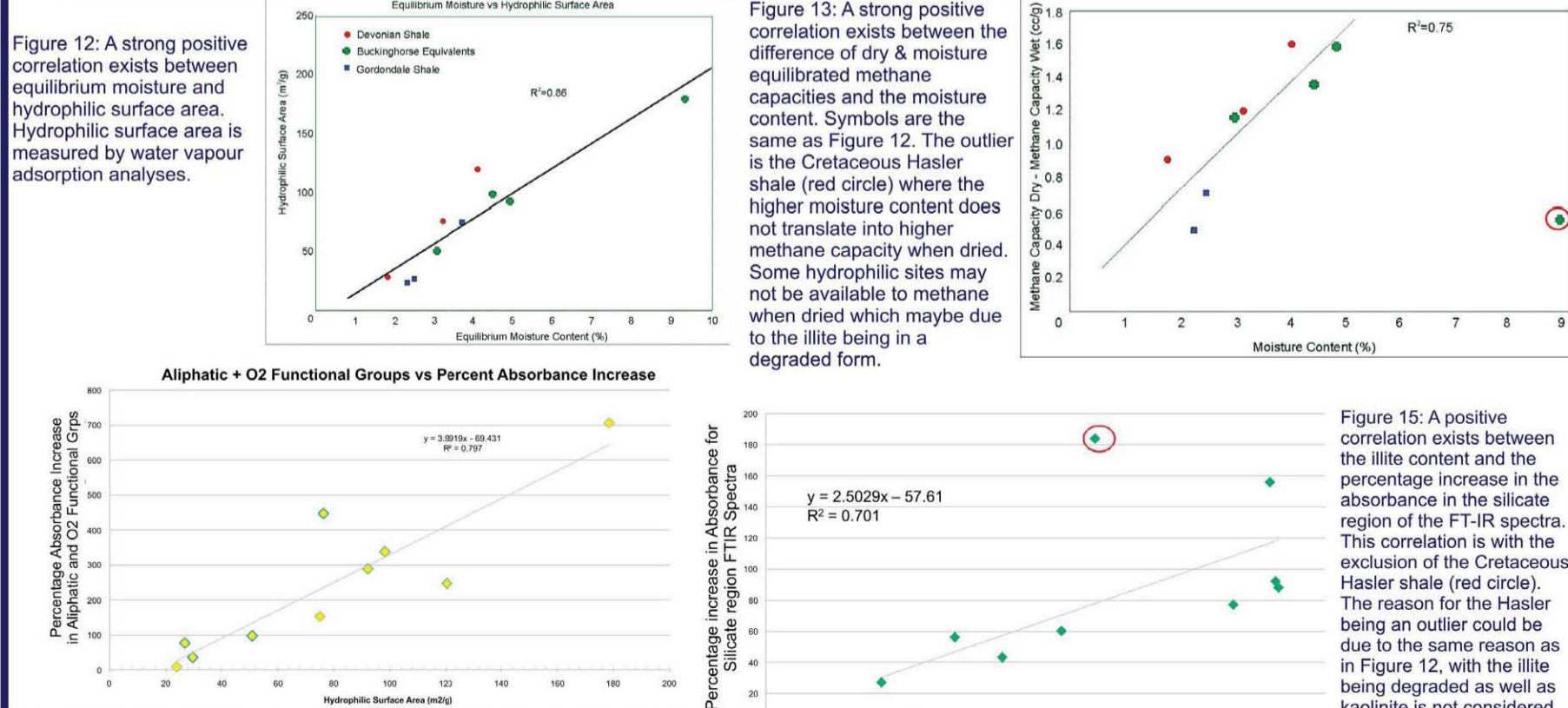


Figure 11: A strong positive correlation exists between the difference of dry & moisture equilibrated methane capacities and the moisture content. Symbols are the same as Figure 12. The outlier is the Cretaceous Hasler shale (red circle) where the higher moisture content does not translate into higher methane capacity when dried. Some hydrophilic sites may not be available to methane when dried which maybe due to the illite being in a degraded form. Figure 12: A strong positive correlation exists between the difference of dry & moisture equilibrated methane capacities and the moisture content. Symbols are the same as Figure 12. The outlier is the Cretaceous Hasler shale (red circle) where the higher moisture content does not translate into higher methane capacity when dried. Some hydrophilic sites may not be available to methane when dried which maybe due to the illite being in a degraded form. Figure 13: A positive correlation exists between the illite content and the percentage increase in the absorbance in the silicate region of the FT-IR spectra. This correlation is with the exclusion of the Cretaceous Hasler shale (red circle). The reason for the Hasler being an outlier could be due to the same reason as in Figure 12, with the illite being degraded as well as kaolinite is not considered which is 12% in this sample.