Self-sealing in sedimentary basins

David Deming, Constantin Cranganu,1 and Youngmin Lee2
School of Geology and Geophysics, University of Oklahoma, Norman, Oklahoma, USA

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[1] Over the last decade, the picture that has emerged from several geologic disciplines is that the Earth’s crust is permeable to great depths and that fluids are more or less constantly moving, transporting both heat and mass and affecting virtually every geologic process. In contrast, workers in the petroleum industry have maintained that sections of the crust contain impermeable pressure seals and hydraulically sealed compartments. We show that these starkly different conceptions can be reconciled by a theory of self-sealing through gas generation in sedimentary basins. The model especially applies to older sedimentary basins where overpressuring cannot be readily explained as the result of ongoing sedimentation and compaction disequilibrium. In our conceptual model, overpressuring is created by catagenic gas generation and maintained by a combination of vertical and horizontal gas capillary seals. Data from the Anadarko Basin in Oklahoma provide support for the self-sealing hypothesis. Well logs reveal the presence of 9 or 10 gas-water interfaces over a 30-m overpressured interval. Capillary pressure measurements show that the force necessary for gas to displace water from a shale is ~3 × 106 Pa, a pressure equivalent to that exerted by a column of water 300 m high. A theory of self-sealing explains the anomalous overpressuring observed in some older sedimentary basins by invoking known mechanisms and forces; it is both parsimonious and falsifiable.

INDEX TERMS: 5114 Physical Properties of Rocks: Permeability and porosity; 9350 Information Related to Geographic Region: North America; 1829 Hydrology: Groundwater hydrology; KEYWORDS: permeability, capillary, gas, Anadarko, pressure seal, overpressure


1. Static and Dynamic Schools

[2] Over the last 10 to 15 years, two distinctly different conceptions of fluids in the Earth’s crust have emerged from separate disciplines. Bredehoeft et al. [1994] have suggested these be called the static and dynamic schools. The founders of the dynamic school were hydrogeologists engaged in discovering, exploiting, and managing groundwater found in highly permeable near-surface aquifers. In 1885, one of the patriarchs of the dynamic school, Chamberlin [1885, p. 137] wrote that “no stratum is entirely impervious”. Although it is understood that there are exceptional materials such as permafrost and salt, the working paradigm of the dynamic school is that fluids flow freely through a permeable crust. In recent years, the dynamic school has been bolstered by several new results. Tests conducted by the German Continental Deep Drilling Program [Huenges et al., 1997] found a permeability of 10−12 m2 at a remarkable depth of 9100 m. Analysis of geothermal data and metamorphic systems indicates an average permeability for the entire lower continental crust of ~10−18 m2 [Ingebritsen and Manning, 1999]. In the oceanic crust, high permeability (10−10 to 10−14 m2) in the upper 500 m facilitates hydrothermal fluid circulation, a profoundly important process that influences the physical, chemical, and biological state of both the solid Earth and oceans [Fisher, 1998; Fisher and Becker, 2000]. Overall, the picture that has emerged over the last decade or so is that the Earth’s crust is a dynamic environment in which fluids are more or less constantly moving, mobilizing, and transporting both heat and mass, altering the geologic and geophysical properties of crustal rocks, and affecting virtually every geologic process. We appear ready to throw out our conception of the crust as an unchanging mass of solid rock and embrace a paradigm wherein the crust is a two-phase medium in a continual process of evolutionary change brought about by fluid-rock interactions [Deming, 1994, 2001].

[3] While the dynamic school has found wide acceptance amongst scientific and academic circles, an entirely different paradigm has been forged by those employed in the petroleum industry [Bradley, 1975; Hunt, 1990; Bradley and Powley, 1994; Cathles, 2001]. The static school has emerged from the experiences of those whose task is to locate and exploit static accumulations of hydrocarbons. The primary tenet of the static school is that there are
anomalously pressured areas in sedimentary basins where flow is prevented by impermeable layers termed pressure seals. A pressure seal was defined by Hunt [1990, p. 2] as a zone of rocks capable of hydraulic sealing, that is, preventing the flow of oil, gas, and water. The term does not refer to capillary seals; the term refers to seals that prevent essentially all pore fluid movement over substantial intervals of geologic time.

Subsequently, the term has often been used in a degraded sense to refer to low-permeability layers which restrict flow; these are more properly referred to as aquitards. The above quote shows clearly that the original intention of the static school architects was to define a pressure seal as a layer of zero permeability. Perhaps the most incredible assertion of the static school is that pressure seals combine to form three-dimensional pressure compartments that are visualized literally as bottles within the crust. Powley [1990] used the term “buried bottle model” to describe these compartments.

In the view of the dynamic school, the claims of the static school seem quite improbable. No one has ever obtained and tested an actual sample of a pressure seal, and the idea of areas in sedimentary basins analogous to sealed bottles is quite fantastic. The concepts of the static school have been criticized as retrogressive, and the resistance of its advocates as “conceptual inertia” [Toth et al., 1991]. Nevertheless, the entire history of science is one of improbable empiricisms triumphing over impeccably crafted and reasoned theories.

2. Anadarko Basin

Many sedimentary basins contain abnormal fluid pressures, most commonly these are above hydrostatic and are referred to as overpressures. The dynamic explanation for the presence of overpressures is a transient imbalance between pressure dissipation and an ongoing geologic process such as sedimentation or hydrocarbon generation [Neuzil, 1995]. Hydrodynamic models appear to work very well for young, actively subsiding basins such as the Gulf Coast Basin of the southeastern United States, where the rapid accumulation of thick sequences of low-permeability shales has resulted in compaction disequilibrium [Bredehoeft and Hanshaw, 1968; Bethke, 1986]. Hydrodynamic models have been less successful in explaining the existence of overpressures in older basins that have not undergone subsidence for tens or hundreds of millions of years. One of these older basins is the Anadarko Basin (Figure 1).

The Anadarko is the deepest sedimentary basin on the North American craton; total sediment thickness in the deepest section exceeds 12 km and consists of sandstone, limestone, and shale of Cambrian to Permian age. The basin originally formed as a rift or aulacogen in late Proterozoic and early Cambrian time. Gilbert [1992] compared the Anadarko Basin in early Paleozoic time to the present-day Michigan and Illinois basins. In the Pennsylvanian, a plate collision to the south gave rise to the Wichita Mountains. Enormous quantities of sediment were shed into the Anadarko depression, and it became a foreland basin. By about 280 Ma, the period of rapid sedimentation had ended. There was some Mesozoic sedimentation that is difficult to reconstruct, followed by 1 to 3 km of Cenozoic erosion [Lee and Deming, 2002].

The Anadarko Basin today contains extensive areas of overpressuring (Figure 2) [Hunt, 1990; Jorgensen, 1993; Al-Shaieb et al., 1992, 1994a, 1994b]. Al-Shaieb et al. [1992, 1994a, 1994b] stated that fluid pressures exceeding hydrostatic generally start at ~2.3 to 3.0 km depth, but return to near-hydrostatic below the Woodford Shale. Within the overpressured area of the Anadarko Basin (Figure 1) high fluid pressures are not ubiquitous, but confined to distinct zones termed compartments. Al-Shaieb et al. [1992, 1994a, 1994b] termed the entire volume occupied by pressured compartments a “megacompartment complex.” Cathles [2001, p. 562] described the Anadarko as possessing “a complex honeycomb structure of overpressuring”.

In our previous work, we evaluated two hypotheses concerning the origin and dissipation of overpressures in the Anadarko Basin [Lee and Deming, 2002]. The first possi-
bility we considered was that present-day overpressures in the Anadarko Basin were a remnant of Paleozoic compaction disequilibrium preserved for 250 Myr. For this possibility to be consistent with the physics of diffusive processes, we found that a pressure seal 100 m thick would be required to have a permeability lower than $10^{-25}$ m$^2$. This permeability is many orders of magnitude lower than the lowest rock permeabilities ever measured; the result is essentially equivalent to requiring zero permeability over 250 Myr.

It is also difficult to explain the existence of overpressures in the Anadarko Basin with a dynamic hypothesis that postulates a balance between pressure generation and leakage. Although there are innumerable theoretical mechanisms for changing fluid pressures in sedimentary basins, in the Anadarko Basin gas generation is by far the most feasible possibility. For example, Neuzil's [1995] review of pressurizing mechanisms concluded that the strongest mechanism for overpressuring in a setting similar to the Anadarko Basin was the generation of liquid petroleum from a solid precursor. Gas generation from either a solid or a liquid can be an even more robust source of overpressuring due to the greater density contrasts involved [Barker, 1990; Osborne and Swarbrick, 1997]. The Anadarko Basin is rich in catagenic gas; in 1980, the ultimate recovery of natural gas from the Anadarko Basin was estimated to be $3.1 \times 10^{12}$ m$^3$ [Rice et al., 1989], an amount approximately equivalent to four times the year 2000 production of natural gas from all of North America. The Anadarko Basin is also believed to be the source of gas found in the nearby Panhandle-Hugoton field, the largest gas field in North America.

Although gas generation is the likely source for the overpressuring observed in the Anadarko Basin today, apatite fission track data indicate unambiguously that the Anadarko Basin was uplifted and cooled starting $\sim 40$–50 Myr ago. The amount of uplift was in the range of 1 to 3 km, and resulted in a minimum cooling of 20°C. This cooling shut down gas generation. As a result, the containment of overpressures in the Anadarko Basin by layers thinner than $\sim 100$ m requires permeabilities lower than $10^{-25}$ m$^2$ [Lee and Deming, 2002]. This is 2 orders of magnitude lower than the lowest shale permeabilities ever measured or inferred [Neuzil, 1994].

Figure 2. Fluid pressure in the Anadarko Basin estimated from (a) mud weights and (b) wellhead shut-in pressures (WHSIPs). Mud weights generally yield maximum estimates of true fluid pressures, while WHSIPs are minimum estimates of fluid pressures. WHSIPs are frequently lower than virgin fluid pressures due to petroleum production. (c) Fluid pressure trends estimated from mud weights and WHSIPs plotted along with fluid pressure in the Bertha Rogers well estimated from mud weights [from Lee and Deming, 2002](AAPG©2002, reprinted by permission of the AAPG whose permission is required for further use.).
Although there are some uncertainties in the results obtained by Lee and Deming [2002], as there must be when attempting to understand any geologic system, the primary conclusion appears to be robust: overpressures in the Anadarko Basin cannot be explained with conventional hydrodynamic models; true aquicludes are required.

3. Gas Capillary Seals

We now suggest that the pressure seals which apparently must be present in the Anadarko Basin are due to capillary forces acting at gas-water interfaces between coarse- and fine-grained clastic rocks. The idea of gas capillary seals is not new, having originated in studies of the unsaturated zone [Ross, 1990]. Consider the case of a fine-grained, low-permeability soil overlying a coarse, high-permeability gravel. If the soil is wetted, a most curious result is obtained. Instead of water flowing preferentially into the high-permeability gravel, the gravel acts as a barrier to flow. Water is retained in the soil pores by capillary forces. Unless the capillary displacement pressure is overcome, the boundary between the fine- and coarse-grained sediment acts as a layer of zero permeability. The concept of gas capillary seals was later applied to sedimentary basins by Larry Cathles and his coworkers at Cornell [Revil et al., 1998; Cathles, 2001]. Sealing by gas capillary forces may also be implied in the “vapor lock” mechanism suggested by Benzing and Shook [1996].

To detect gas capillary seals, we examined 100 logs from oil and gas wells in the deep Anadarko Basin in Roger Mills county, Oklahoma, an area known to be overpressured (Z. Al-Shaieb, personal communication, 2000). In about half of these 100 wells, we identified multiple thin layers of gas. Figure 3 shows typical well logs from one of these wells where gas has preferentially invaded the sandy layers, leaving the shales water-saturated. Over a distance of ~30 m, 9 or 10 gas-saturated layers are identified by the crossover of the density and neutron porosity logs. Neutron porosity logs measure hydrogen ion concentration. Because the concentration of hydrogen in gas is lower than in water, the presence of gas causes the neutron-porosity log to indicate lower porosity. In contrast, the presence of low-density gas causes the density-porosity log to indicate a higher porosity. Thus when gas is present a plot of density porosity minus neutron porosity is positive (Figure 3).

We are aware that these logs are proxy indicators, and crossovers may be created by artifacts in some instances. We were careful to rule out all the alternative interpretations known to us. For example, in sections of a borehole where the diameter increases (“washed out zones”), crossovers will be created by the presence of drilling fluid. However, the caliper log indicates no cavernous zones are present in this instance. The photoelectric log and the gamma ray log indicate that the zones which appear to be gas-saturated are the sandy layers in a clastic sequence of alternating layers of fine and coarser grained sediments. Finally, we have been informed by the drilling company that this is a productive gas zone (Apache Oil Corporation, personal communication, 2000).

The efficacy of the capillary-sealing mechanism can be demonstrated through a simple calculation. The capillary pressure drop ($\Delta P$, kg m$^{-1}$ s$^{-2}$) across a gas-water interface is

$$\Delta P = 2 \left( \frac{1}{r} - \frac{1}{r_c} \right),$$

where $\gamma$ (kg s$^{-2}$) is the interfacial tension between gas and water, $r$ (m) is the pore throat radius of the fine-grained layer, and $r_c$ (m) is the pore throat radius of the coarse-grained layer [Revil et al., 1998]. In the case of alternating layers of sandstones and shales, the sandstone pores are usually larger by at least a factor of 10. Therefore we can approximate

$$\Delta P = 2/r.$$

To estimate the pore throat radius ($r$) of shales in the Anadarko Basin, we made mercury injection measurements
interfacial tension (γ) of a gas-water interface at in situ conditions is 2.5 × 10^{-8} m. The interfacial tension (γ) for a gas-water interface at in situ conditions is 2.5 × 10^{-8} (±20%) kg s^{-2} [Schowalter, 1979]. Thus the pressure drop (∆P) across each gas-water interface could be as great as

\[ ∆P = 3 \times 10^{6} \text{Pa}. \]  

Figure 4. Mercury pressure versus relative mercury saturation for a Pennsylvanian age shale from the Switzer C-5-1 well in the Anadarko Basin (see Table 1). The initial increase in pressure associated with saturations below ~40% is due to surface effects. The pore throat radius is estimated by extrapolating the plateau of the curve to the zero percent saturation and noting the associated pressure; in this example, 69 MPa. See Appendix A for detailed description of the methodology.

Table 1. Capillary Pressures (Pc) and Pore Throat Radii for Shale Samples From the Anadarko Basin

<table>
<thead>
<tr>
<th>Sample Age</th>
<th>Location T-R-S</th>
<th>Well Name</th>
<th>Depth, m</th>
<th>Pc, 10^6 Pa</th>
<th>Pore Throat Radius, 10^{-8} m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pennsylvanian/Morrowan</td>
<td>11N–14W-2</td>
<td>Dickerson 1–2</td>
<td>4775</td>
<td>24.1</td>
<td>31</td>
</tr>
<tr>
<td>Pennsylvanian</td>
<td>12N–23W-14</td>
<td>Taylor 1</td>
<td>3136</td>
<td>69.0</td>
<td>11</td>
</tr>
<tr>
<td>Pennsylvanian/Virgilian</td>
<td>11N–23W-30</td>
<td>Barnett 2–3</td>
<td>2749</td>
<td>49.7</td>
<td>15</td>
</tr>
<tr>
<td>Pennsylvanian/Virgilian</td>
<td>15N–25W-08</td>
<td>Males 3–8</td>
<td>2633</td>
<td>41.4</td>
<td>18</td>
</tr>
<tr>
<td>Pennsylvanian/Missourian</td>
<td>11N–20W-11</td>
<td>Marik 1–11</td>
<td>3260</td>
<td>70.3</td>
<td>11</td>
</tr>
<tr>
<td>Pennsylvanian/Desmoinesian</td>
<td>11N–19W-7</td>
<td>Toele 1</td>
<td>4121</td>
<td>60.0</td>
<td>12</td>
</tr>
<tr>
<td>Pennsylvanian/Missourian</td>
<td>4N–7W-2</td>
<td>W.M. White 1</td>
<td>2933</td>
<td>62.1</td>
<td>12</td>
</tr>
<tr>
<td>Pennsylvanian/Desmoinesian</td>
<td>15N–21W-5</td>
<td>Switzer C-5-1</td>
<td>3480</td>
<td>69.0</td>
<td>11</td>
</tr>
<tr>
<td>Pennsylvanian/Desmoinesian</td>
<td>6N–10W-26</td>
<td>Apache 1–26</td>
<td>2344</td>
<td>62.0</td>
<td>12</td>
</tr>
<tr>
<td>Pennsylvanian/Desmoinesian</td>
<td>9N–19W-5</td>
<td>Walter-Steffes 1–5</td>
<td>4158</td>
<td>70.3</td>
<td>11</td>
</tr>
<tr>
<td>Pennsylvanian/Morrowan</td>
<td>8N–10W-13</td>
<td>Riddle Bradford 1</td>
<td>4824</td>
<td>27.5</td>
<td>27</td>
</tr>
</tbody>
</table>

If the shales are not hydraulically connected in three dimensions, the capillary pressure drops across individual interfaces are additive [Shosa and Cathles, 2001]. In this example, where we have 9 or 10 gas-saturated sands interlayered with water-saturated shales, we have 18 or 20 total interfaces for a maximum possible pressure change of 54–60 × 10^{6} Pa. The magnitude of the maximum overpressuring (above hydrostatic) observed in the Anadarko Basin is ~50 × 10^{6} Pa [Lee and Deming, 2002]. Thus gas capillary sealing is potentially able to contain overpressures of the magnitude observed in this setting.

[16] The efficiency of capillary sealing largely originates in the fact that pressure changes across layered interfaces are additive; this result is not necessarily intuitive or expected, but it was substantiated in laboratory experiments by Shosa and Cathles [2001] and can be explained theoretically. Consider two simple conceptual models (Figure 5). In the first model (Figure 5a), pores are either completely water- or gas-saturated. Initially, the system contains mostly water, but the water is displaced as higher-pressured gas enters the larger pores in the coarse-grained rock (sandstone). For the gas to invade the fine-grained rock (shale), the capillary entry pressure must be exceeded. Once gas displaces water from the first small pore throat, it will flood the entire system. The total sealing capacity of the layered sequence is equal to the capillary pressure of the smaller pores; capillary pressures are not additive across layered sequences. A second model (Figure 5b), first suggested by Cathles [2001], explains how the capillary pressure drops across a layered sequence of coarse- and fine-grained rocks can be additive. In the Cathles model (Figure 5b), the coarse-grained pores each contain a mixture of gas and water. In a gas-rich sedimentary basin like the Anadarko, water near the sites of gas generation is likely to be gas-saturated. As pressure and temperature drop from basin uplift and erosion, gas comes out of solution. Gas is forced out of small-diameter shale pores by capillary pressures, and accumulates at pore entrances. If there is a gas bubble near the entrance of each pore, then for water to move through the system, water must be displaced simultaneously from all of the pores. Capillary forces exist because there is an attractive force between pore walls and water; to displace water simultaneously from all of the pores requires a total force that is equal to the sum of the forces necessary to displace water from each individual pore. Thus the total pressure required is equal to the sum of the capillary pressures inherent in each pore.

4. Difficulties of the Static Concept as it Now Exists

[17] The existence of overpressures that cannot reasonably be explained as resulting from a hydrodynamic process
implies that the primary tenets of the static school [e.g., Bradley, 1975; Hunt, 1990; Ortoleva, 1994] are correct. That is, there exist in some sedimentary basins pressure seals that function as layers of zero permeability over geologic time, and these seals can be spatially distributed in such a way as to create pressure compartmentalization on a variety of physical scales. Although there is a broad empirical basis for these concepts, they have not found wide acceptance outside of the petroleum industry. Before we finally assemble our observations and ideas into a new theory that is internally consistent, let us review what we believe are the shortcomings of static ideas as they are currently postulated.

The existence of overpressuring in settings such as the Anadarko Basin requires three factors. There must be a mechanism to initially generate the overpressures, horizontal and vertical barriers to seal the pressure compartments in three dimensions, and some means of maintaining the seals over geologic time. The response of the static school to these requirements has largely been to invoke explanations that are fragmented, disjointed, and arbitrary [Bradley, 1975; Hunt, 1990; Bradley and Powley, 1994]. The ideas are not intuitively satisfying, and have not resulted in a simplification that reveals an underlying order in nature. No explanation for the creation of overpressures is usually proffered; more importantly, the cause of the overpressuring has not been linked with the sealing in a coherent and internally consistent manner. An especially difficult problem is to explain sealing in all three dimensions. Horizontal seals are supposed to result from mineral precipitation, vertical seals from faults or facies changes. Although either of these mechanisms is possible in some circumstances, the proposals are essentially invoked ad hoc as logical necessities, not as logical consequences of a unified theory. Finally, it seems improbable that seals created by processes such as mineralization could be maintained through geologic time without being breached by faulting.

5. Self-Sealing in Sedimentary Basins

The data presented above illustrate how it is theoretically possible for horizontally oriented pressure seals to be formed by gas capillary forces at interfaces between coarse- and fine-grained sedimentary rocks. It remains for us to show how vertical seals can be formed, tie in the seal formation with the mechanism which created the overpressures in a coherent fashion, and finally show how seal integrity can be maintained over geologic time.

We propose a conceptual model (Figure 6) wherein some sedimentary basins go through a process of self-sealing as a normal part of their life cycle. The key element is the presence of gas; nor is this requirement necessarily
onerous. Davis [1984, p. 189], noted that many sedimentary basins are saturated with gas and that these basins are “never normally pressured.”

[21] When catagenic conditions in a basin are propitious for the formation of gas, overpressures can be generated by the volume change from solid kerogen (or liquid oil) to gas. In low-permeability shales, gas generation is likely to lead to fracturing if pressures cannot diffuse quickly enough through the relatively low matrix permeability. In the case of the Anadarko Basin, these conditions may have been fulfilled during its foreland basin phase in Pennsylvanian time, when organic-rich shales were rapidly buried [Gilbert, 1992]. When fracturing occurs, the orientation of the fracture planes will be parallel to the maximum principal stress, which is vertical. Meissner [1984] documented how the Bakken Shale in the Williston Basin has undergone fracturing induced by oil generation to such an extent that the unit in many places is able to function as a reservoir rock. Gas generation is potentially an even more efficacious mechanism for hydrofracturing, because the volume change from solid kerogen to gas is significantly larger than the volume change from solid kerogen to liquid oil.

[22] As migrating gas enters vertically oriented fractures, it follows the path of least resistance and is driven outward and upward by a combination of catagenic overpressuring and buoyancy forces. When higher-permeability sandstones are intercepted by fractures, the invading gas partially or completely displaces pore fluids as it flows through the high-permeability avenue offered by the sandstone. We are left with a complex system of horizontally oriented gas-saturated sandstones and vertically oriented gas-filled fractures; each acts a capillary barrier to the surrounding water-saturated shale (Figure 6). These horizontal and vertical capillary barriers may seal in overpressures on a variety of physical scales, leading to the compartmentalization observed in sedimentary basins such as the Anadarko.

[23] A sedimentary basin inevitably enters a phase of uplift and cooling, and gas generation subsides. During the long cooling phase, the integrity of the capillary seals is maintained by the fact that the solubility of methane decreases with decreasing temperature and pressure [Price, 1979; Hanor, 1980]. Thus the gas which fills fractures does not tend to diffuse slowly back into the country rock. If anything, the uplift phase promotes the slow dissolution of methane into, rather than out of, pore spaces and fractures. The integrity of the capillary seals is thus maintained over geologic time.

[24] Although this model does not necessarily apply to every sedimentary basin, it appears to be consistent with the geology of the Anadarko Basin, where compartmentalization in Pennsylvanian age rocks is promoted by the presence of lobate bodies and discontinuous lenses of Pennsylvanian sandstones surrounded by shale. This sedimentary architecture arises from the fluvial and fluvial-dominated deltaic environments in which many of these rocks formed [Northcutt and Johnson, 1996].

6. Conclusions

[25] The model we propose to explain the observations of anomalous pressures in some sedimentary basins is simple, and elegantly explains the observations by invoking a single physical mechanism (gas generation). Gas simultaneously provides both the overpressures and the seals. There is nothing hypothetical about the nature of gas capillary forces, they have been measured in the laboratory. The model makes two specific predictions which can be tested. The first is that anomalous pressures are associated with the presence of gas. The second is that ambient fluid (or gas) pressures should undergo rapid changes across capillary barriers. If accurate high-resolution pressure measurements could be made across gas-water interfaces in virgin territory, the model we propose could be tested.

Appendix A. Pore Throat Size Measurements

[26] Pore throat size can be estimated by the use of capillary pressure curves derived from mercury injection
porosimetry (MIP). The MIP data are obtained by forcing mercury at pressures up to 206,850 kPa (30,000 psia) into small voids and pore throats within the rock sample. Pore throats control the access to larger voids (pores) because greater pressures are required to force mercury, or other nonwetting fluid, into smaller spaces [Purcell, 1949; Keighin, 1997]. Thus pore throats are bottlenecks in the system, and it is necessary to exceed their critical capillary pressure in order to inject mercury into pores. Mercury injection pressure is increased in a stepwise manner and time for equilibration between pressure increments is allowed. The step pressure is plotted against the mercury saturation (Figure 4). The parameter derived from MIP curves (Figure 4) is the displacement pressure ($P_d$), which is the pressure required to begin saturating the rock sample with the nonwetting phase (mercury). $P_d$ is obtained extending the slope of the plateau to zero percent mercury saturation [Krushin, 1997]. The pore throat size is calculated using the Washburn equation [Washburn, 1921], modified by Schowalter [1979] [see Krushin, 1997]:

$$r = \frac{2\gamma \cos \theta}{P_c}, \quad (A1)$$

where $r$ is the pore throat radius, $\gamma$ is the interfacial tension of the mercury-air system (0.485 N m$^{-1}$); $\theta$ is the air-mercury-solid contact angle (140$^\circ$); and $P_c$ is the pressure necessary for mercury to displace air. Table 1 shows the mercury displacement pressure converted to pore throat size for 11 shale samples from the Anadarko Basin using a standard contact angle of 140$^\circ$ and an interfacial tension of 0.485 N m$^{-1}$ [Vavra et al., 1992].

Using the technique described above, pressure displacements were measured on eleven shale samples cut from cores (Figure 4 and Table 1), and then pore throat size was calculated using equation (A1). The samples were oven-dried and unjacketed. They were all Pennsylvanian age shales (Desmoinesian through Virgilian) from the Anadarko Basin. Their depths range between 2749 and 4824 m.

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D. Deming, School of Geology and Geophysics, University of Oklahoma, 810 Sarkeys Energy Center, 100 East Boyd Street, Norman, OK 73019, USA. (ddeming@ou.edu)

C. Cranganu, Brooklyn College, Department of Geology, 2900 Bedford Ave., Brooklyn, NY 11210, USA. (cranganu@brooklyn.cuny.edu)

Y. Lee, School of Earth and Environmental Sciences, Seoul National University, Shillim-Dong, Kwanak-Gu, Seoul 151-742, Korea. (ylee23@hotmail.com)