POSSIBLE USE OF WATER ISOTHERMS TO MEASURE POROSITY AND RELATED PROPERTIES OF SHALES

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ABSTRACT

A variable but important component of the gas resource of shale is held in meso- and microporosity. As depth increases, this gas resource component becomes more important and can exceed the resource component held by adsorption on the total organic carbon. This paper introduces a new process to estimate shale porosity on cuttings at surface in a way that is minimally stressful on the shale matrix. The procedure relies on the principles outlined in the Kelvin-Laplace equation, which predicts the way porous media release water as the relative humidity of the surrounding air decreases. Water is lost from successively smaller pores as relative humidity decreases. The weight loss versus relative humidity plot (a water isotherm) therefore can provide information on pore-size distribution and total porosity.

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INTRODUCTION

Shale gas is the new frontier for exploration of unconventional gas. As an example of the interest, land sales largely for the opportunity to explore for shale gas in northeastern British Columbia raised about $1.9 billion in 2008. Interest is high because shale with some total organic carbon (TOC) content is moderately common in the geological rock column. These shales contain small amounts of gas, in part held by adsorption on organic matter and in part held in shale microporosity. Shale is therefore both a source and reservoir rock for methane.

The ability of shale to retain gas (because of its very low permeability) makes it an enormous potential resource; however, this is also a liability in terms of turning the resource into a reserve. The amount of TOC required to convert a "normal" shale into one capable of producing shale gas is small. Productive shales contain TOC contents that range from 1% to 10%. This is the weight percent TOC measured today and is considerably less than the amount present during early maturation of the shale. As organic carbon matures and expels gases, such as methane and carbon dioxide, its volume decreases. A weight percent TOC of 6% at a rank of 0.35% (vitrinite reflectance) is reduced to about 2% TOC when rank increases to 2% based on the difference in moisture and volatile matter contents at the two ranks. As well as expelling methane, the TOC expels heavier gases such as ethane and propane, which are cracked to methane

at ranks greater than about 1.3%. The decrease in TOC volume as rank increases may translate into post-depositional porosity of up to 9% to add to original depositional porosity (Figure 1). All porosity is available to be charged by methane generated during TOC maturation that is in excess of that retained by adsorption on the TOC. This includes methane generated by cracking heavier gases in the oil rank window.
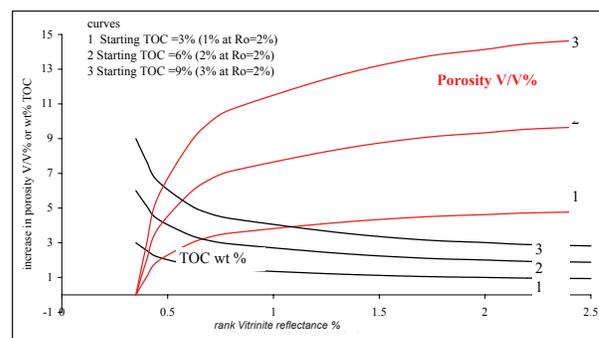
Figure 1. Volume decrease of TOC as rank increases and resulting increase in secondary porosity V/V% - secondary porosity.

In simple terms, for shale to be gas charged, there has to be a balance between the thermal maturity and the ratio of porosity to TOC (Figure 2). There are a lot of variables, so Figure 2 is only a schematic representation. In terms of total resource, the ratio of free gas in porosity to adsorbed
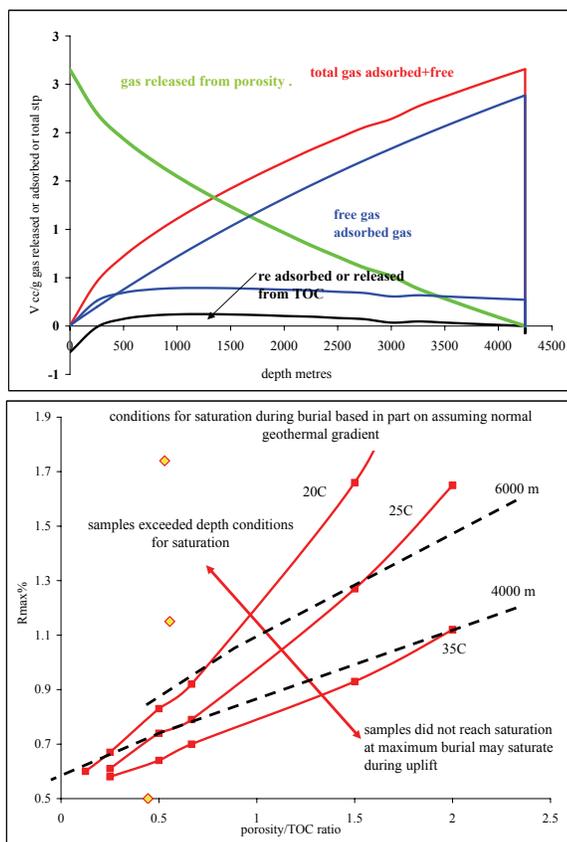
Figure 2. Schematic relationship of ratio porosity/TOC to rank for gas-filled porosity.

gas on TOC will increase with depth. This is because the rate of increase in adsorption capacity of TOC with depth is less than the rate of increase in capacity of porosity to store gas with depth. Porosity, size distribution of porosity, and degree of water saturation are very important properties in estimating the resource potential of shale, assuming there is sufficient TOC to charge the porosity.

Shale porosity can become gas saturated in two ways. First, the excess thermogenic gas generated by the TOC during maturation pushes water out of porosity through interconnected small pores by overcoming hydrostatic pressure plus capillary pressure. Excess gas can also remove water vapour to a degree that depends on the partial pressure of water in the gas phase. This requires a substantial excess of methane greater than that required to fill the porosity at existing pressure and temperature conditions.

Water occupies porosity as free water and as water adsorbed on TOC and kaolinite. Shales contain a high proportion of clay (usually kaolinite), so there is the possibility that some water is held in porosity by adsorption on these clay particles. Under burial conditions, it is possible that excess methane can reduce relative humidity (RH) in porosity enough that water adsorbed on kaolinite is removed in the vapour phase and the adsorption sites (volume) are

then filled by methane. It is unlikely that water adsorbed on kaolinite can be removed during uplift or by biogenic methane that has to access microporosity from external fractures.

Measuring shale porosity is difficult. As the definition of shale implies, it has meso- or microporosity, and differentiating between connected porosity and total porosity is a challenge. Total porosity, which may be greater than connected porosity, is difficult to measure and probably not important for estimating free gas volumes unless diffusion of free gas through pore walls is considered. Another major problem when measuring porosity is that most techniques are applied to samples at surface, not at in-situ temperature and pressure.

Techniques for measuring connected porosity involve infusing mercury or inert gases into dry samples. Mercury infusion under high pressure may not measure the microporosity of interest, which is the connected porosity available for methane molecules. Methane and helium molecules are approximately spherical, with a significant difference in molecular size (CH_4 = 4.3 A° [angstroms]; He = 0.98 A°). Therefore, using an inert gas such as helium may overestimate methane porosity. Water molecules (2.8 A°) are closer in size to methane molecules and might be a better candidate for measuring porosity available to methane. Geophysical logs provide various measurements of porosity and water saturation, but there is always a desire to confirm results with measurements on samples at surface.

This paper describes an alternative method of estimating shale porosity. It involves drying samples by progressively reducing RH to determine volume loss of water and associated weight decrease of samples.

Porosity is calculated using

$$\emptyset = [(SG_{dry} - SG_{wet})/(SG_{dry} - 1)] \times 100$$

where

$\emptyset$ = porosity (volume percent)

SG_{dry} = specific gravity of sample with pore water removed (g/cm^3)

SG_{wet} = specific gravity of the sample with pore water included (g/cm^3)

SG_{wet} is determined using Archimedes' Principle. Samples are weighed and have only surface water removed. The weight loss of the sample after drying to zero RH and dry weight at zero RH provide enough data to calculate SG_{dry}.

The initial assumption is that sample porosity is totally filled with water and that decrease in weight as RH decreases is directly related to removal of water from porosity. Samples are maintained at atmospheric temperature and pressure as RH is reduced. The resulting plot of weight loss versus decreasing RH is a water isotherm. Water isotherms were used in the past to investigate porosity and water retention in coals (See Ryan 2006 for references on the subject).

If porosity is not totally filled with water, then it is possible, using He pycnometry, to measure SG_{dry} to estimate porosity and degree of gas saturation as described later.

BACKGROUND

Gas isotherms are used extensively to study adsorption, pore-size distribution, and diffusion characteristics of solids. Generally, inert gases such as helium, nitrogen, and argon are used, with non-inert gases such as carbon dioxide used less frequently. There is also literature that describes the use of water isotherms to investigate properties of coal, building materials, soil, and organic compounds. Many of these studies are aimed at understanding how these materials hold water, pore-size distribution, and porosity determination. For example, Allardice and Evans (1978) described water isotherms on coal; Likos and Ning (2002) used water isotherms to investigate water adsorption on clays; Carmiet and Roels (2002) used water isotherms to study moisture uptake and porosity of building materials. Studies in these areas have applicability to measurement of porosity in shale cuttings and help provide an understanding of pore-size distribution.

Why construct a water isotherm to measure porosity? It is possible to dry a sample either by heating or putting it in a desiccator at zero RH and weighing the sample before and after drying. Unfortunately this does not address the initial problem—differentiating between water on the surface of shale cuttings and water held in porosity (pore water). Also, drying by increasing temperature may damage samples, rendering the results invalid.

This study uses shale cuttings wet-screened to a particular mesh size; consequently, the first problem is to differentiate between surface water and pore water. Water isotherms make this possible because surface moisture evaporates from samples at higher RH values than does pore water. For most porous rocks, there will not be a distinct break point in the weight loss versus RH curve, as large pores or grain fractures will hold water with about the same tenacity as grain surfaces. Because of the meso- to microporosity in shale, the weight loss versus RH curve shows a distinct break point that separates surface water from pore water (Figure 3).

Many authors divide water isotherms into two main fields: the over-hygroscopic field at high RH, which probably represents surface water, and the hygroscopic field at lower RH, which probably represents water held mainly by capillary force in meso- and micropores (Grunewald 2007). The break in slope in the RH versus weight plots separates these two fields. There does not appear to be a consistent definition of over-hygroscopic water, but one interpretation is that it is surface water adhered to a surface with a tenacity that is related to the liquid–solid contact angle. Water with
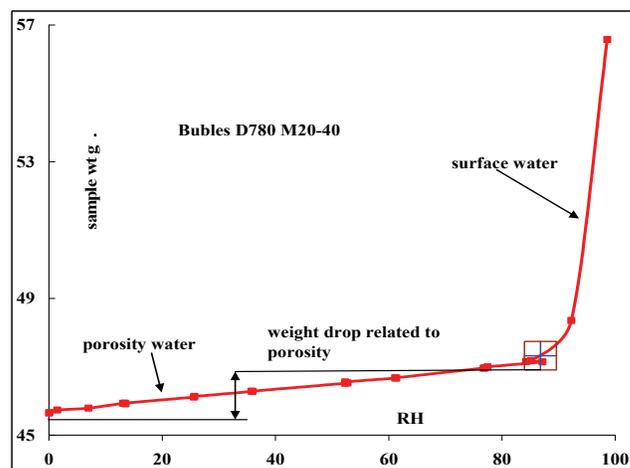
Figure 3. A water isotherm for shale cuttings (20 to 40 mesh size) illustrates the break between surface and pore moisture (Sample Bubles D780).

low contact angles on hydrophilic surfaces will be dried at lower RH than will water with larger contact angles on hydrophobic surfaces.

It is difficult to separate, in the hygroscopic field, water held by capillary forces in small pores from water adsorbed onto clays. A number of papers discuss adsorption of water by clays. Likos and Lu (2002) studied water adsorption on suspended mixtures of smectite and kaolinite at varying values of RH. Curves generally have an inflection point at about 85% RH, which Likos and Lu interpreted as the change from molecular adsorption to capillary condensation. They were studying fine grains of clays in a slurry, so the inflection point could alternatively be the break point between surface moisture and adsorbed moisture (hygroscopic to over-hygroscopic). They did document the adsorption ability of kaolinte at decreasing RH and found that there was about a 2.5% weight loss when RH changed from about 85% to 0%. This would correspond to an apparent porosity of about 6.5% for a sample composed of 100% kaolinite. Shales are not 100% kaolinite, and the ability of a kaolinite slurry to adsorb water is probably much greater than that of kaolinite as a component of solid rock. Is the volume occupied by water adsorbed on kaolinite available to be occupied by methane gas? Aggressively drying a sample in a laboratory would remove this water and influence the calculation of porosity. Calculated porosity might be higher than that available for free gas with a high relative humidity.

Equilibrium moisture content of coal is a laboratory measurement designed to provide an estimate of the moisture-holding capacity of coal. The measurement is done in an atmosphere with 97.6% RH controlled by a saturated solution of KSO_4. This RH value was chosen probably because coal is hydrophobic, and therefore surface moisture is removed at relatively high values of RH compared to rocks that are variably hydrophilic and might retain surface moisture at lower values of RH.

Two water isotherms were constructed for a sample of high-volatile B bituminous coal. Coal of this rank usually has equilibrium moisture (EQ) in the range of 6% to 10%, and the two sample splits have EQ moisture of 6.33% and 6.58%, which agrees with the commercial laboratory EQ moisture analysis made on coal from the same area. The break points in both graphs are at about 98% RH (Figure 4), illustrating the difference in wettability of hydrophobic coal and of hydrophilic shale. Based on the comparison of coal and shale water isotherms, the break point in slope varies based on the degree of hydrophobicity, which is a measure of surface wettability. Careful measurements may indicate subtle variations in wettability, which is closely related to relative permeability.
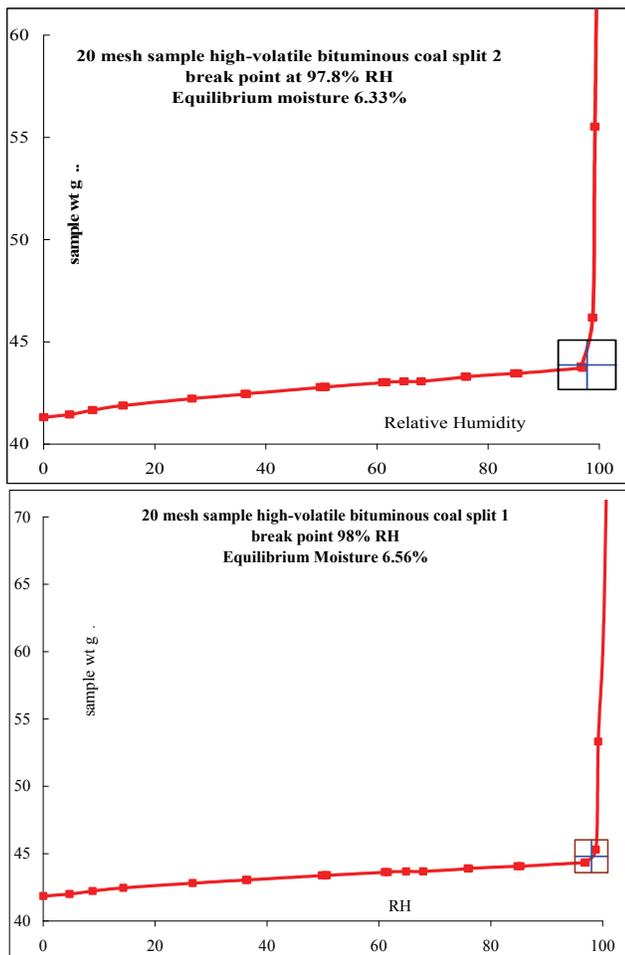
Figure 4. Water isotherms on two samples of high-volatile B coal indicate break points at about 98% RH.

Attempts to do EQ measurements on shales using ASTM (American Society for Testing and Materials) procedures may not produce meaningful results, because the reported water content may include surface moisture. It is probable that surface water is retained by shale until RH values are reduced to about 85%, depending in part on sample size and maybe grain size. An indication of the RH val-

ues separating over-hygroscopic from hygroscopic fields is evident in data from Grunewald (2007) (Figure 5).

KELVIN EQUATION AND PORE-SIZE DISTRIBUTION

The part of a water isotherm that covers the hygroscopic range provides information about cumulative volume of connected pores, distribution of pore sizes, and capillary pressure. Capillary force is an attractive force between liquids and solids that manifests as surface tension and contact angles between solid and liquid. An example of surface tension and capillary pressure is the ability of liquid in a small tube placed in a vessel to rise, against the force of gravity, above the liquid in the vessel. The liquid height is proportional to the diameter of the tube. As the diameter decreases, the liquid height in the tube increases. Thus, surface tension will work against the inclination of water molecules to evaporate when RH of the surrounding gas phase is less than 100%. The effect increases as pore diameter decreases and depends on RH, not on total pressure.

Relative humidity is reduced above a concave meniscus because surface tension forces reduce the ability of water to evaporate. This has the effect of producing a relationship between the radius of the meniscus or pore throat size and the RH below which water will evaporate from the pore and above which water will remain in the pore. The Kelvin equation (also referred to as the Kelvin-Laplace equation) relates pore radius to RH. It also incorporates surface tension, universal gas constant, and temperature (in Kelvin). An explanation of the development of the Kelvin equation and how it relates to analysis of pore-size distribution is given by many authors (for example, Grunewald 2007).

There are a number of forms of the Kelvin equation. The standard form relates pore radius to surface tension and RH:

$$\ln(RH) = -2\sigma/(R_c \rho R T)$$

where

ln	= natural logarithm
σ	= surface tension (N/m)
Rc	= Kelvin mean radius of pore (m)
ρ	= density of liquid (g/cm^3)
R	= universal gas constant (JK^{-1}mol^{-1})
T	= temperature (K)
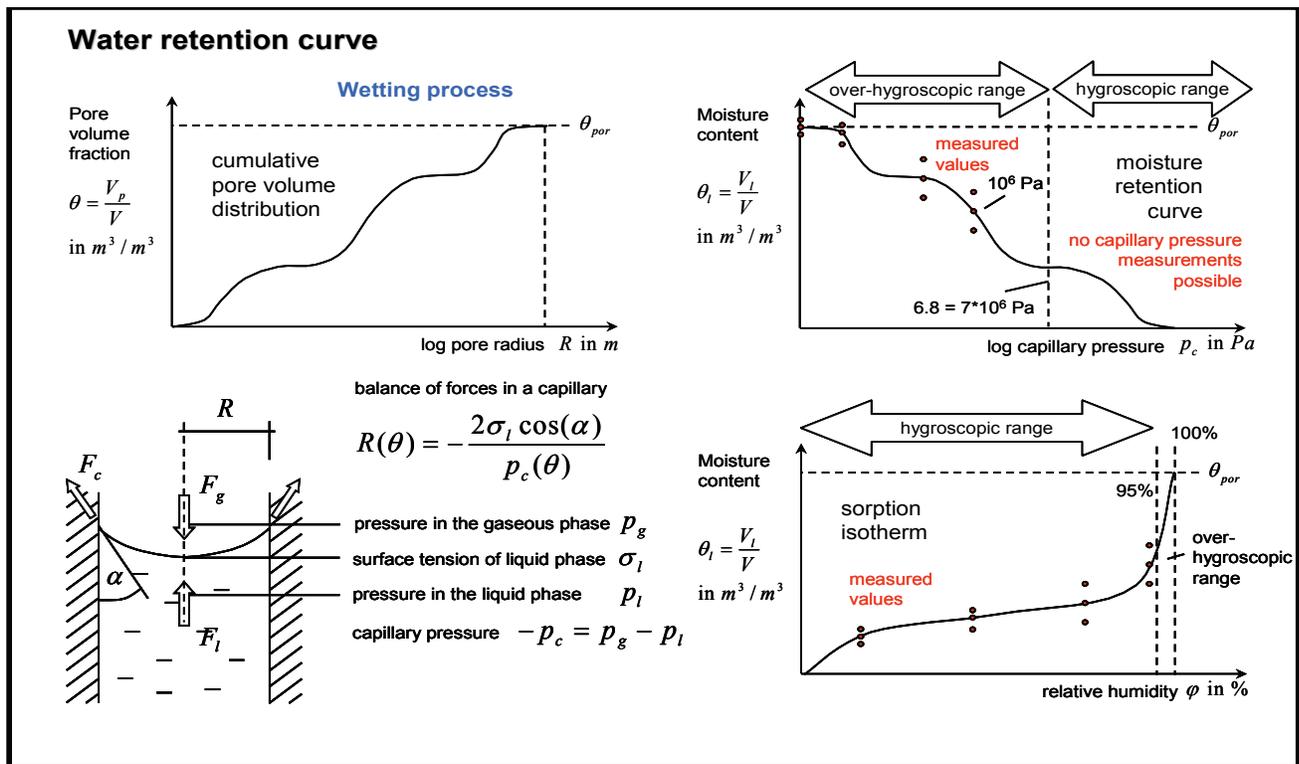
Figure 5. Hygroscopic and over-hygroscopic fields (Grunewald 2007).

Alternatively the Kelvin equation from Wang and Fredlund 2003 can be written as

$$RT\ln(RH) = \sigma V[1/Rc - (P - P_{sat})]$$

where

R	= universal gas constant ($JK^{-1}mol^{-1}$)
T	= temperature (K)
ln	= natural logarithm
σ	= surface tension (N/m)
V	= molar volume (m^3/mol)
Rc	= Kelvin mean radius of pore (m)
P	= vapour pressure (N/m^2)
Psat	= saturated vapour pressure (N/m^2)

Shang et al. (1994) and Prost et al. (1998) use the Kelvin-Laplace equations in the following form:

$$\ln(RH) = [(V)/(RT)]2(\sigma/R_k)$$

where

ln	= natural logarithm
V	= molar volume (m^3/mol)
R	= universal gas constant ($JK^{-1}mol^{-1}$)
T	= temperature (K)
σ	= surface tension (N/m)
R_k	= R_c – t where R_c = actual pore radius and t = adsorbed film thickness

Another form is this:

$$P_c = \rho RT\ln(RH)$$

where

P_c	= capillary pressure (MPa)
ρ	= density of liquid (g/cm^3)
R	= universal gas constant (JK-1mol-1)
T	= temperature (K)
ln	= natural logarithm

Or

$$R_c = -2\sigma[\cos(\alpha)/P_c]$$

where

R_c	= Kelvin mean radius of pore (m)
σ	= surface tension (N/m)
α	= contact angle. The angle α is close to 0, so cos(α) is assumed to be 1
P_c	= capillary pressure (Pa)

Molar volume of water	= 1.8×10^{-5} m^3/mol
Surface tension	= 0.0728 N/m^2
T (degrees Kelvin at stp)	= 298 K
R (universal gas constant)	= 8.314 $JK^{-1}mol^{-1}$

Figure 6 indicates the relationship between RH, capillary pressure, and pore-size distribution predicted by the Kelvin equation. The equation is used in material sciences and in soil sciences, where it is applied to the drying effect of decreased humidity on soils composed of compacted particles with surface water contained in the interstices (Wang and Fredlund 2003). A number of authors have used the Kelvin-Laplace equation and capillary pressure to document pore-size distribution. Dabous et al. (1976) measured pores sizes ranging from 0.4 to 200 µ in coal core using measurements of capillary pressure and the relationship $R_c = -2\sigma \times \cos(\alpha)/P_c$. Prost et al. (1998) used water isotherms to differentiate between water held external to quartz grains from water held in the pores in grains. Pore sizes are 3 to 6 µ (0.003 to 0.006 mm) and 18 to 32 µ (0.018 to 0.032 mm). This falls in the mid range of macropores (0.0001 to 0.1 mm) as used in geological literature. Water is extracted from these pores at 2 distinct RH values.
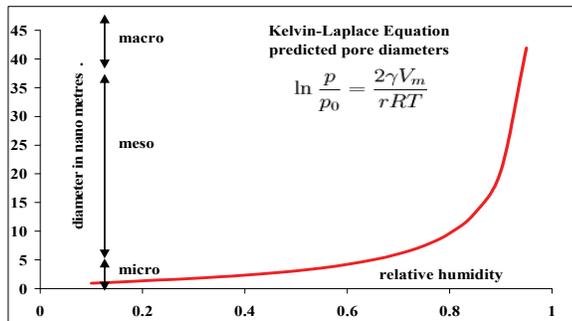
Micro metres = mm (10^{-6} metres)   nano metres = nm (10^{-9} metres)
Angstroms = A (10^{-10} metres)

	Nano metres		Angstroms	
	from	to	from	to
Micro pores	0.2	2	2	20
Meso pores	2	50	20	500
Macro pores	50	10000	500	100 000
20-40 mesh grain Dia	6.4*10 5			
40-60 mesh grain Dia	3.4*10 5			
ratio (grain diameter 20-40m)/(macro pore)			128000	640
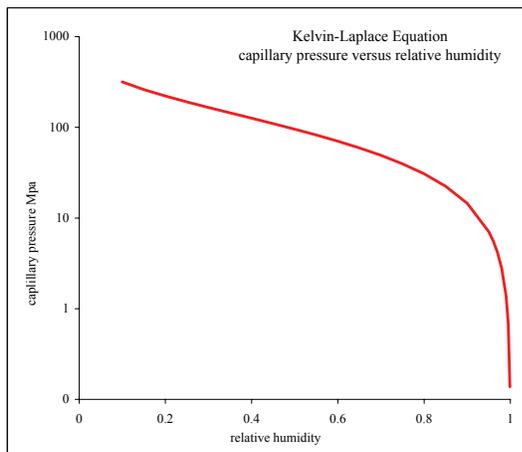
Figure 6. Relative humidity versus pore size (top) and versus capillary pressure (bottom) as predicted by the Kelvin-Laplace equation.

The Kelvin equation provides a value for the Kelvin radius, which is probably an underestimate of the pore size holding moisture at any RH value. It appears that for rocks with mainly meso- and micro-porosity, water isotherms will provide a good way of differentiating between surface water on grains and pore water filling mesoporosity (averaging 0.00001 mm). For samples with porosity in the macropore range, there is confusion between grain surface water and pore water.

In the ideal case, the Kelvin equation provides a pore-size distribution (Figure 6). In general it is difficult to classify the pore-size distribution in a sample. Water escaping from a sample composed of variable connected pore sizes will be forced to travel through both narrow and wide pore throats. The smaller pore throats will tend to control water escape, therefore a water isotherm cannot be used to clearly provide a pore-size distribution.

Inflection points in an isotherm represent minima or maxima in the rate of change in water loss. A plot of $\delta V/\delta(RH)$ versus RH displays these inflection points as maxima or minima, indicating that they represent preferences for particular pore sizes in the pore-size distribution.

FRENKEL-HALSEY-HILL EQUATION

Frenkel (1946), Halsey (1948), and Hill (1952) developed the Frenkel-Halsey-Hill (FHH) equation, which helps demonstrate the state of adsorbed water versus RH rather than pore-size distributions versus RH.

The equation is

$(q/q_m)^n = A/\ln(RH)$

where

q/q_m	= relative saturation = RH
n	= a power term
ln	= natural logarithm
A	= $e_o/(X_m^n RT)$
e_o	= potential for adsorption
X_m	= film thickness (m)
R	= gas constant ($JK^{-1}mol^{-1}$)
T	= temperature (K)
RH	= $[(1 - Ø)/Ø][\rho r/\rho wq]$
Ø	= porosity %
ρ	= density of rock or water (g/cm^3)
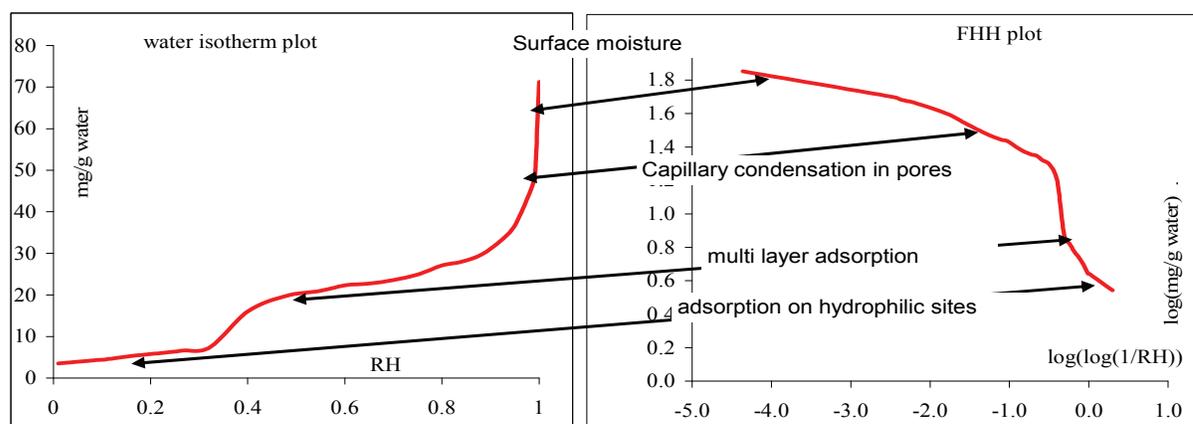
Figure 7. The Frenkel-Halsey-Hill equation demonstrates the relationship between RH and the ways water is held in pores.

The equation can be rewritten as

$$\ln[\ln(1/RH)] = \ln(A) - n[\ln(RH)]$$

or

$$Ln(RH) = \ln(A)/n - Ln[\ln(1/RH)]/n$$

They showed that for intermediate values of RH:

$$\log(1/RH) = k/w^r$$

where

w = water content; k and r are constants

In this form the equation provides a useful plot for differentiating four domains of water retention (Figure 7):

Domain 1 = Monolayer adsorption (adsorption on hydrophilic sites).

Domain 2 = Multilayer adsorption.

Domain 3 = Water held capillary condensation. (capillary condensation in pores).

Domain 4 = External surface water (surface moisture).

Porosity is defined by the water represented by domain 3. Water represented by domains 1 and 2 is probably adsorbed on clays and might not be occupying porosity available for free gas.

The FHH plot demonstrates the way a solid retains water; it does not predict pore sizes. The water retention method is closely related to pore size. Prost et al. (1998) used the FHH equation to break out these four domains of water retention in quartz and Al_2O_3 pastes. Shang et al. (1994) found that the FHH equation fits water desorption isotherms well and is capable of tracking capillary condensation and adsorption processes. They used cuttings and core samples and found that cuttings could be used despite the increase in external surface area.

CAPILLARY PRESSURE

Capillary pressure is the pressure required to initiate fluid movement through pore throats of a particular size. It is dependent on pore size, RH, surface tension, and temperature. Capillary pressure increases as temperature and surface tension increase and decreases as pore size and RH increase. At a particular capillary pressure, there is a value of RH above which the liquid in a pore is stable and below which water will tend to evaporate. This is the equilibrium RH value associated with the specific capillary pressure. At a fixed temperature, capillary pressure increases exponentially as RH decreases and this, in effect, defines the irreducible water content of a porous solid. Irreducible water is found wetting pores and can only be removed by evaporation at very low RH.

Maturation of TOC during burial generates gas in excess of that retained by adsorption. This gas fills pores as temperature and pressure increase with depth of burial. Capillary pressure in pores is fixed mainly by pore size, though it decreases somewhat as surface tension decreases with increasing temperature. Relative humidity in pores increases as temperature (and therefore depth) increases. For pores to survive gas filled, or for gas saturation to increase by displacing water, gas pressure must overcome hydrostatic pressure plus capillary pressure. This is increasingly difficult as pores get smaller but is probably easier as depth increases.

The potential for shale porosity to be gas overpressured is in part dependent on the ratio of porosity to TOC and on rank, as these two parameters define the ability of shale to have excess gas available to move water out of the porosity. As an example, a pore diameter of 0.001 mm has a capillary pressure of about 2.9 MPa, which corresponds to a depth of about 300 m, based on a normal geothermal gradient.

Capillary pressure increases exponentially as pore sizes decrease during burial and compaction. While maturity of TOC is increasing, secondary porosity also is increasing, and excess gas is produced, which may force water out

of pores. As compaction and burial progress, pore sizes decrease, as does the amount of excess gas generated by TOC for each incremental increase in rank. At this stage, capillary pressure increases because of decreased pore size, and external water tries to re-enter pores. Pore pressure also increases because of increasing temperature and decreasing pore volume, making it difficult for water to re-enter small pores. Compaction, increase in temperature, and generation of excess gas all increase the gas pressure in pores. This more than counters the increase in capillary pressure, which will tend to force water back into gas-filled pores.

As TOC matures it produces methane, which under geological conditions will remain as a gas or in solution in water. Once water surrounding TOC is gas saturated, any further gas generated will remain, partially filling the porosity at a pressure that is hydrostatic plus capillary. The percent of porosity that is gas filled may be small, but because water is incompressible, some water will be forced out of the porosity. Generally, rough calculations using plausible values of TOC, porosity, and cumulative gas generated indicate that it is difficult for excess gas to provide sufficient overpressure during burial to overcome hydrostatic and capillary pressure and force all the water out of the porosity. It will force out some water because gas in excess of adsorbed gas is nearly always generated. During uplift, as hydrostatic pressure decreases, pore overpressure may develop and work to force water out of pores. In this case, hydrostatic pressure may appear to be normal, but once new fracture surfaces are developed during completion of the well and pressure is reduced during gas production, there may be a rapid expulsion of water and gas from the porosity as pore gas pressure is able to overcome capillary pressure.

Capillary pressure, acting on a pore of fixed size, increases with temperature and therefore depth. However, the RH value separating evaporation from adsorption increases with temperature so that the net affect is that the capillary pressure acting on liquid in a pore at equilibrium does not change as temperature increases. It is therefore possible to estimate the degree of overpressuring in shale that excess TOC gas must generate in order to push water out of micropores and into fractures.

During uplift, if there is a dry gas phase (biogenic gas with low RH) in fractures, then excess gas can remove water from pores by evaporation and effectively erode water from shale porosity working inwards from fractures. Water in contact with methane will become saturated with methane in solution. Methane in solution that comes in contact with TOC surfaces will adsorb onto TOC surfaces. It is therefore possible for the TOC in shale to be adsorption saturated, but harder for the porosity to become gas saturated.
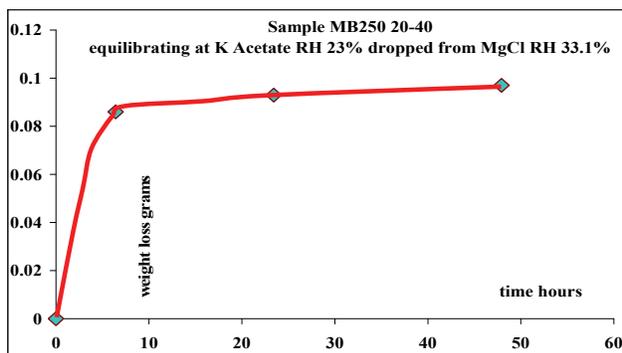
Figure 8. The graph of weight loss over time at a set relative humidity is similar to a desorption curve.

IMPLICATIONS FOR DIFFUSION

The weight loss of a sample is not dependent on the time for which it is held at a particular RH value, as long as an equilibrium time of about one day has elapsed; rather it is dependent on the RH value (Figure 8). The weight loss versus time plot is very similar to a desorption curve for methane, and consequently, it is possible to use the equivalent of sorption time to comment about the diffusivity, or micropermeability, of a sample.

Permeability in shale is often very low, and if the rock is not fractured into small blocks, then diffusion may be the process that limits gas production. There is probably not a single diffusion coefficient in effect. Some gas molecules move to grain boundaries, accessing larger connected pores (a weight loss versus time plot at a higher RH step), and some gas molecules move to grain boundaries, accessing smaller connected pores, and experience a slower diffusion (as measured by a weight loss versus time plot at a lower RH step). It therefore becomes possible to construct time versus water loss plots for different initial and final RH values. This is equivalent to constructing desorption curves, each one providing a sorption time constant for a different component of the gas resource represented by the fraction of porosity associated with the RH step.

WATER FILM THICKNESS

Film thickness or wettability on grain boundaries provides information on physical characteristics of rock that influence relative permeability of gas flow along fractures. It is possible to estimate the thickness of the wetting surface by using dry sample weight and average grain diameter to estimate total surface area of all grains (TS). At each RH above the break in slope separating surface water from pore water, the weight of water is equivalent to identifying a volume of water, which, when divided by TS, provides the thickness of the water layer. The rate at which this thickness decreases as RH decreases (towards RH at break point) is a measure of hydrophobicity, which affects the relative per-
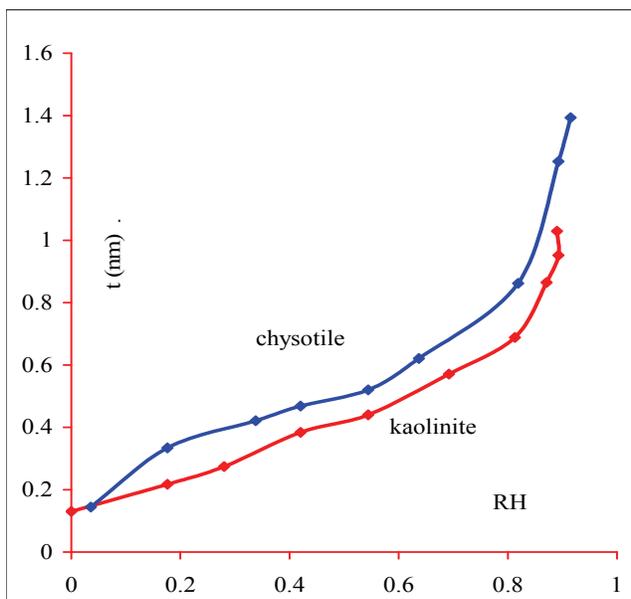
Figure 9. The thickness (t) of the water film on a mineral grain is a function of relative humidity (RH). Data from Hagymassy et al. (1969).

Figure 10: A desiccator with a relative humidity meter inserted. The desiccator contains two samples above a dish containing a salt solution that maintains a specific humidity.

meability of gas. It is possible to estimate water film thickness on dispersed grains using an equation developed by Hagymassy et al. (1969) (Figure 9). Data from Hagymassy et al. (1969) and Prost et al. (1998) suggests that the water film thickness decreases rapidly at RH values greater than about 85% on grains of kaolinite and that below 86% RH, the decrease is much slower. This is equivalent to an external expression of a water isotherm that is measuring water loss from internal pores.

SAMPLE PREPARATION AND ANALYSIS PROCEDURE

Sample porosity is measured using moderately coarse shale cuttings that have been kept water-saturated (with formation water if possible) since retrieval. The assumption is made that at atmospheric pressure, free gas is completely replaced by water in all pores. Samples are wet-screened to a number of size fractions. In this case samples were separated into size fractions greater than 20 mesh, 20 to 40, 40 to 60, 60 to 100, and less than 100 mesh. Size fractions are kept water-saturated prior to analysis.

Most of the samples analysed in this study were screened to 20 to 40 mesh. At this size, a single grain is over 20 000 mesopore diameters wide. A water-soaked sample weighing about 50 g is placed in a modified desiccator (Figure 10), which holds two such samples. Modifications to the desiccator include replacing the domed top with a flat top; inserting a small fan (the type found in laptop computers); and drilling an insert tunnel so that the RH probe can be inserted into the desiccator. A number of chemicals that

provide relative humidity control points at about 10% RH steps are used (Table 1).

A series of saturated salt solutions are placed in the desiccators in sequence to decrease RH from 100% to 0%. The first solution is a saturated solution of KSO_4, and the final compound is dried $CaCl_2$. Samples are weighed once RH has stabilized at the RH value maintained by each solu-

TABLE 1. SALT SOLUTIONS USED TO CONTROL RELATIVE HUMIDITY OF SAMPLES.

Sequence for relative humidity control	
saturated solutions	humidity %
Water	100
potassium sulfate	97.6
potassium chloride	85.1
sodium chloride	75.7
sodium bromide	59.1
magnesium nitrate	54.38
potassium carbonate	43.2
magnesium chloride	33.1
potassium acetate	23.11
lithium chlorite	11.3
baked calcium chloride	0

tion. It takes about 1 to 2 days for sample weights to equilibrate at each new RH value as defined by a new saturated salt solution. Samples have to be weighed quickly when periodically removed from desiccators because they will either lose or gain weight, depending on whether RH in the desiccator is greater or less than ambient room RH.

SAMPLING CONSTRAINTS

The first problem during construction of a water isotherm for measuring porosity is to differentiate between surface water and water that is held in porosity. This is critical when using cutting samples. All RH versus weight plots for shale samples have a distinct break point that occurs at
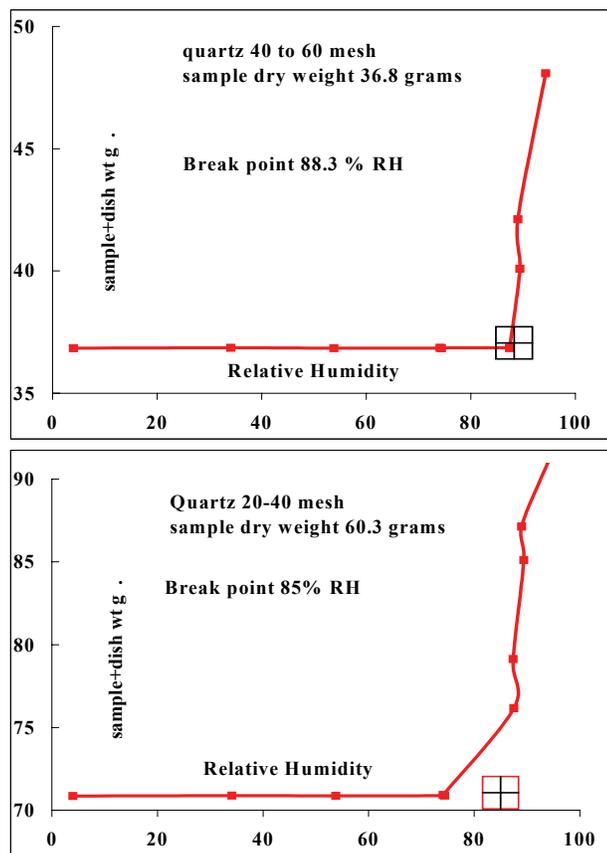
Figure 11. Water isotherms of quartz grains screened to 20 to 40 mesh and 40 to 60 mesh.

about 86% RH (Figure 3). The RH value of 86% appears to separate removal of surface water from pore water, based on the fact that the same break point is seen in water isotherms on screened quartz grains (Figure 11). Samples of quartz grains screened to 20 to 40 mesh and 40 to 60 mesh were analysed, and both have zero porosity below a RH value of about 86% (no decrease in weight as RH decreases below 86%).
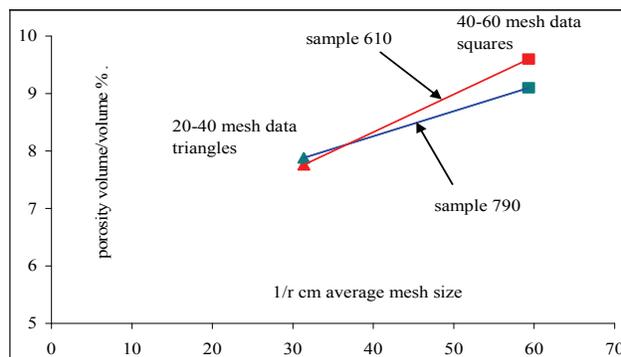
Figure 12. Relationship of porosity to mesh size of shale cuttings. Mesh size decreases to the right.

A correlation between particle size and porosity is expected. As grains get smaller, there is better access to porosity, especially non-connected porosity. This effect is related to the ratio of surface area to grain volume (1/radius). As grain size increases (1/radius approaches zero), porosity measurement converges on true connected porosity, which will be a minimum value. Smaller grain size samples will have higher estimated porosities (Figure 12), and this is probably a surface-area effect. By screening samples to a constant grain size, relative porosities should be valid, but all values will need to be corrected for absolute connected porosity. There should also be a correction based on the compressibility of the solid to correct porosity measured at surface to actual porosity at depth, but that is outside the scope of this paper.

IMPLICATIONS FOR TOTAL ORGANIC CARBON (TOC)

The small amount of organic material in shales adsorbs water as well as methane. The amount and mechanism of water adsorption is indicated by water isotherms. Generally water retained at 50% RH on coal is considered to be mono-layer adsorbed (Mahajan and Walker 1971). This water will be extracted at low values of RH and may influence porosity calculations, as will water adsorbed on kaolinte. It is unlikely that this water will ever be removed to provide porosity for free gas, because it would require low values of RH or very high capillary pressures to force it out. In a gas-saturated shale, there is a portion of porosity that has strongly adsorbed water (or irreducible water), which should not be considered part of a porosity calculation. This water is removed only when samples are dried by decreasing RH to values approaching zero. Present calculations of effective porosity may be too high, and therefore calculated values of the degree of effective gas saturation may be too low and resource estimates too high.

Identification of water adsorbed by TOC may be possible by using the shape of water isotherms to partition equilibrium moisture between capillary, condensed, multilayer adsorbed, and mono-layer adsorbed water. Once this relationship is established, if the rank of the TOC material is known, then it is possible to estimate the amount of TOC based on the amount of water removed in the RH range 10% to 0%.

DETAILS OF POROSITY AND APPARENT DEGREE OF SATURATION CALCULATIONS

Calculation of porosity requires the specific gravity of sample with water-filled pores (SG_{wet}) and skeletal specific gravity with no water in pores (SG_{dry}). The procedure is documented in Table 2 and is as follows:

1. Split sample into two subsamples.

2. For one subsample, remove surface water (dry to 86% RH) and weigh sample (Table 2; a1).

3. Use Archimedes' principle (water immersion) to measure subsample volume at 86% RH and calculate SG_{wet} (Table 2; a2 a6).

4. Second subsample, dry to 86% RH weight then weigh again at 0% RH (Table 2; a3 and a4).

5. Use the SG_{wet} value from first subsample and wet weight second subsample to calculate 86% RH volume of second subsample (Table 2; a7).

6. Calculate water-filled volume of second subsample (Table 2; a2, a3).

7. Calculate SG_{dry} of second subsample using dry weight and dry volume (Table 2; a9).

8. Calculate porosity from RH data using

$$\text{Ø} = (SG_{dry} - SG_{wet})/(SG_{dry} - 1) \times 100$$

Ø = porosity, volume %,

1 = assumed SG of water filling all pores (Table 2; a10).

9. Calculate porosity using He pycnometry data (Table 2; a11).

10. Calculate total pore volume using SG_{wet} RH 86% and SG_{dry} He Pycnometry (Table 2; a12).

11. Using porosity from RH 86% to 0% and porosity using He pycnometry, calculate apparent % gas saturation (Table 2; a13) as described in detail below.

TABLE 2. METHOD FOR CALCULATING CONNECTING POROSITY AND DEGREE OF SATURATION.

	Calculation of degree of saturation and porosity		
	Sample 1 is saturated with water then put in the desicator Sample 2 is put into the desicator as received The water saturated SGwet is measured on sample 1 the wieght loss is measured on sample 2 from 86% RH to 0%RH The SGdry is measured using He pycnometry		
	Calculation of porosity and % saturation Example Calculation		
a1	sample 1 water saturated weight at 86% RH	**60**	
a2	Sample 1 water saturated volume at 86% RH	**24**	
a3	Sample 2 wet wt 86% RH	**56.00**	
a4	Sample 2 dry wt 0% RH	**55.00**	
a5	SGdry by He injection	**2.65**	
a6	sample 1 water saturated SGwet	**2.5**	a1/a2
a7	Sample 2 wet volume	**22.4**	
a8	weight water filled pore volume sample 2	**1.00**	(a3-a4)
a9	SGdry sample 2 from RH 86% and RH 0%	**2.57**	a4/(a7-a8)
	SGwet sample 2 from 86% RH and 0% RH		
a10	Porosity calculated using RH data	**4.46**	(a9-a17)/(a9-1)*100
a11	porosity calculated using He SGdry	**9.09**	(a5-a6)/(a5-1)*100
a12	total pore volume in sample 2	**2.08**	(a11/100*a4/a5/(1-a11/100)
a13	gas saturation	**51.82**	(a12-a8)/a12*100
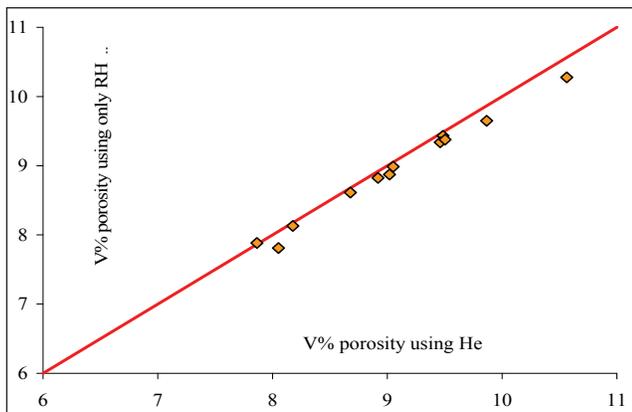
Figure 13. Plot of porosity V, (volume %) calculated using only desiccator data against porosity calculated using He pycnometry and desiccator data.

There are two ways of calculating porosity for samples that are completely water saturated. One uses only data from the desiccator, the other uses He Pycnometry and desiccator data. For the data presented here, the two methods produce similar estimates of porosity (Figure 13). Using the split-sample approach provides a way to calculate degree of gas saturation of the porosity as it exists in the samples under atmospheric conditions for samples not fully water saturated.

Shale porosity at depth may be partially or completely gas filled or water filled. Physical measurement of the degree of gas saturation in porosity at surface is difficult. As a sample is retrieved, pressure decreases and gas escapes from porosity and is replaced by water. This process might be slow if the porosity is composed of meso- or micropores with restricted inter-connecting throats, and larger fragments may still preserve evidence of the degree of gas saturation. The degree of gas saturation at surface will be different than that at depth. Gas expands as pressure decreases, whereas the water volume changes very little. If a sample is crushed to a finer size and a water isotherm measured, then the weight of water loss from 86% RH to 0% RH may help determine degree of saturation when compared to data from a second sample that is completely water saturated.

It is possible to estimate degree of saturation using a combination of He Pycnometry and RH data if samples are not 100% water saturated (i.e., gas saturation > 0%). The procedure requires two sub-samples, one as-received (sample 2, Table 2) and one water-saturated (sample 1, Table 2). The SG of sample 1 is measured at 86% RH (= SG_{wet} sample 1). Sample 2 is put into the desiccator as-received, and the weight at 86% RH and at 0% RH are measured. SG_{dry} is measured using He Pycnometry on sample 1, and the total porosity is calculated using SG_{dry} (1) and SG_{wet} (1). The pore volume in the second sample 2 is calculated using its dry weight with SG_{dry} and total porosity calculated from sample 1. This volume is compared to the weight loss (= water volume) when drying sample 2 to calculate the percent gas saturation (Table 2). The validity of the estimate depends on the history of sample 2 since it was collected during drilling operations.

During uplift gas expands in porosity and will force water out. Rock decompresses and this may increase porosity and tend to pull water in. Once at or close to surface, if the sample is wet, water will tend to displace gas in the porosity because of capillary pressure. There are many uncertainties in estimating degree of gas saturation in porosity for samples brought to surface. Water in pores is in contact with methane and may be a mixed gas on the external side of the throat. This means that there is a concentration gradient for methane in solution in the water and there will be diffusion movement of methane out of the pores despite the effect of capillary pressure to trap gas in pores.

Using He pycnometry to calculate SG_{dry} may result in values that are too high because the He molecule is smaller than the methane molecule and may access additional sites. If this is the case, then the calculated total porosity will be too high, as will the percent gas saturation. This could result in a significant overestimation of resource.

In cases where percent gas saturation is high, it is possible that RH is very low, and this could mean that the ability of the TOC to adsorb methane is increased. A number of studies indicate that adsorption of low- and medium-rank coals increases if they are dried below equilibrium moisture. Resource estimates on gas-saturated shales may be too low because they use isotherms measured on water equilibrated samples (100% RH) to estimate the adsorbed gas component of the resource.

An alternative approach that uses water chemistry to estimate percent gas saturation may be possible. The chemistry of formation water can be measured to provide a fingerprint that is very different from surface water. For rock that is partially saturated with formation water, if dried at surface and then washed in a known volume of pure water it is possible to calculate the amount of formation water contained in the porosity by changes in the chemistry of the wash water.

SAMPLES

Cuttings samples were provided by a number of companies. They were kept saturated with formation water when possible until ready for preparation. Hudson Hope Gas provided 24 cuttings samples of the Lower Cretaceous Moosebar Formation intersected in hole b-43-A/94-B-1 (WA report number 21477) over a depth range of 250 to 490 m. Petro-Canada provided samples from three holes: Bubbles C-25-G/94-G-8 (WA report number 21577), PC Town d-36-C/94-G-1, and PC West Beg C-046-C094-G-01, each covering part of the interval from 350 to 800 m.

depth	RH break point	dry wt	wt loss RH 86%-0%	Gamma ray counts	SGdry He	SGwet measured	SGdry calc from SGwet measured	SGwet calc using SGdry He	porosity using SGdry He and Sgwet calc	porosity V% using SGdry calc from SGwet measured	V% Porosity using SGwet measured and plot	EQ 86%RH
Hole	B-43-A/94-B-1											
250	85.5	47.919	0.921	90.95	2.6532			2.573	4.85			
260	86.2	52.191	1.139	94.79	2.6551			2.564	5.48			
270	84.4	54.262	1.338	90.77	2.6677			2.565	6.17			
280	86	48.151	0.759	93.43	2.661			2.594	4.03			
290	89.3	49.398	0.892	91.68	2.666			2.589	4.59			
300	89.5	45.239	0.761	93.65	2.6659			2.594	4.29			
Hole	C-025-G/094-G-08											
610	86.4	45.444	1.596	134	2.6834	2.558	2.706	2.538	8.61	8.68	8.8	
670	86.9	48.439	2.061	129	2.6916	2.589	2.776	2.518	10.28	10.56	9	
720	86.6	48.237	1.853	135	2.7112	2.564	2.728	2.550	9.43	9.49	8.2	
750	86.9	47.7	1.74	145	2.7062	2.572	2.728	2.553	8.98	9.05	7.5	
780	90	45.646	1.814	140	2.6873	2.581	2.754	2.524	9.65	9.86	9.2	
790	86.3	48.246	1.844	137	2.6947	2.570	2.734	2.536	9.34	9.46	8.7	
Hole	PC west Beg c-46-C/94-G-1											
350		41.99	1.64	122	2.6498	2.528	2.688	2.495	9.38	9.50	9.502	3.759
410		32.25	1.032	116	2.6744	2.536	2.667	2.542	7.88	7.86	7.863	3.101
450		44.66	1.42	76.7	2.6643	2.613	2.754	2.534	7.81	8.05	8.052	3.082
Hole	PC town d-36-C/94-G-1											
370		27.27	0.993	120.32	2.6744	2.567	2.722	2.526	8.87	9.02	9.05	3.513
380		24.38	0.808	91.64	2.6701	2.549	2.687	2.534	8.13	8.18	8.177	3.208
410		31.73	1.156	78.96	2.6562	2.537	2.687	2.510	8.82	8.92	8.92	3.515
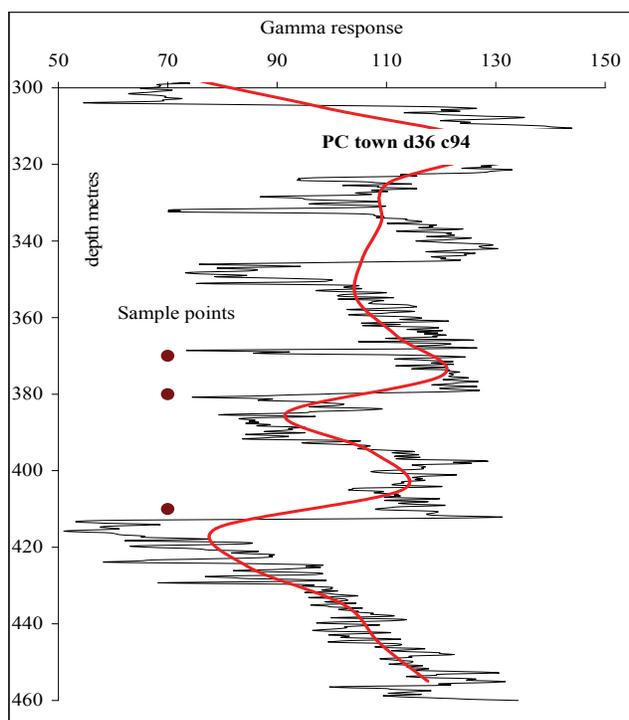
Figure 14. Example of gamma log with smoothing and sample points.

After a measurement protocol was established, 12 samples were analysed. Six samples from hole b-43-A/94-B-1; six samples from hole C-25-G/94-G-8; three samples from hole PC Town d-36-C/94-G-1; and three samples from hole PC West Beg C-046-C094-G-01. All samples represent 10 m intervals (Table 3). Samples were generally collected to represent the maximum range in gamma readings from geophysical logs (Figure 14).

DISCUSSION

Porosity values measured for the 12 samples range from 4 volume % to over 10 volume % (Table 3). They are in the range of what is expected, but at present there is no independent way to verify these values. Some general comments can be made about the data. Calculation of porosity using a weight at a low (but not zero) RH may provide a means of correcting for water adsorbed on kaolinite. Water isotherms may provide information on pore-size distribution; however in this study there do not appear to be different segments in the water isotherm plots with varying slopes indicating different amounts of water held in pores of various sizes. The SG$_{dry}$ value measured using He pycnometry is generally lower than the value calculated from

desiccator data (Figure 15). This is because samples were not maintained at exactly 0% RH during shipment for He pycnometry.

Gamma counts usually respond to K, U, or Th. These data have a poor correlation with K and therefore must be responding to U or Th. Porosity, SG_{dry}, and Al content all increase as gamma counts increase (Figure 16). The correlation of increased gamma with higher SG_{dry} and Al_2O_3 content (low SiO_2 content) reflects the higher SG of clay minerals compared to quartz. The increase in SG_{dry} values increase with Al_2O_3/SiO_2 ratios. This indicates that the higher SG values of clay minerals compared to quartz are influencing SG_{dry} values more than variable amounts of TOC, which has low SG and which tends to increase in content as Al_2O_3/SiO_2 ratio increase. There is no relationship of porosity to %K, so that illite is not effecting porosity estimation by adsorbing large quantities of water. It is not clear whether gamma counts correlate with estimated porosity, because there are clearly two populations of data.

Trace element contents of shales provide information on depositional environment and on the potential to retain TOC. Major oxide chemistry, on the other hand, can provide indications of potential porosity and fracability. The basic chemistry of the samples indicates a low CaO content and high SiO_2 content compared to average shale (Figure 17). The figure also shows data from the Barnett Shale estimated from mineral content data (Jarvie 2006), data estimated from mineral composition data in Ross and Bustin (2008), and average illite and kaolinite compositions in terms of the three oxide parameters. Figure 17 also includes an estimate of the relationship of total clay content to Al_2O_3/SiO_2 ratio (estimated from data in Ross and Bustin

[2008],), which allows the clay content of samples in this study to be estimated.

Porosity is influenced by mineral composition, burial history, and rock properties. In this study, porosity increases as Al_2O_3/SiO_2 ratio increases (Table 4), indicating either a positive relationship of kaolinite (i.e., negative correlation to silica content) or an adsorption effect by kaolinite. Ross
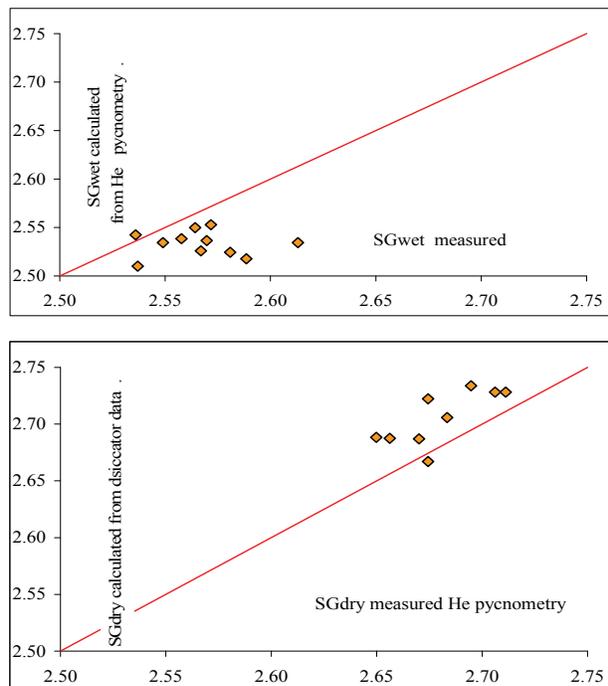
Figure 15. Comparison of SG_{dry} data determined using He pycnometry and calculated from desiccator data and similar comparison for SG_{wet}. Units for SG (specific gravity) are g/cm³.
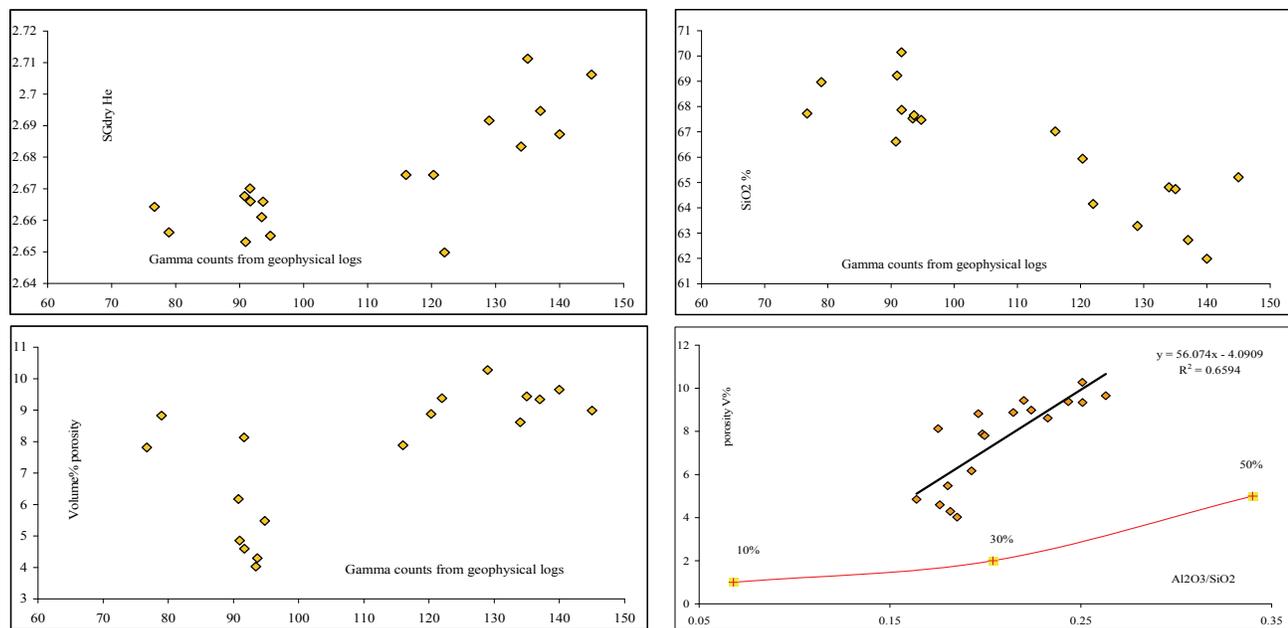
Figure 16. Plot of SG_{dry} (g/cm³) measured using He pycnometry versus gamma counts from geophysical logs.
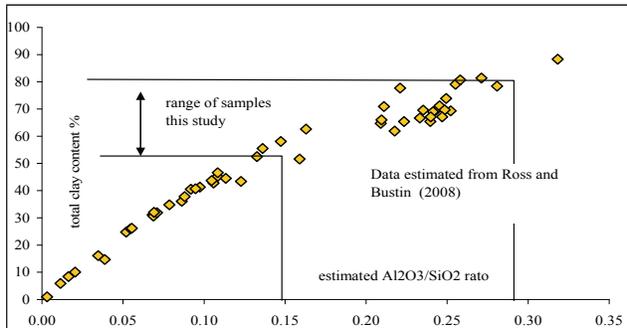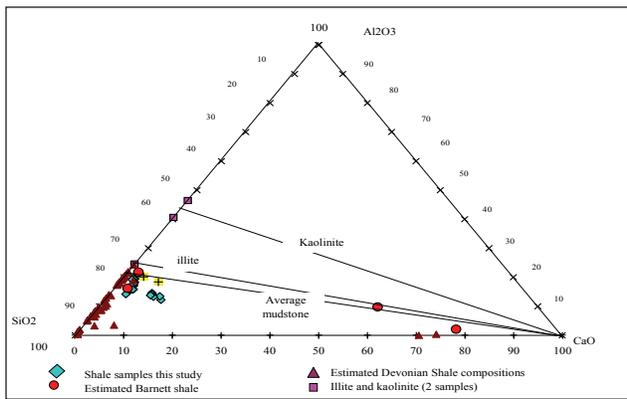
Figure 17. Major oxide chemistry of samples compared to average shale from Clarke (1924).

and Bustin (2008) report a negative correlation between silica content and porosity in Devonian Muskwa and lower Besa River mudrocks in northeastern British Columbia (Figure 18). They provide a table of mineral content data from which major oxide chemistry can be estimated assuming mineral compositions of quartz, kaolintie, illite, and calcite and making the assumption that these four minerals account for most of the rock. Once this is done, it is possible to estimate the relationship of porosity to silica content and of porosity to TOC for the samples (Figure 18). The porosity data from this study are plotted in Figure 18 and fall along the same trend of increasing porosity with decreasing silica content.

Low silica content is preferred for high porosity and potentially high free-gas content; however, rocks with high silica content are easier to fracture. The amount of TOC tends to increase as silica content decreases. A compromise has to be made in terms of preferred high silica content for ease of fracture stimulation during well completion and preferred low silica content for potentially higher gas

TABLE 4. LINEAR CORRELATION OF SOME ROCK CHEMISTRY AND WATER ISOTHERM DATA. UNITS: POROSITY, VOLUME%; SG, G/CM³; GAMMA RAY, COUNTS/SEC.

	Al_2O_3/SiO_2	porosity	SG dry	K_2O	gamma	P_2O_5
Al_2O_3/SiO_2	1.00					
porosity	0.81	1.00				
SG dry	0.58	0.57	1.00			
K_2O	0.44	0.54	-0.22	1.00		
gamma	0.82	0.66	0.78	0.06	1.00	
P_2O_5	-0.58	-0.79	-0.50	-0.25	-0.52	1.00

content. Ease of fracturing is related to Poisson's ratio and Young's modulus. These two rock parameters are not independent—Young's modulus increases as Poisson's ratio decreases. Rock property constants *lambda* (incompressibility) and *mu* (rigidity) are derived from Young's modulus and Poisson's ratio (Goodway et al. 2006). Figure 19, which is a simplified version of a plot of *lambda* versus *mu* from Goodway et al. (2006), illustrates the fracture potential of rocks and the preferred values of *mu* and *lambda*. The figure also shows a trend in porosity and *lambda* and *mu* values for common rock-forming minerals.
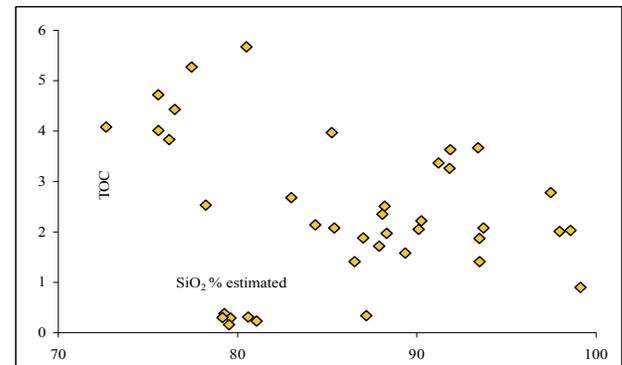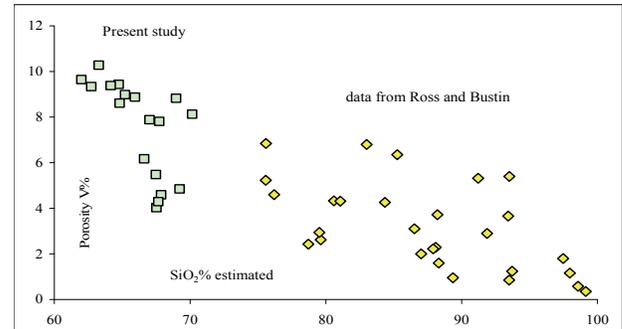
Figure 18. Estimated relationships of porosity and TOC to silica content (data from Ross and Bustin 2008).
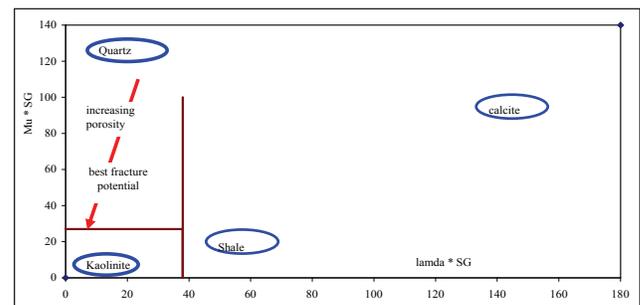
Figure 19. Relationship of fracture potential to rock properties; figure is a simplified version of a figure in Goodway et al. (2006) Lambda (incompressibility), Mu (rigidity), SG specific gravity.

CONCLUSIONS

- It is possible, using water isotherms, to measure porosity of shale cuttings. This is important because cuttings are much more readily available than core samples.

- The water isotherm approach to remove water is much less stressful on samples than using heat to dry samples or high-pressure mercury injection of gases of different ionic size.

- The water isotherm method allows for differentiation of surface water from pore water and makes it possible to use cuttings for porosity determination. However, there are indications that a correction must be made to the connected porosity measurement based on the grain size of the cuttings.

- The method provides information on the degree of hydrophobicity, which relates to relative gas permeability.

- It is possible to obtain information about pore-size distribution.

- A careful analysis of the time it takes for moisture to escape samples at each RH step should provide information on gas escape rate, whether it is described as diffusion or flow based on micropermeability.

- Combining the water isotherm approach with He pycnometry provides a way of estimating gas saturation.

The next stage for this study is to partner with industry so that core can be collected for porosity measurements and can provide samples for comparative analysis of porosity using crushed core samples as proxy for cuttings. In addition, consideration should be given to redesigning the desiccators and attaching dedicated humidity meters with continuous digital readout.

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