Investigation of the hydrocarbon source rock potential of selected Carboniferous black shales in southern Ireland and south-west Portugal

PIP project number IS12/08

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March 1st, 2015

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Introduction

Organic maturation (based on measurement of vitrinite reflectance) is an essential tool for unravelling the thermal histories of black shale successions and establishing relations to hydrocarbon (gas) generation and storage zones.

With ongoing hydrocarbon exploration on and around Ireland, the mid-Carboniferous (Serpukhovian) Clare Shale is a prospective, organic-rich, black, marine shale unit that is mainly preserved beneath younger Serpukhovian clastics in the Clare Basin (CB), onshore western Ireland (Figure 1-1 a). Its maximum thickness is approximately 300 m. The early Serpukhovian is also represented by black, marine shales in the Dublin Basin (DB) and adjacent areas but, with the notable exception of the Kingscourt Outlier, most of the unit has been removed by erosion. However, the Serpukhovian in this basin is also underlain by a thick succession of Mississippian limestones and shales, many of which also have high TOCs.

For comparison, two black shale successions in other regions are discussed. To the south, the mid-Carboniferous black shale succession of the 'South Portuguese Zone' (Southwest Portugal) includes the Bordalete and Quebradas formations. Several black shales sequences of mid to late Carboniferous age are also interbedded with turbiditic sandstones of the Mira and Brejeira formations to the east (Figure 1-1b).

The second reference section is Newfoundland and Labrador, on the conjugate margin to western Ireland. There, black shale successions occur in the Mid-Carboniferous, (Serpukhovian) strata of the Mabou, Deer Lake and Barachois groups of the Bay St George, Deer Lake and St Anthony basins (Figure 1-1 c). In contrast with the Irish and Portuguese basins, the black shales in this region are in large part fluvio-lacustrine in origin.

The Clare Shale and the overlying clastic rocks in the Clare Basin are post-mature in terms of dry gas preservation based on vitrinite reflectance, coal rank and spore colour (Clayton *et al.* 1989, Fitzgerald e*t al.* 1994, Goodhue 1996, Goodhue and

Clayton 1999, Corcoran and Clayton 2001). However, most of the maturity data have been derived from rock units overlying the Clare Shale, as outcrop and subsurface coverage is extremely limited. A further problem is that weathering of the shale at outcrop and in relatively old cores and cuttings has led to extensive oxidation of vitrinite that may have either raised or lower reflectance by a significant amount.

Resulting from the work programme completed under the terms of its Clare Basin Licencing Option, Enegi Oil Plc (2012, 2013) announced, *"Total recoverable resource estimates for the Option area of between 1.49 TCF and 3.86 TCF."* This clearly suggests that the maturity of much of the Clare Shale is believed by Enegi to be below the dry gas preservation limit.

The Carboniferous rocks in the DB vary considerably in maturity, from within the oil window to mature with respect to dry gas generation. Data from this basin are largely derived from deep, cored, mineral exploration boreholes in the Navan area (Fernandes 2000, Fernandes & Clayton 2007). Correlatives of this succession are source rocks for hydrocarbons currently being produced onshore UK and offshore in the UK Sector of the Irish Sea.

In southwest Portugal, the Quebradas Formation represents more-or-less the whole of the Serpukhovian. It is also closely comparable to the Clare Shale in terms of its lithological character and thermal maturity. As in the Clare Basin, the maturity of the succession has been determined mainly from VR determinations from underlying and overlying strata, rather from the Quebradas black shales themselves. The high maturity of the Devonian and Carboniferous rocks in this region was interpreted by McCormack *et al.* (2007) as the result of conductive heating with peak temperatures having been attained during and after Variscan deformation. However, recent research on sections penetrated by a deep borehole has suggested advective heating associated with Variscan uplift as a more probable cause (Fernandes *et al.* 2012).

Far to the west, Serpukhovian Mabou, Deer Lake, and Barachois group strata carry a broad range of immature through overmature thermal maturation signatures reflecting complex and diverse onshore and offshore histories of Late Paleozoic orogenesis with Mesozoic rifting and sea floor spreading. The least mature rocks are outliers upon older Precambrian and Lower Paleozoic igneous and metamorphic basement. The most mature strata are offshore and beneath thick Mesozoic cover.

This project aimed to further investigate the maturity of the Clare Shale Fm and the lower part of the Ross Sandstone Fm in the Clare Basin and to interpret the results, comparing them with Southwest Portugal. The thermal maturity of the Dublin Basin was assessed and both basins were evaluated for gas storage potential. The results of this study are of considerable significance and will contribute to the definition of the extent, organic maturation and source rock potential of black shales in the areas studied. This work may also result in the establishment of some important guidelines for future hydrocarbon exploration in the onshore and offshore basins of southern Portugal and Ireland.

1 Material and Methods

1.1 Sampling

Samples were collected from the Clare Basin, Dublin Basin (Ireland) and the 'South Portuguese Zone' (SPZ) of Southwest Portugal (Figure 1-1).

In total 136 samples were collected and analysed from outcrops and boreholes (Table 1-1).

1.1.1 Clare Basin

In terms of the Clare Basin, the sampling strategy was to obtain equally spaced samples through the Clare Shale Formation and the lower part of the Ross Sandstone Formation. The first area investigated was Ballybunnion (Co. Kerry) near the Castle and along Bay 2 (Kelk, 1960).

10 samples were collected from GSI Borehole 09/04 from Kildysart (a.k.a. Kildysert), Co. Clare. 2 samples were obtained from Loop Head and Fisherstreet, Co. Clare. A condensed section was sampled at St. Brendan's Well (near Lisdoonvarna), Co. Clare, where 4 samples were taken from the base of the section, just above the phosphate bed, and from a much siltier overlying unit (equivalent of the Ross Sandstone).

1.1.2 Dublin Basin

Samples from the Dublin Basin were obtained from Tara Mines boreholes N1442 and N1909, and from GSI borehole 13-01 drilled in Kentstown, Co. Meath (now stored in the Geological Survey of Ireland (GSI) core storage facility in Sandyford). Seven core samples were collected from N1442 and 18 from N1909. 27 core samples were taken from this borehole with an average sampling spacing of 10 m. Of the 27 samples, 7 were used for adsorption-desorption experiments. An additional 4 samples (B25-B28) were collected from the Irish Cement quarry at Donore (Co. Meath), but only 2 (B25 and B28) were productive for vitrinite.

1.1.3 South-West Portugal

Two samples were obtained from an outcrop of the Quebradas Formation at its type section at Quebradas (QB1 and QB3) and 44 from the Mertola Formation in Borehole AC-1 (Figure 1-1). More details concerning sample locations are included in Appendix 1.

1.1.4 Maritime Basin in Newfoundland and Labrador

Serpukovian strata on and around the coasts of Newfoundland and Labrador are among the least studied rocks in Atlantic Canada. Work on regional variations in source rock quality and maturity is currently underway in another Provincial Government programme. It will become available soon. This review will offer a summary of currently available background data and a useful comparison with Irish strata.

1.2 Analyses

The numbers of analyses completed are summarised in Table 1-1. Localities sampled with number of samples taken together with their labels.

Total Organic Carbon (TOC) was analysed in 158 samples.

X-ray diffraction (XRD) analysis was completed on 41 samples because lithological variation was observed in the samples from both the Dublin and Clare Basin, and it was deemed important to assess this for the characterisation of samples analysed by the other methods.

A sub-set of 24 samples (Table 1-3) was sent to Dr. Cortland Eble (Kentucky Geological Survey). These were prepared in accordance with ASTM International

Standard D-2013-07 (ASTM International, 2009) by first crushing them to -8 mesh (2.36 mm screen openings) using a hammer mill crusher. The samples were then halved using a sample riffler. One half was used for the construction of petrographic pellets. The other half was further reduced in size to -60 mesh (250 micron screen openings), using a pulverizer, for CH_4 and CO_2 gas isotherm analysis, the determination of total organic carbon content (TOC) and Rock-Eval pyrolysis (performed by GeoMark Research Ltd).

Twenty samples were selected for adsorption analysis and assessment of reservoir condition. These analyses were performed by RMB Earth Science Consultants Ltd., BC, Canada. Seventeen samples were assessed for CO_2 adsorption and 3 for methane adsorption.

All analyses completed are summarized in Appendix 1.

1.3 Total Organic Carbon (TOC)

TOC content can be measured directly or determined by difference between the total carbon content and inorganic carbon content. TOC analyses were completed using both methodologies and the results compared.

1.4 Vitrinite Reflectance

Vitrinite reflectance (R_{o}*ran*) is a measure of the percentage of incident light reflected from the surface of vitrinite particles in a sedimentary rock. The determination of the R_{o}*ran* followed the ASTM D7708-11 standard (ICCP, 1998).

1.5 Rock-Eval Pyrolysis

Around 100 mg of pulverised sample were heated in both pyrolysis and oxidation ovens in a series of stages from 100 to 850 ° C. During Rock-Eval Pyrolysis, samples are heated in inert conditions (in helium or nitrogen). The organic compounds emitted are detected by a flame ionization detector (FID), while the amount of CO and CO_2 emitted are measured by infrared detectors (IR). A thermocouple registers the temperature variations.

Initially, the sample temperature is maintained at 300 °C for several minutes, enabling generation of the hydrocarbons already produced by the rock (S1 peak). The kerogen is then cracked thermally (S2 peak) by increasing the temperature 25 °C per minute until a temperature of 850 °C is reached. CO_2 production increases during the second phase, creating the S3 peak. Tmax, the temperature at which maximum generation of hydrocarbons occurred was recorded when this was possible.

Other indices were extrapolated from the Rock-Eval pyrolysis in order to characterise the source rock:

- Hydrogen Index (HI): derived from the ratio of H over TOC and is defined (S2/TOC*100). The higher the HI, the higher is the oil generating potential of the kerogen
- Oxygen Index (OI): derived from the ratio of CO_2 to TOC (S3/TOC*100). This is useful for determining the kerogen type and the maturation stage.
- Production Index (PI): derived from the hydrocarbons produced during all the heating stages (S2/(S1+S2))

These Indices can be plotted against each other to interpret the data.

1.6 X-Ray Diffraction

Mineralogy is an important aspect of the characterisation of both conventional and unconventional reservoirs (Figure 1-2). Mineralogy controls the pore network and the initial mineral composition affects the nature and the magnitude of diagenetic transformation during burial. Mineralogy is even more important in shale gas exploitation because it influences the mechanical properties of the rocks and how easily they can be fractured. Shales have a variable mineral composition, the understanding of which is fundamental in creating a reliable petrophysical and geomechanical model (Euzen, 2011). Mineralogy also impacts on shale brittleness. Clay-rich shales are more difficult to fracture, since they tend to deform under stress, whereas siliceous mudstones tend to fracture more easily.

Swelling clays (smectite), when present, can create problems, especially in shallow shales, when water-based fracturing fluids are used. If carbonate-rich shale is treated with acids, this can potentially increase the risk of releasing fines (Rickman e*t al.*, 2009).

A representative 40 g from each sample was powdered in a Retsch PM100 ball-mill. A 1 g subsample of this was ground to a powder by hand in an agate pestle and mortar and placed in a cavity mount before being analysed in the XRD. The XRD trace was interpreted using phase-matching software[1]. The interpreted traces are presented in the result section while the traces are provided in Appendix 2.4.

1.7 Adsorption Experiments

Samples for adsorption determination were collected from different areas around the Clare Basin and the Dublin Basin. The adsorption experiments were completed using an assumed reservoir temperature of 40 °C. The samples were crushed to (at

[1] Bruker AXS, Diffrac.EVA software, 2012 Release, Version 3.0.

least) -60 mesh. A 2 g split was used for moisture and ash analyses following ASTM procedures.

Isotherms were measured on custom-made apparatus based on the design of a system built by CSIRO, Lucus Heights, Australia. The apparatus is based on Boyle's Law. A known volume of gas within a reference cell is used to dose a sample cell containing the sample. The amount of gas adsorbed in the sample cell is then determined, based on change in pressure in the sample cell. Normally, 100 g of sample is used for these analyses.

The 'Langmuir Isotherm' (Figure 1-3) describes the sorption capacity of a rock with pressure at a specific temperature. Only a certain amount of gas can be sorbed to the surface at a fixed pressure and when the pressure drops, this gas is progressively released as a free gas into the pore system.

1.8 Figures and tables

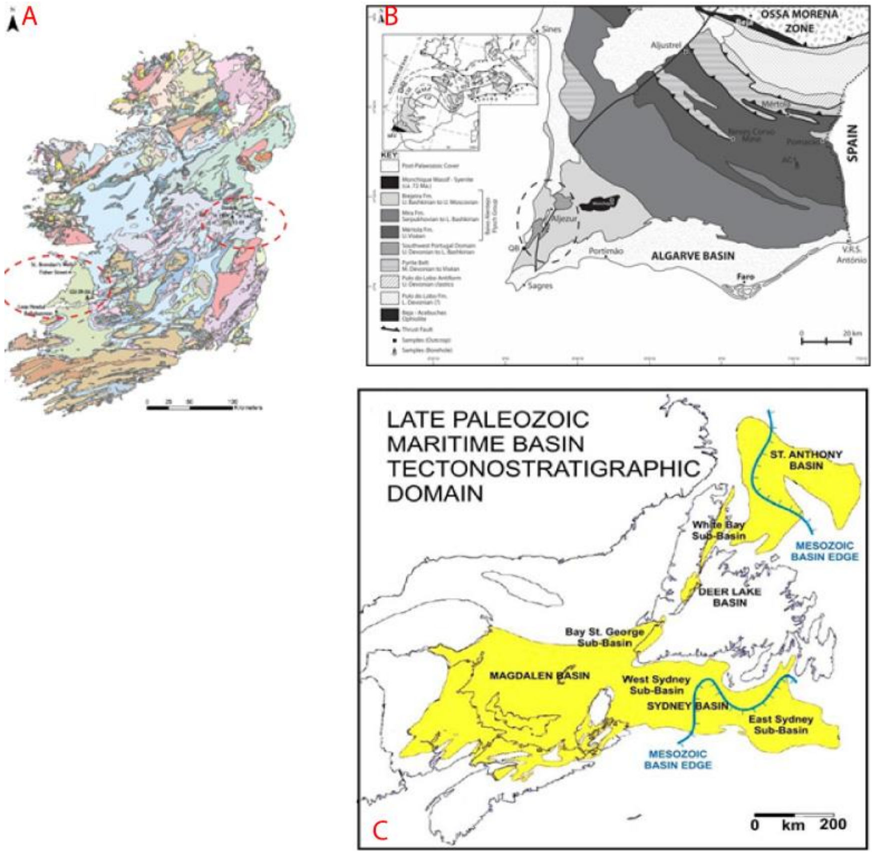

Figure 1-1. Areas investigated: a) a simplified bedrock geology of Ireland with the location of the basins (Dublin basin in the east and Clare basin in the south-west). b) Location of the SPZ in Portugal. c) Tectonostratigraphy map of Late Paleozoic basins in Atlantic Canada (from Lavoie et al. (2009); Hu and Dietrich (2010))

Locality/Borehole	County	State	No. of Samples	Labels
Ballybunnion	Kerry	Ireland	18	B1-B18
St. Brendan's Well	Clare	Ireland	4	B19-B22
Fisherstreet	Clare	Ireland	1	B23
Loop Head	Clare	Ireland	1	B24
Donore	Meath	Ireland	4	B25-B28
GSI 09-04	Clare	Ireland	10	B29-B38
GSI 13-01	Meath	Ireland	27	B39-B65
N1442	Meath	Ireland	7	B66-B72
N1909	Meath	Ireland	18	B73-B90
Quebradas	Faro District	Portugal	2	QB1 &QB3
AC-1	Faro District	Portugal	44	AC1-1/AC1-44
TOTAL			136	

Table 1-1. Localities sampled with number of samples taken together with their labels.

Analyses	Completed	Planned	Comments
TOC	158	150	109 (TCD)+ 24 (KGS)
VR	91	50	17 samples were barren
Rock-Eval	24	41	
Adsorption	20	20	
SEM	0	20	Difficulties in accessing the machine
XRD	41	-	

Table 1-2. Analyses carried out and number of samples analysed.

Sample	**Location**	**Sample**	**Location**
B1	Ballybunnion	B29	GSI 09/04
B2	Ballybunnion	B32	GSI 09/04
B5	Ballybunnion	B34	GSI 09/04
B8	Ballybunnion	B37	GSI 09/04
B11	Ballybunnion	B38	GSI 09/04
B18	Ballybunnion	B44	GSI 13/01
B19	St. Brendan's Well	B52	GSI 13/01
B22	St. Brendan's Well	B56	GSI 13/01
B23	Fisherstreet	B60	GSI 13/01
B24	Loop Head	B64	GSI 13/01
B25	Donore	QB1	Quebradas
B28	Donore	QB3	Quebradas

Table 1-3. Samples sent to the Kentucky Geological Survey.

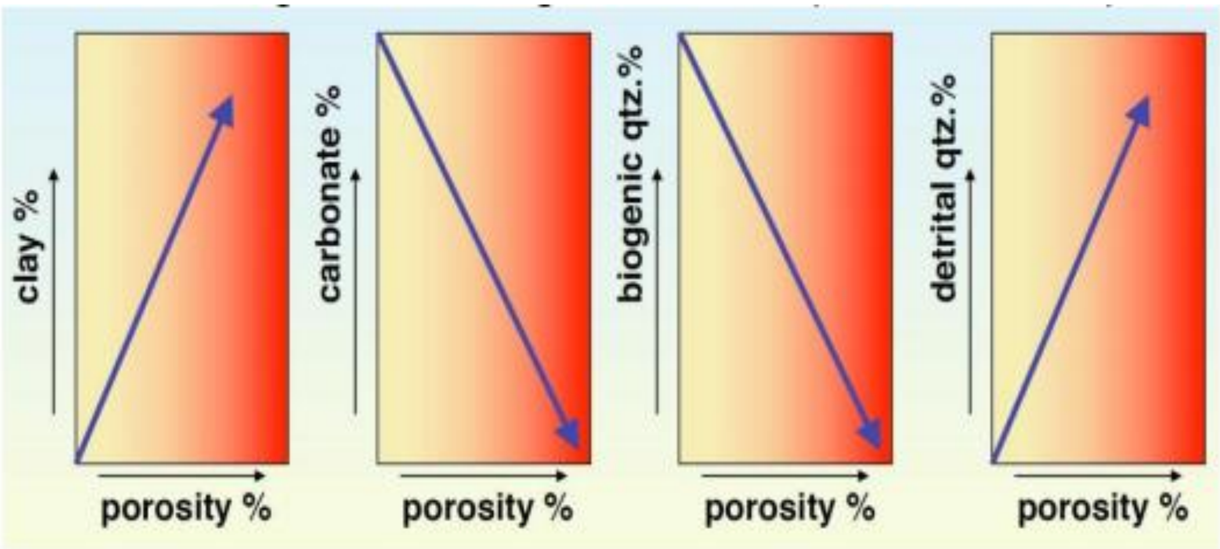

Figure 1-2. Influence of mineralogy in shale (Bustin, 2010)

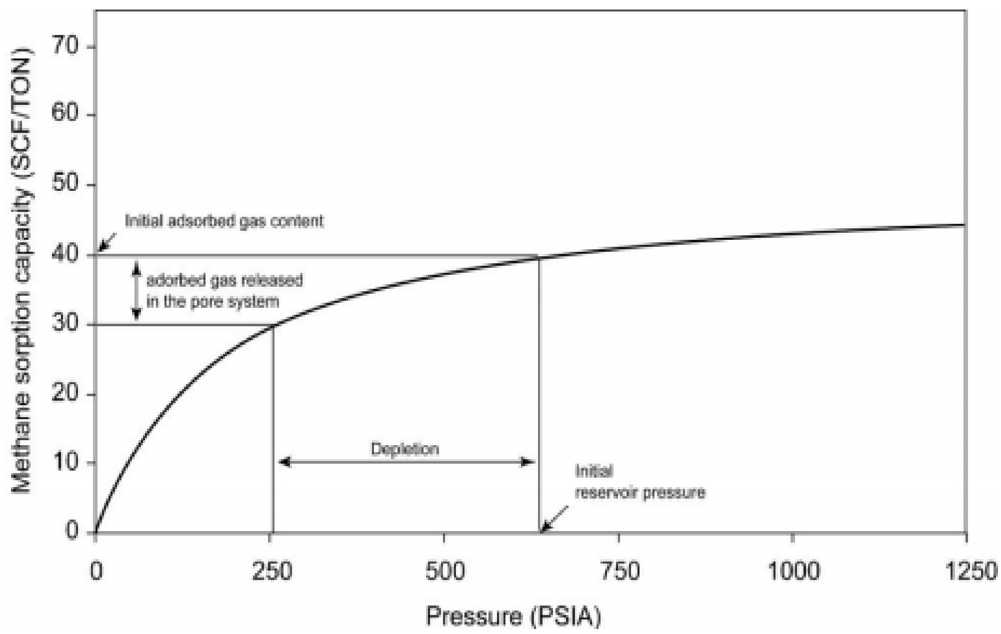

Figure 1-3. Langmuir isotherm

2 Results

2.1 Clare Basin

2.1.1 TOC

TOC values are summarised for all the samples in the Clare Basin in Figure 2-1. The detailed results from each sample are included in Appendix 2.1. The assumed depths to which samples have been buried are speculative and are based on interpreted stratigraphic relationships. Therefore, the data are plotted only for comparative purposes.

The samples from Ballybunnion show values of TOC above 1% in most cases, with four samples well above 4%. The minimum value recorded was 0.82% (B7) and the highest was 8.11% (B18). The Total Ash Yield varied from a minimum of 73 % to a maximum of 94%. TOC results obtained from samples B1 and B8 by the TCD and KGS differ significantly (Figure 2-2). These analyses were carried out on different splits of the samples, which could explain these differences.

In the case of sample B1, the TOC is classified as “good” (2.4%) by KGS but “excellent” (5.4%) by TCD. Sample B8 shows good potential (3.7%) on the basis of the TCD result but has poor potential (0.3%) from the KGS result. The samples are more organic rich towards at the top of the Limestone and at the base of the Clare shale and they get leaner in the Ross Sandstone. The other two outcrop samples from Fisherstreet (B23) and Loop Head (B24) show that both of them are potentially excellent source rocks having with TOC values of 9.6% and 11.9% respectively. The TOC analyses from GSI borehole 09-04 show that the samples range from very good to excellent, except for one sample that has a TOC value of 1%.

2.1.2 Vitrinite Reflectance

$R_{o}\textit{ran}$ for the Clare Basin samples are summarised in Figure 2-3. The Vitrinite Reflectance values obtained from the Ballybunnion samples (B1-B18) are all in the gas generation zone, with $R_{o}\textit{ran}$ > 4.0%. Similar values were obtained from the other two outcrop samples from Fisherstreet (B23) and Loop Head (B24). (R_o*ran* from B23 - 5.02 % and B24 - 5.33%).

The values obtained from GSI Borehole 09-04 range from 4.43 to 4.81% placing the samples in the post-mature window (Figure 2-4). The relative stratigraphic positions are accurate only for the borehole samples; the outcrop values are only plotted for general comparative purposes without an exact spacing. Detailed results can be found in Appendix 2.2.

KGS analyses (Table 2-4) produced lower values than those from TCD. Hackley *et al.* (2015) showed in an interlaboratory exercise that vitrinite reflectance measurements have low repeatability and reproducibility in high maturity kerogen samples. However, the TCD values fall within the range predicted from the results from other types of analysis. Mean R_o*ran* ranges from 2.8 to 5.2 %, indicating very high levels of thermal maturity. In terms of coal rank, these samples would be classified as semi-anthracite (R_o*ran* 2.0 – 2.5 %), anthracite (R_o*ran* 2.5 – 4.0 %), and meta-anthracite (R_o*ran* >4.0%).

Three samples (B8, B29 and B37) had bimodal reflectance distributions, which are labeled as high (H) and low (L) in Table 2-4. In high rank material, vitrinite and inertinite reflectances converge, which makes discrimination between the two maceral groups very difficult in most cases. Furthermore, the most of the organic material exists as finely comminuted particles of vitrinite (vitrodetrinite), and inertinite (inertodetrinite), which typically are very small in size (commonly <10 µm).

2.1.3 Rock-Eval

The samples from Ballybunnion, Fisherstreet, Loop Head and St. Brendan’s Well (Table 2-2) showed that the potential of the source rock in these areas is very low. The complete dataset (S1, S2, S3 and Tmax) is included in Appendix 2.3. The S1 peak is very low which could be due to the gas generated in the rock having been released over time. If solid bitumens were present, the S1 peak would be higher. Since the S2 peaks (Figure 2-5a) are lower than 0.2 mg HC/g of rock, all of the Tmax values were rejected (Peters, 1986). The remaining hydrocarbon potential is very low and all the samples fall in the dry gas zone.

The core samples from GSI Borehole 09-04 confirm the previous data. They have a poor oil potential index (S2 peak always below 0.1 %mg HC/g). All Production Index (PI) values lie within the range 0.4 - 1 (Figure 2-5b). In case the of the outcrop samples, oxidation has reduced the S1 and S2 peaks, also affecting the PI Index.

The S2 peaks are very low, as is the Hydrogen Index (Figure 2-5c) suggesting a gas prone source rock. This is also evident in the Pseudo Van Krevelen Plot (Figure 2-6) where the samples lie horizontally along the oxygen index (x-axis). These results are also affected by the thermal history of the samples, as type III kerogen could have been degraded to type IV kerogen. It is also clear from Figure 2-7 is that despite the good potential from a TOC point of view, the section sampled could only generate dry gas.

2.1.4 XRD Analysis

Semiquantitative analyses from XRD from outcrop samples in the Clare Basin (Ballybunnion, St. Brendan's Well and Loop Head) are summarised in Figure 2-8.The samples from St. Brendan's Well are rich in quartz, albite, muscovite, pyrite and gypsum, and in one case (B22) dolomite. Chlorite group clays were always present.

A sample from the marine band at Loop Head contained only quartz, albite and muscovite. The samples from Ballybunnion are rich in quartz, feldspars (albite or oligoclase), muscovite and clinochlore. Pyrite, the third most abundant mineral present, was found in samples B7, B8 and B9. Carbonates were found in the form of calcite and dolomite (B18 had only calcite, B3 only dolomite while B8 both calcite and dolomite).

Samples from GSI Borehole 09/04 were rich in quartz, muscovite, clinochlore and pyrite (Figure 2-9); five contained gypsum. Calcite and dolomite were present together (B30, B32 and B37) and individually (B31, B34 and B35). Albite was detected in all samples except B34 and B38.

Many classifications of organic-rich mudstones have been published. The SCore ternary mudstone classification scheme (Gamero *et al*., 2012) is used to classify the samples collected in this report. This diagram is based on the relationship between cores and logs. QFM (quartz, feldspars and micas), Carbonates and Clay are the corners points. In total, 16 classes of mudstones can be defined. The most promising shale gas prospects are dominated by non-clay minerals.

Most of the samples collected from the Clare Shale and lower part of the Ross Sandstone formations (Figure 2-10) are siliceous mudstones (having a quartz + feldspar + mica content > 50%).

The Mineral Brittleness Index (MBI) was calculated for the Clare Shale and Ross Sandstone formations (Figure 2-11) following Wang and Gale's (2009) equation:

$$MBI\ (\%) = \frac{(WQFM + WCAR)}{(WQFM + WCAR + WCLAY + TOC)} * 100$$

Where WQFM, WCAR, WCLAY stand for dry weight of quartz, feldspar and micas (QFM), Carbonates and Clays respectively. This equation also takes TOC into consideration as a ductile material like the clays. It should be noted that this equation is only a first qualitative assessment of the mechanical properties of the shales. Calculation of the elastic parameters of the rocks (Young's Modulus and Poisson's ratio), which assess the 'weakness' of the shales (where no chemical bonds are present) was beyond the scope of this project. Most of the samples investigated have MBI > 40%, reaching a maximum of 95%. Therefore, all appear relatively brittle.

2.1.5 Adsorption

Adsorption curves for the samples from Ballybunnion are shown from Figure 2-12 to Figure 2-15.

B1 and B2 had the highest TOC (6.23 and 5.76% respectively) and therefore, the highest adsorption capacity. Samples B11 and B18 had the lowest adsorption capacity. Sample B11 has the lowest TOC value (0.32%) while B18 had a higher TOC content (2.62%) (Table 2-3).In sample B18, the inorganic matrix adsorbed much less CO_2 than the other samples. Samples B19 and B22 (Figure 2-13) have similar TOCs (2.73 and 2.29% respectively).

The only sample collected from a 15 m section of black shales (equivalent to the lower part of the Ross Sandstone Formation) at Fisherstreet Bay (Figure 2-14) has a high TOC (7.05%) and low moisture content (0.89%). Although the thickness is much reduced in the area, this section has a considerable CO_2 adsorption capacity. Most of the samples have not reached a state of equilibrium where a CO_2 monolayer is formed. The reason for this is unclear.

Samples B34 and B37 (Figure 2-15) had the highest TOC content (8.39 and 7.11% respectively) and higher moisture content compared to B29. This probably explains why these samples have a higher adsorption capacity. Sample B 34 was also run for methane adsorption analysis (Figure 2-16). As expected from work by Grobe *et al.* (2010), Methane adsorption was less favourable than CO_2. The CO_2/CH_4 ratio at high pressure (around 730 PSIA) is around 1.79 (Figure 2-16). Previous observations that CO_2 adsorption increases with both TOC (Figure 2-18) and moisture content (Figure 2-17) were confirmed (Grobe *et al.*, 2010, Nuttal *et al.*, 2005).

2.1.6 Figures and tables

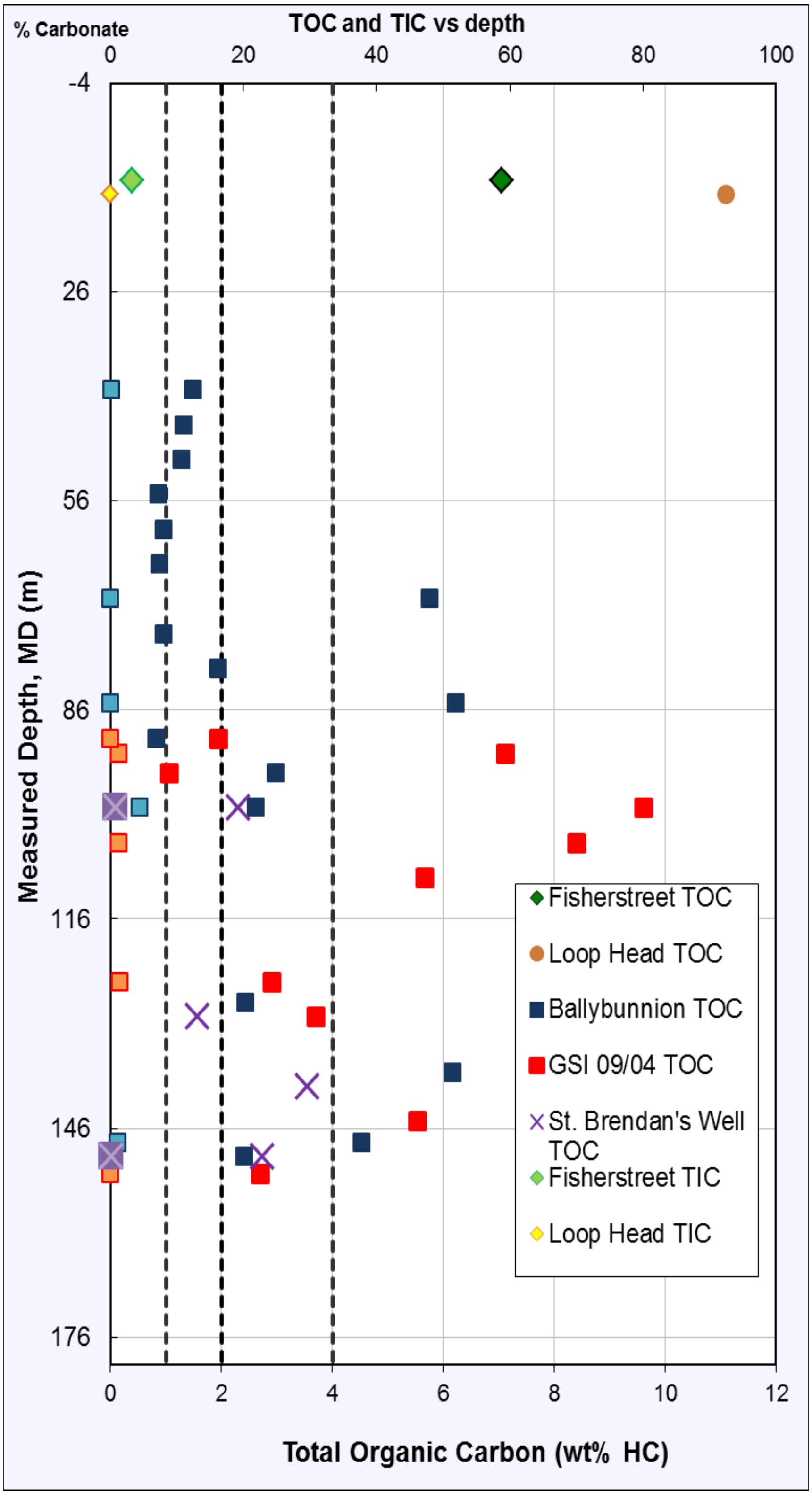

Figure 2-1. TOC values for the Clare Basin samples.

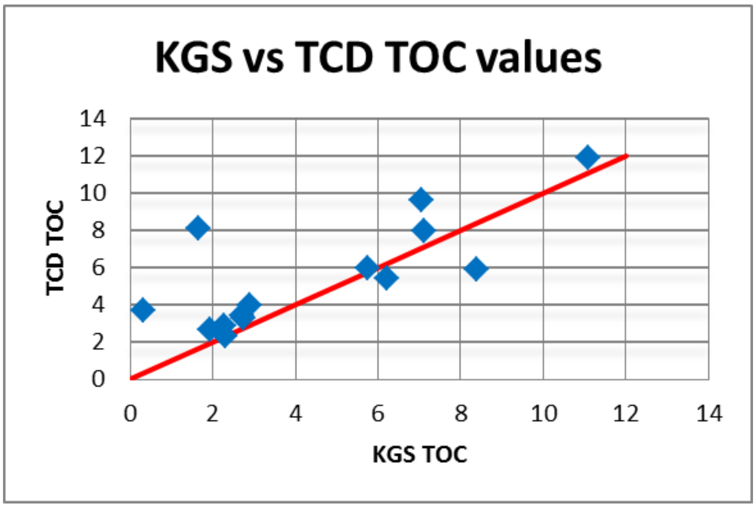

Figure 2-2. Comparison between TOC values obtained from the Kentucky Geological Survey and Trinity College Dublin. These measurements are not from the same split of samples.

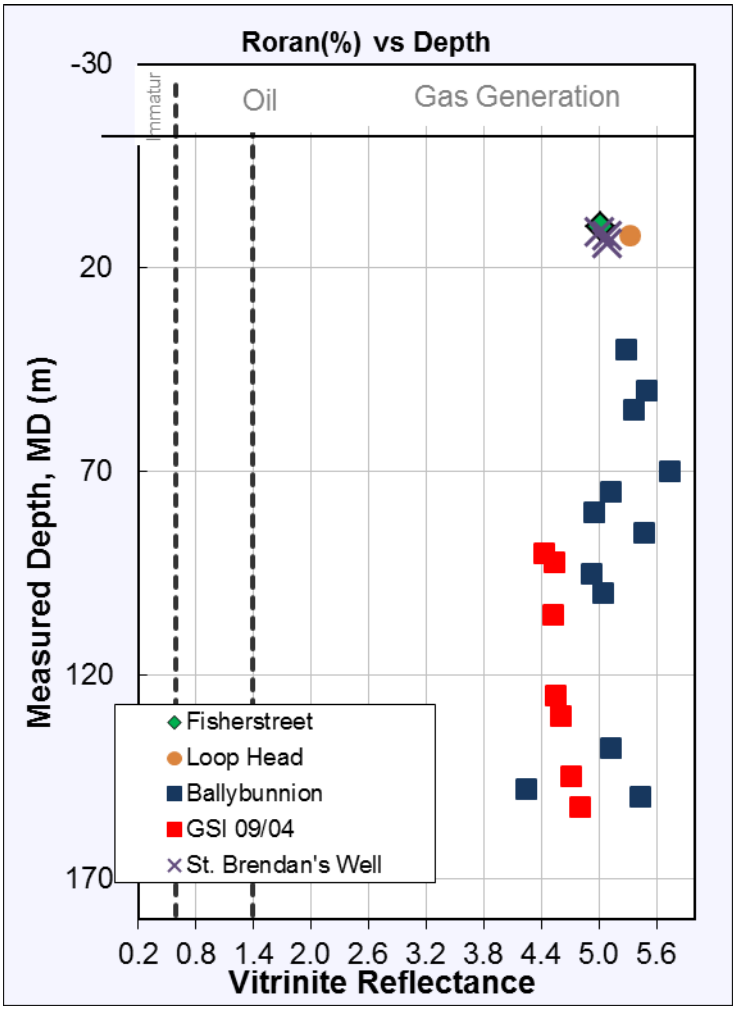

Figure 2-3. Vitrinite Reflectance variation with depth for the Clare basin samples.

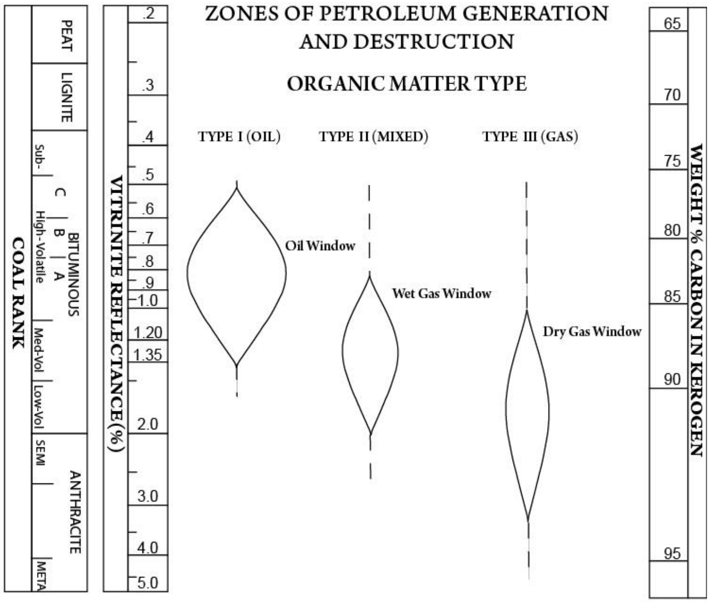

Figure 2-4.Thermal maturation chart showing different showing common thermomaturation (rank) determination parameters (Dow, 1977).

Samples	R_{Oran} (%)	SD	Measurements
B1	4.01	0.24	50
B2	3.75	0.17	56
B5	3.84	0.19	50
B8 H	3.75	0.19	51
B8 L	3.11	0.19	15
B11	3.94	0.27	50
B18	3.79	0.15	51
B19	3.73	0.18	50
B22	3.51	0.22	54
B23	3.74	0.1	58
B24	4.33	0.1	54
B29 H	3.25	0.17	33
B29 L	2.80	0.13	20
B32	3.33	0.16	53
B34	3.31	0.14	52
B37 H	5.23	0.18	24
B37 L	4.6	0.22	50
B38	3.23	0.15	61

Table 2-1.Vitrinite Reflectance measurements from Clare Basin samples made by KGS.

	Index (S2x100/TOC)	Index (S3x100/TOC)	Conc. (mg HC/mg CO2)	Norm. Oil Content	Index (S1/(S1+S2))
B1	1.66	8.30	0.20	0.83	0.33
B2	0.88	8.61	0.10	1.10	0.56
B5	0.70	2.61	0.27	2.43	0.78
B8	0.68	32.43	0.02	2.70	0.80
B11	1.53	3.05	0.50	1.53	0.50
B18	0.16	5.78	0.03	0.80	0.83
B19	0.37	4.76	0.08	1.47	0.80
B22	3.06	10.48	0.29	2.18	0.42
B29	1.85	2.96	0.63	1.85	0.50
B32	1.38	20.34	0.07	1.72	0.56
B34	0.72	2.50	0.29	1.19	0.63
B37	0.70	2.95	0.24	1.13	0.62
B38	0.51	9.26	0.06	1.03	0.67

Table 2-2. Rock-Eval parameter for the Clare Basin Samples.

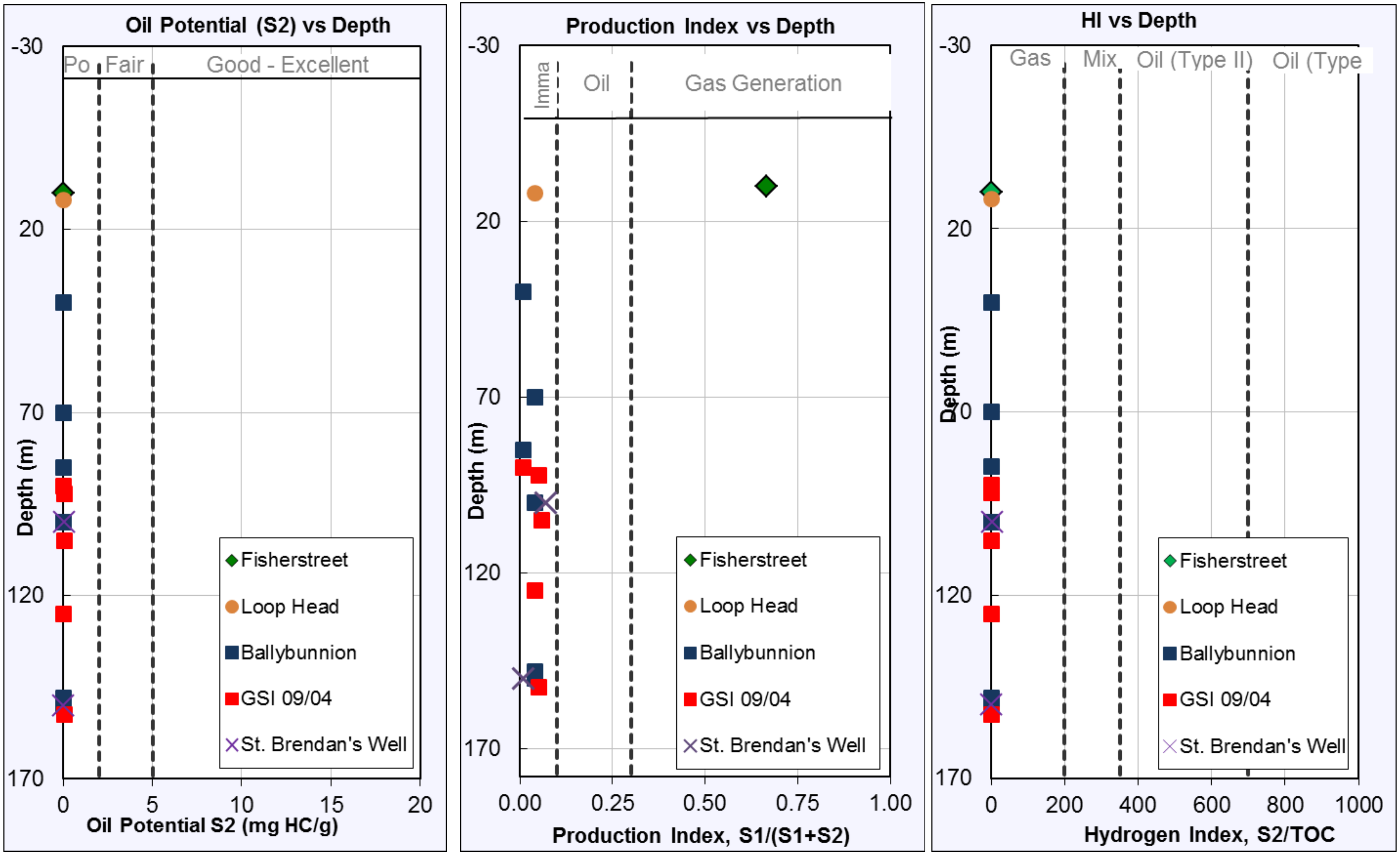

Figure 2-5. a) Oil Potential Index; b) production Index; c) hydrogen index for the Clare Basin samples.

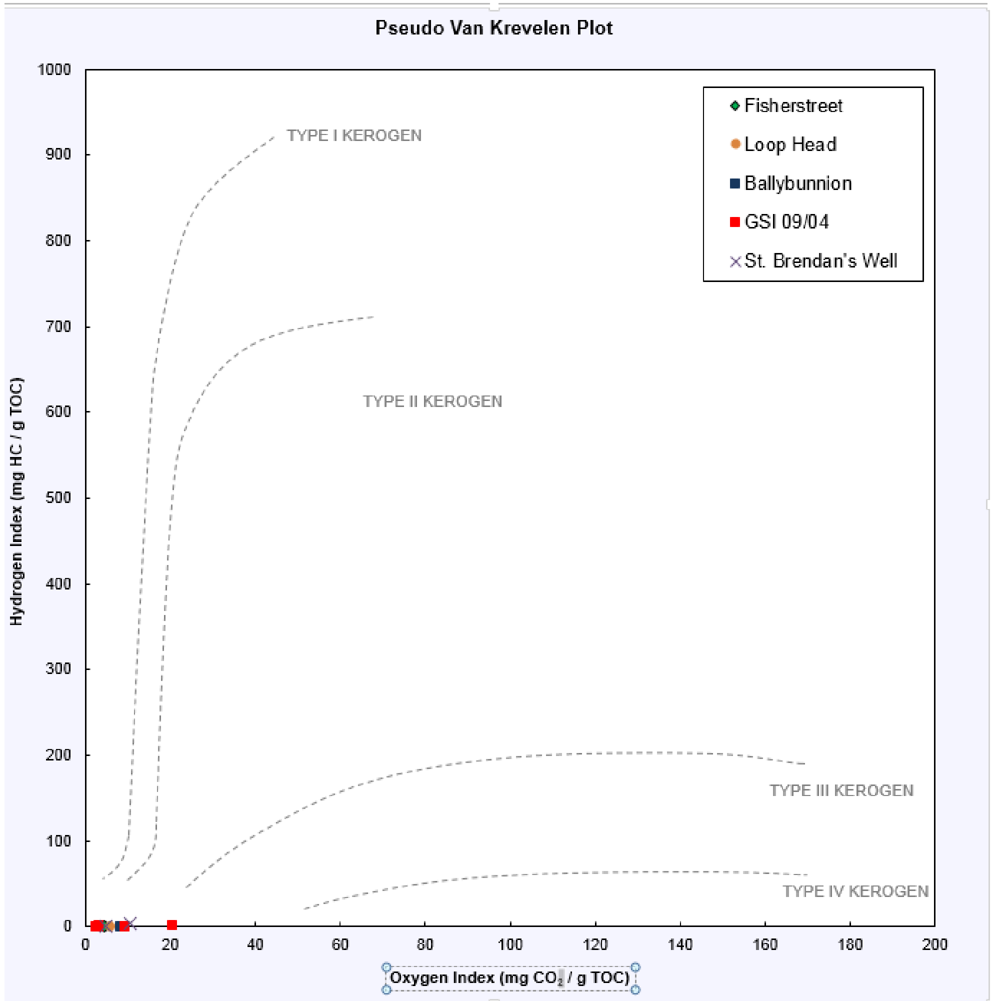

Figure 2-6. Pseudo Van Krevelen Plot for the Clare Basin samples.

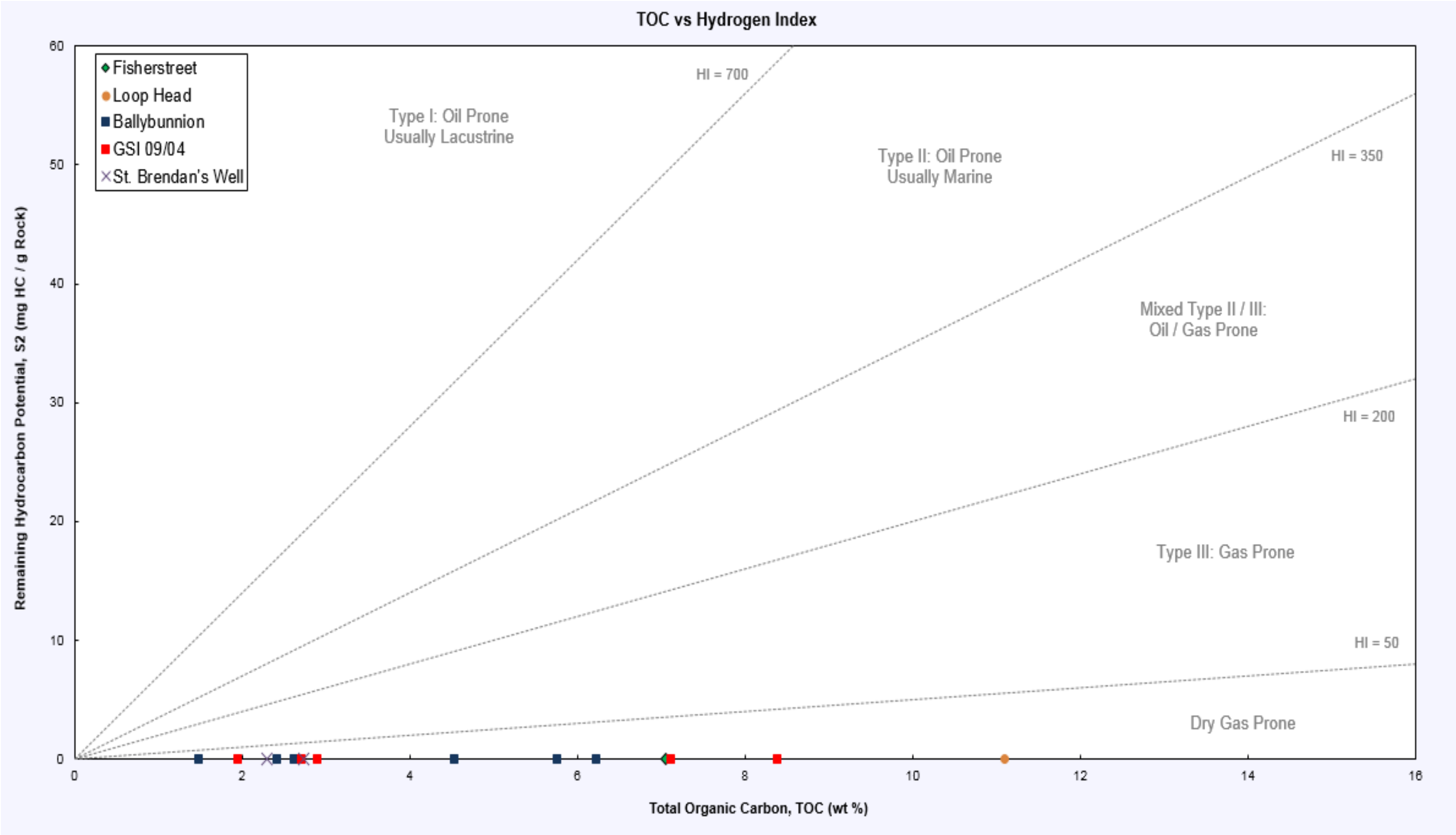

Figure 2-7. TOC vs Hydrogen Index for the Clare Basin Samples.

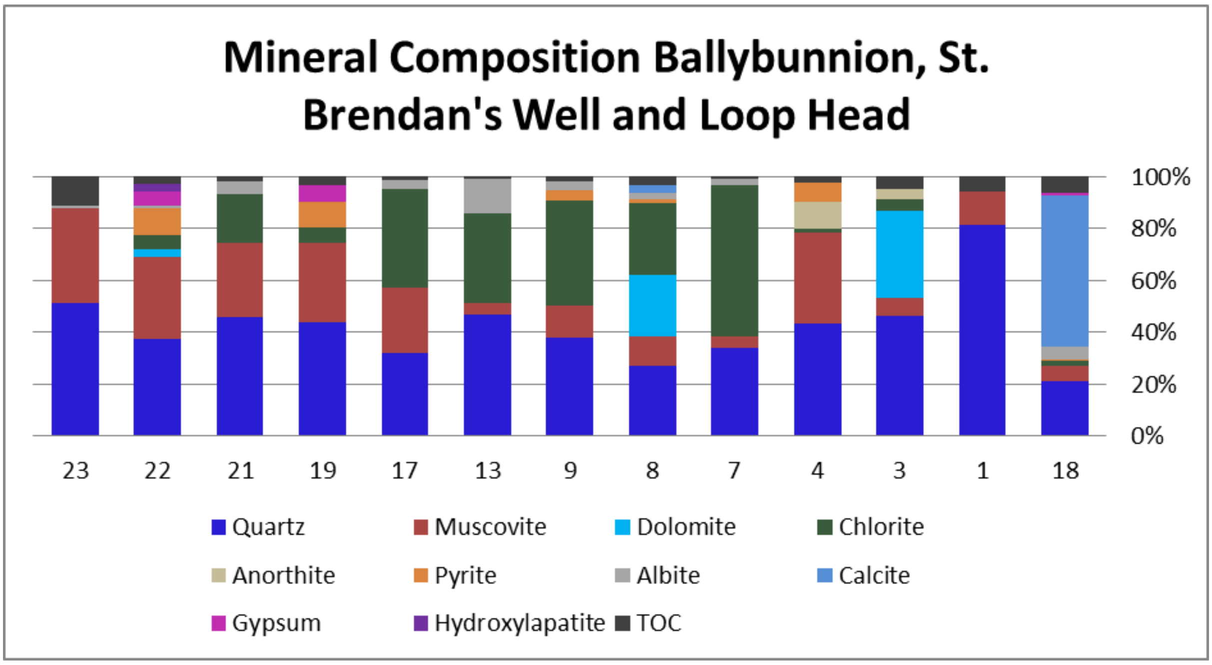

Figure 2-8. Semi-quantitative mineral composition for the outcrop samples in the Clare Basin.

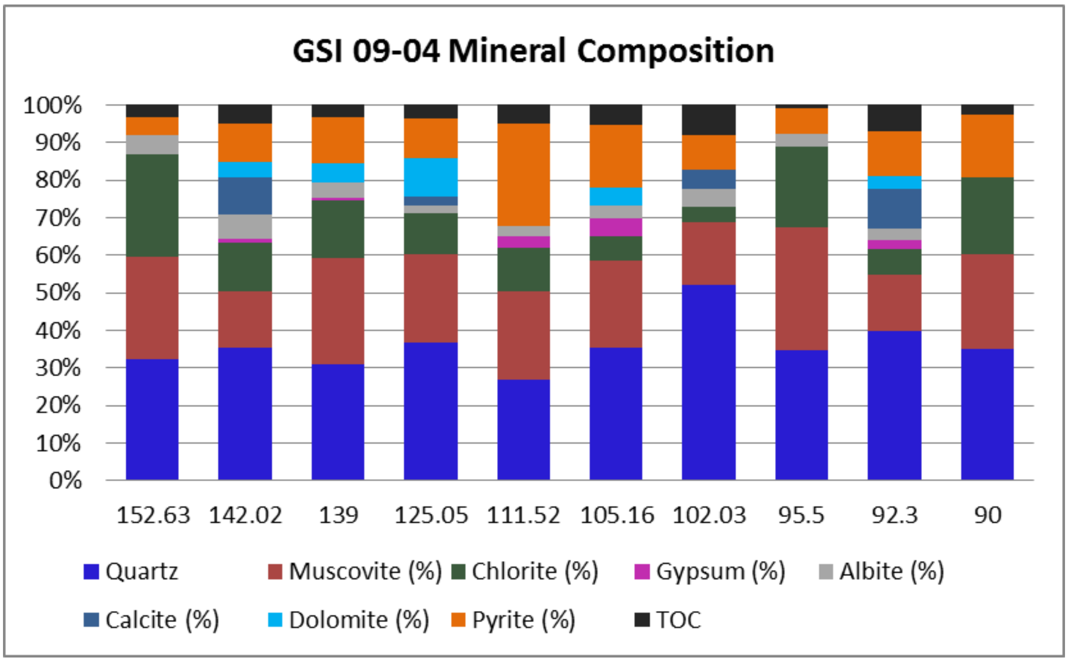

Figure 2-9. Semi-quantitative mineral composition for samples from GSI Borehole 09-04.

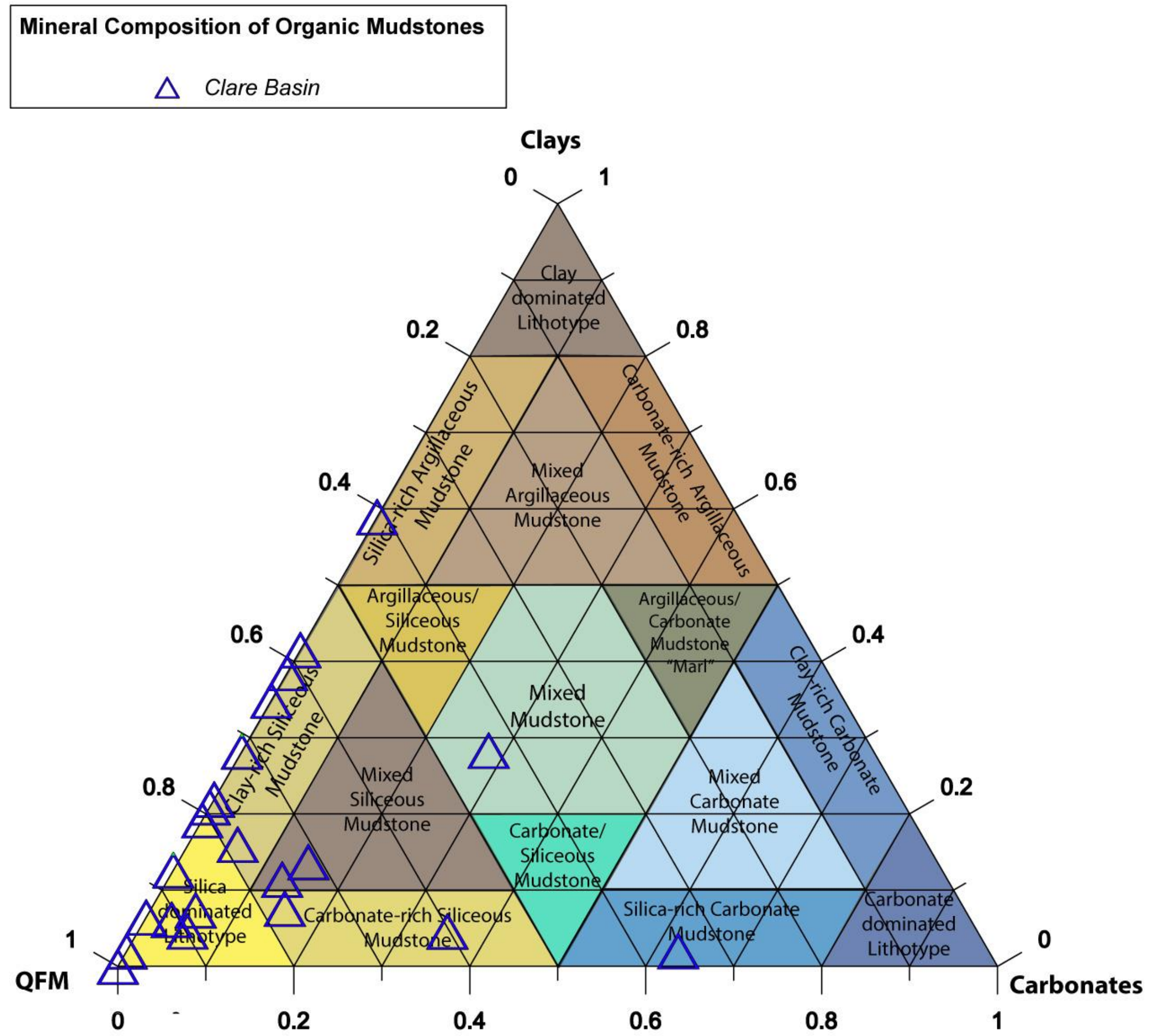

Figure 2-10. Organic-rich mudstone classification for the Clare Basin samples from Gamero *et al.* (2012) with blue triangles representing samples analysed.

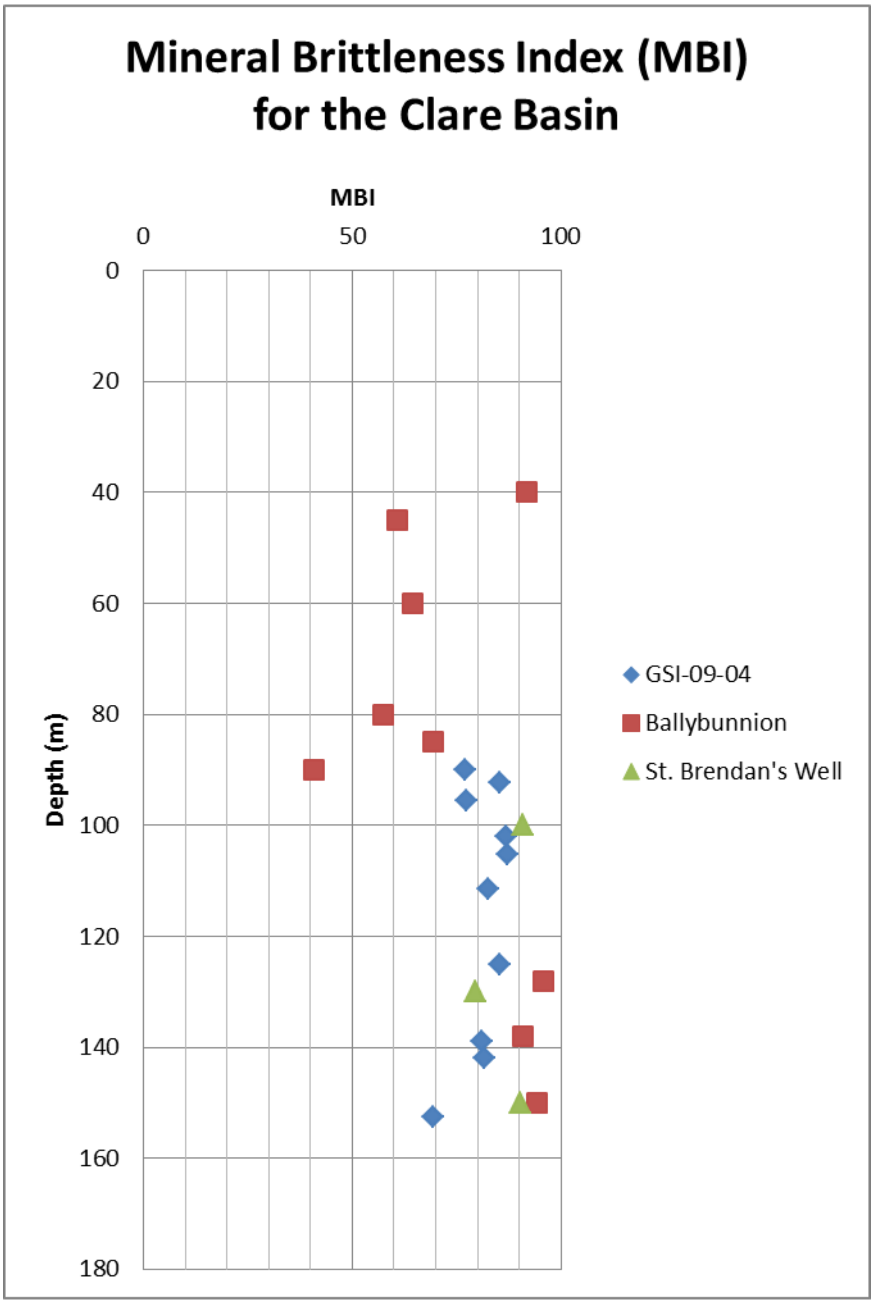

Figure 2-11. Mineral Brittle Index calculated for the samples from the Clare shale and Ross Sandstone formations in the Clare Basin.

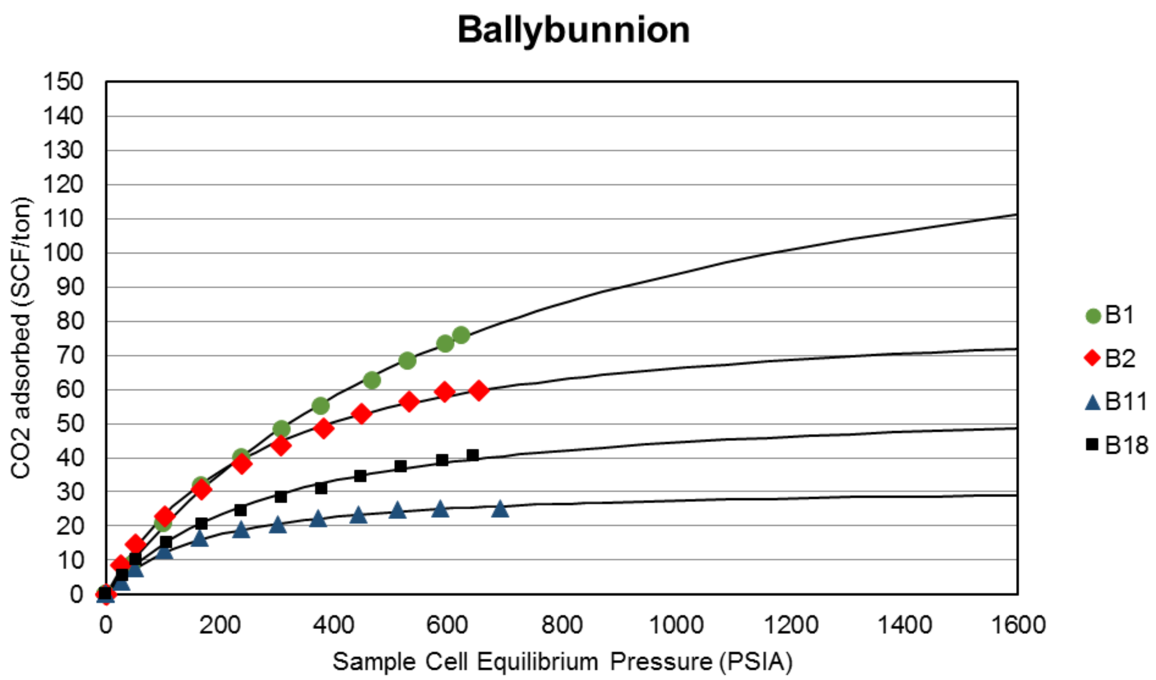

Figure 2-12. CO_2 adsorption curves from Ballybunnion samples.

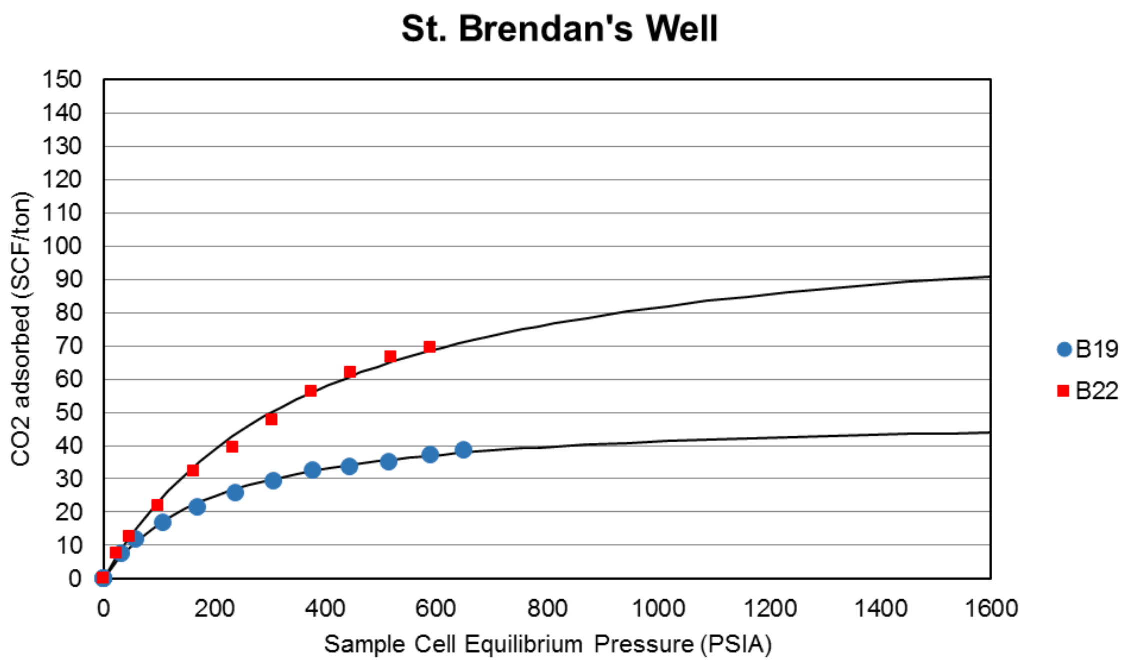

Figure 2-13. Adsorption Curve for the samples from St. Brendan's Well.

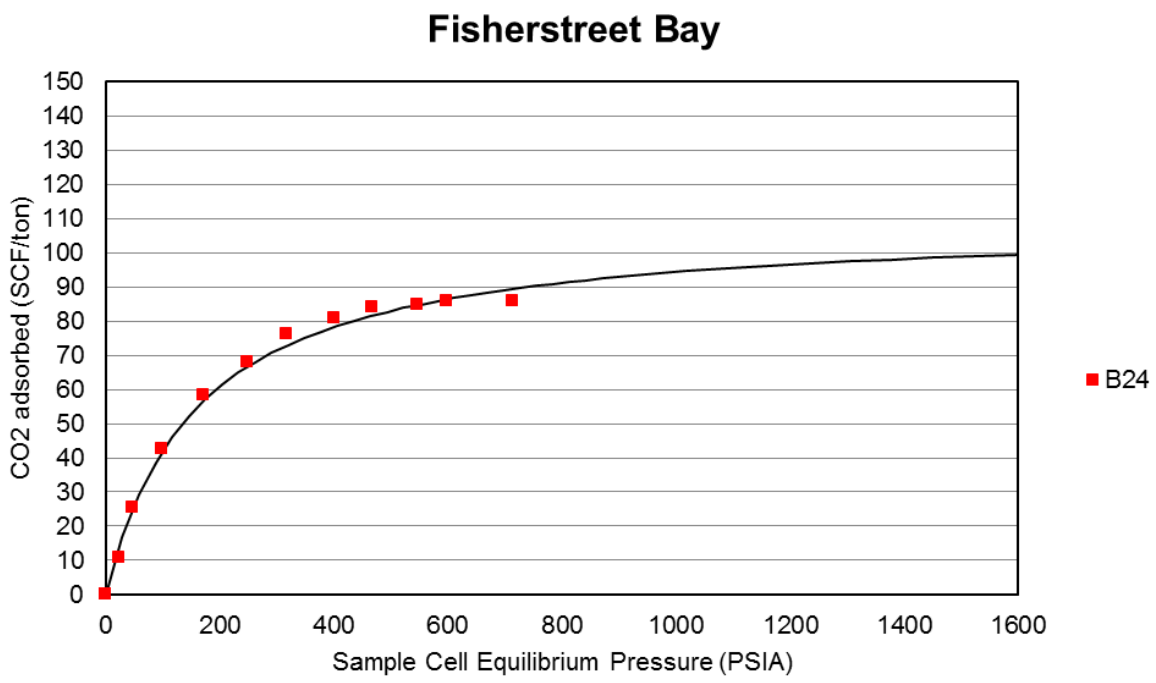

Figure 2-14. Adsorption Curve for the samples from Fisherstreet Bay.

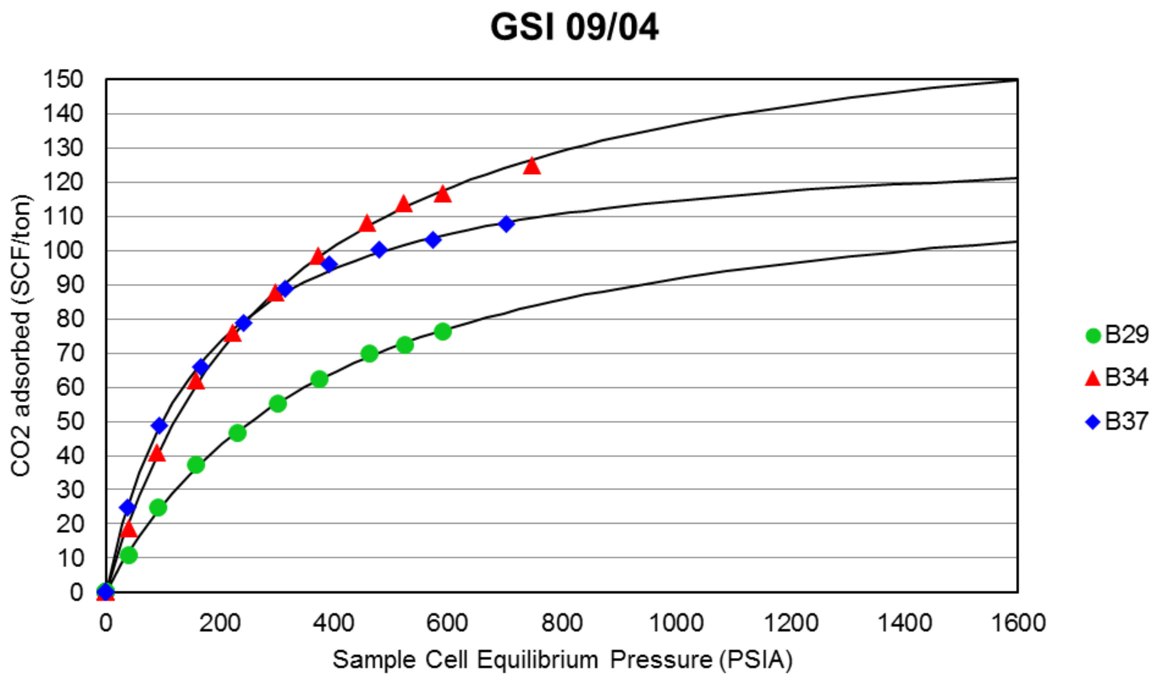

Figure 2-15. Adsorption Curve for samples from the GSI Borehole 09/04.

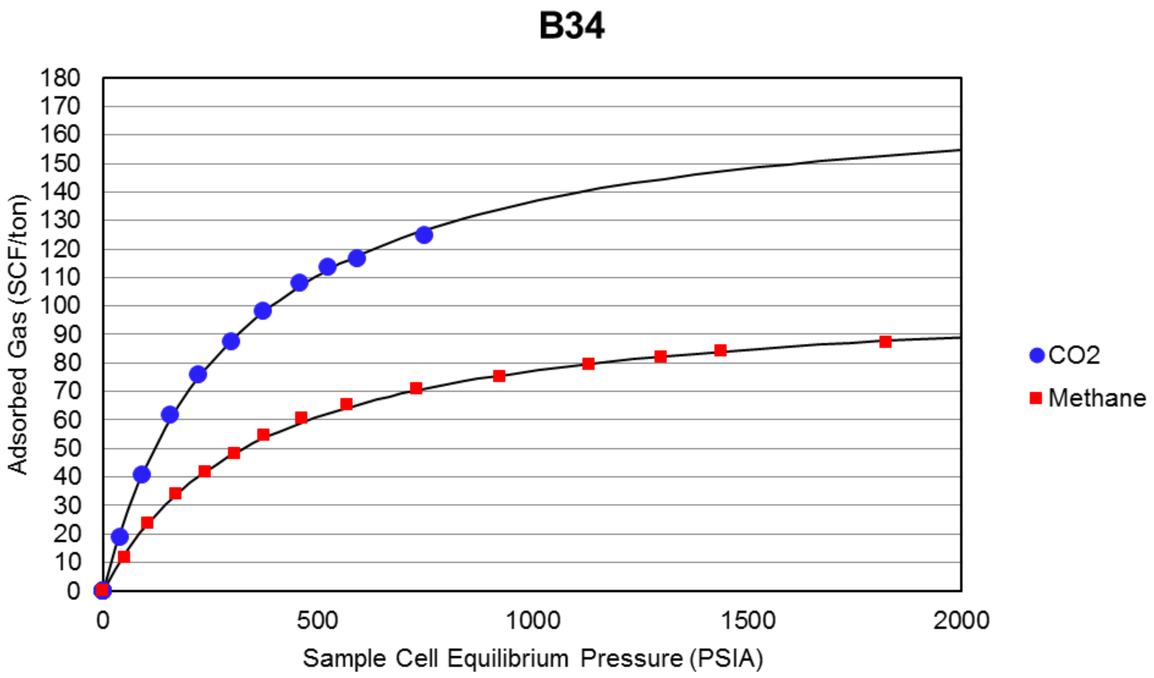

Figure 2-16. CO_2 vs CH_4 adsorption Curve for B34.

Samples	Moisture Content (%)	TOC *	Pressure (PSIA)	Adsorbed Gas (ft3/ton)*	TIC*	Ash Yeald (wt%)*
1	1.19	2.41	594.80	73.39	0.02	90.99
2	1.21	4.53	593.06	59.29	0.01	91.38
11	0.84	0.32	586.97	25.01	6.42	76.16
18	0.56	2.62	589.87	39.24	0.08	93.58
19	2.29	2.73	588.56	37.26	0.08	89.73
22	1.32	2.29	589.00	69.45	0.69	89.59
23	0.83	7.05	597.20	85.82	3.25	79.94
29	0.85	2.70	590.00	76.30	0.02	93.01
34	1.69	8.39	590.93	116.77	1.18	83.91
37	1.69	7.11	573.98	102.97	1.17	85.52

Table 2-3. Moisture content, TOC and Adsorbed CO_2 for all samples from the Clare Basin. * KGS analyses.

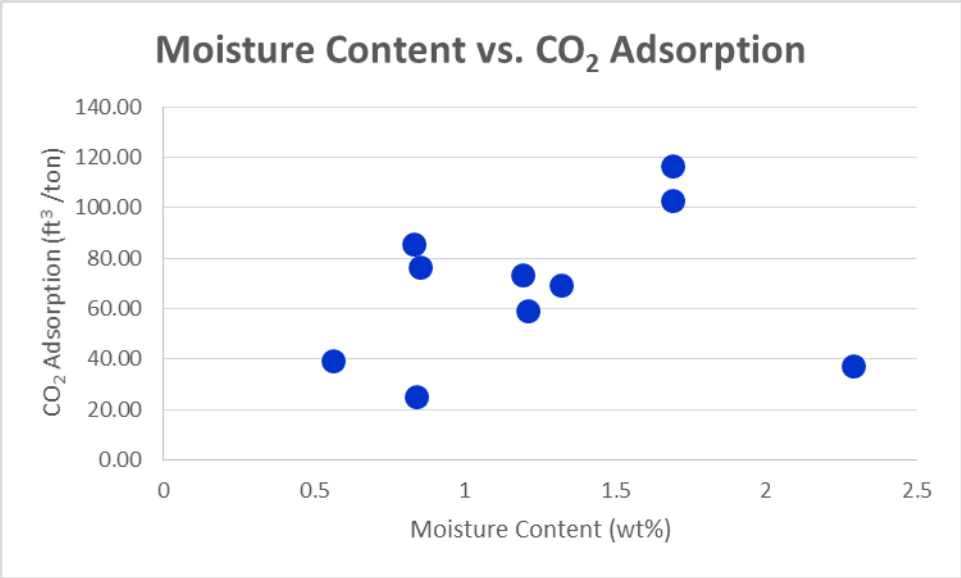

Figure 2-17. CO_2 adsorption vs. Moisture content.

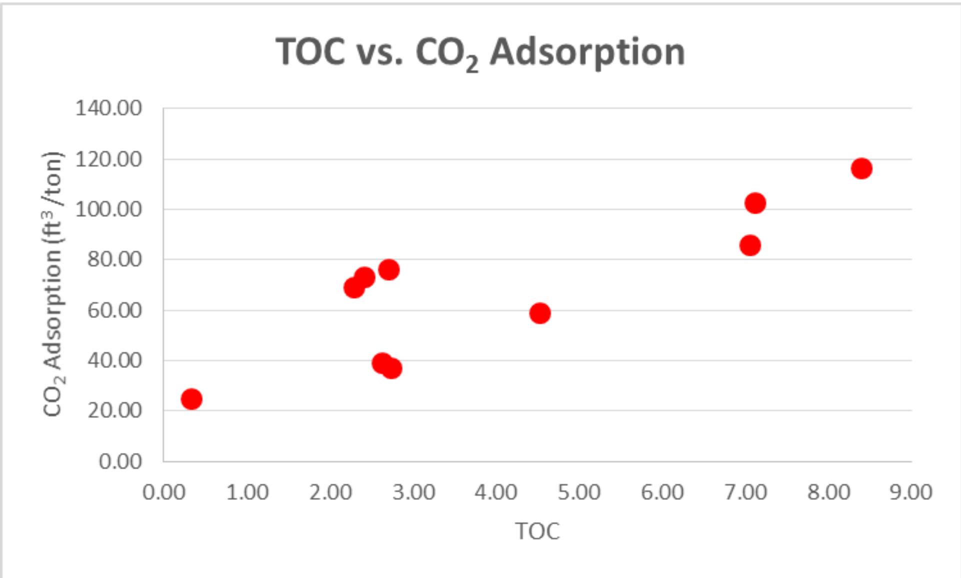

Figure 2-18. CO_2 adsorption vs. TOC.

2.2 Dublin Basin

2.2.1 TOC

TOC values for N1909 samples are shown in Figure 2-19; values for Donore and GSI 13-01 are shown in Figure 2-20. Complete datasets for each sample are included in Appendix 2.1.

Borehole N1909 TOCs range from 1.01% to 3.34%. TOCs range from fair to good; most are around 2%.

The TOC from the Donore outcrop samples (B25- B28, in green), were all above 4%, with a maximum value of 5.58% for B28.

GSI Borehole 13/01 samples (in red) have TOC values ranging from 1.31% to 13.62%. TOCs are high, with nine samples classified as excellent. The discrepancy between the KGS and TCD TOC measurements (Figure 2-21) is probably due to different splits of the same samples having been analysed in the two labs.

2.2.2 Vitrinite Reflectance

Thermal maturity indicators for the samples from Donore and the GSI 13/01 borehole are shown in Figure 2-23; Donore R_o*ran* results are shown in green and GSI 13/01 results in red. Tmax (in yellow) is only reported for the GSI 13/01 samples because these are the only ones with a Rock-Eval pyrolysis S2 peak. Therefore, calculated R_o*ran* values (blue) were only obtained for the GSI 13/01 samples. Relative stratigraphic positions are only accurate for GSI Borehole 13/01; the positions shown for the the Donore samples are extremely tentative in view of the absence of bio- or lithostratigraphic correlations.

The N1909 samples range from 0.8% to 1.4% R_o*ran*, increasing with depth. Since most samples were dominated by AOM, some R_o*ran* readings could have been underestimated (Figure 2-22). Samples collected from the N1442 were barren.

Detailed Vitrinite Reflectance data for the Dublin Basin are included in Appendix 2.2. The Donore samples (B25 and B28) showed a $R_{o\,ran}$ of 2.25% and 2.79% respectively (Figure 2-23). B26 and B27 were not productive for vitrinite reflectance. The GSI 13-01samples show a very noisy vitrinite reflectance distribution but a poorly defined gradient can still distinguished.

All the measured values fall in the gas-window and are consistently higher than the 'equivalent' values calculated from Tmax (from Rock-Eval analysis). Values vary from 1.80 % to 3.84% $R_{o\,ran}$ but some of these are less accurate because of low numbers of measurements made. The KGS results range from 1.54 to 2.05%. These samples are classified as low volatile bituminous, and occur within the dry gas window (Table 2-4).

2.2.3 Rock-Eval

Rock-Eval pyrolysis results are reported in Appendix 2.3. In terms of HC source rock potential, samples B25 and B28 were poor (Figure 2-24), since the S2 peak was well below 0.1 mg HC/ g rock (0.01 and 0.06 mg HC/g rock respectively).

Since the S2 peak was so low and broad, the Tmax values could not be picked accurately. The effects of surface weathering were evident on the rock samples which may explain the reduction of the S1 and S2 peaks with the increase of the S3 peak. As a consequence, the Hydrogen Index (Figure 2-25a) was reduced and the Oxygen Index increased, thereby affecting the Production Index (Figure 2-25b).

The samples from GSI Borehole 13/01 showed low S2 peaks and the Tmax was therefore obtained for only four samples (Figure 2-23) varying from 464 °C to 514°C. These fall in the gas generation window. The Equivalent VR gradient based on calculated vitrinite reflectance values is steeper than that obtained from measured vitrinite reflectance. The kerogen quality plot (Figure 2-26 and Figure 2-27) showed that all the samples fell in the dry gas–prone area with type III / type IV kerogen dominant. It is likely that with oxidation and increasing thermal maturity the samples shifted down from a Some transformation in kerogen from type III to type IV may have resulted from maturation and/or weathering.

In contrast, the Tmax results placed the samples in the wet condensate gas and dry gas zones between the oil and gas windows (Figure 2-28 and Figure 2-29).

2.2.4 XRD Analysis

Mineral phases present in the samples from GSI Borehole 13/01 borehole are summarised in Figure 2-30. Quartz is always present with muscovite, albite and pyrite present in most samples. Samples B40 and B52 also contain calcite together with dolomite, while B53, 55, 56 and 65 contain only dolomite. Siderite was present in two samples (B57 and B64). Clay minerals are always present, mainly chlorite group and less frequently as kaolinite and illite.

The samples were plotted on a ternary diagram (Figure 2-31) for organic-rich mudrock classification (Gamero *et al*, 2012). Most of the samples are Clay-rich siliceous Mudstones and in the Silica dominated lithotype. Two samples (B53 and B55) were completely dolomitised

Mineral Brittleness Index (MBI) was calculated following Wang and Gale (2009):

$$MBI\ (\%) = \frac{(WQFM + WCAR)}{(WQFM + WCAR + WCLAY + TOC)} * 100$$

All the samples are brittle since the MBI is above 48% (Figure 2-32). See page 19 for discussion of method.

2.2.5 Adsorption

CO_2 can be stored in the inorganic matrix of shales and also in the organic matter (adsorbed). The organic matter typically accounts for 50% of the total porosity with moisture content also playing a major role.

Sample B25 had a much higher TOC and moisture content that B28 (Table 2-5), and could store more than twice the amount of CO_2.

Five samples from GSI Borehole 13-01 (B44, B52, B56, B60 and B64) were selected for analysis. B52 had the lowest moisture content (0.96%) and a relative high TOC (3.32%) compared with the other samples. B60 had the highest TOC content (4.53%). Therefore, it is obvious that these intervals have the potential to store the highest volumes of CO_2. Sample B44, which had the highest moisture content (2.16%) and the lowest TOC (1.43%) is the least favourable. The CO_2 adsorption capacity of the shale appears to increase with depth.

Overall, the GSI Borehole 13-01 (Figure 2-34) shows a higher CO_2 adsorption capacity than the samples from Donore (Figure 2-33). Samples B44 and B60 were run for methane adsorption (Figure 2-35). The latter appears to be much better than the former. As previously stated, both preferentially adsorb CO_2 over CH_4.

2.2.6 Figures and tables

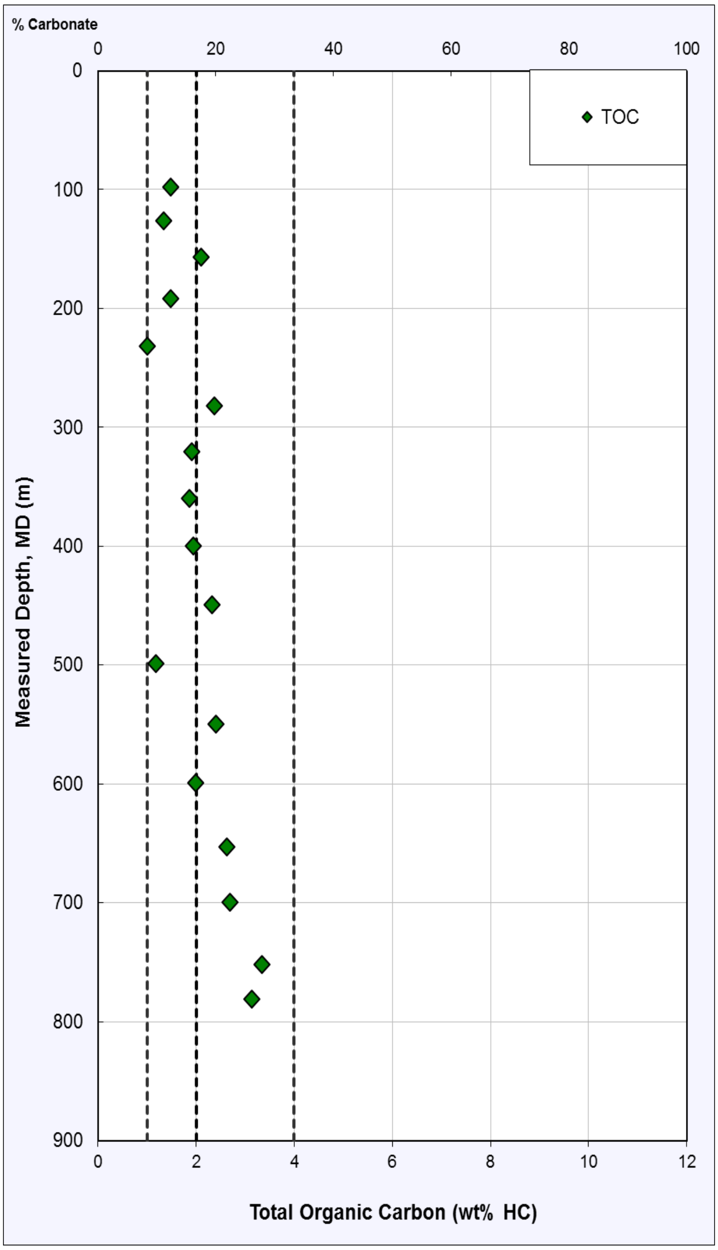

Figure 2-19. TOC values for Borehole N1909.

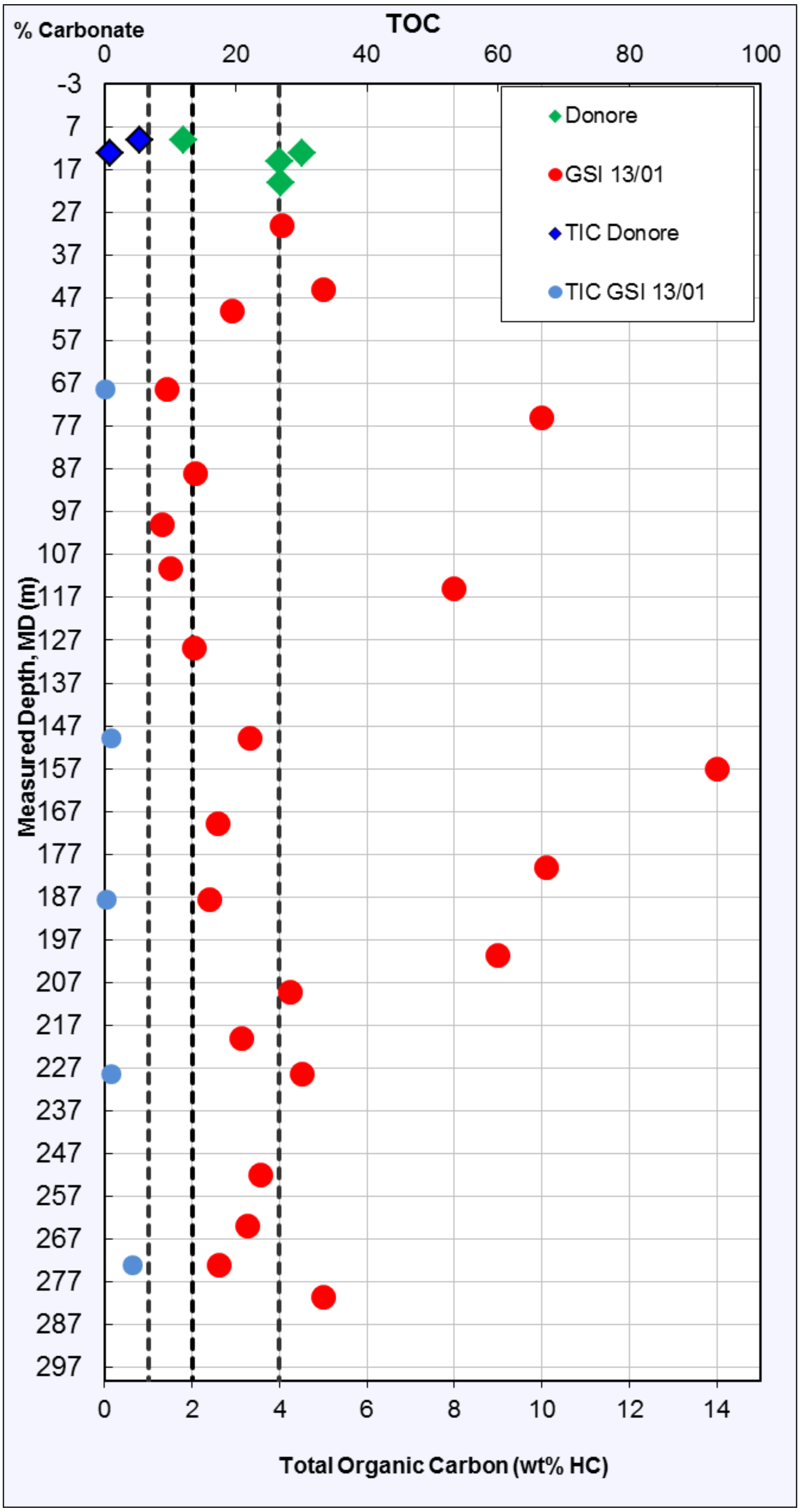

Figure 2-20. Dublin Basin TIC and TOC.

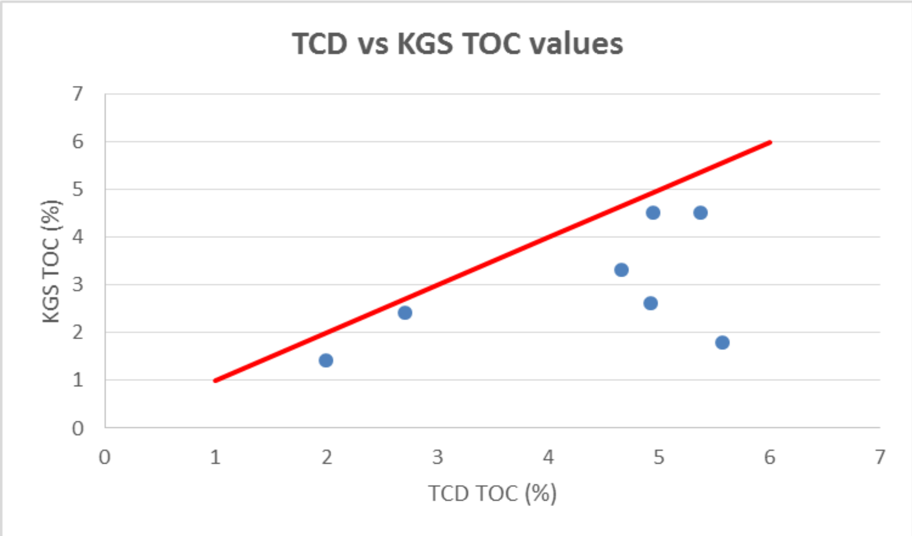

Figure 2-21. TCD vs. Kentucky Geological Survey TOC measurements.

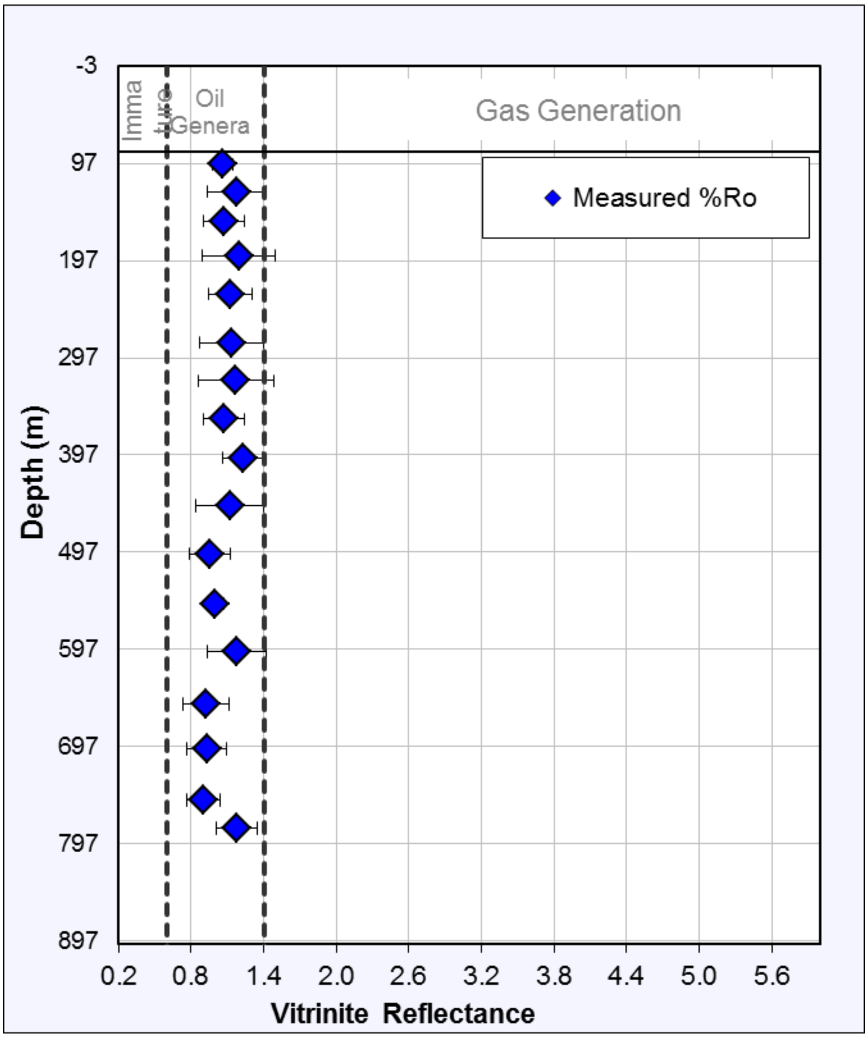

Figure 2-22. Vitrinite Reflectance distribution with depth in borehole N1909.

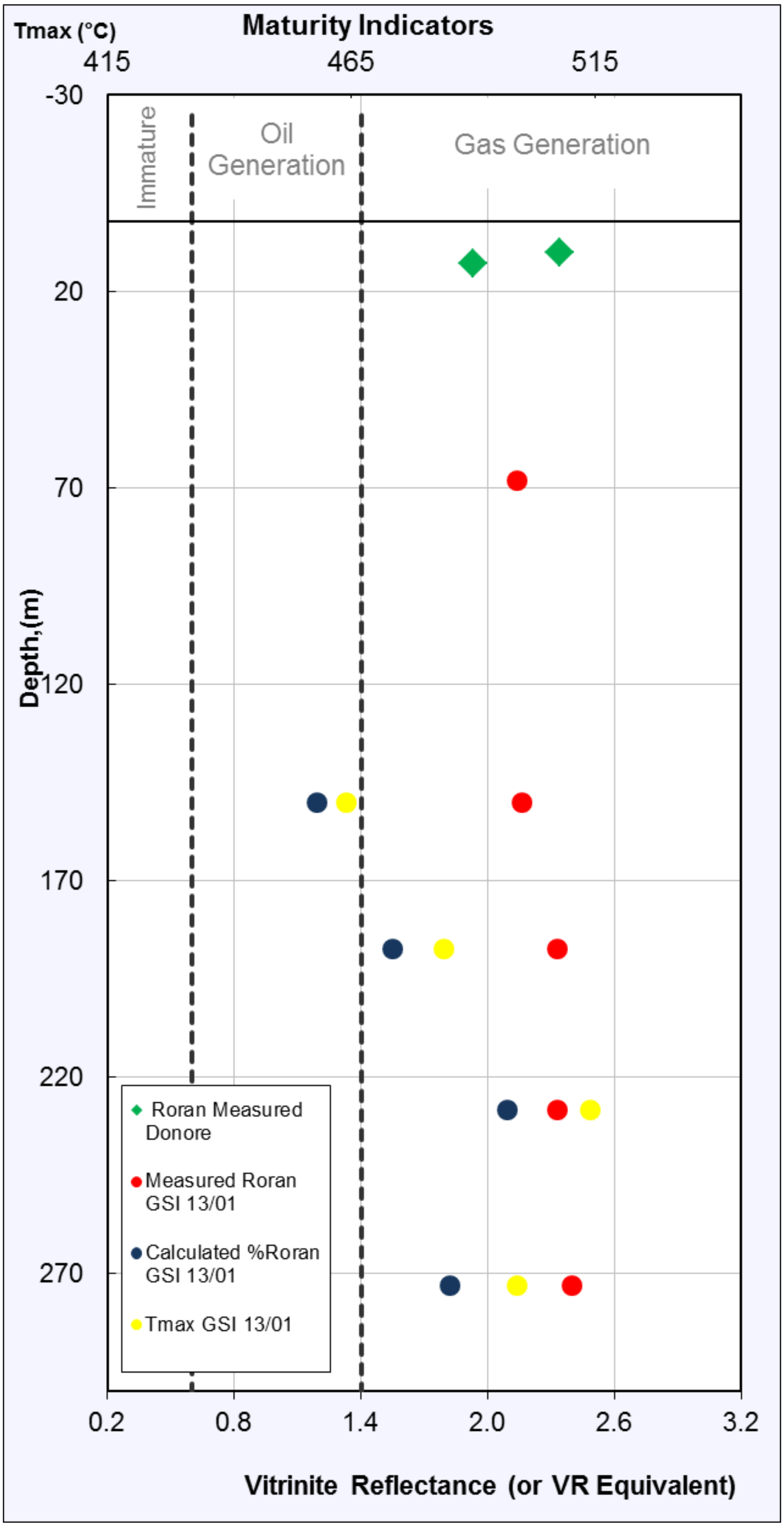

Figure 2-23. Vitrinite Reflectance, Tmax and Calculated Vitrinite Reflectance for the Donore and GSI 13/01 samples.

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Samples	R_{oran} (%)	SD	Measurements
B 25	2.04	0.1	56
B 28	2.05	0.12	50
B 44	1.54	0.08	50
B52	1.59	0.06	52
B56	1.82	0.08	55
B60	1.71	0.08	51
B64	1.89	0.1	55

Table 2-4. KGS Vitrinite Reflectance measurements

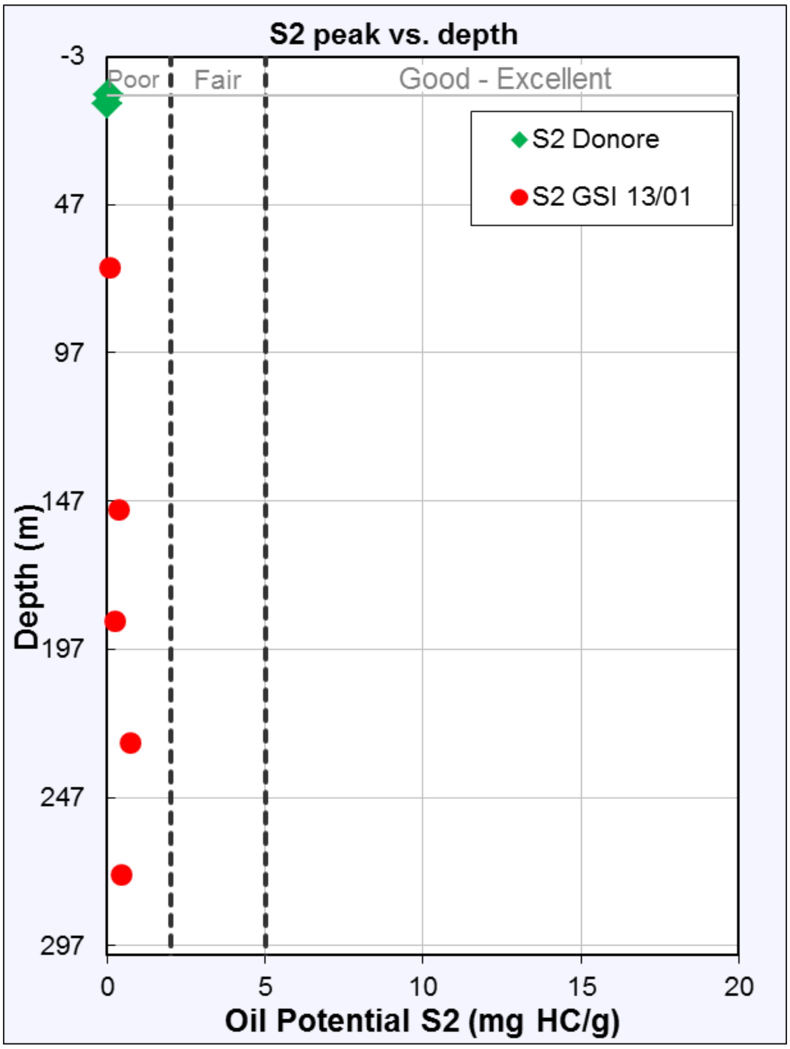


Figure 2-24. Oil Potential (S2 peak) for the Donore and GSI 13/01 samples.

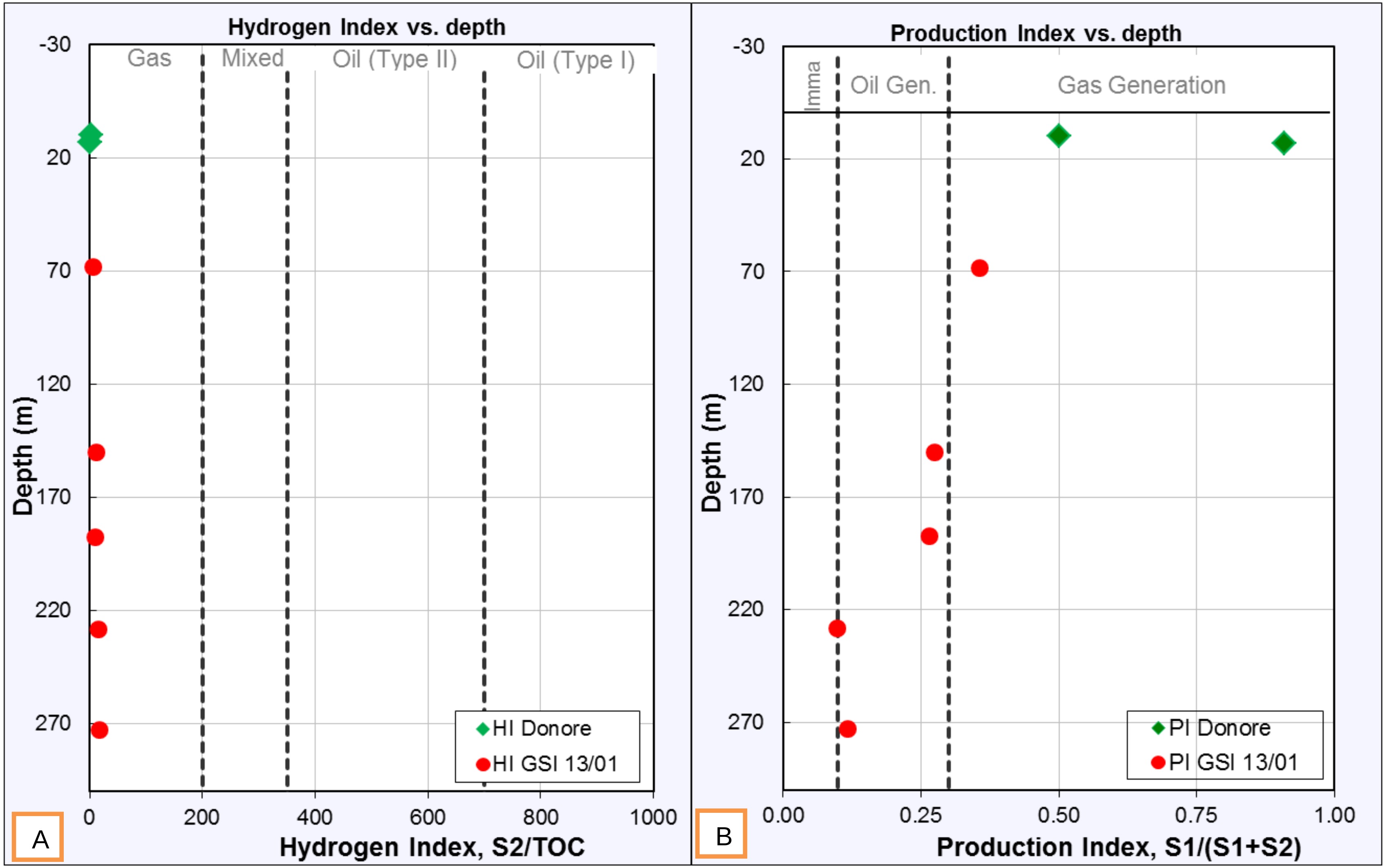


Figure 2-25. Hydrogen Index (a) and Production Index (b) for the Donore and GSI 13/01 samples.

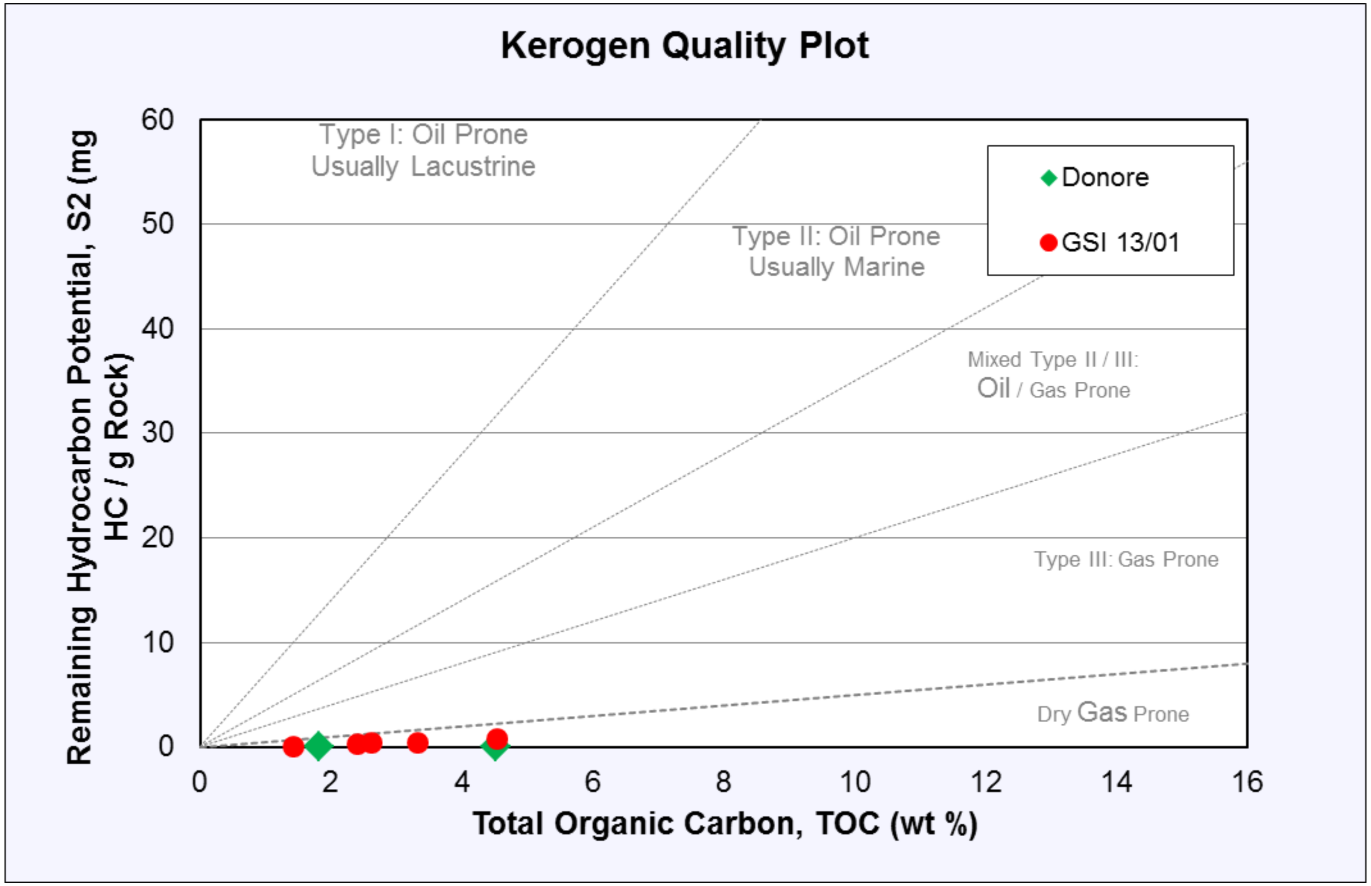


Figure 2-26. Kerogen Quality plot for the GSI 13/01 and Donore samples.

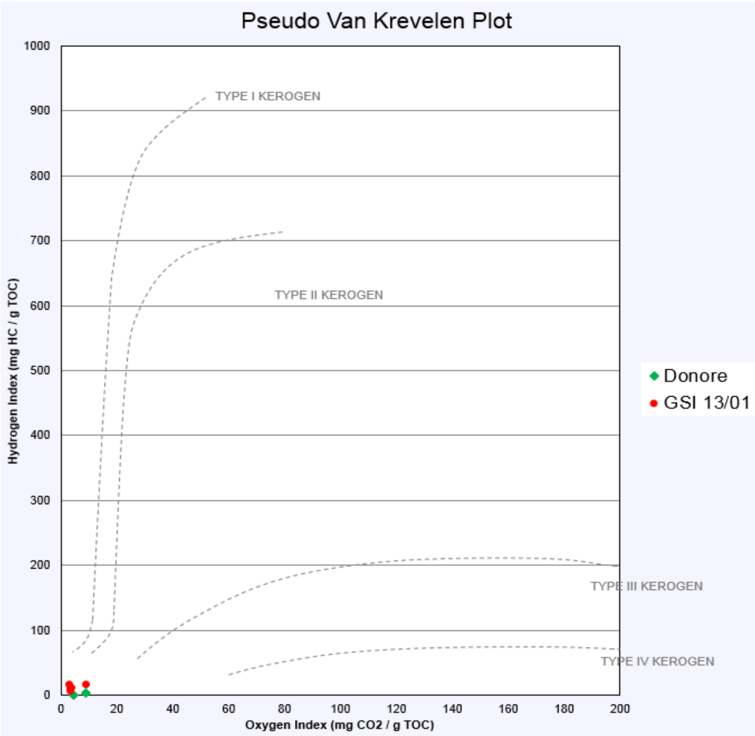


Figure 2-27. Pseudo Van Krevelen Plot for the Dublin Basin samples.

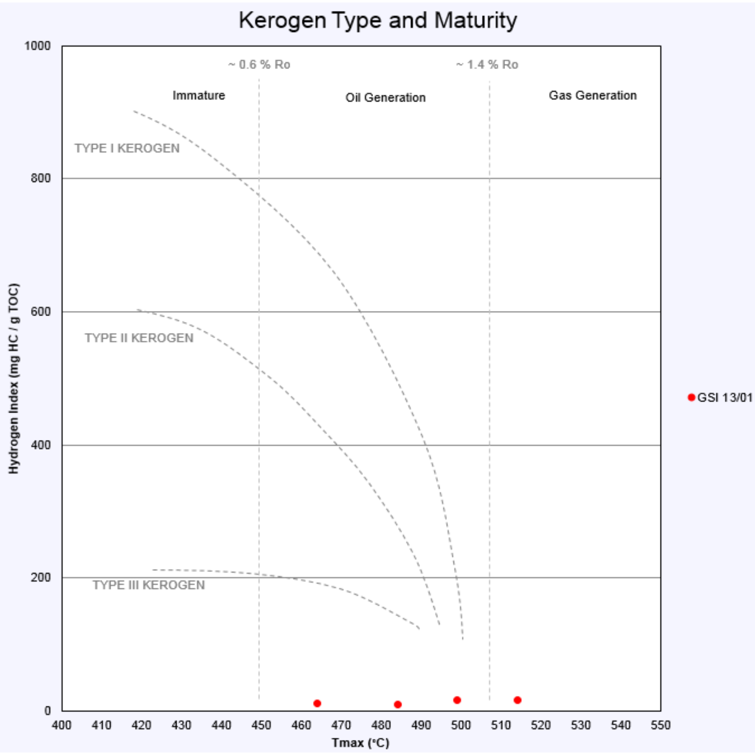


Figure 2-28. Kerogen type and maturity of the GSI 13/01 samples based on Tmax and Hydrogen Index.

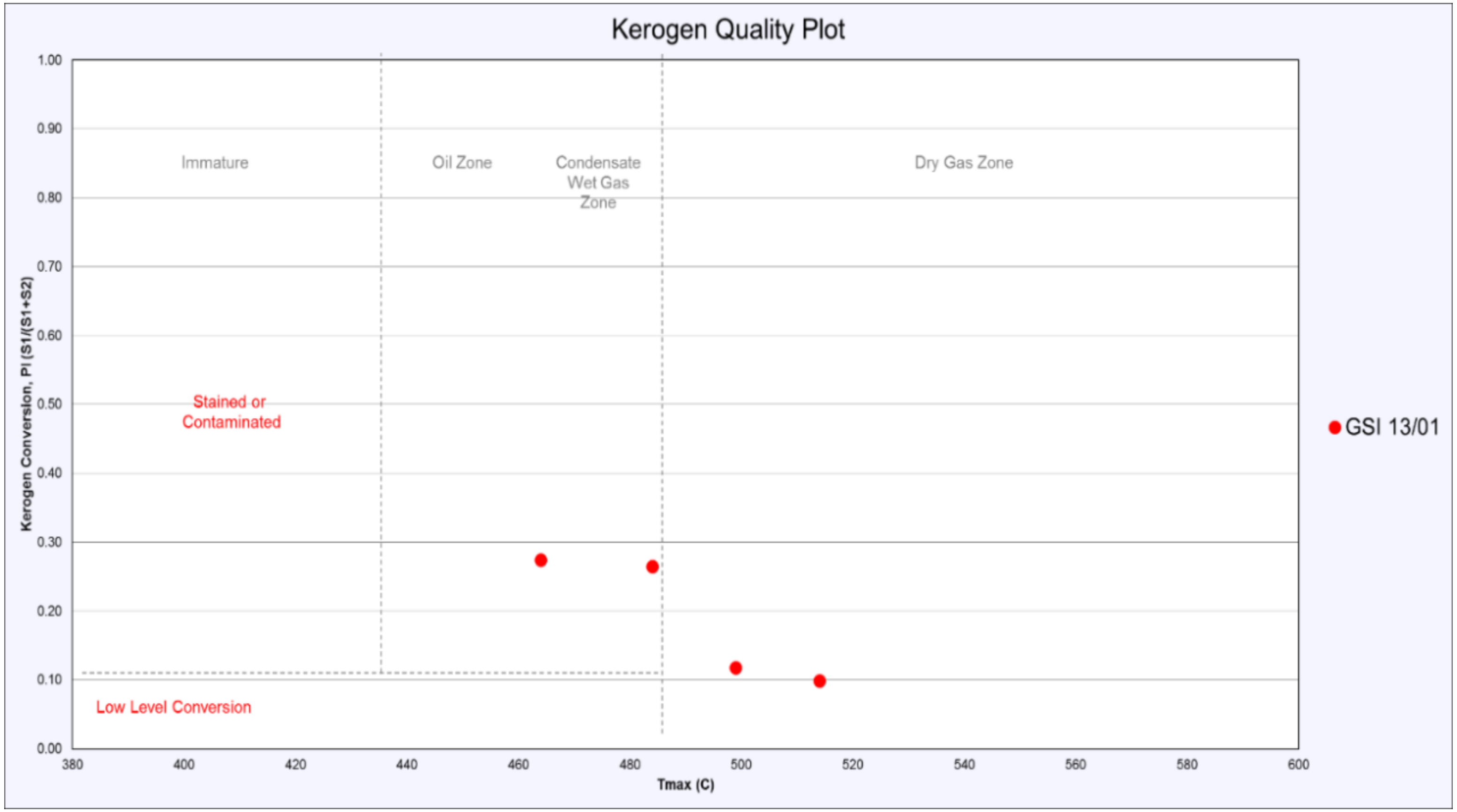


Figure 2-29. Tmax vs Production Index for the GSI 13/01 borehole.

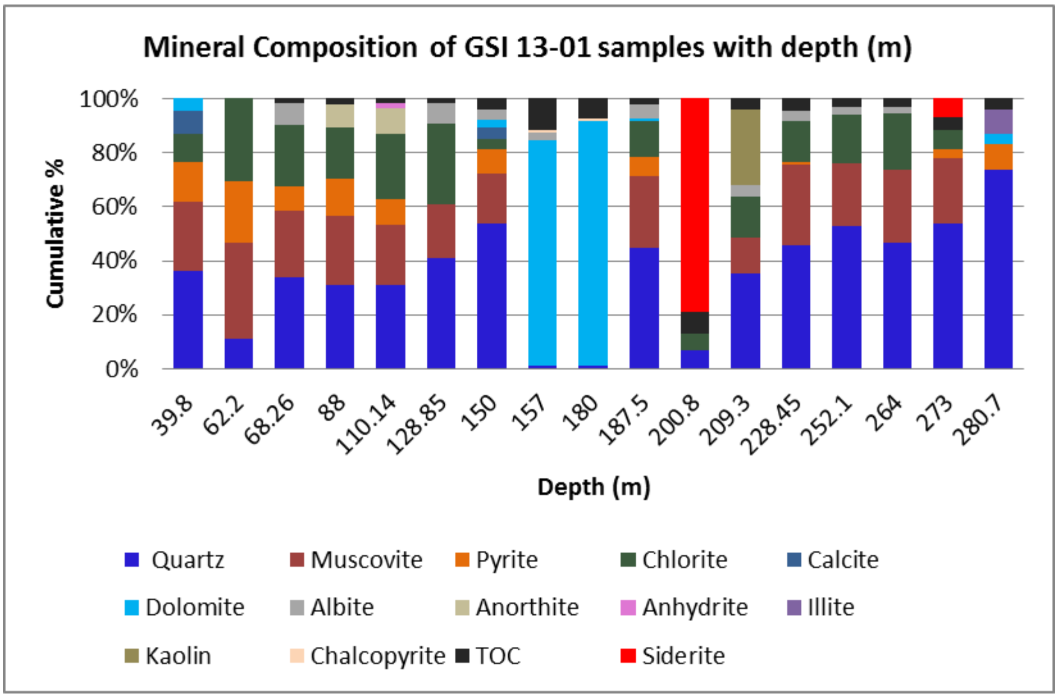


Figure 2-30. Semi-quantitative mineral composition for the GSI 13-01 samples.

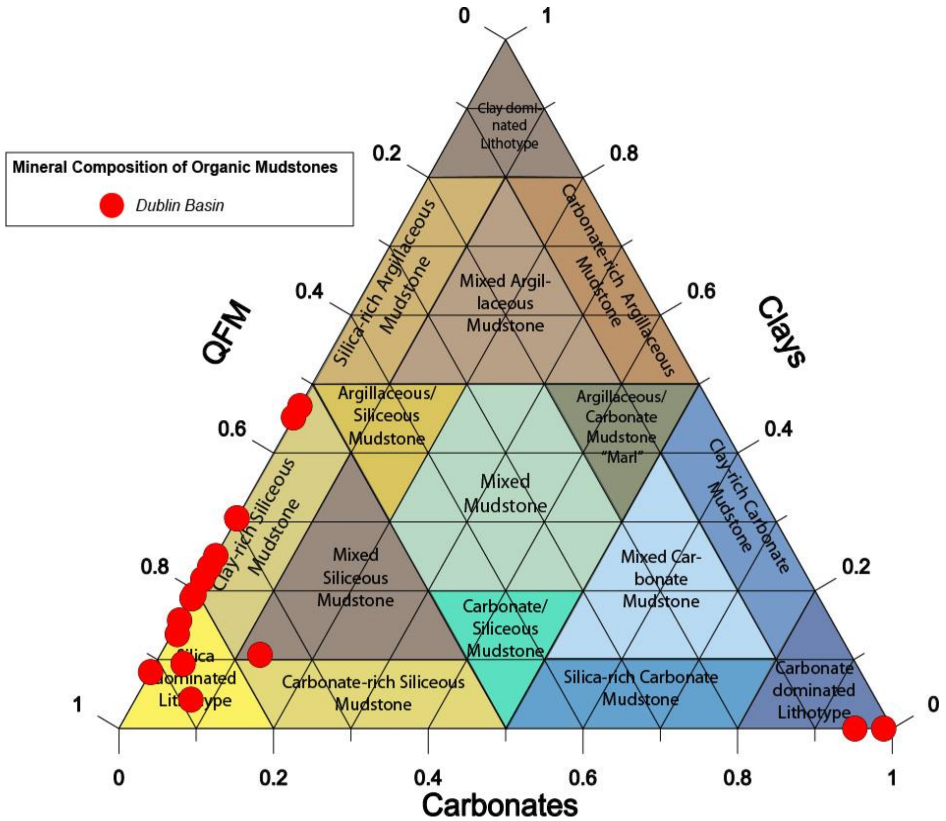


Figure 2-31. Classification of GSI 13-01 organic mudstone samples (after Gamero *et al.*, 2012) with red circles marking analysed samples.

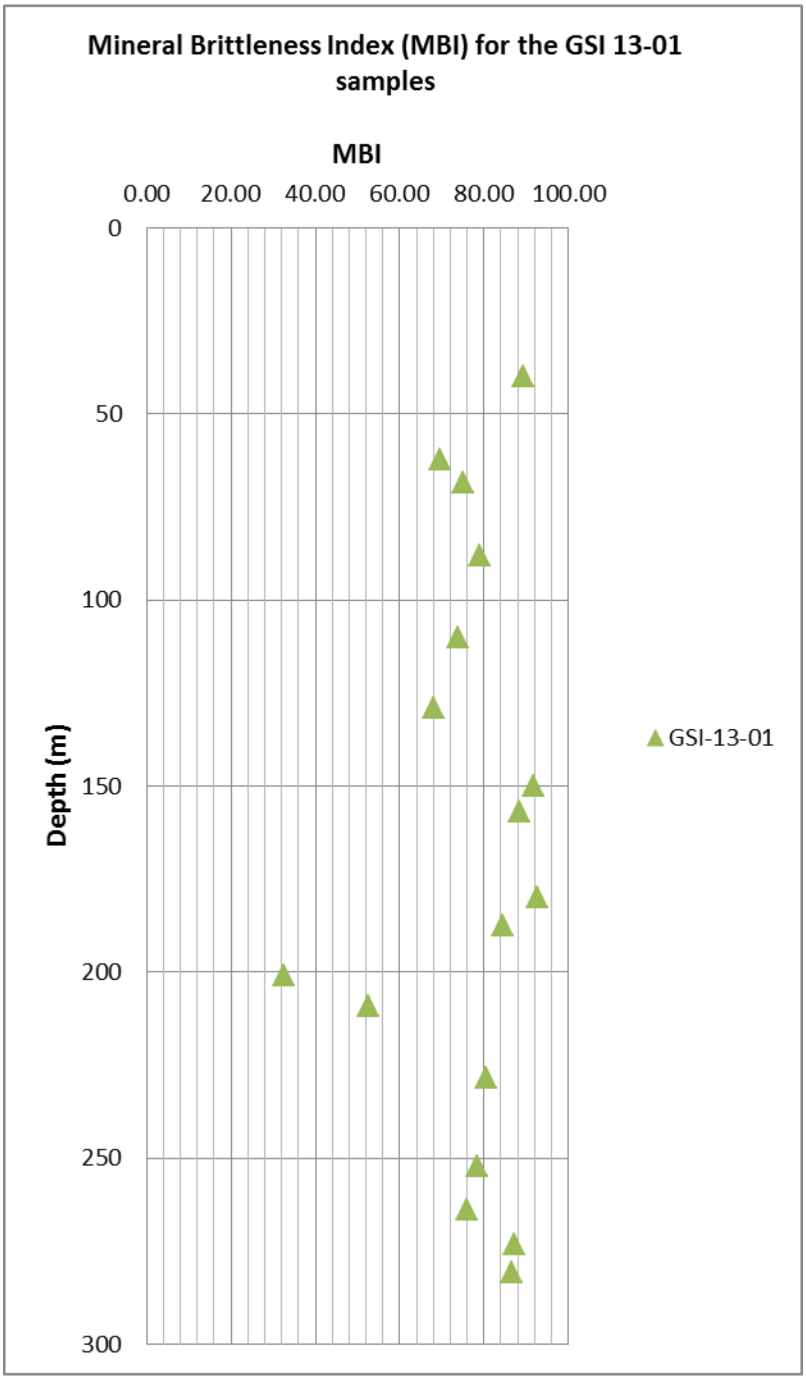


Figure 2-32. Mineral Brittleness Index calculated for the GSI 13-01 samples.

Samples	Moisture Content (%)	TOC *	Pressure (PSIA)	Adsorbed Gas (ft3/ton)*	TIC*	Ash Yeald (wt %)*
B 25	1.71	4.52	727.51	86.66	0.86	87.93
B 28	0.61	1.81	743.51	39.25	5.31	79.95
B 44	2.16	1.43	679.21	33.46	0.06	91.13
B 52	0.96	3.32	715.76	93.60	0.97	90.27
B 56	1.66	2.41	677.04	75.12	0.26	93.10
B 60	0.61	4.53	660.80	101.17	1.06	88.27
B 64	0.83	2.62	768.70	101.98	4.35	81.07

Table 2-5. Moisture content, TOC and Adsorbed CO_2 for all the samples from the Dublin Basin. * KGS analyses.

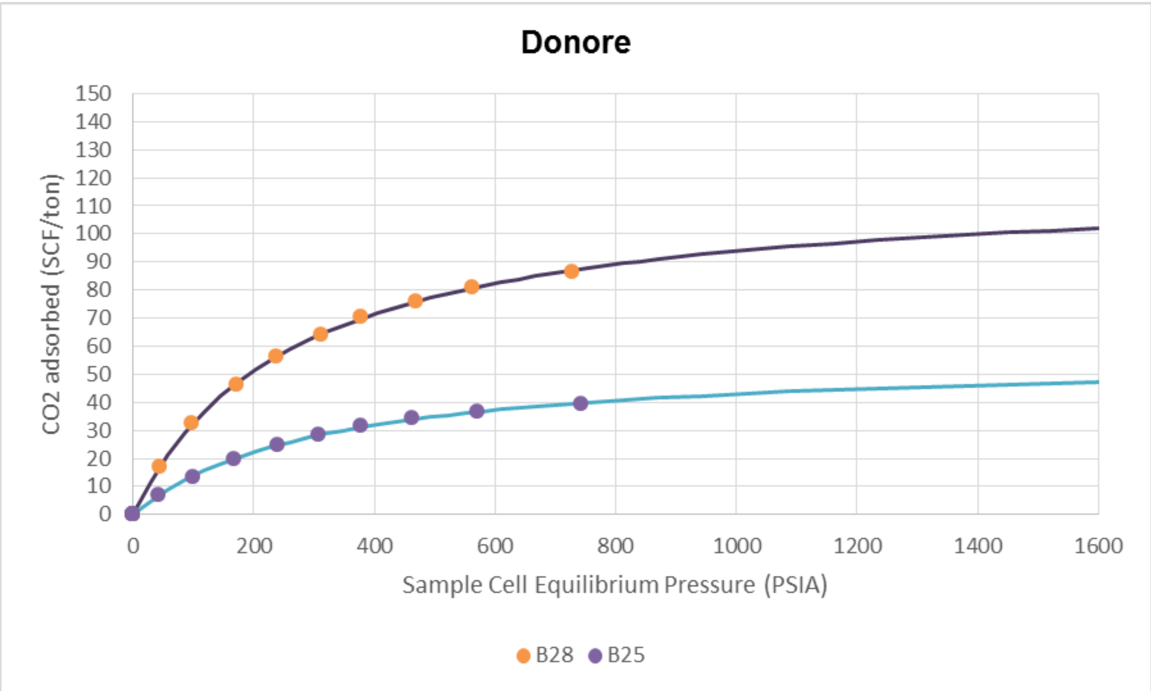


Figure 2-33. CO_2 adsorption curve for the Donore samples.

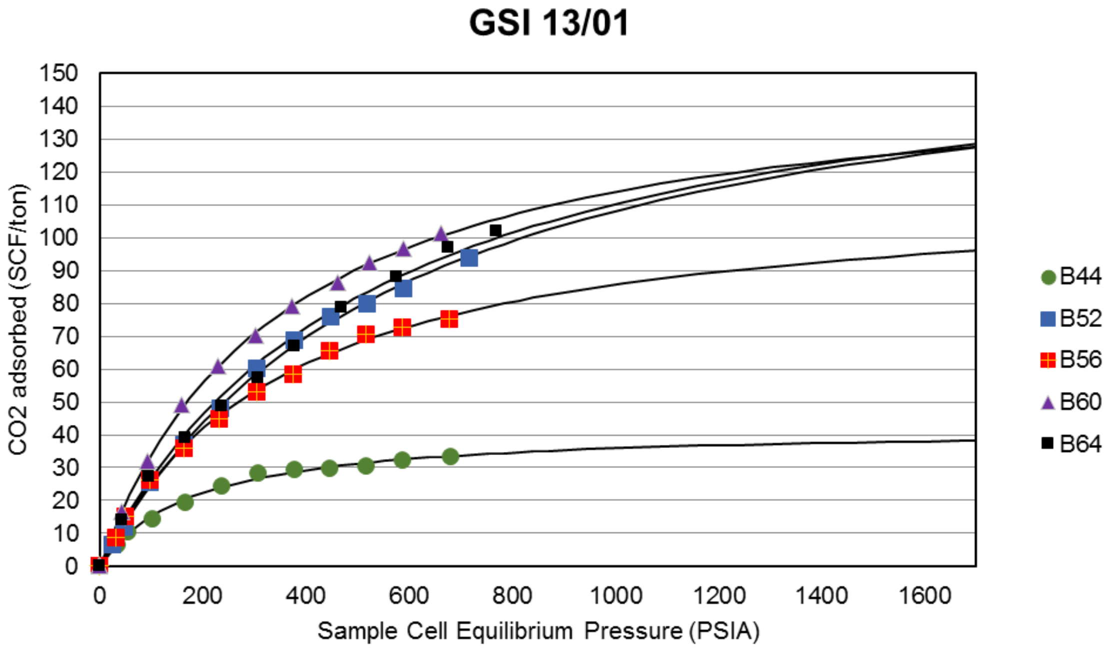


Figure 2-34. CO_2 adsorption curves for the samples from the GSI 13/01 borehole.

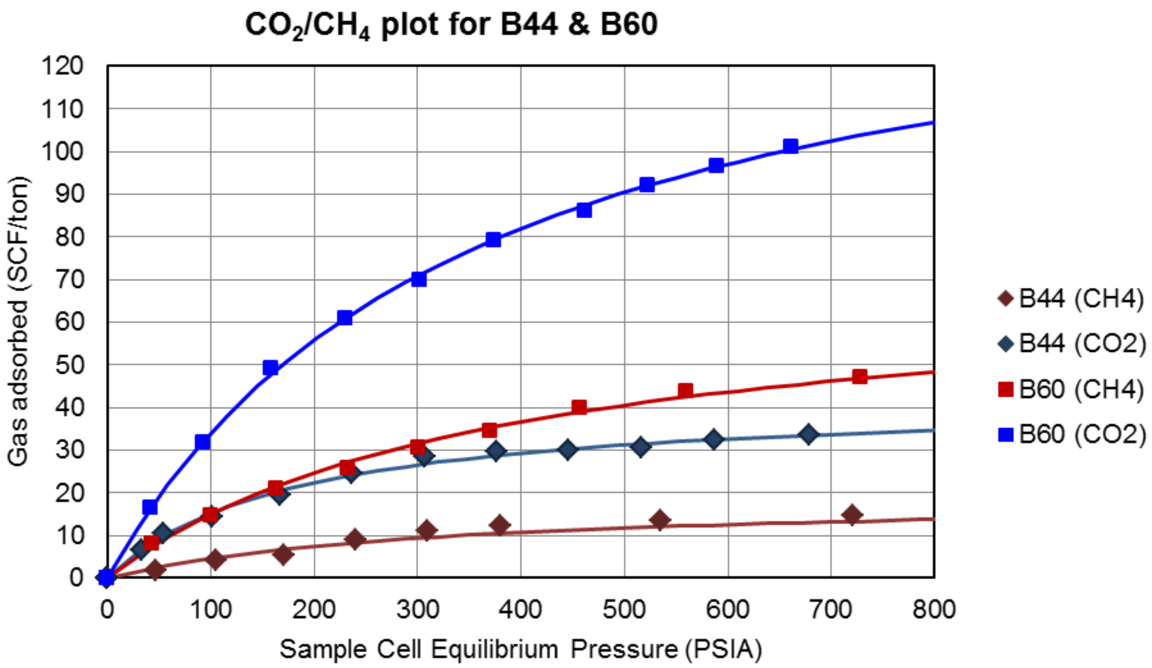


Figure 2-35. CO_2/CH_4 ratio in samples B44 and B60.

2.3 Southwest Portugal

2.3.1 TOC

TOC values (Figure 2-36) from the Quebradas Formation (QB1 and QB3) were both just below 5% (4.95 and 4.99%). Since these values are > 4%, they appear to have excellent potential. In contrast, samples from the Mertola Fm from Borehole AC1 show poor potential with all TOCs <1.5%. The relative stratigraphic positions of the samples are extremely tentative. All TOC values are included in Appendix 2.1

2.3.2 Vitrinite Reflectance

Vitrinite Reflectance measured from these two samples was 3.13 and 3.35% (Table 2-6).These confirm previously published values, and suggest the section is post-mature. The KGS results show bimodal reflectance distributions, which are labeled as high (H) and low (L) (Table 2-7).

2.3.3 Rock-Eval pyrolysis

Rock-Eval pyrolysis results are included in Appendix 2.3.3. The S1 peaks were less than 0.1 mgHC/g rock for both QB 1 and QB 3. The remaining source oil potential (S2 peak) was less than 0.01 mg HC/g rock for QB 1 and 0.14 mg HC/g for QB 3 (Figure 2-37).

Both of the samples showed poor oil potential (Figure 2-38). Since these were outcrop samples, that had probably undergone some weathering, both of the S2 peaks are probably lowered and the S3 peaks increased. This would significantly affect the production Index.

The PI (Figure 2-38) for QB 1 was 0.83 while was 0.36 for QB3. It appears that both QB1 and QB3 were mature.

Since the Hydrogen Index is very low for both samples (QB1 and QB3), these lie near the origin in the pseudo Van Krevelen plot (Figure 2-39), without giving a clear indication of the kerogen quality.

In the kerogen quality plot (Figure 2-40) both samples fall in the dry gas zone.

2.3.4 Figures and tables

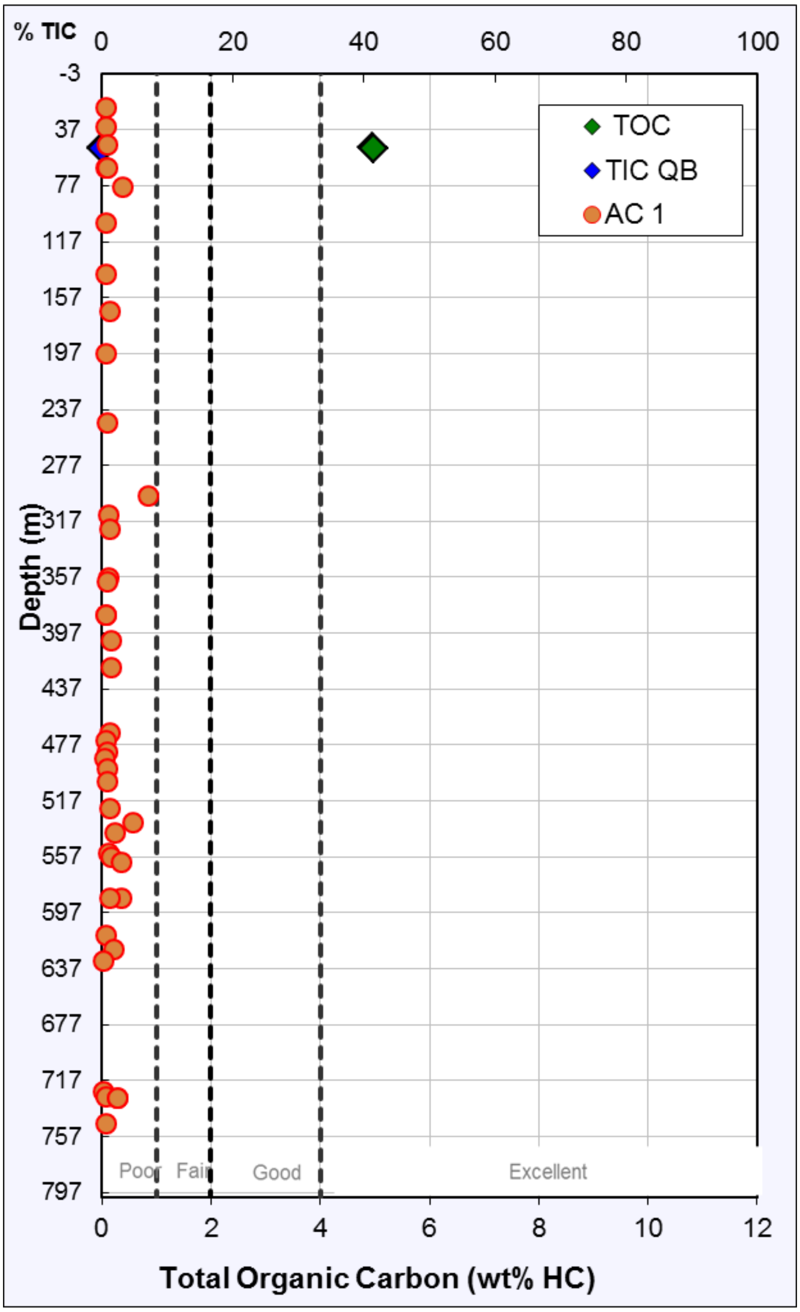


Figure 2-36. TOC values for the Quebradas Fm (in green) and the AC1 (in red) samples.

Samples	R_{oran} (%)	SD	Measurements
QB1	3.13	0.43	50
QB 3	3.35	0.59	50

Table 2-6. Vitrinite Reflectance Values for the Quebradas Fm samples.

Samples	R_{oran} (%)	SD	Measurements
QB 1 H	**2.42**	**0.17**	**50**
QB 1 L	1.88	0.12	38
QB 3 H	**2.34**	**0.16**	**73**
QB 3 L	1.96	0.11	24

Table 2-7. Vitrinite Reflectance measurements from the Quebradas Fm. from KGS.

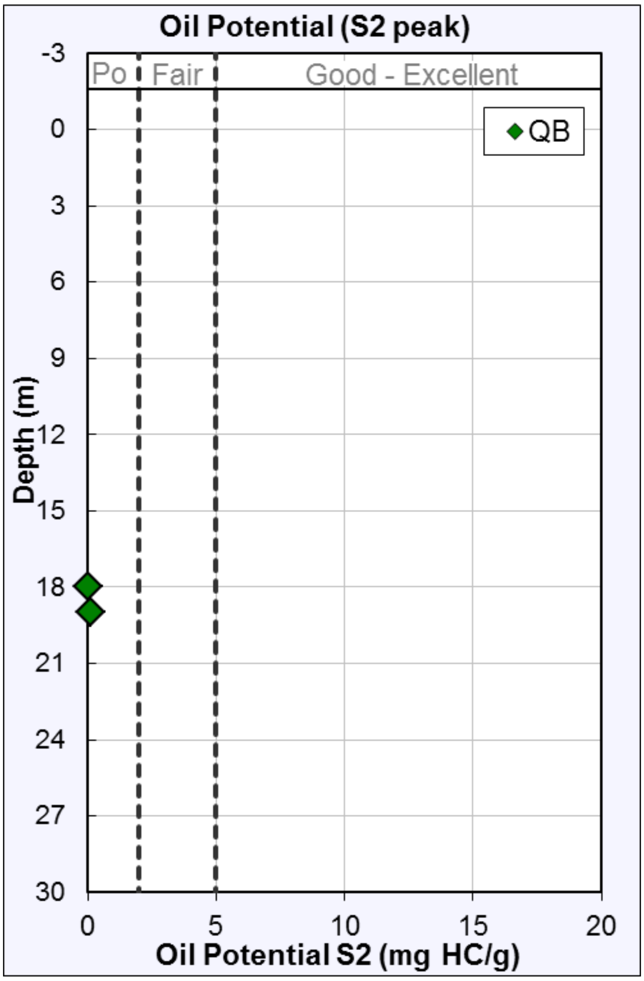


Figure 2-37. Remaining Oil Potential (S2 peak) for the Quebradas Fm

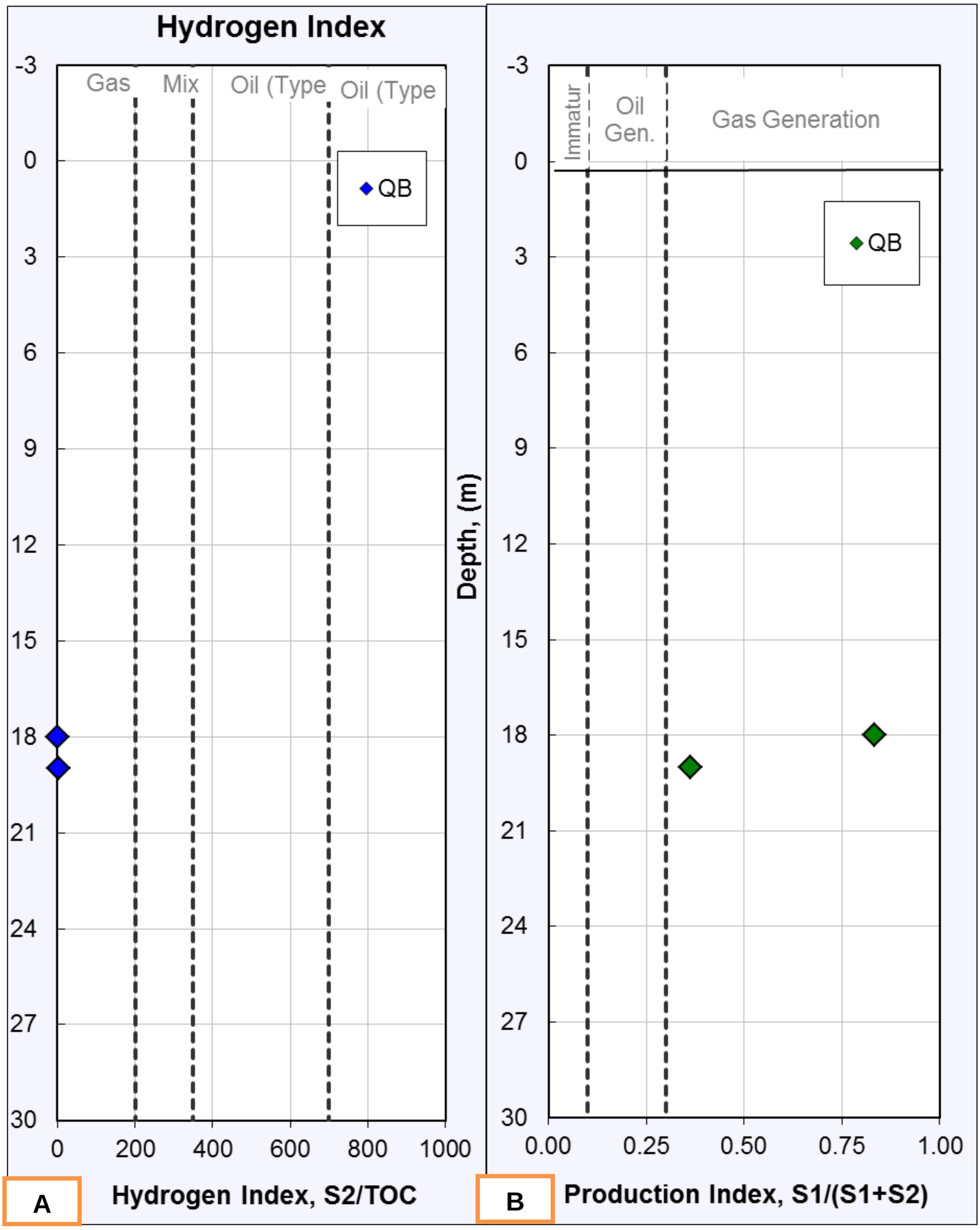


Figure 2-38. Hydrogen Index (a) and Production Index (b) for the Quebradas Fm.

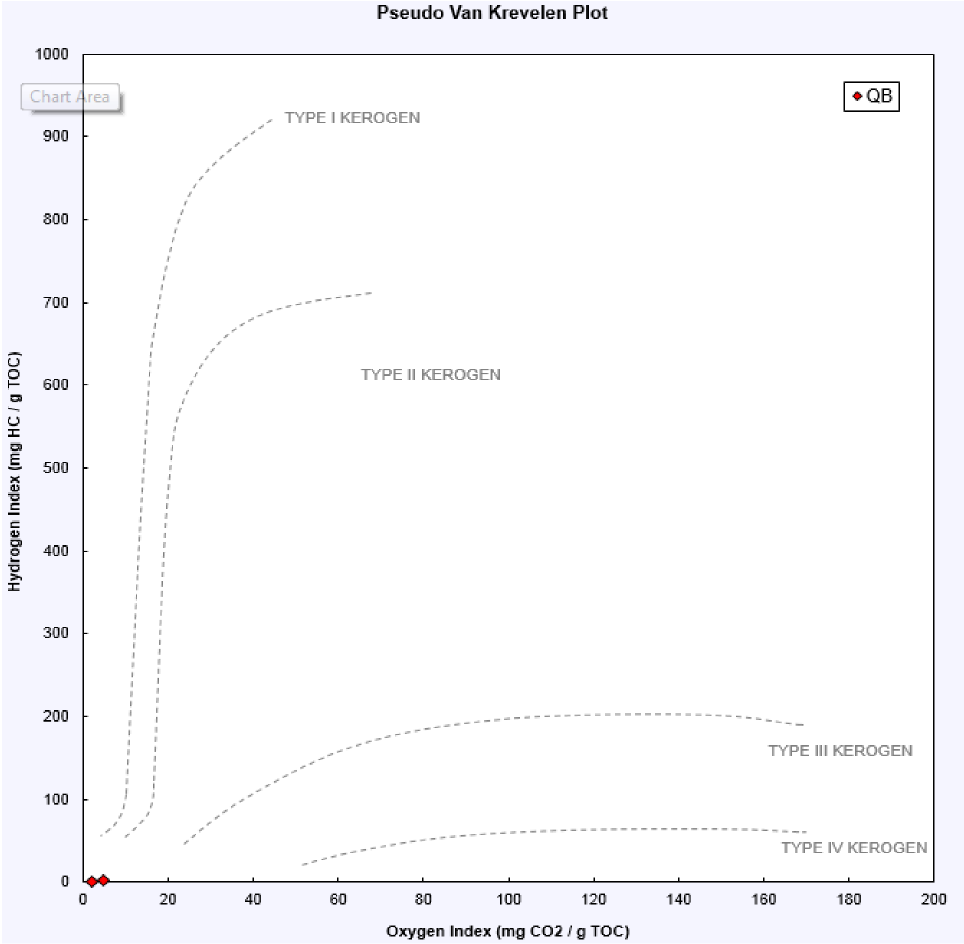


Figure 2-39. Pseudo Van Krevelen Plot for the Quebradas Fm.

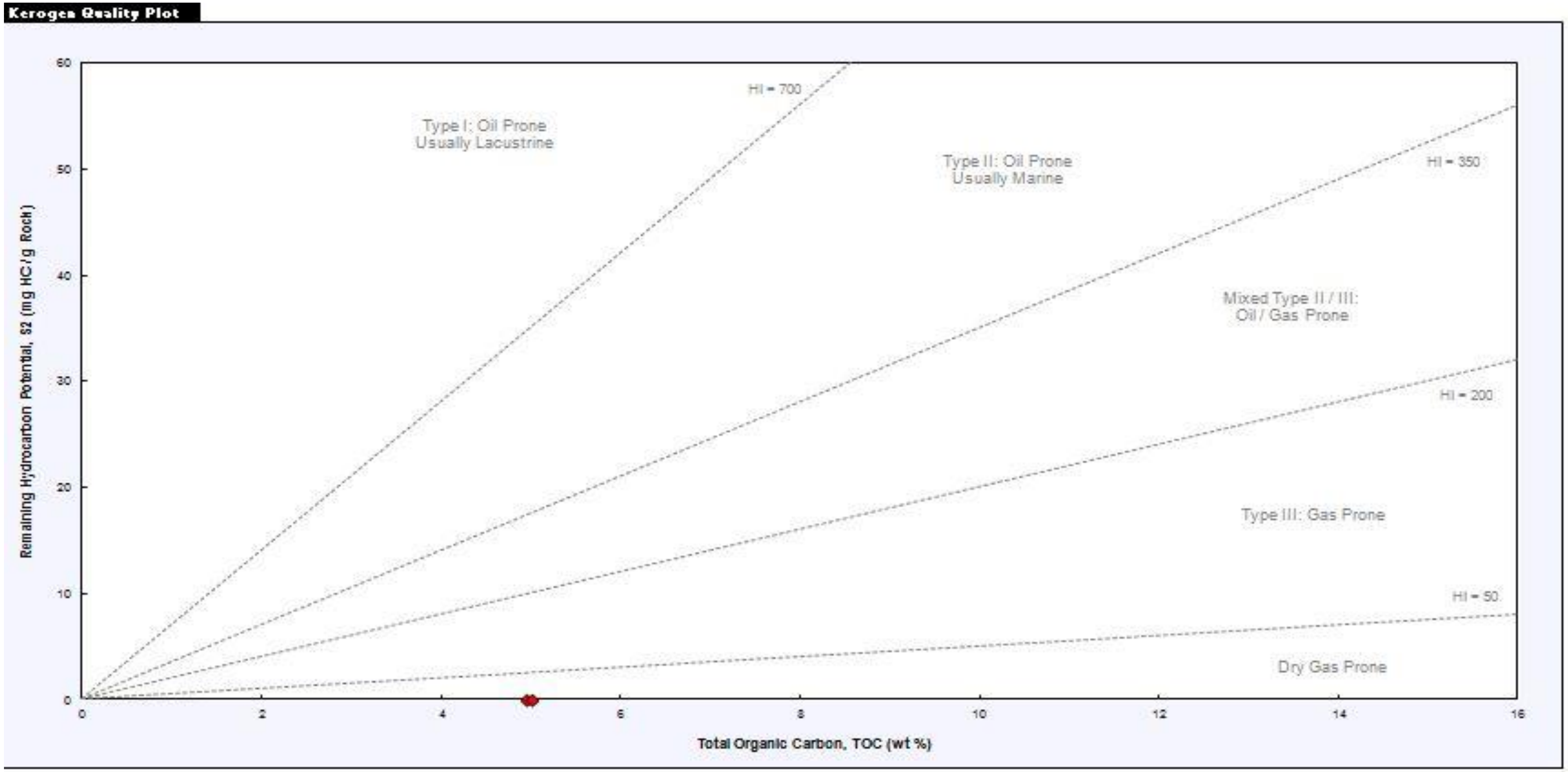


Figure 2-40. Kerogen quality plot for the Quebradas Fm.

2.4 Upper Paleozoic strata of Newfoundland and Labrador

The geology of the Upper Paleozoic strata of Atlantic Canada is broadly described as belonging to the Maritime Basin Tectonostratigraphic Zone (Lavoie et al. 2009). For the province of Newfoundland and Labrador, the Maritime Basin Tectonostratigraphic Zone (Figure 1-1c) is a complex of 5 distinctive sedimentary basins or subbasins covering an area of more than 250,000 km^2 (Giles, 2008; Hu and Dietrich, 2010). All of these basins are linked in one way or another to older tectonic events or plate sutures. The Sydney Basin, south of Newfoundland, is on or about the boundary between the Avalonia and Africa (Meguma Terrane), and at least in part beneath the Laurentian Channel. The Deer Lake Basin is an Appalachian intermontane feature on the boundary of the early Paleozoic Humber and Dunnage Tectonostratigraphic Zones. The St Anthony Basin, on the east Newfoundland continental shelf, lays on Humber and Dunnage zone boundaries, and was once in proximity to the ancient Irish margin.

A recently completed scoping study (Burden et al., in press) gathering most research reports and publications for the Paleozoic sedimentary strata of western and northern Newfoundland and Labrador shows, after 1960, about 2400 papers focused on all aspects of Paleozoic sedimentary strata, and with fewer than 300 references on all upper Paleozoic (Maritime Basin) petroleum system geology (Table 2-8)

Comprehensive studies of this area are limited to a small number of theses (e.g. Gall, 1984; Solomon, 1986; Hendriks, 1991) and a number of government reports (e.g. Hyde, 1979; Kalkreuth and Macauley, 1989; Hamblin et al., 1995; 1997; Hu and Dietrich, 2008; 2010; Lavoie et al., 2009; Kelly and Burden, 2011.). Online Provincial and Federal government databases offer additional details (e.g. well reports) on geophysics and drilling activities.

2.4.1 TOC

Compiled reference data for petroleum studies of the Deer Lake and St Anthony basins can be sparse, and particularly for the St Anthony Basin. Onshore, in the Deer Lake basin, a relatively new well, Werner Hatch #1 has been released into the public domain. Logs for organic richness and hydrocarbon potential of these Serpukhovian rocks (Figure 2-41) show TOC values as high as 8% and with many over 2% (Brooker, 2010). Likewise, the S2 Hydrocarbon potential is also high and indicating that dark, muddy Rocky Brook strata are good to excellent source rocks.

2.4.2 Vitrinite Reflectance

Vitrinite reflectance samples (Figure 2-42) from outcrop studies reported in Hyde et al., (1988), show pronounced differences between immature and marginally mature, Serpukhovian, Deer Lake Group strata and overmature Tournaisian Anguille Group strata.   Offshore, in the St Anthony basin, vitrinite maturation profiles (Figure 2-43), from the NRC Basin Atlas show a sharp jump in maturity between Tertiary and Carboniferous rocks. Serpukhovian, Barachois and Mabou Group strata are at the bottom of the oil window and in the zone of wet and dry gas.

2.4.3 Rock-Eval pyrolysis

Rock-Eval pyrolysis analyses for Werner Hatch #1 in the Deer Lake basin (Figure 2-44) show Serpukhovian, Rocky Brook strata entering the zone of hydrocarbon production but not at the point of peak generation. Farther north, at Conche, and on the edge of the St Anthony Basin, Hamblin et al (1995) report a Tmax >440º C, and a HI < 250 mg HC/g, and indicating Tournaisian strata are thermally mature and near the bottom of the oil window.

2.4.1 Figures and Tables

BASIN	DATABASE (>1960 -Abst.)	PETROLEUM SYSTEM REPORTS					
		TOTAL ROWS (HC-SYSTEM)	SOURCE	RESERVOIR	SEAL	MATURATION	TIMING
Anticosti	1510	338	176	196	83	139	203
St George	500	201	64	64	138	50	60
Deer Lake	252	114	92	67	26	52	45
Sydney	198	103	64	48	45	52	42
St Anthony	135	56	34	28	21	25	30
Total Columns	NA	622	307	285	218	233	284
Total Database	2420	NA	346	318	239	266	323

Table 2-8. Summary of numbers of technical and research reports available for Paleozoic sedimentary basins of Newfoundland and Labrador (numbers are post 1960 and do not contain Abstracts). In examining this chart, the total number of records for – say – the St Anthony Basin is 135, with 56 reporting something about the five Petroleum System elements. From those 56 reports, 34 contain some information about petroleum source rocks.

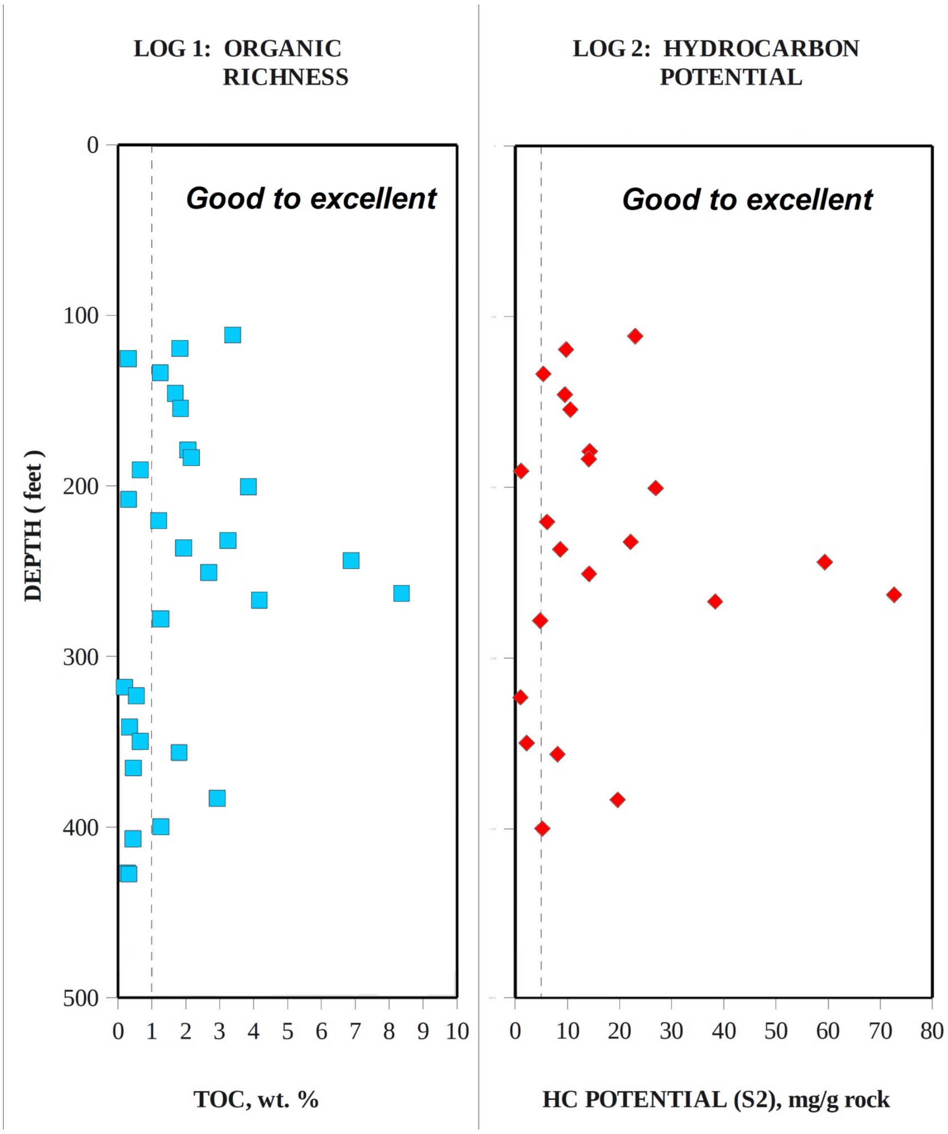


Figure 2-41. Organic richness and hydrocarbon potential logs for Werner Hatch #1, Deer Lake Basin, show significant source rock development in dark, lacustrine mudstones of the Rocky Brook Formation (Data from Brooker, 2010).

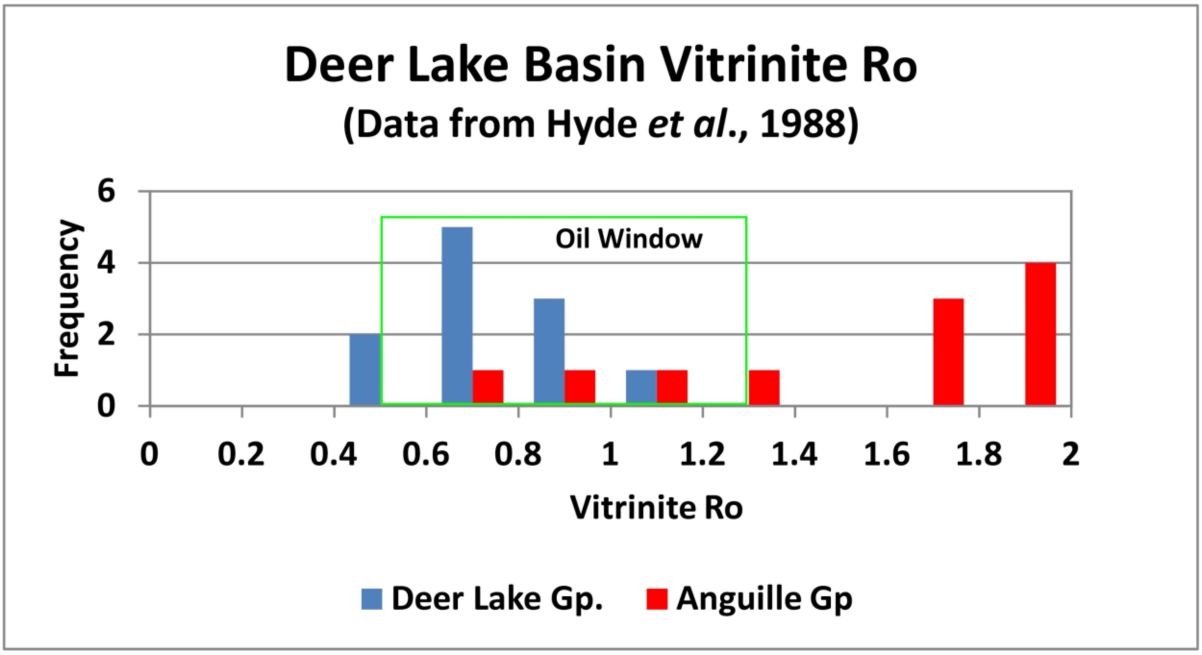
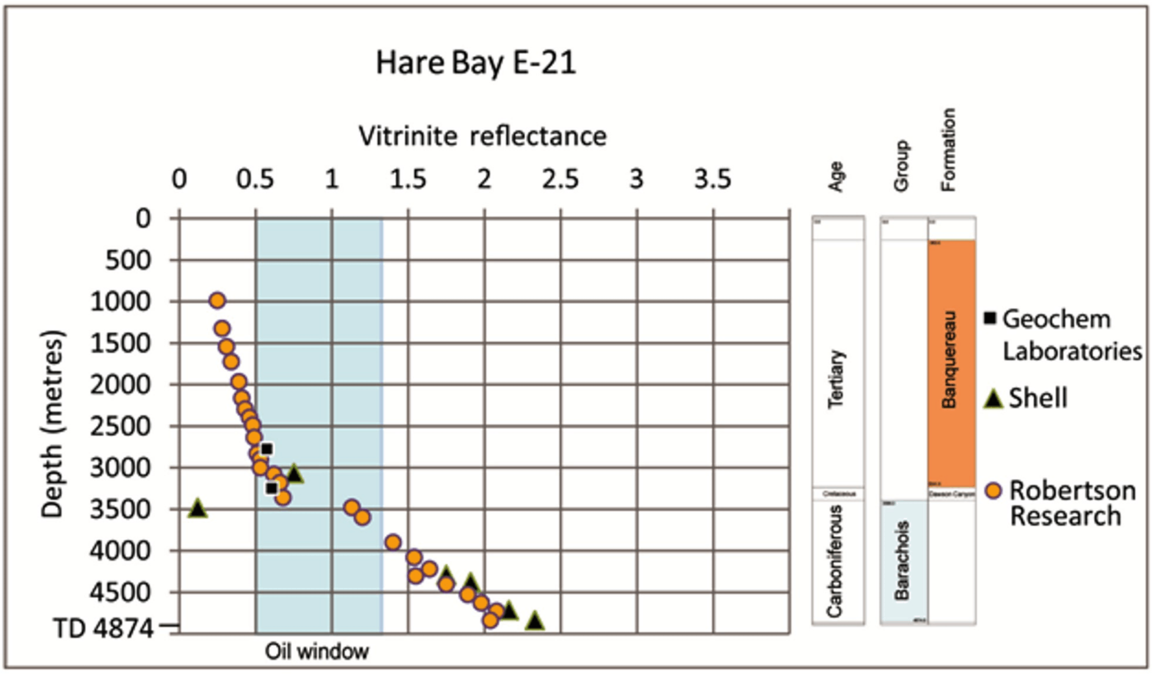


Figure 2-42. Vitrinite data from Hyde et al. (1988) illustrating significant differences in thermal maturity between Serpukhovian, Deer Lake Group and Tournaisian, Anguille Group rocks in the Deer Lake Basin.



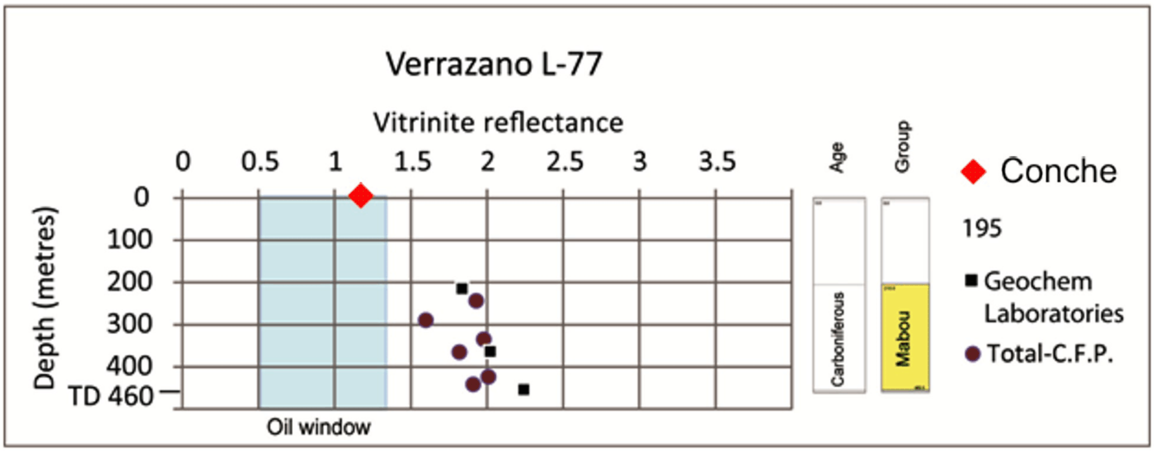


Figure 2-43. St Anthony Basin vitrinite reflectance data for the Hare Bay E-21 and Verrazano L-77 offshore wells (from the NRC, Earth Sciences Sector, Basin Database, CNLOPB Schedule of Wells, 2007, Hu and Dietrich (2010). Conche (red diamond) is an average of Anguille Group outcrop data from Hamblin et al. (1995), and showing that older (Tournaisian) St Anthony Basin strata onshore, on the edge of the basin, remain in the oil window.

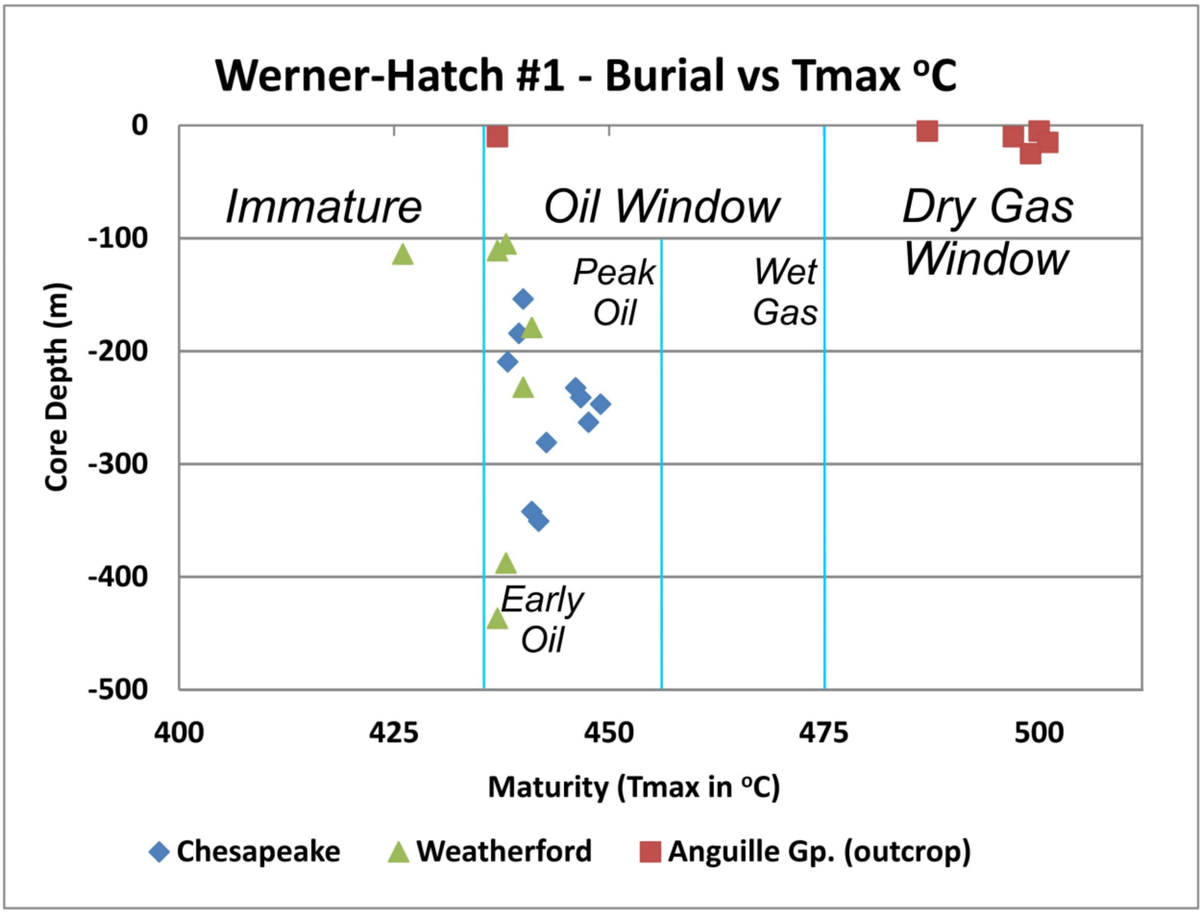


Figure 2-44. Rock-eval Tmax values show the Rocky Brook Fm inside the oil window but not at the critical point for peak oil generation (Tmax > 450° C). The figured Anguille strata (from Mukhopadhyay, 2010) are from outcrops on flower structures. These older Tournaisian rocks show significant differences as strata that are almost entirely outside the oil window. Differences between Weatherford and Chesapeake labs should be viewed as statistical noise from sample variability

3 Discussion

Most of the samples from the Dublin and Clare Basins tend to fall in the clay-rich siliceous mudstone and Silica dominated classes. A few samples are carbonate rich. Figure 3-1 compares the new Irish data with the most important US shale gas plays. Compared to the USA, the Irish samples are richer in quartz, feldspar and micas. All the results from the Dublin and Clare Basins are more similar to the Barnett Shale or Fayette Shale than the Marcellus Shale. Larger amounts of quartz, feldspar and micas tend to increase the brittle behaviour of rocks, rendering them more prone to fracture. In terms of shale gas assessment, minor amounts of clays reduce gas adsorption potential. The amount of organic matter present is also an important factor.

Overall, the Clare Shale and the Quebradas Formation are both post-mature with regard to dry gas generation. In the Dublin Basin, Borehole N1909 spans the boundary between the oil window and the wet gas zone whereas the other sections investigated are placed in the dry gas zone though less reliable rock-eval pyrolysis results suggest that some samples lie in the wet gas zone. In general, equivalent VR values from Rock-Eval analysis were consistent with measured Vitrinite Reflectance.

Only borehole samples gave reliable information, since oxidation of outcrop samples could have affected the results obtained. Furthermore, gas generated could have escaped from these samples over time. Oxidation of samples during weathering can reduce the TOC values (Leythaeuser, 1973; Clayton & Swetland, 1978; Peters, 1986 and Stanley, 1987).

The clay mineral assemblages identified by XRD, could have adsorbed gas during the pyrolysis and reduced the S2 peak (Peters, 1986). This effect (Espitalié et al. 1984, Katz, 1983 and Peters, 1986) causes a reduction of the hydrogen index (HI). Illite and montmorillonite produce the greatest effect with calcite less important (Dembicki et al. 1983; Peters 1986).

Although the carbonate content is not high, the Oxygen Index (OI) can be affected by the presence of Siderite. This mineral decomposes at low temperatures, generating

CO_2 and therefore increasing the S3 peak. Siderite was only observed in two samples (B57 and B64).

In terms of CO_2 adsorption, the rocks investigated in the Clare Basin have more potential than those in the Dublin Basin. It is also important to note that the Clare samples do not show an increase in adsorption capacity as happened with the GSI 13-01 samples. This suggests that lithology is the primary factor that has determined adsorption, rather than compaction. The present investigation has also confirmed the conclusions of Nuttal *et al.* (2005) that CO_2 adsorption increases with TOC, and of Grobe *et al.* (2010), with Moisture Content.

It was also confirmed that, with increasing thermal maturity, organic matter preferentially adsorbs CO_2 compared to CH_4. The mean CO_2: CH_4 ratio determined decreases from 2.2 at low rank to 1.7 at higher rank (Figure 3-2).

The shales studied were also qualitatively assessed in terms of rock mechanics by calculating the Mineral Brittleness Index from the semi quantitative XRD analyses.

The samples show a brittle behaviour with values well above those reported from the major unconventional plays in the USA.

With regard to long-term CO_2 sequestration, the mineral trapping mechanism is the most important process. This is influenced by the primary mineral composition of the reservoir. Siderite and ankerite require Fe^{2+} which can be supplied by chlorite (Xu *et al.*, 2005). Dawsonite can be precipitated after that Na^+ is supplied by the dissolution of oligoclase (Xu *et al.*, 2005).

3.1 Figures and tables

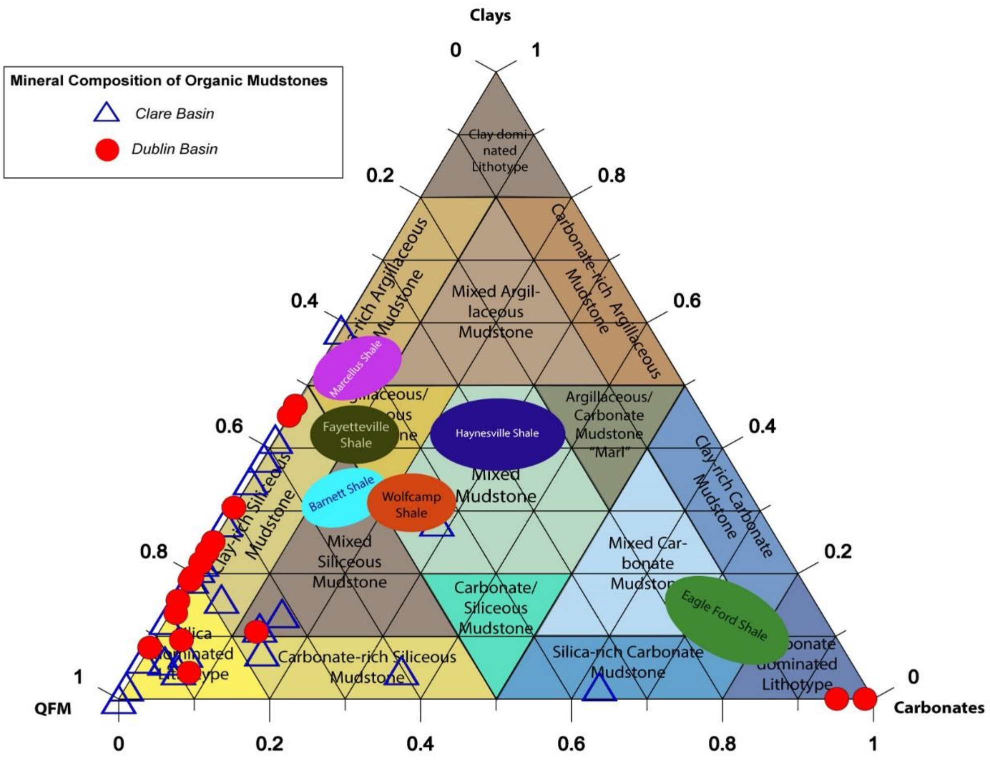


Figure 3-1. Organic-rich classification of the samples compared to the main US shale gas plays.

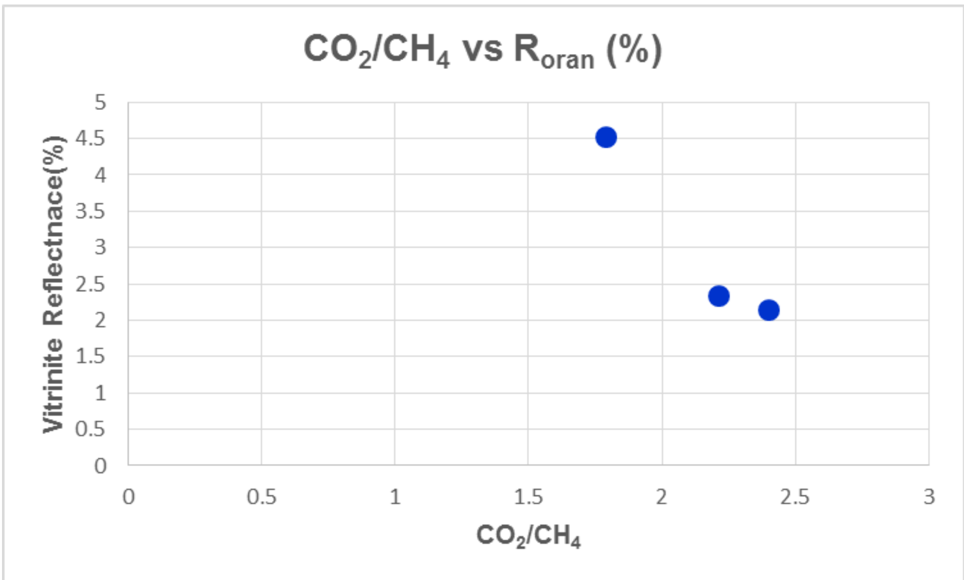


Figure 3-2. CO_2/CH_4 variation with Vitrinite Reflectance for all the samples.

Acknowledgements

This project was part-funded by the Irish Shelf Petroleum Studies Group (ISPSG) of the Irish Petroleum Infrastructure Programme Group 4. The ISPSG comprises: Cairn Energy Plc, Chrysaor E&P Ireland Ltd, Chevron North Sea Limited, ENI Ireland BV, Europa Oil & Gas (Holdings) plc, ExxonMobil E&P Ireland (Offshore) Ltd., Husky Energy, Kosmos Energy LLC, Maersk Oil North Sea UK Ltd, Petroleum Affairs Division of the Department of Communications, Energy and Natural Resources, Providence Resources plc, Repsol Exploración SA, San Leon Energy Plc, Serica Energy Plc, Shell E&P Ireland Ltd, Sosina Exploration Ltd, Statoil (UK) Ltd, Tullow Oil Plc and Woodside Energy (Ireland) Pty Ltd.

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