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Scanning-Electron-Microscope Petrographic Evidence for Distinguishing Organic-Matter Pores Associated with Depositional Organic Matter versus Migrated Organic Matter in Mudrocks

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ABSTRACT

Organic-matter (OM) pores are an important constituent of mudrocks and comprise the dominant or subsidiary pore network of many shale-gas and shale-oil systems. New research suggests that OM pores form not only in kerogen, as originally proposed, but also in solid bitumen and pyrobitumen. Identifying the type of nanometer- to micrometer-sized organic matter that is present in mudrocks is extremely difficult, if not impossible, using a scanning electron microscope (SEM). However, distinguishing whether the OM-pore hosted organic material exists in place or has migrated would allow the determination to be made whether the original organic material was kerogen or bitumen. Through the analysis of an extensive collection of SEM photomicrographs, we have determined that there are several petrographic criteria that can be used to separate depositional versus migrated organic matter. These criteria include: (1) organic matter occurring after cementation in mineral pores, (2) fossil body-cavity voids filled with organic matter, (3) dense, spongy pore texture of the organic matter, (4) abundant contiguous pores filled with organic matter having a spongy pore network, (5) no alignment of pores in organic matter (aligned OM pores are present in kerogen), (6) cracks in organic matter related to devolatilization, and (7) anomalously larger bubbles associated with development of two hydrocarbon phases.

To help understand the concept of depositional and migrated organic matter and associated OM-pore development, we present an idealized history of OM-pore development and evolution with increasing thermal maturation. Original depositional organic material is composed of kerogen, which can be transformed to bitumen and then oil, gas, solid bitumen, and pyrobitumen (char) during thermal maturation. When bitumen is produced from the kerogen, it can migrate into the mineral pore network and later transform to solid bitumen or pyrobitumen.

The final pore network within the mudrock may be dominated by OM pores. It is important to distinguish depositional organic-matter–hosted OM pores versus migrated organic-matter–hosted OM pores because the final OM-pore network and connectivity pathways are dependent on the proportions of the distribution of these two organic matter states. Migrated organic-matter–hosted pores mimic the three-dimensional distribution of the original mudrock mineral pore network and provide more extensive contiguous permeability pathways than isolated organic matter.

INTRODUCTION

Organic-matter (OM) pores are a common constituent in mudrocks and form the dominant or subsidiary pore-network of many shale-gas and shale-oil systems (e.g., Loucks et al., 2009, 2012; Curtis et al., 2010; Milner et al., 2010). Recent research by Bernard et al. (2012a, 2012b) suggested that organic-matter pores form not only in kerogen and solid bitumen, as originally proposed by Loucks et al. (2009, 2012) and Reed and Loucks (2013), but mainly form in pyrobitumen. Bernard et al. (2012a, 2012b) based their supposition on results from synchrotron-based scanning transmission x-ray microscopy analysis (STXM) that allowed the differentiation of organic matter, which includes kerogen, solid bitumen, and pyrobitumen, at the nanoscale level in mudrocks. Without STXM, it is very difficult, if not impossible, to identify organic-matter types in consolidated rocks without having to destroy the sample. However, it is possible to distinguish original depositional associated (in place) organic matter (kerogen or its alteration products, solid bitumen and/or pyrobitu-

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men) from migrated organic matter (solid bitumen or pyrobitumen). This identification is significant because it allows us to differentiate OM pores developed in depositional organic matter from OM pores developed in migrated organic matter.

The major goal of this investigation is to identify OM pores that have formed in depositional organic matter (kerogen and its products, solid bitumen and/or pyrobitumen) versus those that formed in migrated organic matter (solid bitumen and/or pyrobitumen). Specific objectives are (1) present an idealized history of OM-pore development and evolution associated with increasing thermal maturity; (2) outline several scanning electron microscope (SEM) petrographic criteria for differentiating OM pores that developed in depositional organic matter from OM pores that developed in migrated organic matter; and (3) present concepts on the significance of OM pores in depositional versus migrated organic matter. Addressing these objectives will increase our understanding of pore networks and permeability pathways in shale-gas and shale-oil systems.

METHODS AND DATA

OM pores in shale-gas and shale-oil systems are generally developed in aggregates or patches of organic matter having very fine-grain size—commonly less than a few micrometers in diameter (e.g., Loucks et al., 2009). These patches of organic matter may be composed of depositional kerogen, solid bitumen, and/or pyrobitumen, or they may be composed of migrated solid bitumen and/or pyrobitumen. The dimensions of the depositional organic matter are controlled by the original size of the kerogen particle or aggregate and later deformation associated with compaction, whereas the dimensions of matter of migrated origin are controlled by the size of the hosting pore. In both cases, the organic matter patches in intact mudrock samples are commonly too small to be investigated using standard light microscopy techniques; therefore, we used a field-emission scanning electron microscope (FESEM) to accomplish our study of the organic matter and associated pores.

Broad-ion-beam (BIB) milling was used to provide a flat surface for FESEM examination. Such surfaces have only minor topographic variations that are related not to differences in hardness of the sample but, rather, to slight variations in the path of the Ar-ion beam (see Loucks et al., 2009, for more information). The majority of samples were prepared using a Leica EM TIC020 ion mill, although other ion mills have been used. Generally, an accelerating voltage of 8 kilovolts and a gun current of 2.8 milliamperes have proven effective in producing relatively flat surfaces on mudstone samples, making them suitable for very high-magnification imaging.

Imaging was conducted using multiple field-emission SEM's, but primarily using an FEI Nova NanoSEM 430. Mineral identifications and phase identification maps were made using a Bruker XFlash® SDD energy dispersive spectroscopy system. Secondary electron (SE) images were acquired for documentation of topographic variation, and backscattered electron (BSE) images were acquired for delineation of compositional variation. Imaging using a FESEM equipped with an in-lens SE detector provided greatly increased detail of nanometer-scale features. This imaging provided important information on lithologic variation and general locations of pores throughout the sample. In order to prevent beam damage, low to moderate accelerating voltages (1–15 kilovolts) were generally used, particularly when imaging organic matter. Spot sizes varied, depending on magnification. Working distances were mostly 3 to 7 millimeters.

The Bureau of Economic Geology of the Jackson School of Geosciences at The University of Texas at Austin has a large collection of SEM mudrock photomicrographs taken from more than a dozen shale-gas and shale-oil systems. Many of these photomicrographs are of organic matter and OM pores. This library of SEM photomicrographs was used to investigate the nanometer- to micrometer-scale petrography of organic matter in shale-gas and shale-oil systems.

REVIEW OF OM-PORE PARAGENESIS

The evolution of organic matter with burial is directly related to increases in temperature (e.g., Tissot et al., 1974; Miki et al., 1991). As kerogen is subjected to increased maturation, bitumen and petroleum are generated and solid bitumen and pyrobitumen can form. In this paper, we use the definitions for organic matter, kerogen, bitumen, solid bitumen, and pyrobitumen from the online American Geological Institute (AGI) Glossary of Geology (2014): (1) organic matter is any liquid or solid composed of organic material; (2) kerogen is insoluble organic material that can be converted to petroleum products through thermal maturation; (3) bitumen is a generic term applied to a variety of hydrocarbons (wide range of viscosities) such as petroleum, asphaltites, and can include other non-hydrocarbon components; (4) solid bitumen is very viscous bitumen able to preserve pores; and (5) pyrobitumen is a hard, nonvolatile substance composed of hydrocarbon complexes (similar to char). Mastalerz and Glikson (2000) divided bitumen into pre-oil bitumen and post-oil bitumen. Pre-oil bitumen is generated at lower maturity and migrates only short distances into adjacent pores. This fits the definition of bitumen used in this paper. Post-oil bitumen (our pyrobitumen) is generated later (higher maturity) and is the residue of the oil. These are simple, working definitions for use in this paper and for further clarification we refer the reader to the vast literature (e.g., Tissot and Welte, 1984; Hunt, 1996) on this subject. It is important to note that organic geochemists consider the major difference between bitumen/solid bitumen and pyrobitumen is that bitumen and solid bitumen are soluble in carbon disulphide, whereas pyrobitumen is mostly insoluble in carbon disulphide (e.g., Tissot and Welte, 1984; Hunt, 1996).

Loucks et al. (2009) recognized that in the Mississippian Barnett Shale in the Fort Worth Basin, OM-pore development was related to the thermal maturation of organic matter. However, it is still uncertain within what type of organic matter OM pores developed. Loucks et al. (2009) suggested OM pores formed in kerogen, and Reed and Loucks (2013) also suggested that some OM pores are in what they interpreted as solid bitumen. Bernard et al. (2012a, 2012b) concluded that OM pores form in pyrobitumen. The observations by Bernard et al. (2012a, 2012b) are very important in understanding the development and distribution of OM pores. They were able to document different types of organic matter in both the Mississippian Barnett Shale in the Fort Worth Basin and in the Jurassic Posidonia Shale in northern Germany. To make these observations, Bernard et al. (2012a, 2012b) used STXM-based C–XANES spectroscopy techniques. STXM is synchrotron-based transmission spectromicroscopy technique, using a monochromated x-ray beam produced by synchrotron radiation (Bernard et al., 2012a, 2012b). Bernard et al. (2012a, 2012b) noted that use of this technique allowed imaging of the organic matter at the 25-nanometer scale and also allowed the collection of XANES spectroscopic measurements. XANES stands for x-ray absorption near edge structure. Bernard et al. (2012a, 2012b) show that this technique provides spectral data on the bonding environment of carbon in organic compounds, which can be used to differentiate kerogen, solid bitumen, and pyrobitumen. An example of the mixture of the different organic matter types from the work of Bernard et al. (2012b) on the Barnett Shale is shown in Figure 1. The photomicrographs show the organic matter distribution in three samples of differing thermal maturity from three wells. Using STXM-based C–XANES spectroscopy, Bernard et al. (2012b) were able to identify gas-mature kerogen, solid bitumen, and pyrobitumen at the nanometer to micrometer scale. Their work shows the complexity of the evolution and distribution of organic matter.

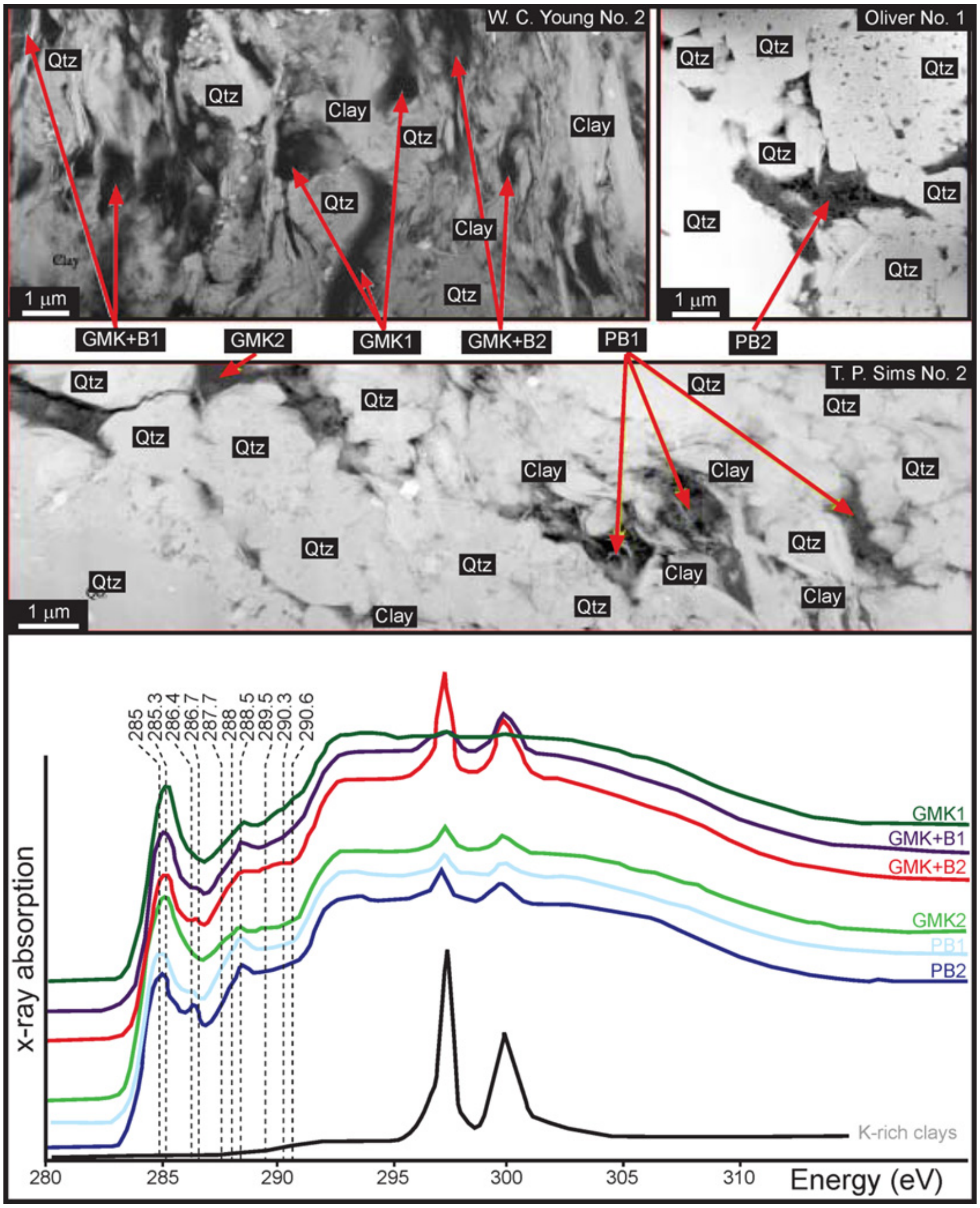

Figure 1. Transmission electron microscope (TEM) and C–XANES analysis of three samples from the gas window of the Mississippian Barnett Shale, northern Fort Worth Basin. Photomicrographs display different types of organic matter and their distribution. GMK = gas mature kerogen, B1 and B2 = solid bitumen, PB1 and PB2 = pyrobitumen, and Qtz = quartz. C–XANES spectra data aid in identifying organic matter type. See Bernard et al. (2012b) for discussion of C–XANES spectra analysis. Redrawn from Bernard et al. (2012b) and published with permission of International Journal of Coal Geology and Sylvain Bernard (*Laboratoire de Minéralogie et de Cosmochimie du Museum*, Paris, France).

On the basis of their work in the Barnett and Posidonia shales, Bernard et al. (2012a, 2012b) concluded that only the pyrobitumen in gas-window-maturity samples contained OM-pores. However, Reed et al., (2014) showed evidence that OM pores are also present in organic matter from oil-window-maturity samples, which might preclude such pores from being related to pyrobitumen produced at higher temperature thermal maturity levels. More analysis of organic matter from different shale-gas and shale-oil systems exposed to a variety of thermal stress levels needs to be completed before we can conclude definitively which organic material or materials actually produce OM pores.

An important question related to this discussion of OM pores is not just what type of organic matter the pores formed in, but whether the organic matter remains in place or has migrated. Depositional organic matter can evolve during thermal maturation from depositional kerogen, into bitumen, solid bitumen, and finally into pyrobitumen. In contrast to depositional organic matter, migrated organic matter present in mineral pores will initiate as bitumen or oil (Lewan, 1991) and may then evolve into solid bitumen and/or pyrobitumen. The initial bitumen is expelled into adjacent mineral pores and can form a continuous organic matter network (Lewan, 1987). Lewan (1987, 1991) suggested that thermal decomposition of the organic matter produces a net volume increase, creating the pressure differential necessary to force the bitumen to migrate into mineral pores. As will be addressed in the discussion section, the distribution of depositional organic matter is very different from that of migrated organic matter. To help understand the concept of depositional and migrated organic matter and associated pore development, an idealized history of OM-pore development and evolution with increasing thermal maturity is discussed below and shown in Figure 2. This figure is meant to portray a simple compositional and fabric rendition of a mudstone. The authors refer the reader to Loucks et al. (2012) and Milliken and Day-Stirrat (2013) for more detailed discussions of mudrock fabrics and diagenesis. Also, in this figure we use vitrinite reflectance (Ro%) to designate the stage of hydrocarbon maturation. The reader is referred to Dembicki (2009) for a review of the concept of the Ro% scale.

Figure 2A shows the original, noncompacted muddy sediment containing rigid grains of quartz and calcite and ductile grains of clay and kerogen. Both interparticle and intraparticle pores are present. Some rare inherited OM pores, related to the original type III (woody) kerogen, can be present, but generally exist only in the larger woody particles (Figs. 3A and 3B) or in some amorphous type II kerogen. Figure 2B is the same sediment sample after shallow burial corresponding to a Ro of ~0.4%. Porosity is lost through mechanical compaction, particularly as the ductile kerogen is squeezed between rigid grains. Thermal maturity is too low for the development of OM pores. With burial, cementation takes place (Fig. 2C). Cements form in interparticle and intraparticle pores, but cannot form where kerogen has occluded mineral pores. In Figure 2D, the sample is more deeply buried and reaches a Ro of ~0.75%. The rock is now in the oil window. Generated bitumen is expelled from the kerogen, migrating into adjacent interparticle and intraparticle mineral pores (Lewan, 1991). However, because of factors not fully understood but possibly related to capillary pressure associated with pore-throat size, not all visible mineral pores are filled. OM pores may form in the kerogen but be filled with oil and therefore difficult to recognize. Also, some migrated bitumen or oil may transform to solid bitumen, which can contain OM pores. Figure 2E shows the sample at a higher temperature and deeper burial depth corresponding to a Ro of ~1.3% or greater. At this temperature, several processes can occur. Gas can evolve from the depositional kerogen and create easily recognizable pores in the kerogen. The bitumen in the kerogen may transform to solid bitumen or pyrobitumen, producing pores in the process. Also, the bitumen and oil in the mineral pores can transform to solid bitumen and pyrobitumen, with associated OM pores.

Thus, the depositional organic matter can contain a complex pore network consisting of OM pores associated with kerogen, solid bitumen, and pyrobitumen. All these OM pores are within the original kerogen grain boundary. OM pores can also develop in mineral pore spaces where bitumen and oil migrated. With advanced thermal maturation, the bitumen and oil in the mineral pores can form solid bitumen and pyrobitumen, with associated OM pores. These OM pores are recognized by being in organic matter that is within former intraparticle mineral pores such as fossil body cavities or in organic matter in former mineral pores that are lined with cement. The cement and cement overgrowths indicate that the pore was open, allowing precipitation of the cement and the overgrowths. Then bitumen and/or oil migrated into the mineral pore. Petrographic characteristics of migrated organic matter are presented in the next section.

As mentioned earlier, standard petrographic or SEM methods cannot easily define very fine organic matter type; however, standard SEM methods can help distinguish whether the organic matter exists in place or has migrated into mineral pores. Origin of OM pores associated with depositional organic matter can be related to kerogen, solid bitumen, or pyrobitumen, whereas OM pores in migrated organic matter can only be related to solid bitumen or pyrobitumen.

SEM PETROGRAPHIC EVIDENCE FOR DISTINGUISHING DEPOSITIONAL ORGANIC-MATTER–ASSOCIATED VERSUS MIGRATED ORGANIC-MATTER–ASSOCIATED OM PORES

By analyzing a large collection of SEM photomicrographs, we have determined several petrographic characteristics that can be used to separate depositional versus migrated organic matter and, in turn, determine whether OM pores are related to original depositional kerogen or related to bitumen and oil that migrated into mineral pores. These petrographic characteristics are discussed below using SEM photomicrograph examples.

Evidence or criteria for transported solid bitumen/pyrobitumen-related pores include (1) organic matter occurring after cementation in mineral pores, (2) fossil body-cavity voids filled

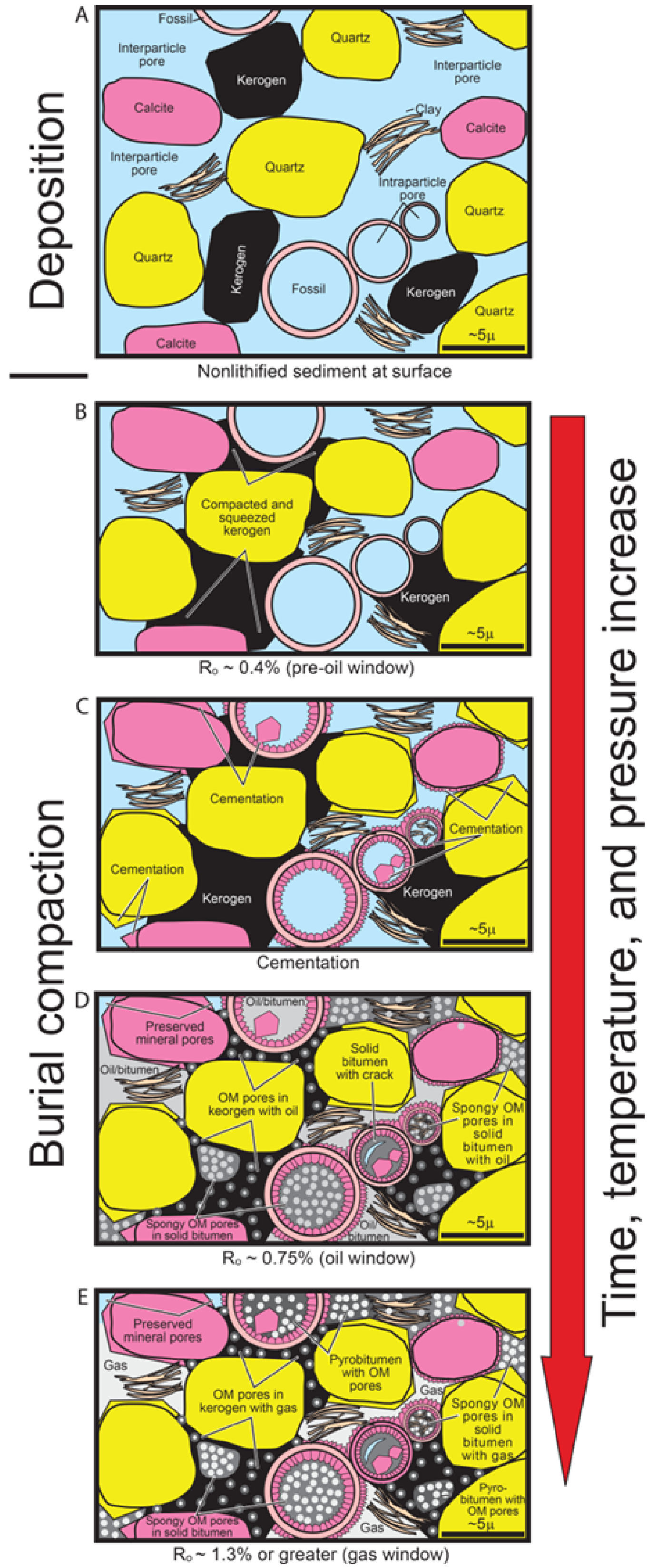

Figure 2. Idealized history of OM-pore development and evolution with increasing thermal maturation.

with organic matter, (3) dense, spongy pore texture of the organic matter, (4) abundant contiguous pores filled with organic matter having a spongy pore network, (5) no alignment of pores in organic matter (aligned OM pores are present in some kerogen),

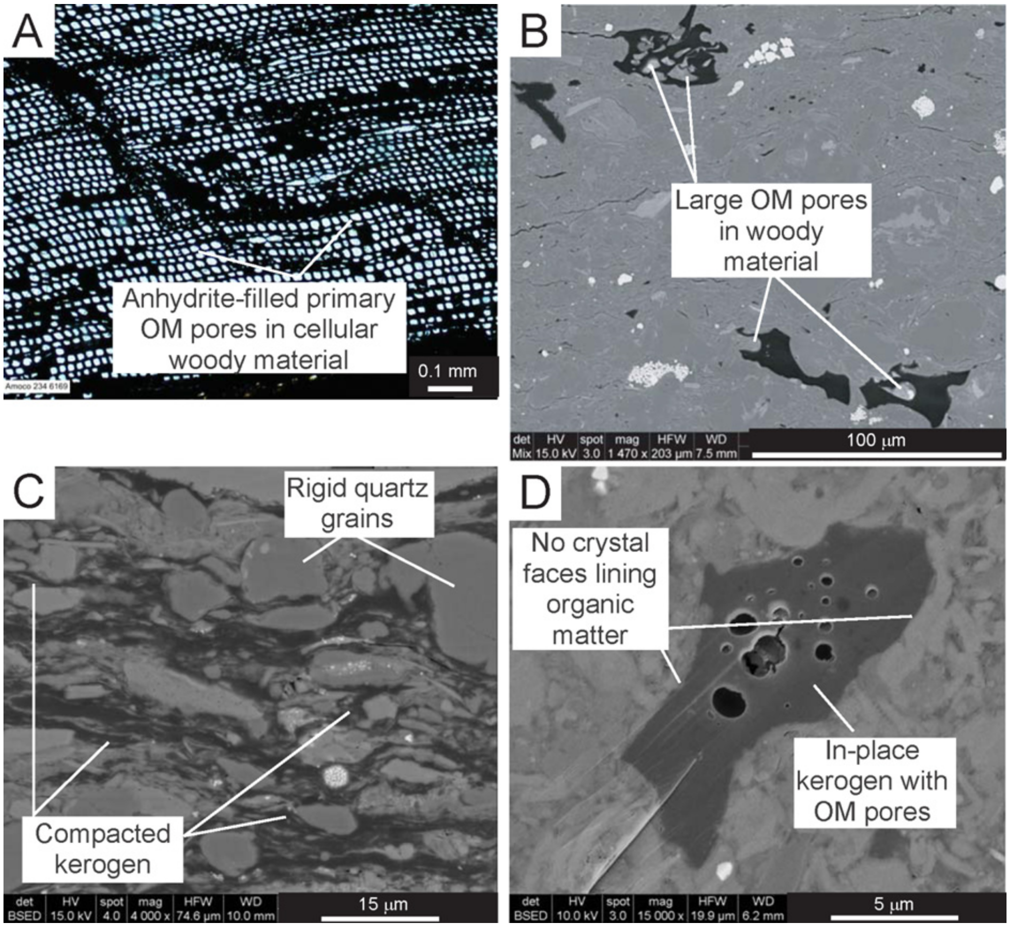

Figure 3. (A) Thin-section photomicrograph of woody organic matter with anhydrite-filled original OM pores. Permian Clear Fork Formation, Ector County, Texas, Amoco GLDU 234, 6168 ft. (B) SEM photomicrograph of woody material chips containing large original OM pores. Upper Cretaceous Skull Creek Formation, Niobrara County, Wyoming, Cities Service Federal CM No. 1, 10,207 ft, calculated Ro = 1.1%. (C) SEM photomicrograph of compacted kerogen. Kerogen is generally composed of compacted micrometer-sized organic particles/aggregates and may occur in seams. The kerogen in this photomicrograph has squeezed around rigid grains, eliminating any visible primary intraparticle mineral pores. Mississippian Barnett Shale, McCulloch County, Texas, Houston Oil and Mineral Johanson No. MC1–1, 1086 ft, calculated Ro = 0.51%. (D) SEM photomicrograph of organic matter interpreted to be depositional kerogen or byproduct. Organic matter shows no crystal growth between it and adjacent minerals. Upper Cretaceous Eagle Ford Formation, Frio County, Texas, Quintana Halff No. 1, 6458 ft, calculated Ro = 0.75%.

(6) cracks in organic matter related to devolatilization, and (7) anomalously larger bubbles associated with development of two hydrocarbon phases.

Criterion 1: Kerogen is a ductile organic-matter particle that fills space between more rigid grains in a mudrock. As a result of its ductility, kerogen will compact and squeeze between the more rigid grains occluding adjacent pore space (Figs. 2B and 3C). This property is well shown in a low Ro sample from the Barnett Shale (Fig. 3C) in which abundant organic matter has squeezed between adjacent rigid grains. The organic matter shows no visible pore development at the SEM scale of observation and the lack of development is related to the low calculated Ro (0.51%) of the sample. As a direct result of the squeezing of the organic matter, no mineral pore space is available for later cementation, and the organic matter is in direct contact with the detrital mineral grains (Fig. 3C). Another example of depositional kerogen (or direct alteration product) is shown in Figure 3D. In contrast, bitumen and oil may have migrated into mineral pores after the initiation of cementation. In such a situation, the migrated bitumen or oil would fill the cement-lined pores and the cement would separate the bitumen or oil from the mineral grain (Figs. 4 and 5). In some cases, if migration was initiated during crystal growth, some bitumen or oil can be included in the crystals. Also, mineral pores tend to fill with authigenic cement crystals. The bitumen or oil may reside where cement does not totally occlude the pore (Figs. 4A and 4B). The migrated organic matter may form OM pores with increasing thermal maturation. Excellent examples of this criterion are shown in Figures 4B–4D and 5C. Figure 5C shows a former mineral pore lined with well-developed crystal faces. The porous solid bitumen or pyrobitumen fills in around the crystal overgrowths, indicating the bitumen entered the mineral pore after crystal growth. In the central globigerinid chamber of Figure 4B, several crystals of calcite with well-developed crystal faces are surrounded with solid organic matter. This organic matter entered the intraparticle pore space as bitumen or oil after the stage of crystal growth. The organic material is now either solid bitumen or pyrobitumen.

Criterion 2: Depositional kerogen particles fill interparticle mineral pore space between grains. Very rarely will kerogen be reworked by biological activity into intraparticle mineral pores (body cavity pores). Therefore, where intraparticle pores are filled with organic matter, especially where organic matter totally fills the chamber, the organic matter most likely migrated into the chamber as bitumen or oil (Figs. 4B and 4C). Figure 4B shows an Eagle Ford Shale sample in which a globigerinid has three chambers, each filled with cement and/or organic matter that is interpreted to be solid bitumen (Ro of ~0.8% appears too low for the organic matter to be pyrobitumen). The lower left chamber is totally filled with porous solid bitumen. A thin rim of calcite overgrowth lines the chamber. The middle chamber shows calcite cement rimming the chamber and several larger calcite crystals in the chamber. Paragenetically, the solid bitumen overlies the authigenic calcite cements, indicating that the present-day bitumen must have migrated as bitumen or oil into the chamber after the calcite precipitated. The devolatilization cracks (discussed below) support the supposition that the fill material is solid bitumen. The upper right chamber is filled with authigenic kaolinite booklets. This chamber, too, is lined with a rim of calcite crystal overgrowths. The porous solid bitumen overlies the calcite cement rim and fills in between the kaolinite booklets, indicating late emplacement of the organic matter by migration of bitumen and oil.

Criterion 3: In many examples where the above two criteria indicate migrated organic-matter material, the organic matter appears to have a well-developed spongy texture produced by numerous OM pores (Figs. 4C, 4D, and 5). The examples pre-

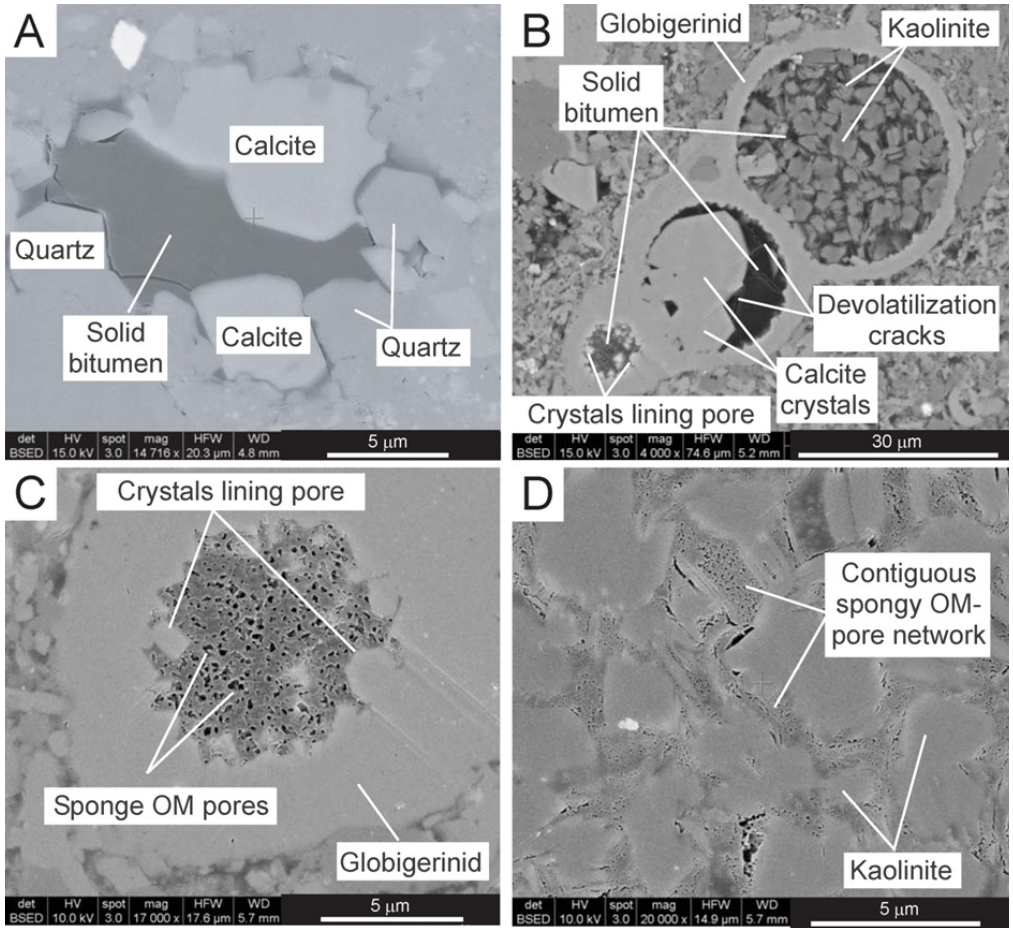

Figure 4. (A) SEM photomicrograph of former mineral pore now lined with quartz and calcite overgrowths. Remaining mineral pore space filled with solid bitumen or pyrobitumen showing no pore development. Lower Bexar Member of Lower Cretaceous Pearsall Formation, LaSalle County, Texas, Tidewater Oil Mable Wilson No. 2, 11,755 ft, calculated Ro = ~1.2%. (B) SEM photomicrograph of multichambered globigerinid with early calcite crystals followed by organic-matter emplacement. Middle chamber exhibits well developed calcite crystals that precipitated before formation of solid bitumen. Solid bitumen contains devolatilization cracks. Upper Cretaceous Eagle Ford Formation, Zavala County, Texas, Gose Hassett No. 3, 6214 ft, calculated Ro = ~0.8%. (C) Close-up of bottom left chamber shown in B. Solid bitumen in intraparticle pore after calcite crystal growth, and solid bitumen shows a spongy OM-pore network. (D) Close-up of upper right chamber shown in B. Authigenic kaolinite precipitated in intraparticle pore before oil migrated into remaining pore space. Oil is now solid bitumen, showing a contiguous spongy OM-pore network.

sented in Figures 4C, 4D, and 5 show migrated organic matter having a well-developed spongy texture containing numerous OM pores. Evidence for migration of organic matter in each example is that the organic matter overlies crystal overgrowths, indicating the crystals precipitated first in mineral pores and, subsequently, bitumen or oil migrated into the mineral pores. Figure 4D also shows a devolatilization cracks suggestive of solid bitumen or pyrobitumen. This spongy texture was most commonly observed in migrated organic matter, but could also form in solid bitumen or pyrobitumen associated with depositional kerogen thermal evolution. No depositional kerogen associated spongy organic matter was seen in low-maturity samples and therefore is not believed to be related to original pores in the kerogen.

Criterion 4: Solid bitumen or pyrobitumen with spongy textures, as discussed above in criterion 3, is commonly abundant in numerous adjacent pores (Figs. 4D, 5D, and 6A). As shown in Figures 4B and 4D of an Eagle Ford Shale sample, several contiguous areas of organic matter are characterized by the spongy pore network. The organic matter overlies authigenic crystal of calcite, indicating the organic matter is later in the paragenetic sequence, therefore suggesting that the pore-filling organic matter initiated as migrated bitumen or oil. On the basis of the association of the contiguous, spongy organic matter with crystal overgrowths, it is suggested that contiguous, spongy organic matter is solid bitumen or pyrobitumen that initiated as migrated organic matter. In this sample, the calculated Ro is ~0.8% and, on this basis, we interpret it to be solid bitumen.

Criterion 5: Nonalignment or random orientation of OM pores in organic matter appears to be associated mainly with migrated organic matter (Figs. 4D, 5C, and 5D). Aligned elongate OM pores have been observed mainly in depositional organic matter. An example from the Eagle Ford Shale (Fig. 6B) displays such alignment of elongated pores. The absence of authigenic crystals along the mineral walls or within the organic matter in Figure 6B suggests that the organic matter is still kerogen or a byproduct. The alignment may be related to the original structure of the kerogen (Loucks et al., 2009). This criterion needs more investigation because the origin of the OM-pore alignment is unknown and may be multifactorial, creating some uncertainly.

Criterion 6: Devolatilization can create cracks in solid bitumen and pyrobitumen (Figs. 4B and 6C). Such cracks have not been observed in organic matter interpreted to be kerogen. The walls of the cracks can be smooth (Fig. 4B) or rough (Fig. 6C) and may have organic matter bridges perpendicular to the cracks (Fig. 6C). It is important to note that these devolatilization cracks may have formed during or after coring, but they are still indicative of solid bitumen and pyrobitumen. Similar devolatilization cracks have been observed by the authors at a larger scale in solid bitumen/pyrobitumen-impregnated sandstone and carbonate megapores.

Criterion 7: As migrated bitumen or oil transforms to solid bitumen or pyrobitumen, gas or oil trapped in the pore may produce anomalously large bubbles (Fig. 6A and 6D). Hydrous pyrolysis experiments have shown that bitumen decomposes in part to oil (Lewan, 1985). We suggest that when the oil is removed from a mineral pore by migration or evaporation, a large bubble pore might remain. Figure 6D shows migrated organic matter overlying euhedral calcite crystal faces with a bubble at the center of the upper right former mineral pore.

Criteria 1 and 2 above are near-conclusive evidence that the

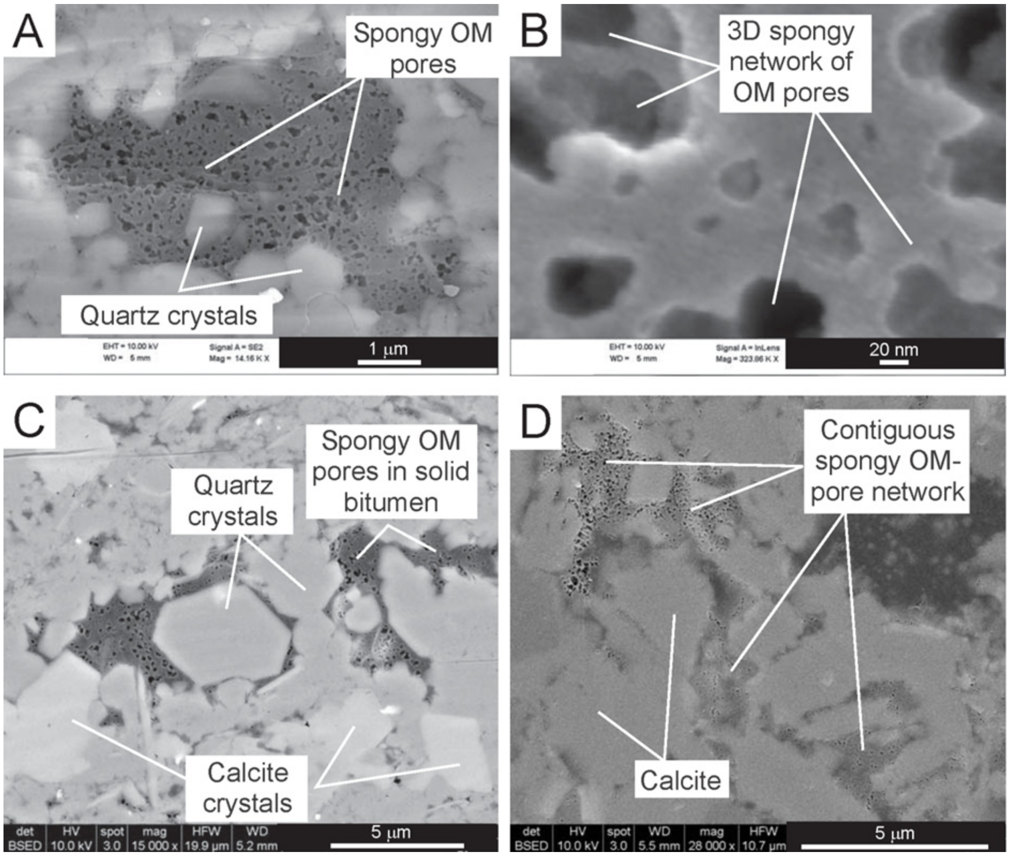

Figure 5. (A) SEM photomicrograph of former mineral pore lined with quartz crystals. Some quartz crystals are in center of pore but are probably connected to the pore wall in the third dimension. Remaining space filled with solid bitumen or pyrobitumen having spongy OM-pore texture. Mississippian Barnett Shale, Erath County, Texas, EOG French Ranch No. 1, 4676 ft, calculated Ro = 1.25%. (B) Close-up of spongy OM-pore texture shown in A. (C) SEM photomicrograph of mineral pore lined with quartz and calcite crystals. Solid bitumen or pyrobitumen displays a spongy OM-pore texture. Mississippian Barnett Shale, Wise County, Texas, Texas United Blakely No. 1, 7111 ft, calculated Ro = ~1.9 to 2.2%. (D) SEM photomicrograph of a contiguous spongy-textured OM-pore network. Organic matter (now solid bitumen) migrated into mineral pores after formation of calcite crystal overgrowths on calcite allochems. Upper Cretaceous Eagle Ford Formation, Zavala County, Texas, Gose Hassett No. 3, 6214 ft, calculated Ro = ~0.8%.

organic matter presently found in the pores has migrated into these pores, whereas criteria 3 to 7 are not as conclusive, but still provide supportive evidence for migration of organic matter as bitumen or oil. As with all petrographic criteria for interpretation and timing of paragenesis, multiple observations must be collected and integrated to form a reasonable conclusion. The above criteria allow a preliminary assumption of whether OM pores are associated with original depositional kerogen in place or with byproducts of kerogen maturation (e.g., bitumen or oil) that has migrated into mineral pores. In conjunction with maturity data, the above criteria allow for preliminary conclusions of whether the migrated organic matter is solid bitumen and/or pyrobitumen.

DISCUSSION

The above sections establish the concept that OM pores form within depositional kerogen and its migrated bitumen/oil-associated products, solid bitumen and pyrobitumen. This concept is important in understanding the origin and distribution of OM pores and the connectively of the OM-pore network.

The size of the organic-matter patches, whether in-place or migrated, will be controlled by two different processes. Depositional organic matter starts out as kerogen. The sizes of kerogen particles and aggregates will be controlled by the original size of the precursor material, near-surface degradation processes (biological and mechanical), energy level of the depositional environment, and oxygenation level of the depositional environment. Mudstone datasets observed by the authors indicate that type II organic matter, common in shale-gas and shale-oil systems, appears to have a very-fine particle size of less than 10 micrometers. The distribution of the depositional organic matter can vary from isolated individual particles (Figs. 3D, 6B, and 7) to local concentrations of particles, such as along laminae (Figs. 3C and 7) (Loucks et al., 2009). The sizes of patches of migrated organic matter are controlled by the size of the mineral pores into which the bitumen or oil migrated. Therefore, the compacted pore network at the time of migration will control both the range in sizes and distribution of migrated organic matter. Mineral pore sizes at different compacted states of the mudrock will vary considerably. Observations from numerous shale-gas and shale-oil systems indicate that the mineral pores in compacted mudrock range from a few nanometers to several micrometers.

Therefore, OM-pore networks will be a function of the combination of depositional organic-matter–associated OM pores and migrated organic-matter–associated OM pores. If at the time of hydrocarbon generation all previous open mineral pores have been destroyed by compaction or cementation, then all the OM pores would be confined to the depositional organic matter. In this case, we suggest that the resulting pore network would be limited because many of the OM pores would be in isolated organic matter particles (Fig. 7). As organic matter becomes more concentrated, such as along laminae (Fig. 7), connectivity and, hence, permeability is likely to increase. Migrated organic matter that fills the associated three-dimensional mineral pore network would more likely have a better three-dimensional OM-pore network than would the isolated depositional organic material with pores (Fig. 7). The solid bitumen in the former mineral pores would have occluded these pores, but would have also produced OM pores. These OM pores would be much smaller than the original mineral pores (Fig. 7) and associated permeability would be immensely lower. Therefore a combination OM-pore network consisting of OM pores in depositional and migrated organic matter would be expected to produce a pore network of higher reservoir quality than a pore network associated with only depositional organic matter. The combination OM-pore network would have enhanced three-dimensional connectivity that would produce more continuous permeability pathways than isolated organic matter alone.

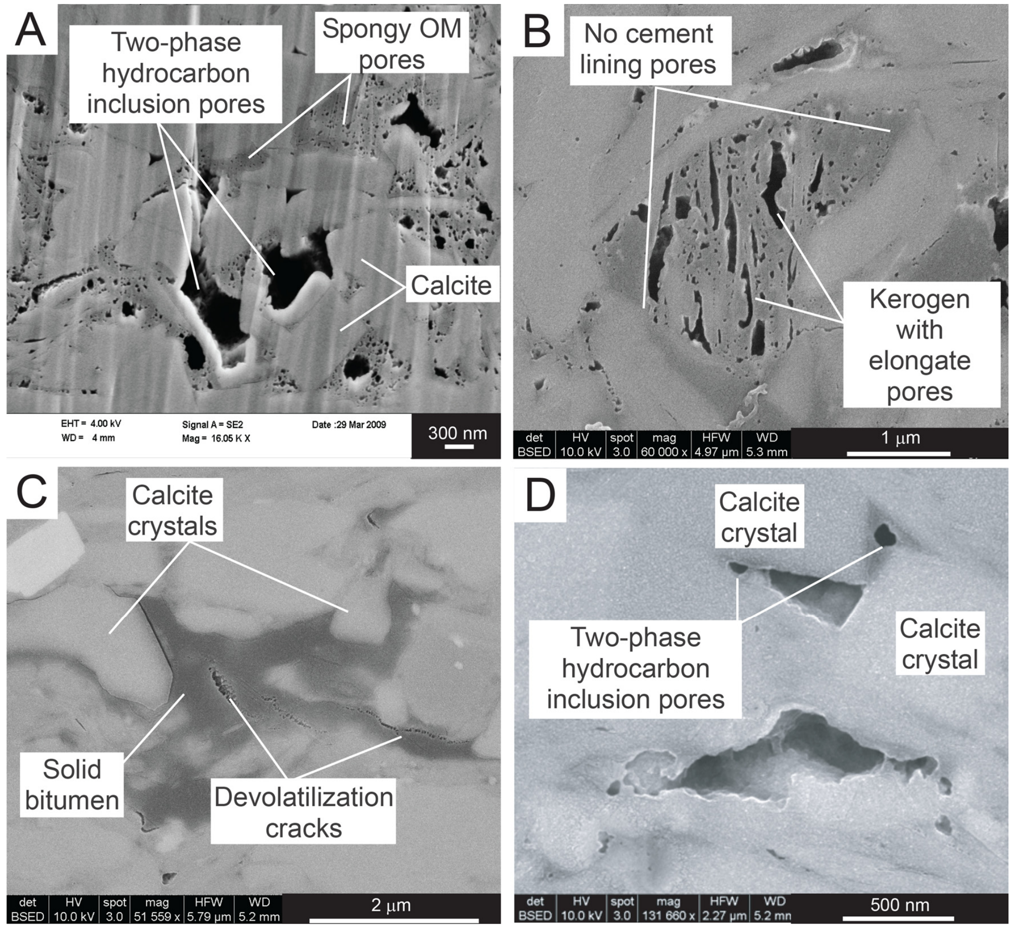

Figure 6. (A) SEM photomicrograph of contiguous spongy-textured OM-pore network. Organic matter, now solid bitumen, migrated into mineral pores after calcite crystal overgrowths formed on calcite allochems. Some larger pores might be OM pores associated with two-phase hydrocarbon inclusions (liquid and gas). Upper Cretaceous Eagle Ford Formation, DeWitt County, Texas, Shell Hay No.1, 13,818 ft, calculated Ro = ~1.5%. (B) SEM photomicrograph of organic matter with elongated aligned OM pores. Organic matter interpreted to be depositional kerogen because it lies directly in contact with mineral grains. Upper Cretaceous Eagle Ford Formation, DeWitt County, Texas, Shell Hay No. 1, 13,814 ft, calculated Ro = ~1.4%. (C) SEM photomicrograph of solid bitumen or pyrobitumen in former mineral pore, showing devolatilization cracks. Organic matter overlies calcite crystal overgrowths, indicating that organic matter migrated into mineral pore after cementation. Pine Island Shale Member of Lower Cretaceous Pearsall Formation, Atascosa County, Texas, Humble Pruitt No. 1, 9700 ft, measured Ro = 0.78%. (D) Photomicrograph of mineral pore where part of pore filled with solid bitumen or pyrobitumen containing bubbles that we interpret as having formed by two-phase hydrocarbon inclusion. Pine Island Shale Member of Lower Cretaceous Pearsall Formation, Atascosa County, Texas, Humble Pruitt No. 1, 9700 ft, measured Ro = 0.78%.

Another possible advantage of bitumen and oil migrating into mineral pores is that this process may inhibit the total occlusion of mineral pores by late-burial cementation. At the early stage of bitumen/oil migration, the mineral pores could be prime shale-oil reservoirs because of their general larger size. However, with later occlusion by solid bitumen in these mineral pores, the permeability of the mineral pore network would at first drastically decrease. However, with the formation of the OM pores, some permeability would be resurrected.

An additional observation in shale-gas and shale-oil system OM pore networks is that some of the mineral pores contain migrated organic matter, whereas other mineral pores are still migrated organic matter free. One suggestion we can provide for this observation is that pore-throat sizes within a mudrock pore system vary greatly. Therefore, the pores connected by larger pore throats are saturated with bitumen and/or oil, whereas the pores connected by smaller pore throats are left empty of bitumen and oil.

CONCLUSIONS

As research on the origin of OM pores continues and our knowledge increases, we find that understanding OM-pore networks becomes more complex. We now recognize that OM pores can be present in several types of organic matter, including kerogen, solid bitumen, and pyrobitumen. Also, we have found that organic matter hosting OM pores can be depositional (kerogen or its later alteration products, solid bitumen and pyrobitumen) or migrated (solid bitumen and pyrobitumen). To identify the type of organic matter hosting OM pores in consolidated samples (actual distribution within a consolidated sample) is difficult, if not impossible, without STXM-based C–XANES spectroscopy. However, there are several SEM petrographic criteria that can be used to discriminate depositional versus migrated organic matter and, in turn, understand whether OM pores are related to original depositional kerogen or related to bitumen and oil that migrated into mineral pores.

An important concept provided by the present investigation of depositional organic-matter–hosted OM pores versus migrated organic-matter–hosted OM pores is that the final pore network and connectivity pathways are dependent on the distribution of these two states of organic matter. Migrated organic-matter–hosted OM pores mimic the three-dimensional distribution of the original mineral pore network and provide more contiguous permeability pathways than isolated depositional organic matter alone (Fig. 7).

At present there are no investigations that have looked at reservoir quality relative to depositional versus migrated organic matter. Future quantitative analysis of reservoir quality based on different proportions of OM pores associated with depositional organic matter versus migrated organic matter is necessary in order to be able to understand reservoir quality in mudrock systems.

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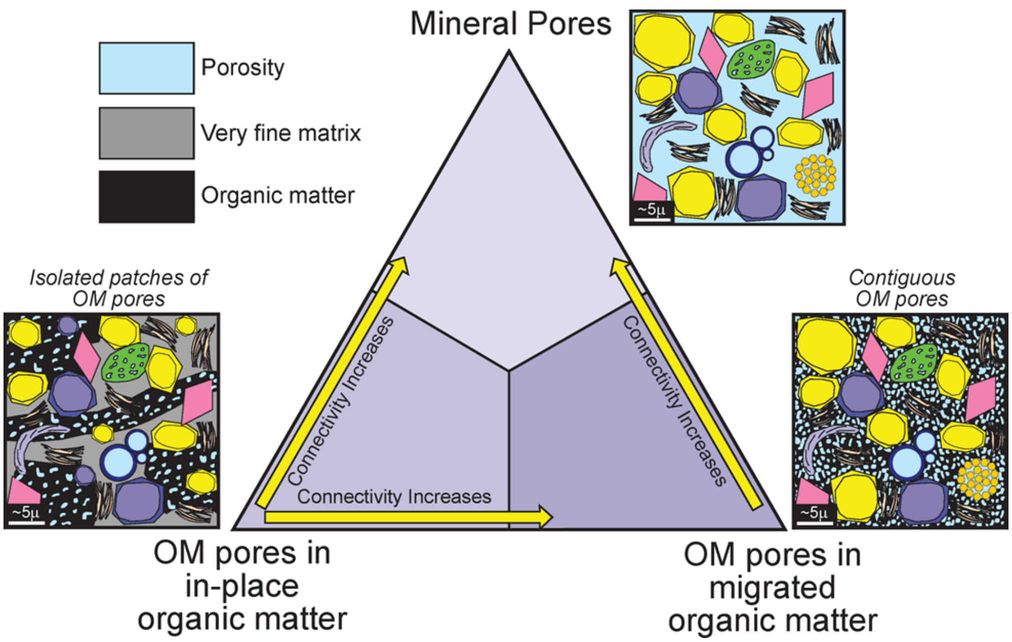

Figure 7. Ternary diagram showing end members (with schematic representations) of mudrock pore networks. Pore network can be combination of mineral pores, OM pores in depositional organic matter, and OM pores in migrated organic matter. We suggest that, as proportions of OM pores in migrated organic matter and mineral pores increase, connectibility increases, resulting in better permeability pathways.

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