Common Themes in the Formation and Preservation of Intrinsic Porosity in Shales and Mudstones – Illustrated with Examples Across the Phanerozoic
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Abstract
In shales, intrinsic porosity is considered a direct outcome of those processes that are active during deposition and early compaction of a shale succession. They are typically in the micrometer to nanometer size range, and unrelated to processes that produce fragmentation-related porosity later on in burial history.

An examination of six shale successions, ranging in age from Cambrian to Cretaceous shows that, in spite of considerable variability of composition, depositional setting, and compaction history, there are several pore types that seem universal. Three types of pores that recur are phyllosilicate framework (PF) pores, carbonate dissolution (CD) pores, and organic matter (OM) pores. PF-pores are defined by a framework of platy phyllosilicates and range in size from 5 nm to more than 1000 nm. CD-pores typically occur along the periphery of dolomite and calcite grains and range in size from 50 nm to more than 1000 nm. OM-pores occur within kerogen blebs and organo-clay aggregates, and range in size from 10 nm to several 100 nm.

When organic matter content and shale maturity are considered, the following relationships emerge: 1) at high organic matter content (>10% TOC) many PF-pores are filled with kerogen/bituminite in immature shales; 2) in mature shales these same fills contain abundant OM pores or are partially removed; 3) organic matter that has seen partial degradation before compaction (e.g. bituminite) develops abundant OM pores in shales that have reached maturity; but 4) non-degraded organic matter (e.g. alginite, inertinite) does not develop pores. In shales with comparatively low TOC (less than 7%) a large proportion of the PF-pores are open, likely connected, and potentially able to transmit gas. PF-pores are also more common as clay content increases, but more critically, their abundance hinges on the presence of pressure shadows generated adjacent to "hard" grains (quartz, feldspar, dolomite, calcite, pyrite) that resist compaction. They also occur in compaction resistant cavities (e.g. foram tests). CD-pores appear to form late in diagenetic history. The requisite pH drop was likely due to the formation of carboxylic and phenolic acids when kerogens reacted with silicates in a briny solution at elevated temperatures (~ 80° to 120° C). When carbonate content is low (a few %), CD-pores constitute only isolated porosity. However, in shale intervals that contain abundant carbonate, and where carbonate grains are concentrated into laminae, CD-pores probably are an important facilitator of gas migration.

In many shale gas plays natural fracture systems are considered a key aspect in the assessment of producibility. Yet, with a typical fracture spacing at the decimeter scale, gas still has to migrate some distance to these fractures. Thus, the intrinsic porosity of the shale is a crucial variable that needs to be understood for a realistic evaluation of long term production. Petrographic evaluation of shale porosity provides a much needed “reality check” for “method driven” measurements (mercury injection, nitrogen adsorption) of porosity and permeability.

Introduction
Typical shales are terrigenous elastic dominated sedimentary rocks with a dominant grain size below 63 microns, and constitute approximately two thirds of the sedimentary rock volume (Schieber, 1998). Whereas most of these have long functioned as the seals that prevent hydrocarbons from escaping from their reservoir, a subset of carbonaceous (organic-rich) shales has for many years also served as a source of natural gas. In fact, the first natural gas well in the US that tapped Devonian black shales beneath Fredonia, New York, was drilled in 1821, almost four decades before the much better known Drake Oil Well near Titusville, Pennsylvania, considered the birthplace of the oil industry. Yet, although shale gas has been produced in the eastern US for more than a century, for most of that time its contribution to the overall production has been marginal.

Over the past decade, however, shale gas has become a rapidly growing source of natural gas in the US, spurred by technological advances, such as horizontal drilling and hydraulic fracturing techniques. Increased shale gas production has
been essential to offset declining production from conventional gas reservoirs. Statistical data from DOE data bases show a 30% increase in US natural gas reserves from 2003 to 2008, owing largely to shale gas development.

Early studies of gas producing shales focused on Devonian black shales of the eastern US, strata that have long been known to produce natural gas from fractured as well as nonfractured shale intervals (Broadhead et al., 1982). Petrographic examination of porosity in these and other shales requires electron microscopy. Yet attempts to produce sufficiently thin and undisturbed samples of shale for transmission electron microscopy was long hampered by the difficulties with avoiding mechanical damage inflicted by microtome knives (Davies et al., 1990). The application of ion milling, a sample preparation technique developed by material scientists (Bollinger and Fink, 1980), has helped to overcome this limitation and has enabled imaging of pore spaces and mineral interrelationships at the magnifications needed for shale studies (Jiang et al., 1990; Hover et al., 1996; Rask et al., 1997; Schieber, 1998, 2002). Ion milling is now the technique of choice for the study of shale porosity (Tomutsa et al., 2007), and in this contribution I will illustrate pore characteristics of several shale successions with high resolution TEM and SEM images of ion milled specimens. The focus is on pores that are intrinsic to the shale matrix, rather than on fracture-related porosity.

Methods

Samples of the Cambrian Eau Claire Formation, the Ordovician Maquoketa Shale, and the Devonian New Albany Shale were collected from drill cores stored at the core library of the Indiana Geological Survey. Samples of the Devonian Geneseo Shale of New York were collected from a core drilled near Lansing in Tompkins County, N.Y., and currently stored at the laboratory of Dr. Carl Brett of the University of Cincinnati. Samples of the Cretaceous Mancos Shale were collected from cliff exposures in the Book Cliffs of Utah. The latter sample set was prepared for TEM observation (JEOL 1200 EX STEM) via mechanical thinning followed by ion milling from both sides (Gatan 600 Duomill). Thin slices of the other samples were mounted on a custom designed sample holder and mechanically polished on the top surface. The sample holder was then placed into a Gatan 600 Duomill and the polished surface was ion milled at a low incidence angle for several hours. Milled surfaces were then examined without conductive coating with a FEI Quanta 400 FEG in low vacuum mode. All samples are oriented perpendicular to bedding.

In terms of thermal maturity, the New Albany Shale samples are considered immature (Comer et al., 1994), the Eau Claire and Maquoketa Shale samples were heated to the low end of the oil window (Grathoff et al., 2001), the Mancos Shale samples were within the oil window (Nuccio and Roberts, 2003; Machent et al., 2007), and the Geneseo Shale was heated to supermaturity (Weary et al., 2000).

Pore Types

Phyllosilicate framework (PF) pores are the most ubiquitous pore type in all samples. They consist of triangular openings that are defined by a lattice-work of randomly oriented clay mineral platelets (Fig. 1).

![Figure 1: Fabric and PF-pores in sample of New Albany Shale. (A) Low magnification SEM image showing planar fabric due to compaction, and compression around resistant larger grains. Dark streaks consist of kerogen. (B) Enlargement of yellow-framed area in (A). Planar-compressed fabric still dominant. (C) Enlargement of red-framed area in (B). Shows largely randomly oriented clays that define triangular openings, here termed phyllosilicate framework (PF) pores.](image)

These triangular pores range in size from a few nanometers to more than a micron, and in an overall planar fabric that is compaction dominated (Fig. 1), they are best developed in pressure shadows adjacent to larger compaction resistant grains (silt, sand, fossil debris, etc.) and in spaces between such grains (Fig. 2).
Figure 2: (A) Domains of randomly oriented clay minerals (dashed outlines) with triangular PF-pores in pressure shadow of quartz silt grain. (B) Space between small quartz silt grains protects PF-pores from collapse. Bending of clay flakes (arrows) suggests that at least in part the interstitial clays are of detrital origin. SEM images, samples from New Albany Shale.

The defining clay mineral platelets, although typically at most a few microns in size, appear to have multiple origins. They can show textures suggestive of detrital origin, such as bending and splintering due to compaction, as well as piercing and differential compaction when oriented near-vertical (Figs. 2, 3).

Figure 3: (A) SEM backscatter image that shows bending of large detrital clays and mica flakes around pyrite framboid (center) and quartz grains. (B) Random clay fabric with PF-pores. Clay flakes marked with * are considered clearly detrital and define a lattice framework of compaction protected space. Black arrows: b marks compactional bending of clays around quartz grains, s marks splintering of clay flake due to compression, and p marks piercing by clay flake. White arrows mark “wrapping” of clays due to compaction. (C) Subvertical clay flake pierces underlying clays due to compaction (black arrow). All images from New Albany Shale. Det SSD indicates backscatter image, Det LFD indicates secondary electron image.

Whereas images from Figs. 1, 2, and 3 are all from the Devonian New Albany Shale of Indiana, Fig. 4 illustrates that PF-pores are common textural feature in multiple other shale successions. TEM images from the Cretaceous Mancos Shale (Figs. 4 A, B, C) show sharply defined triangular pores as small as 10 nm, and mineral growth within these clay mineral defined voids (Fig. 4A). The fill is apatite in the latter image, but quartz is probably most common, followed by carbonates. In Fig. 4C we see thin clay packages with layer terminations in upper half of image, and clays with a fine grained felted look in the lower half of the image. Both these features are suggestive of diagenetic growth.

In the Devonian Geneso Shale PF-pores up to several microns in size occur. The latter are typically defined by frameworks of larger detrital clay flakes (Fig. 4D), as well as splits (Fig. 4E) of larger clay flakes. Diagenetic mineral growth (Fig. 4E) is in many places observed in association with such large pores. This type of growth can keep PF-pores open by enclosing the ends of clay flakes that project towards such minerals, such as seen in Figs. 4, F and G. Cementing the ends of
clay flakes in position prevents the collapse of these pores at the same time as a pressure shadow is maintained near the compaction resistant cement mineral.

Figure 4: Examples of phyllosilicate framework (PF) pores, all surfaces perpendicular to bedding, images oriented stratigraphic up. (A), (B), (C), PF-pores in Mancos Shale tongues (Cretaceous) from the Book Cliffs of Utah. TEM images of double ion milled samples. Randomly oriented matrix clays define triangular pores that range in size from 10 to 100 nm. In (A), central pore is partially filled by diagenetic apatite. (D and E) Large PF-pores in Devonian Geneseo Shale from New York. In (E) two clearly detrital clay flakes (marked 1 and 2) have been deformed and split by compactional forces. The split in flake 2 (black arrow) is kept open by a
diagenetic calcite grain (marked as qu. (F) PF-pores in the Maquoketa Shale (Ordovician) of Indiana. The best developed PF-pores are found in the pressure shadows near the pyrite grain in the center of the image. Inset shows detail of one of these pore areas. The clay flakes have been “trapped” in overgrowth of adjacent grain (also pyrite). (G) Well developed PF-pores in shales from the Eau Claire Formation (Cambrian) of Indiana. In this image as well, the clay minerals of the shale matrix are randomly oriented and define triangular pores. The smaller, straight/idiomorphic clay flakes probably grew in pore spaces. The red arrows point out clay flakes that have become “trapped” (or “clamped”) in overgrowth of a quartz grain at right.

Carbonate dissolution (CD) pores are commonly observed when there are carbonate grains (most commonly dolomite and calcite) scattered through the shale matrix, or when carbonate grains have been reworked into thin lag deposits. Dissolution rarely removes entire grains (Fig. 5A). More commonly partial dissolution along the carbonate grain margins is observed (Fig. 5). In the latter case the dissolution results in seams of corroded and vuggy carbonate mineral that range in width from a few tens to several hundreds of nanometers. Within these seams pores are either irregular in shape or still retain rectangular outlines due to the structure of the carbonate substrate (Fig. 5D). There is no sign of collapse into these cavities, and they do not appear to be filled with secondary minerals.

Organic matter (OM) pores can occur wherever there is organic matter present in the form of kerogen blebs and depend on the grade of maturity (Dow, 1977; Tissot et al., 1987). In immature rocks, ion milled kerogen will have a smooth appearance like that exhibited by samples from the Devonian New Albany Shale (Fig. 6A,B). In rocks that have reached maturity, bubble-like voids of variable size (a few nm to more than a micron) are observed. These are exemplified by samples from the Devonian Geneseo Shale (Figs. 6 C, D, and E) and the Ordovician Maquoketa Shale (Fig. 6F). The Geneseo kerogens exhibit a wide range of pore sizes within single kerogen blebs, as well as what appears to be large pores (Fig. 6E) that are lined with the same carbon-rich material that is found in the kerogen blebs. OM-pores are also present in the Maquoketa Shale, but are not as well and pervasively developed (Fig. 6F).

The type of organic matter also appears to influence the OM-pore formation. In general terms, kerogen blebs that are linked to bacterially degraded organic matter (such as bituminite) show well developed OM-pores in mature rocks, but degradation resistant organic matter (e.g. alginite, inertinite) in the same sample may not develop any, or very few pores.

Discussion

The most ubiquitous pore type seen in above examples, the phyllosilicate framework (PF) pores, have also been pictured in reports from other shale units that were investigated with high resolution electron microscopy (e.g. Yau et al., 1987; Li et al., 1995; Hover et al., 1996; Rask et al., 1997; Masuada, 2001). In these latter publications, however, the focus was on details of the smectite-illite transformation during burial diagenesis. As a consequence, the associated triangular pores were only mentioned in passing, if at all. Phyllosilicate transformation in the “Zone of Intermediate Burial Diagenesis” (Surdam et al., 1991) has been amply documented from many sedimentary basins, and involves the change from smectite to interlayered illite/smectite or to chlorite and/or interlayered chloride/smectite (e.g. Li et al., 1995; Hover et al., 1996). Contingent on local factors, these phyllosilicate fabrics developed at a burial depth of some kilometers and the implicit idea has been that they are not predicated by original depositional fabrics. Thus, one could simply argue that PF-pores are to be expected in any shale succession with a sufficient clay content that has been buried deep enough for the onset of the smectite-illite transformation. On the other hand, the observation that PF-pores seem to be associated with lattice frameworks of detrital clay flakes (Fig. 3B) that impart partial protection from compaction, and with pressure shadows of compaction resistant larger grains (Fig. 2), suggests that depositional fabric leaves a significant imprint on the developing diagenetic fabric parameters.

The edge to face particle arrangements seen in detrital clay lattice frameworks (Fig. 3B) could for example be a depositional fabric component that reflects deposition of clays from flocculation. This type of fabric has been observed in other ancient shales and has been attributed to a flocculation origin (e.g. O’Brien et al., 1994). Floccule formation occurs in clay suspensions regardless of salinity (Schieber et al., 2007), and is generally considered a fabric characteristic for clay deposition in a wide range of environments (Bennett et al., 1991). Whereas these initial card-house structures are prone to flattening via compaction (Bennett et al., 1991), partial preservation in pressure shadows, such as illustrated in Figs. 2 and 4, is to be expected. In fact, next to clays, silt grains of variable composition are the most common component of many shales (Potter et al., 2005), and it is probably not a coincidence that a negative correlation between silt content and seal quality has been observed (Dawson and Almon, 2002). Observations presented here predict that with increasing silt content there should be an increase in the pressure shadowed volume containing PF-pores. This in turn should cause an increase in porosity/permeability and result in a decrease of seal quality.

The diagenetic dimension of PF-porosity is illustrated in Figs. 3 and 4. The clay platelets in Figs. 4A, B, G are quite uniform and idiomorphic, and strongly suggest diagenetic growth related to the smectite-illite transformation (e.g. Li et al., 1995; Hover et al., 1996). In clay-rich shales this style of PF-pores is common in interstitial spaces defined by lattice frameworks of detrital clay flakes (Fig. 3B), but it is also a general feature of any void spaces that remain at the onset of burial diagenesis (e.g. pores in siltstone beds, open spaces in fossil tests, etc.). Although diagenetic cementation can potentially occlude PF-pores, it more typically serves to keep them open. Either by acting as a proppant (Fig. 4A, E), or by partially engulfing clay platelets during growth and “clamping” them in place. Whereas fundamentally any diagenetic
Figure 5: Manifestations of carbonate dissolution in several shale successions. (A) A secondary pore in the Devonian New Albany Shale due to partial dissolution of a dolomite (do) grain. (B) Corrosion and porosity formation (arrows) along the margins of a dolomite grain in the Devonian New Albany Shale. (C and D) Comparable margin dissolution (ca=calcite grain) and porosity
formation in the Ordovician Maquoketa Shale. (D) Detail of grain margin dissolution pointed out with large arrow in (C). (E and F) Dissolution along dolomite grain (do) margins (arrows) in the Devonian Geneseo Shale of New York.
mineral can function in this capacity, authigenic silica is most commonly observed. Most likely this is so because silica is released into the pore waters during the smectite-illite conversion (e.g. Abercrombie et al., 1994) and thus can reach supersaturation and precipitate (e.g. Hover et al., 1996).

Because the smectite conversion overlaps with the onset of chemical reactions involving kerogens, the latter have a tendency to fill PF-pores. In the case of abundant kerogen, to see all PF-pores filled with kerogen, such as in the New Albany Shale (Fig. 6), is typical. In contrast, when we look at organically lean units such as in the Cambrian Eau Claire Shale (Fig. 4), PF-pores remain open even after deep burial and a long diagenetic history. Thus, it seems likely that in low TOC shales only a fraction of the PF-pores will be occluded by kerogen.

Secondary porosity development through corrosion of carbonate grains (Fig. 5) implies acidic pore waters and a drop of pH. Research on oil field brines and pore water evolution during burial (e.g. Hayes, 1991; Surdam et al., 1991) suggests that the initial stages of smectite transformation are followed by (and overlap with) decarboxylation of kerogen and a buildup of carboxylic and phenolic acids in the temperature range from 80° to 120° C (MacGowan and Surdam, 1990). In sandstones this stage is associated with formation of secondary porosity (e.g. Hayes, 1991; Surdam et al., 1991) and destruction of carbonates. It seems therefore a reasonable conjecture that the carbonate dissolution observed in Fig. 5 is likewise linked to organic acid formation. Because the initial amount of organic matter in a shale will place limits on the amount of organic acids that can be generated in this way, it seems likely that dissolution porosity of this type is best developed in organic-rich shales. In the overall context, and given that no diagenetic clays were observed in any dissolution cavities, one may conclude that in the studied examples the smectite conversion was largely concluded by the time organic acid production peaked and induced carbonate dissolution. As long as carbonate content is low (a few %) and carbonate grains are scattered through the rock matrix, it is likely that this type of pores will form isolated pockets. However, when in this occurs in shale successions with abundant carbonate (10% or more), and where carbonate grains have been reworked into thin laminae, CD-pores are probably important for facilitating gas migration.

The bulk of liquid hydrocarbon generation in sedimentary successions occurs in the next diagenetic stage, after smectite conversion and organic acid generation (e.g. Hayes, 1991; Surdam et al., 1991). Production of liquid hydrocarbons due to kerogen maturation, followed by outward migration of these liquids, seems to be an appealing and logical explanation for the formation of variably shaped OM-pores (Fig. 6) in previously uniform and dense appearing kerogen blebs. Because of the higher temperatures required for that step, abundant OM-pores should only be expected in rocks that have reached maturity. The observation that the best developed OM-pores occur in the Geneseo Shale, a rock unit that has been heated to reach Ro values of 1.5 and higher (dry gas window; Weary et al., 2000), whereas the similarly organic-rich but immature New Albany Shale (Ro values ~0.5; Comer et al., 1994) shows no OM-pores at all, clearly supports that assumption.

Conclusions

Although only a fraction of the shales that I worked on over the past decades were examined at the level of detail to image pores directly and unequivocally, petrographic parallels and an understanding of the origin of larger textural features suggest that the pore types illustrated here should be common to many shales, and particularly those that are likely targets for natural gas production. Whereas a given shale unit can have unique qualities that affect pore preservation and formation, such as the early diagenetic silicification in the Barnett Shale (Loucks and Ruppel, 2007), the three pore types illustrated above seem ubiquitous.

The unifying theme for PF-, CD-, and OM-pores is that their generation appears to be an integral part of the diagenetic history of a given shale succession, and intimately linked to the formation of new clay minerals and the maturation of organic matter. Thus, they are a product of diagenetic history, rather than a survivor of diagenesis, another reason why they should be a common element in all gas-prone shale successions. Because they are integral (or intrinsic) to the shale matrix, it is likely that they are a key control for gas transfer from the shale volume to the fractures that allow us to withdraw such gas.

From the observations made on the four shale units examined for this contribution, one can at first approximation make the following generalizations:

1) Phyllosilicate framework (PF) pores typically have an inherited depositional component, and a diagenetic component that relates to clay mineral growth during smectite conversion. Pressure shadows and compaction protected areas help to preserve PF-pores. PF-pores may be the reason for the observed correlation between silt content and permeability of some shale units. To a point, higher clay contents imply more abundant PF-pores, but high clay contents (50% or more) are probably detrimental because they imply lower silt contents.

2) In shales with “high” organic matter content (>10% TOC) PF-pores are likely filled with kerogen/bituminite in immature shales, whereas in “lean” shales many of the PF-pores may remain open in spite of considerable burial. In the latter instance PF-pores are likely connected and potentially able to transmit gas.
3) Kerogen fills of PF-pores and other void spaces will contain abundant OM-pores in shales that have reached maturity. “Structured” macerals, such as alginate or inertinite are less likely to develop OM-pores than partially degraded macerals (e.g. bituminite).

4) CD-pores appear to form late in diagenetic history and are probably related to formation of carboxylic and phenolic acids in the course of kerogen maturation. Isolated porosity is generated at low carbonate contents, but connected pores may result when carbonate is abundant (>10%) and has been winnowed into laminae.

5) Although fracture systems are an important element for shale gas production, at a fracture spacing on the order of decimeters and even meters, gas still has to migrate from the enclosed shale volumes to these fractures. Thus, the intrinsic porosity of a given shale unit is a crucial variable that needs to be understood for a realistic evaluation of long term production. This contribution is a shale petrographer’s approach to understand pore formation and preservation in shales. I am of course cognizant that petroleum engineers use different methodologies to that end, such as mercury porosimetry (Thompson et al., 1987) and nitrogen low pressure isotherm analysis (Sing, 2001). Porosity and permeability data derived from these data, however, need not necessarily show a close match to independently derived porosity and permeability data because there are multiple simplifications and assumptions (Sing et al., 1985) that fail to do justice to the inherent complexity of fine grained sediments (Soeder, 1988). Therefore, petrographic evaluation of porosity provides an invaluable “reality check” for these “method driven” measurements of porosity and permeability.

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