

POROSIMETRY MEASUREMENT OF SHALE FABRIC AND ITS RELATIONSHIP TO ILLITE/SMECTITE DIAGENESIS

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Abstract—The extent of illite/smectite (I/S) reactions is linked with quantitative measurements of shale fabric in a suite of samples from a lower Frio Formation well. Greater illitization of the I/S clays is found in laminated shales that possess a larger pore surface area/pore volume (SA/V) of $3.21 \times 10^6 \text{ cm}^{-1}$ than the adjacent massive shale lithofacies with a SA/V of $1.97 \times 10^6 \text{ cm}^{-1}$. Mean pore diameter in both shale lithologies is 0.0145 micrometers, though in the laminated shale distributions are skewed towards more smaller-sized pores. While no direct permeability measurements were made, estimates of permeability that are based on simple physical models using SA/V suggest that lower permeabilities are associated with laminated shales. The trend of greater illitization at higher SA/V values is contrary to expectations that reaction extent is enhanced by greater permeabilities, such as created by silt laminations in shale. The limitations of estimated permeabilities emphasize that porosimetry measurements of shale fabric are useful for estimating the access of material to all reaction sites, and do not just describe the effect of a few large pores that dominate permeability. Greater reaction extent in the laminated shales is associated with the accessibility of fluids to more pore space than in the massive shales.

Key Words—Illite/Smectite, Shale fabric, Mercury porosimetry.

INTRODUCTION

A previous study demonstrated the relationship between the extent of illite/smectite (I/S) diagenesis and shale fabric (Howard, 1987). Within a short interval of the lower Frio Formation of South Texas, I/S clays in laminated shales had a greater proportion of illite layers than I/S clays in the massive shale lithofacies. Classification of shale fabric was subjective and based primarily on the presence of fine-silt laminations. Silt-sized quartz was dispersed throughout the massive shale lithology, while in the laminated shales the silt was found in thin 0.1–1.0 mm thick laminae. These silt laminations were separated vertically by several millimeters, and formed both laterally continuous layers and discontinuous lenses.

For this interval in the Frio Formation it was proposed that the amount of available pore surface controlled the extent of the I/S reaction. In this context, pores are defined as the void space large enough to promote fluid flow, excluding the smaller interparticle and intraparticle voids less than 0.005 micrometers in diameter that do not contribute to fluid flow. It is important to distinguish between the available surface area of a pore and its total surface area. In this paper available pore surface area refers to the portion of the pore space that contributes to the fluid flow paths. It is expected that any measurement of available pore surface area would be less than the total surface area.

It was suggested that fluid conduits formed by the silt lenses in the laminated shales served to create a greater pore surface area/volume (SA/V) than found in the massive shales. This concept of silt laminations enhancing fluid flow in shales was illustrated by natural

gas production figures for Devonian shales where a positive correlation between rate of production and number of silt laminations was observed (Nuhfer *et al.*, 1979). Therefore, the connection between fluid permeability and pore surface area/volume in laminated shales suggested by Howard (1987) needs to be re-evaluated. For a normal distribution of pore sizes in a porous medium, an increase in SA/V should result in a decrease in permeability (Dullien, 1975). The question remains as to why the laminated shales of the Frio Formation, which might be presumed to have higher permeabilities, also have larger values of SA/V than the adjacent massive shales.

The purpose of this note is to assess further the relationship between shale fabric and degree of illitization in the light of quantitative measurements of pore surface area and pore volume.

METHODS

Preparation and analysis of the clay minerals is described in Howard (1987). For this study, expandability of mixed-layer I/S as a measure of diagenetic reaction extent was determined by X-ray powder diffraction peak positions (Srodoń, 1980, 1984). The terms used interchangeably to denote reaction extent for I/S clays include either the loss of expandable smectite layers or the increase of non-expandable illite layers.

The original 60-m section of core from a well in South Texas was stored for several years, exposed to fluctuations in room temperature and humidity. Drying occurred during this time, but there was no large-scale shrinkage or cracking of the core. Twenty horizontal

plugs 2.0 cm in diameter and 3.75 cm in length were cut from the core. A kerosene bath was employed as the large smectite component in these shales precluded the use of water as the cutting and saturating fluid. Samples were oven dried at a temperature of 80°C in order to remove as much interstitial water as possible without inducing severe desiccation effects. The sample plugs exhibited no shrinkage or cracking after this drying. Porosity and grain density were measured by standard buoyancy methods on the shale plugs saturated with Isopar-M[®], an isoparaffinic hydrocarbon. Isopar was useful in saturating smectite-rich rocks since it minimized swelling.

Attempts to measure bring permeability on the core plugs were not successful, since the lower limit for the procedure was 0.01 millidarcies. A simple physical model of nonintersecting capillary tubes, where the total cross sectional area is equal to the sample porosity, was used to calculate shale permeability. The Carman-Kozeny relationship used in the model for estimating permeability, k , is

$$k = C_k \frac{\phi^3}{(1 - \phi)^2 S^2} \quad (1)$$

where C_k is a shape factor equal to 0.2, ϕ is the porosity and S is the pore surface area-to-volume ratio (Wyllie and Splanger, 1952). Values for the porosity and surface area term were obtained from the core measurements.

Characterization of the pore space was done by mercury injection porosimetry. Porosimeters generate a pressure-volume intrusion curve of a non-wetting fluid as it is forced into the pore space. The size of pore invaded by the mercury is related to the pressure necessary to overcome capillary forces by the Washburn equation

$$P_c = \frac{-2\gamma \cos \theta}{r} \quad (2)$$

where P_c is the capillary pressure, γ is the surface tension of the non-wetting fluid (480 dyne/cm for mercury), θ is the contact angle between the wetting and non-wetting phases (140° for air/mercury) and r is the pore radius (Lowell and Shields, 1984). Porosimetry intrusion curves can be converted directly to pore size distributions by application of the Washburn equation (2). This transformation assumes that the porous medium is a bundle of nonintersecting tubes, which is clearly an unreasonable assumption for most sedimentary rocks. The transformation to pore sizes also is misleading because mercury intrusion is a percolation phenomenon, where the filling of a network of pores occurs as a sequential process (Lane *et al.*, 1986; Wall and Brown, 1981). In order for an interior pore to be filled, it must be connected to the outer surface by a

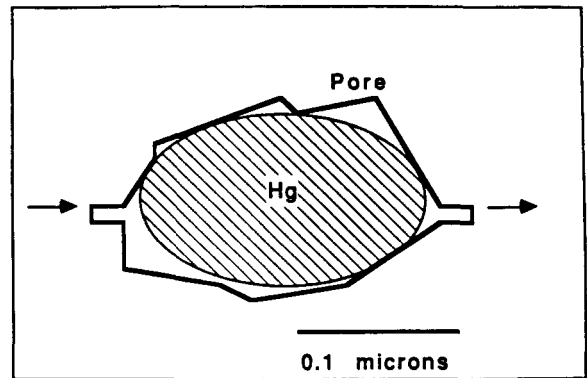


Figure 1. Pore space diagram illustrating the difference between effective and total pore volume. Insufficient pressure to force the high surface tension mercury into the smallest pores allows some of the pore volume to remain unfilled. Porosimetry measures the perimeter of the intruded mercury as surface area rather than actual pore surface.

series of already-filled pores. This simple physical model suggests that the intrusion measurement is influenced as much by pore throat diameters as by pore body diameters (Dullien, 1975; Larson and Morrow, 1981). Despite these concerns that absolute pore sizes are not measured, information obtained from porosimetry remains useful in characterizing relative pore space dimensions.

Intrusion data also contain information on the volume of pore space and its surface area. Surface area (SA) is determined from the PV work required to cover the pore surface with mercury (Lowell and Shields, 1984),

$$SA = \frac{1}{\gamma \cos \theta} \int_0^{V_{\max}} P \, dV. \quad (3)$$

This surface area value reflects the fraction of the pore space whose walls are wetted by mercury at a specified pressure and does not represent the total surface area of the pore space as would be measured by adsorption of gas molecules. This can be visualized as a smooth circle that inscribes a pore, but does not sense any nanometer-scale roughness on the pore wall (Figure 1).

Porosimetry curves were measured with a Quantachrome Autoscan 60 having a pressure range of 15 to 60,000 psi, corresponding to pore radii of 7.1 to 0.0018 micrometers. The instrument utilized a continuous pressure ramp, rather than discrete pressure jumps, to minimize pressure lags (Winslow, 1984). Large chips of shale, 5–10 mm diameter, were used to minimize low pressure intrusion due to surface irregularities and pores (Borst, 1982). The shale chips were oven dried to 110°C. The weight loss of the chips due to this heating was roughly 1.0% for both massive and laminated shales. There was no apparent shrinkage or cracking of the shale chips resulting from the heating. The filling

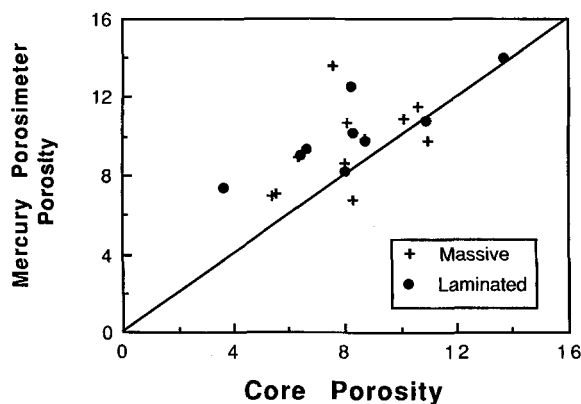


Figure 2. Porosity values for Frio shale samples as determined by standard buoyancy methods and the total intrusion volume of mercury. There is greater scatter for the massive (+) than for the laminated (●) samples. Line represents 1:1 for reference only.

procedure for the porosimeter included a second heating step under vacuum to complete the outgassing. The large sample size used to minimize surface intrusion effects had the adverse side effect of inhibiting total dehydration of the shale prior to the porosimetry measurement. In order to minimize compressive heating effects and to ensure complete intrusion, slow scan rates and instrument runs of about thirty minutes were used. Intrusion volume in the porosimeter was measured by very small capacitance changes as the height of mercury in the glass penetrometer changed. Between 300–400 data points were collected during each pressurization sequence. Porosity was determined from the weight-normalized volume of mercury intruded into the sample. It is expected that the porosity measured by mercury porosimetry would be less than the porosity measured by buoyancy methods because of the limited intrusion pressures employed. Volume distribution curves were calculated from the derivative, $dV/d(\log P)$.

RESULTS

The I/S clays vary from 96 to 50% of expandable layers. The eleven massive shale samples have I/S clays with a mean of 83% expandable layers. The I/S clays in the laminated shales average 61% expandable layers. The range of expandabilities in each shale lithofacies overlaps the other, but a *t*-test indicated that at 95% confidence the sample populations differed.

Porosity measured on Isopar-saturated plugs for the twenty shale samples chosen for this study ranges from 3.6 to 13.7% (Table 1). There is no clear relationship between shale fabric and porosity. The massive and laminated shales have mean porosities of 8.1 and 8.2%, respectively, though the range of porosity for the laminated shales included the suite minimum and maximum. Grain densities determined from Isopar satu-

Table 1. Laboratory results, Frio shale samples.

Sample	Lithologic fabric	% Exp	Porosity	SA (m ² /g)	SA/V (cm ⁻¹)
1	M	85	6.3	5.5	1.99
2	M	83	7.6	6.0	1.68
3	M	73	5.4	5.6	2.41
4	L	54	3.6	7.2	4.81
5	M	66	8.7	8.4	2.17
6	L	57	6.4	10.8	3.86
7	L	53	8.0	10.0	2.91
8	M	83	8.0	5.5	1.58
9	M	96	5.5	4.1	1.74
10	M	85	8.3	5.9	1.67
11	M	85	10.6	12.3	2.61
12	L	60	8.3	11.7	3.29
13	L	65	10.9	13.5	2.74
14	L	70	8.7	10.5	2.79
15	M	95	11.0	5.4	1.85
16	L	80	13.7	15.3	2.42
17	M	80	10.1	9.6	2.16
18	M	85	8.1	6.5	1.86
19	L	52	6.6	10.4	3.66
20	L	60	8.2	8.4	2.40

M = massive, L = laminated; % Exp = percentage of expandable layers in I/S clay; SA = surface area from mercury porosimetry, 15–60,000 psi; SA/V = surface area-to-volume ratio, $\times 10^6$.

ration vary from 2.35 to 2.58 g cm⁻³. These grain densities are significantly lower than expected values of 2.65 g cm⁻³ based on mineralogy, and are more in line with anticipated bulk densities of shales. The combination of low grain densities and porosity values determined from Isopar saturation suggests that not all the interlayer and interparticle water was removed by the initial 80°C drying procedure. A grain density of 2.4 g cm⁻³ is equivalent to one water layer associated with a 2:1 layer, low-Fe content clay, such as a Na-saturated smectite.

Porosity determined from the mercury intrusion volumes is slightly greater than the Isopar saturation values (Figure 2). The greater porosities obtained from mercury porosimetry were unexpected. Experience with a wide range of sandstones and carbonates indicates that all of the void space is not filled at the maximum intrusion pressure of 60,000 psi. This results in porosities that are several percent less than standard buoyancy measurements. The incomplete drying of these shale samples and the resultant lower porosities measured with Isopar saturation is the best explanation for the reversal of porosimetry and buoyancy method porosity results. The additional drying step before the porosimetry measurements also may have contributed to their higher porosity values.

The porosimetry curves for all the shale samples are similar, with a single inflection point between 4000 and 12,000 psi (Figure 3a). These inflection points correspond to throat diameters of 0.028 to 0.009 micrometers. Mean throat diameters varied between 0.03 and

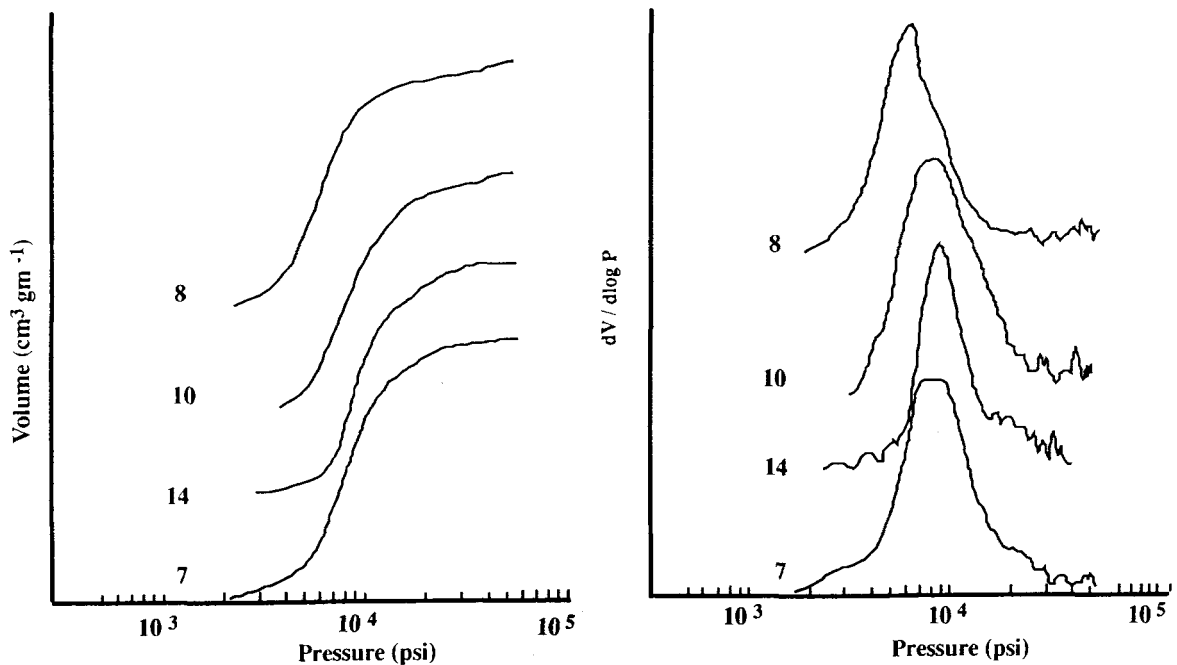


Figure 3. Mercury intrusion curves for shale samples with similar porosities of 8.0%. Samples 8 and 10 are massive shales while 14 and 7 are laminated shales. (A) Cumulative intrusion volume curves over the pressure range 300 to 60,000 psi. (B) Volume distribution curves [$dV/d(\log P)$] indicate unimodal distributions around 1000 psi.

0.009 micrometers. These values fall within the range of shale pore sizes observed in shales older than 50 m.y. and/or buried to greater than 1200 m (Borst, 1982). There was little if any low pressure (<1000 psi) intrusion, thus surface artifacts skewing the size distribution are minimal. There was also little intrusion beyond 20,000 psi, the cutoff for 0.005 micrometer diameter pores. The volume distribution curves are unimodal, with some variability in sharpness (Figure 3b). One third of the samples have broader volume distribution curves, and all but one came from the massive shale lithofacies. There is no correlation between mean throat diameter and the percentage of I/S expandable layers.

Surface area determined by mercury porosimetry between 15 and 60,000 psi varies between 4.0 and 15.0 $m^2 g^{-1}$. The massive shales have a mean surface area of 6.8 $m^2 g^{-1}$, while the laminated shales have a higher mean of 10.9 $m^2 g^{-1}$. The surface area measurement from mercury porosimetry represents a fraction of the pore surfaces rather than a summation of all the clay mineral surfaces (Sills *et al.*, 1973). Since the calculated surface area is the integral of PdV, and given equal porosity for each shale type, these surface area results indicate that the laminated facies contains a greater percentage of smaller (higher intrusion pressure) pores. It is interesting to note that the two shale fabric types do not have significantly different mean and median pore sizes. There is a poor correlation between mean throat size and the surface area even though it is ex-

pected that larger surface areas would be associated with smaller sized pores. This suggests that central tendency indicators such as mean pore size do not adequately describe the entire distribution.

Pore surface area-to-pore volume (SA/V) values were calculated using porosity and grain densities from Iso-par saturation, and the porosimetry surface area. The lower porosity values from the buoyancy method were chosen over the porosimetry values because of greater confidence in reproducibility. The SA/V results were shifted slightly with a bit more scatter when porosity results from porosimetry were used. The SA/V values for these shales range from 1.5 to 4.8 $\times 10^6 cm^{-1}$ (Table 1). The massive shales have a mean SA/V of 1.97 $\times 10^6 cm^{-1}$ while the mean SA/V for the laminated shales is 3.21 $\times 10^6 cm^{-1}$. A statistical t-test indicates that the two populations are significantly different.

Permeabilities estimated from the Carman-Kozeny relationship range between 0.04 and 11.8 nanodarcies. The permeabilities for the laminated shales include the largest and smallest values. The distribution of calculated values does not follow the pattern observed in Devonian gas shales where laminated shales have larger permeabilities than massive shales. The mean estimated permeability for the laminated shales is 2.66 nanodarcies compared to 4.04 nanodarcies for the massive shales. There is little correlation with the I/S reaction extent and the estimated shale permeability, though those samples with a lower percentage of ex-

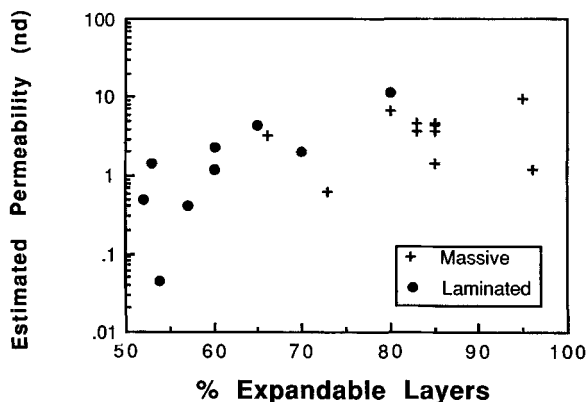


Figure 4. Estimated shale permeability in nanodarcies based upon a Carman-Kozeny relationship and illite/smectite reaction extent as measured by the percentage of expandable layers. (+) Massive, (●) laminated.

pandable layers have lower calculated permeabilities (Figure 4).

The key point of these results is the relationship between the pore surface area/pore volume of the shale samples and the extent of I/S diagenesis (Figure 5). Reaction extent, as determined by the decrease in I/S expandable layers, is strongly correlated with the experimentally measured SA/V. The laminated shales contain I/S clays with a greater proportion of nonexpandable illite layers. The laminated shales also have higher surface areas than the massive shales. This is reflected in the higher SA/V values.

DISCUSSION

On first thought, reaction extent for clay diagenesis should be positively correlated with shale permeability. Higher flow rates are shown to enhance reaction rates towards stable mineral assemblages in laboratory and natural hydrothermal deposits (Dibble and Tiller, 1981). Qualitative relationships between flow rates and clay authigenesis in sandstones are also observed in some geological settings (Whitney and Northrop, 1987; Ramseyer and Boles, 1986). Since there are no direct permeability measurements for the Frio shales, this anticipated correlation cannot be tested.

Permeability estimates, however, do not support this model. Estimated permeabilities for these Frio shales range from 0.04 to 11.8 nanodarcies. While the trend is hardly conclusive, the lower permeability samples correspond to those with less expandable I/S clays (Figure 4). This pattern contradicts the idea that reaction extent in shales is associated with higher flow rates. It must be remembered that these permeability values are only estimates based on a very simple physical model of capillary tubes. While the overall estimated values are reasonable for shales, the variations in permeability among the different shale samples may fall

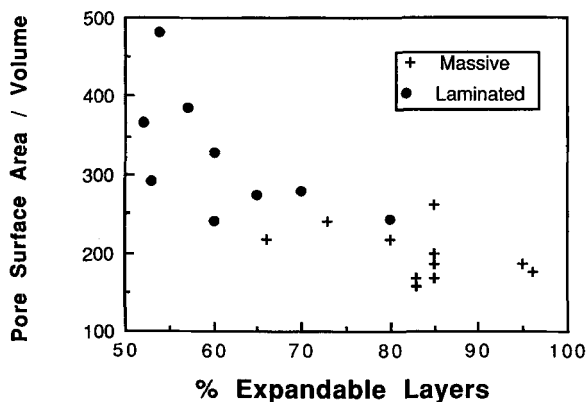


Figure 5. Illite/smectite reaction extent, as measured by the percentage of expandable layers, is controlled by the surface area-to-volume ratio of the shale samples. The laminated (●) shales have a wider range of SA/V at lower percentages of expandable layers than the massive shales (+).

within the porosity and surface area measurement error. The purpose of estimating shale permeability was to (1) demonstrate that the association of I/S reaction extent and shale fabric may not be related to the presence of silt laminations that act as fluid conduits increasing permeability, and (2) that other factors pertaining to shale fabric may be more important.

The interpretation of mercury porosimetry results is not a simple and straightforward process. Given that the mean pore size of each distribution is the same, then the increased SA/V found in the laminated shales suggests a greater proportion of smaller pores. This could manifest itself as broader or skewed pore-size distributions. Such interpretations of measured porosimetry curves are obscured by the percolation nature of porosimetry measurements.

Recent work on pore size distributions in shales using proton Nuclear Magnetic Resonance (NMR) relaxation curves is inconclusive in determining whether laminated shales have broader or skewed distributions (Howard, unpublished). Pore size information from NMR is obtained from rates of proton relaxation enhanced by available surface area. The NMR results do indicate that room-dried samples contain roughly 5% fluid-filled porosity not associated with interlayer water. This water is removed upon drying at 110°C. Mean pore size determined from NMR relaxation results for these samples is approximately 0.1 micrometers, approximately an order of magnitude greater than the porosimetry-derived values.

The determination of I/S reaction extent in this study was based on the stacking model of smectite and illite 2:1 layers into MacEwan crystallites, where the proportion of each layer type in the stack was determined by X-ray powder diffraction methods. An alternative method of assessing I/S reaction extent is based on measurements of illite particle thickness (Eberl and

Środoń, 1988). Measurements of particle thickness in clays found in North Sea shales determined that illite particle morphology was dependent upon pore size, where more euhedral illite laths were found in larger pores (Glasmann *et al.*, 1989). The implication from the North Sea results for the Frio samples is that shales with larger pores should contain more developed laths, therefore more illitic I/S assemblages than shales with smaller pores.

The pore dimension measurements on the Frio samples indicate that the North Sea model is not applicable to these samples. Mean pore size as measured by mercury porosimetry varies little for the Frio shales, despite the wide range of I/S expandabilities. Since SA/V is the inverse of the hydraulic radius of the pore, the trend of pore surface area/volume with percent expandability (Figure 5) is opposite that observed in the North Sea study. Based on the hydraulic radius estimates, the Frio shales with smaller pores have more illite components in the I/S clays than the shales with larger pores.

A key difference between the Frio shales and the North Sea shales is that diagenesis in the latter was characterized as a "hydrothermal event," with the introduction of warm, reactive fluids before compaction. In contrast, Gulf Coast diagenesis is compaction-dominated, where illite crystallite growth occurs in micropores resulting in anhedral morphologies (Glasmann *et al.*, 1989).

It is important to remember that the measurements of pore surface area were made on consolidated oven-dried shale, rather than on finely crushed powders, as is done with standard gas adsorption techniques. The porosimetry method measures the accessible surface area of the pore space instead of the total external surface area of the clay minerals. The concern that all of the porosimetry results are artifacts of the drying procedures used in sample preparation is very real. However, the absence of significant weight loss, or shrinkage of the samples during sample preparation, suggests that any artifacts in the pore geometry were not introduced by the measurements.

It is reasonable to expect that reaction extent in I/S clays should be directly related to permeability. The apparent contradiction between I/S expandability and SA/V for the various Frio shales is explained as follows: Permeability (as calculated in various simple physical models) is controlled by the presence of a few large pores with corresponding small SA/V values (Dullien, 1975). One way of interpreting the results of the SA/V measurements for these shales is to recognize that the presence of a greater number of small pores in the laminated shales results in more access to clay sites for illitization. Porosimetry measurements of shale fabric are more relevant to the access of material to all reaction sites, rather than to the effect of only a few large pores. More complete absolute pore size distributions

in shales are required to further the connection between fluid flow rates and I/S reaction extent.

The importance of distinguishing the scale at which porosimetry samples the pore volume is illustrated in the difference between total and pore surface area. Total surface area measured by gas adsorption methods on powdered samples is often included in geochemical rate expressions as the availability of reactive species to reaction sites (Steeffel and Lasaga, 1990). Surface area determined on intact core plugs by mercury porosimetry, or even gas adsorption methods, is less than total surface area. The presence of the pore network restricts access to only those reactive sites that are on the surface of pores. Porosimetry results from intact pore networks yield better estimates of the availability of reactive sites to fluid flow and should be incorporated into evaluation of kinetic expressions for I/S diagenesis.

CONCLUSIONS

Laminated shales contrast with massive shales in the Frio Formation. The laminated shales are composed of a more illitic I/S clay, reflecting greater reaction extent under the same temperature and pressure conditions. The porosities of these two shale lithologies are the same, while permeabilities are too low to be measured. Mercury porosimetry measurements of these shales indicate that pore or throat sizes are the same in the two shale types, but that the laminated shales have significantly higher pore surface areas. Therefore, the normalized SA/V values for the laminated shales are greater than those measured in the massive shales. Based on physical models it is expected that greater reaction extent occurs in shales with higher permeability. This is contradicted by permeabilities calculated using the SA/V values; smaller permeabilities and smaller pore sizes are predicted for the laminated shales. Since the laminated and massive shales have equal mean pore sizes, it is proposed that the larger SA/V found in the laminated shales is associated with a greater proportion of smaller pores than found in the massive shales. Greater reaction extent in the laminated shales is therefore associated with accessibility of the fluid to more clay sites lining the smaller pores. For slow reactions that occur over periods of geologic time, the absolute permeability becomes less important in determining shale reactivity than the ability of the fluids to reach as many reactive sites as possible.

Porosimetry is a dynamic measurement technique that responds to the shale fabric in a network of pores and throats. Crushed and powdered samples do not represent the actual pore network, and therefore the surface area of powdered samples is a poor measure of the accessibility of fluids to clay mineral reaction sites in consolidated shales. Porosimetry is the preferred method to use when evaluating the effect that rock texture has on diagenesis.

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