Research Article

Petrographic Characterization and Maceral Controls on Porosity in Overmature Marine Shales: Examples from Ordovician-Silurian Shales in China and the U.S.

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The pore structure characterization and its controlling factors in overmature shales are keys to understand the shale gas accumulation mechanism. Organic matter in source rocks is a mixture of various macerals that have their own specific evolutionary pathways during thermal maturation. Pores within macerals also evolve following their own path. This study focused on petrographic characterization and maceral controls on porosity in overmature marine shales in China and the United States. Shale from Ordos Basin in China was also selected as an example of overmature transitional shale for maceral comparison. Organic petrology techniques were used to identify maceral types and describe morphological features in detail; scanning electron microscopy techniques were then used to document the abundance and development of pores within macerals. Helium measurement, mercury intrusion capillary pressure, and CO2 adsorption were especially applied to quantify the pore structure of Wufeng-Longmaxi shale from Sichuan Basin in China. The vitrinite reflectance equivalent of the studied overmature samples is ~2.4%. The macerals within the studied marine shales are composed mainly of pyrobitumen and zooclasts. At this maturity, pyrobitumen develops abundant gas-related pores, and their volume positively correlates to gas content. Three types of pyrobitumen and its related pore structure are characterized in Wufeng-Longmaxi shales. Zooclasts contribute to total organic carbon (TOC) content but little to porosity. When the TOC content is above 1.51% in Wufeng-Longmaxi samples, the TOC content positively correlates to quartz content. Organic matter strongly controls micropore development. Pores of diameter ~ 0.5 nm provide a significant amount of micropore volume. Clay mineral and quartz contents control micro- and macropore increments in organic-lean shales. MICP results indicate that pores within 3-12 nm and 900-2500 nm account for a major contribution to pore volume obtained. Determining the proportions of pyrobitumen to zooclasts within the total organic matter in pre-Devonian organic-rich marine shales is important in predicting porosity and gas storage capacity in high-maturity shales.

1. Introduction

Elucidating the pore network and its evolution in gas shales is a key topic in unconventional oil and gas exploration because many studies have shown that shale pore structure is one of the most important factors controlling gas storage capacity ([1]; Jarvie et al. 2007; [2–13]). Shale pores have been divided into micropore (<2 nm), mesopore (2-50 nm), and macropore (>50 nm) based on pore size [14]. Researchers also divided pores into interparticle pore, intraparticle pore, and
organic matter (OM) pore based on pore types and position
[15–20]. Previous studies suggest that various controlling
factors influence the abundance of pores, such as total
organic carbon (TOC) content and mineralogy [5, 16, 17,
21–23]. Quantitative assessments of pore volume and pore
size distribution analyzed by scanning electron microscopy
(SEM) imaging and gas adsorption techniques revealed that
OM porosity is a significant component of the pore networks
of shales [3, 5–7, 24–26]. Most researchers concluded that
TOC content has a positive relationship with porosity in
shales [4, 16, 18, 27–29]. For example, Mastalerz et al. [16]
suggest that OM contributes micropores to total porosity in
organic-rich marine shales. Also reported in the literature
are cases that do not show a strong TOC-porosity correlation
perhaps because of the presence of a significant inorganic
porosity fraction [15, 18, 23, 30–36]. A growing number of
researchers have suggested that porosity is influenced by
mineralogy and rock fabric [17, 31, 37]. For example, Masta-
lerz et al. [16] observed that total porosity increases with clay
and quartz content and decreases with carbonate content. Ji
et al. [38] and Chen et al. [39, 40] concluded that the biogenic
quartz in marine shale was typically accompanied by abun-
dant pores, whereas the quartz in marine-continental transi-
tional shale or continental shale had little influence on the
pore structure. Milliken et al. [17] proposed higher clay con-
tent may allow the collapse of OM pores and interparticle
pores, especially for deeply buried shales that have under-
gone immense compaction [40].

The effects of thermal maturation on porosity have
recently attracted more attention because of the growing rec-
novation that the porosity of OM is a function of thermal
maturity [4, 16, 18, 27, 29, 41, 42]. For example, Curtis
et al. [4] used focused ion beam milling combined with scan-
ing electron microscopy (FIB-SEM) techniques to inves-
tigate the organic porosity within Woodford shale, finding
that secondary organic porosity is absent in samples having
vitrinite reflectance (VR) values < 0.9% but does occur in
samples having VR > 1.23%. Mastalerz et al. [16] examined
the evolution of porosity with maturation in a suite of five
New Albany Shale samples spanning a maturity range from
immature (VRs = 0.35%) to postmature (VRs = 1.41%),
observing that total porosity and total pore volume show a
significant decline from immature to late mature and then
regain higher values in the postmature sample. However,
their data were limited to shales having VR values < 1.41%.
That study suggests that porosity change with maturity is
the response to oil and gas generation. In addition, there is
a growing awareness that different macerals have different
pore characteristics and that the evolution of porosity with
maturity is maceral-dependent [43–47]. A maceral is an
organic component of coal and shale. The type, amount,
and origin of macerals in shales are a function of their depo-
sitional environment. For example, the liptinite group
includes oil-prone macerals containing compounds of a
mainly aliphatic nature, and upon thermal evolution, they
produce hydrocarbons [48, 49]. The vitrinite group origi-
nates from lignin and cellulose, partly from tannins of the
woody tissues of plants [47, 50–52], and is considered to be
gas-prone. Liu et al. [45] studied maceral evolution in New
Albany Shale (NAS) as an example of kerogen type II marine
shale at the early mature to postmature stage. They show that
amorphous organic matter (AOM) and alginites are the dom-
inant organic components in their early mature samples,
whereas solid bitumen becomes the dominant OM in sam-
ples in the oil window and even higher-maturity stages. They
concluded that secondary organic nanopores developed in
solid bitumen when oil and gas were generated and expelled.
Vitrinite and inertinite did not contribute much to porosity.
Haeri-Ardakani et al. [53] discussed OM assemblage in
Utica shale samples, consisting of type II marine kerogen
(i.e., chitinozoans, graptolite, and liptinite) and migrated
bitumen. They also concluded that bitumen is the only
organic fraction that contributed to total porosity for Utica
shale samples in the oil window but not for samples in the
dry gas window [43].

Pore structure is constantly changing under the com-
bined effect of the thermal transformation of OM, and the
major control on shale pores at the overmature stage (range
from 1.5% to above 2.5%) remains unclear. The characteriza-
tion of porosity of various macerals in marine shale has
mostly been done on mature rocks where various macerals
are present and easy to identify [45, 47, 53]. However,
researchers also have different opinions on maceral identi-
cation in overmature shales. For example, Liu et al. [45] pro-
posed that AOM and alginites in New Albany marine shales
disappeared at the late mature stage. Hu et al. [54] identified
two types of alginate in overmature Longmaxi marine shales
in China. Besides, much less is known about the influence
of macerals on pore characteristics in high-maturity shales.
It remains unclear how the original OM evolves and how sec-
ondary products influence the overall porosity at the overma-
ture stage. Some researchers concluded that zooclasts also
contribute to porosity and, as such, are an important compo-
nent in gas storage [55, 56], but how zooclasts evolve during
maturation and how they differ from other macerals remain
unclear. In general, detailed organic petrology studies are
limited to high-maturity shales.

In this study, Late Ordovician to Early Silurian overma-
ture shales in China and the U.S. were chosen for petro-
graphic and porosity characterization. Most representative
samples come from the most productive marine shales in
Sichuan Basin in China (Figure 1), which have reached a
maturity equivalent to VRs = 2.3–3.0% [57–61]. Many
economically important high-maturity gas shales are of pre-
Silurian age, and they are characterized as a different mineral
and maceral composition which controls pore development
[62–64]. Specifically, this investigation is aimed at studying
(1) the pore type characterization in the overmature stage.
Both the marine and transitional shales are selected for mac-
eral comparison. Our study uses a combination of optical
microscopy and SEM to characterize OM in postmature
shales. Optical microscopy can evaluate the color, reflectance,
and morphology of OM and can identify maceral types [44,
65]. SEM observations of ion-milled argon allow us to exam-
ine nanometer-scale OM-hosted pores in shales [2, 66, 67].
This investigation is also aimed at studying (2) the pore
structure characterization in overmature marine shales and
major control factors on porosity. We chose CO2 gas
adsorption and mercury injection capillary pressure (MICP) analysis as tools of this study. Our study contributes to an understanding of maceral types and the control of SEM-detectable pores in different OM types in typical overmature pre-Paleozoic shales and aids in evaluating the pore structure control factors, occurrence, and storage of gas in overmature shale reservoirs.

2. Samples and Experimental Method

To characterize OM populations and pore structures, we used Wufeng-Longmaxi shale samples interpreted as being overmature from sedimentary basins in China. Wufeng-Longmaxi shales are from Sichuan Basin located in the southwest of China (Figure 1). Samples N1 and N12 were selected from a drilled core in Changning County, Sichuan Basin (Figures 1 and 2). The samples came from an interval of 2481 to 2576 m in depth, covering the Late Silurian to Early Ordovician time period (Table 1). Shales cover the gas-productive Wufeng-Longmaxi Formation. These sediments have been deposited on a deep-sea continental shelf and were interpreted to be overmature marine shales [34, 55, 61, 68–70]. Detailed sample information of Wufeng-Longmaxi shale is listed in Table 1.

Additional overmature shales of similar age and maturity from basins in China and the U.S. were also selected only for maceral comparison with Wufeng-Longmaxi shales. Two of them are also marine shales, and the other is marine-continental transitional shale. Marine shales include Utica shale and Xiuwu shale. Ordos shale belongs to transitional shale. The sample TRA-10 is an example of Early Silurian Utica shale from Appalachian Basin in the U.S. Utica shale is one of the most important gas-producing formations in North America [43, 53, 71–73]. A sample from Xiuwu Basin is characterized as an overmature marine shale deposit at the Ordovician time period [74]. Xiuwu shale is expected to have the highest maturity among marine shales. A shale sample from Ordos Basin is an example of a marine-continental transitional shale deposit in Carboniferous [75–77].

2.1. TOC, XRD, and Porosity Analysis of Wufeng-Longmaxi Shale

The TOC content and mineralogical composition were analyzed in the State Key Laboratory of Petroleum Resources and Prospecting at the China University of Petroleum in Beijing. The TOC contents of the shale samples were measured using a Leco CS230 carbon/sulfur analyzer. Samples were crushed to powder < 100-mesh size, and then 1 to 2 g samples were pyrolyzed up to 540°C. Samples were crushed to 300-mesh size for X-ray diffraction (XRD) analysis using a Rigaku
D/max-2500PC diffractometer at 40 kV and 30 mA. Crushed samples were mixed with ethanol, hand-ground, and then smear-mounted on glass slides. They were further scanned from 2° to 70° at a step of 0.02° and 2-second step time at room temperature.

The pore structure measurements were performed at Renqiu Jiechuang Petroleum Technology Corporation. Combined MICP and CO$_2$ adsorption were applied to quantify pore structure for different pore sizes. The pore size classification in this study follows the International Union of Pure and Applied Chemistry [78] and other recent pore studies (e.g., [79–81]).

Low-pressure gas adsorption measurements with carbon dioxide (CO$_2$) were conducted on a Micromeritics ASAP-2020 apparatus. The shale samples were crushed to 60-mesh size (180 μm). Detailed procedures could be found in Mastalerz et al. [16]. CO$_2$ gas adsorption was used to characterize micropores (<2 nm in diameter). The density functional theory (DFT) [82, 83] method was used to calculate the specific surface area and pore size distribution based on the adsorption curve.

Mercury intrusion data were collected on a Micromeritics Autopore 9520 instrument. The mercury pressure increases from 0 to 400 MPa. Pore size distribution was determined using the Washburn equation [84]. Pore throat size ranging between 3 nm (0.003 μm) and 3 × 10$^3$ nm (300 μm) was characterized. The mercury injection and withdrawal capillary curves were used to predict the behavior of fluids during pressure changes in reservoirs. Pore size distribution can be displayed as cumulative or log differential curves of pore volume or surface area. The log differential curves ($dV/d\log D$ or $dS/d\log D$) are widely used for comparing relative pore volumes and characteristics of pores [65, 85].

Total porosity measurements were carried out with ULTRAPORE-300 using a helium expansion method. The gas contents of the shale samples were analyzed by the Research Institute of PetroChina Southwest Oil & Gasfield Company. They were measured using direct methods, according to a procedure similar to the USBM method [86], and indirect methods following the sorption isotherm procedure described in the literature [87, 88].

**Figure 2:** Compositional analysis, total organic carbon (TOC) content, helium porosity, and gas content of selected Wufeng-Longmaxi shale samples (N1 to N12) at different depths.
Table 1: Lists of Wufeng-Longmaxi shale samples from Sichuan Basin and their depths, porosities, total organic carbon (TOC) contents, and mineral contents. Gas contents are also included. Gas contents include lost gas, desorbed gas, and remaining gas.

| Sample ID | Depth (m) | TOC (total organic carbon content, %) | Porosity (helium, %) | Clay mineral content (%) | Quartz (%) | Pyrite (%) | Carbonate (%) | Feldspar (%) | Gas content (m³/t) |
|-----------|-----------|--------------------------------------|----------------------|-------------------------|------------|------------|--------------|-------------|-------------------|
| N1        | 2481      | 1.23                                 | 5.23                 | 43.0                    | 38.3       | 3.1        | 12.5         | 3.1         | 1.62              |
| N2        | 2487      | 0.96                                 | 4.35                 | 46.3                    | 27.4       | 1.1        | 20.3         | 4.9         | 1.38              |
| N3        | 2498      | 0.89                                 | 4.47                 | 35.0                    | 47.0       | 2.0        | 10.1         | 5.9         | 1.34              |
| N4        | 2503      | 1.07                                 | 4.22                 | 36.6                    | 40.7       | 1.1        | 13.5         | 8.1         | 1.42              |
| N5        | 2513      | 1.31                                 | 4.53                 | 34.3                    | 36.0       | 1.5        | 16.0         | 12.2        | 1.55              |
| N6        | 2534      | 1.51                                 | 5.30                 | 38.2                    | 40.3       | 1.5        | 13.1         | 6.9         | 1.98              |
| N7        | 2540      | 2.15                                 | 5.25                 | 35.6                    | 43.9       | 2.6        | 12.6         | 5.3         | 2.33              |
| N8        | 2554      | 2.98                                 | 5.30                 | 26.0                    | 55.1       | 3.6        | 12.0         | 3.3         | 2.41              |
| N9        | 2563      | 3.39                                 | 5.47                 | 25.1                    | 46.8       | 3.7        | 20.7         | 3.7         | 2.54              |
| N10       | 2567      | 3.52                                 | 5.67                 | 16.2                    | 64.8       | 2.7        | 14.3         | 2.0         | 2.61              |
| N11       | 2573      | 3.19                                 | 5.22                 | 15.9                    | 54.6       | 2.1        | 24.5         | 2.9         | 2.63              |
| N12       | 2576      | 4.18                                 | 5.88                 | 11.8                    | 59.3       | 2.7        | 22.3         | 3.9         | 3.08              |

2.2. Organic Petrology and Scanning Electron Microscopy (SEM) Analysis. Each core sample was cut into ~2 × 1.5 cm fragments. Organic petrology and SEM observations were carried out in the same area; reflected light microscopy was used to identify OM, whereas SEM was used to visualize pores, as well as to evaluate changes in the rock fabric resulting from different mineralogies.

Samples were argon-ion-milled with Gatan 600 DuoMill using a custom-designed sample holder and then observed and analyzed using field emission- (FE-) SEM (Quanta 200F) in low vacuum mode at the China Petroleum Exploration Research Institution. FE-SEM was performed using a Hitachi S-4800 FE-SEM microscope with an accelerating voltage of 1.0 kV. Samples were not coated. The analyzed areas were photographed/mapped to enable the subsequent identification of the same OM particles under a microscope. All SEM images were taken under secondary electron imaging mode. Considering the heterogeneity of shales, 60 evenly spaced SEM pictures were taken within the sample to document the morphology and pore development of OM particles. In the same areas where SEM photomicrographs were taken, organic macerals were identified using reflected light microscopy (Leica DFC310 FX) at Indiana University in Bloomington, Indiana, USA. To evaluate the maturity of the samples, the reflectance of graptolite and/or pyrobitumen was measured under reflected white light and oil immersion, with 25 readings recorded.

2.3. Micro-FTIR. Micro-FTIR measurements were performed with a Nicolet 6700 spectrometer connected to a Nicolet Continuum microscope operating in reflectance mode. For micro-FTIR mapping, the smallest aperture size used for the area analysis is 25 × 25 μm. Details about instrumentation were presented by Wei et al. [89]. Briefly, Micro-FTIR spectra were obtained at a resolution of 4 cm⁻¹, using a gold plate as a background. The spectra cover a wavenumber range from 650 cm⁻¹ to 4000 cm⁻¹. The OMNIC program was used for spectral deconvolution, curve fitting, and determination of peak integration areas. Reflectance micro-FTIR spectra were subjected to Kramers-Kronig transformation. Peak assignments of spectra were based on Painter et al. [90, 91] and Wang and Griffiths [92].

3. Results

3.1. Compositional Analysis, TOC, Helium Porosity, and Gas Content of Wufeng-Longmaxi Shale. Twelve Wufeng-Longmaxi samples from one well at different depths were chosen for this study. The analyzed TOC content, mineral composition, and helium porosity results of Wufeng-Longmaxi shale (N1 to N12) are presented in Table 1. Relationships between depths and those geochemical parameters are shown in Figures 2 and 3. In the well, the TOC content decreases upward in the section, ranging from 4.18% to 0.89%, and the gas content has a similar decreasing trend with shallower depths. Mineralogically, the quartz and clay mineral contents are the main components, accounting for ~46% and ~30%, respectively, in the studied samples. The average value of carbonate content is ~16%, and pyrite and feldspar contents are minor (a few percent, on average). Samples N1 to N7 at shallower depths have relatively lower quartz and carbonate contents but higher clay mineral content compared to samples at greater depths. Quartz content exhibits a weak positive relationship with TOC content ($R^2 = 0.69$) for all twelve studied Wufeng-Longmaxi shales (Figure 3(b)). However, quartz content is obviously correlated with TOC content in shale with clay content < 38% (approximately equal to the mean value of clay content in the twelve studied samples), while no obvious relationship is shown with increasing TOC in shales with high clay content (>~35%). Furthermore, clay content shows an obvious negative relationship with TOC content ($R^2 = 0.84$). The helium porosity of the samples was between 4.22% and 5.88%. The result shows that the gas yield ranged from 1.34 to 3.08 m³/t of rock. Overall, the TOC content, helium porosity, quartz and carbonate contents, and gas content increase...
Figure 3: (a) Relationship between depth and total organic carbon (TOC) content (%), mineral content (%), helium porosity content (%), and gas content (m$^3$/t) of Wufeng-Longmaxi shales. (b) Crossplot of quartz content vs. TOC content. Crossplot of clay mineral content vs. TOC content. The marked numbers are contents (%) of clay minerals of Wufeng-Longmaxi shales.
with depth, especially when depth is at 2540 m and deeper. The measured mean reflectance of pyrobitumens in sample N9 at 2573 m is 2.22%, and three equations were used to calculate equivalent vitrinite reflectance (VRo): (1) VRo = (0.618 × BRo (bitumen reflectance)) + 0.4 = 1.77% [93]; (2) VRo = (BRo + 0.41)/1.09 = 2.41% [94]; and (3) VRo = (BRo − 0.059)/0.936 = 2.31% [95]. Even though the values obtained range in amounts, they all indicate a postmature stage and dry gas window.

3.2. Organic Petrology and Maceral Morphology

3.2.1. Wufeng-Longmaxi Shale. Reflected light microscopy and SEM were used to identify and describe different macerals (Figures 4(a) and 4(b)). Photomicrographs of the same areas at the same scale were taken using those two methods (Figures 5 and 6). Under incident white light, a large number of gray structureless OM were observed in Wufeng-Longmaxi shale; those small OM particles (less than 10 μm) are pyrobitumens. Some pyrobitumens occur as speckles disseminated in the shale matrix (Figures 4(a), 4(b), and 5(d)), and some occupy interparticle pores and microfractures (Figures 4(c) and 4(d)) or are present inside zooclasts and mineral grains (Figures 4(e) and 4(f)). We divided pyrobitumens into three types depending on morphology and pore distribution within the particle. The most abundant type is pyrobitumen I, which has no specific shape and fills in intergranular pores and cracks of minerals (Figures 4(c)–4(f)). Occasionally, larger pieces (several micrometers in size) of pyrobitumen (type II) were also observed (Figures 4(g) and 4(h)). Pyrobitumen II featured an intact shape, which does not distribute around microfractures nor surround minerals. Their shapes are not fixed due to compaction and other effects, with diameters ranging from 1 μm to more than 10 μm. They have clear edge outlines. Pyrobitumen III featured a unique surface different from types I and II. The surface is not smooth but displays uniform pellets inside (Figures 4(i) and 4(j)). Pellets are easily recognized under SEM pictures. This OM is composed of small aggregates of quasispherical bacteria. The diameters of the pellets range from 300 to 400 nm. Affected by compaction, some pellets are flattened to form flat spheres.

Other organic components are fragments of structured zooclasts, including graptolite and chitinozoan (Figures 5(a)–5(d)). The graptolite fragments are grayish-white under reflected light and are characterized by biological morphologies with sharp outlines. Commonly, they are stacked or are forming laminae with a fibrous or threadlike structure (Figures 5(a), 5(b), and 6(a)–6(d)). Void space in these graptolite fragments could be filled with carbonates or quartz. Chitinozoan fragments generally have a segment or scalene shape (Figures 5(c), 6(e), and 6(f)), with a chamber confined by the cell wall. Most zooclast particles seem to be filled with minerals, and OM remains only along the edges. Wufeng-Longmaxi shale samples have the same maceral types at different depths, but the total OM content and relative proportions of pyrobitumen and zooclasts vary. Sporadically, some bodies similar in form to acritarchs could also be found (Figures 6(g) and 6(h)). An acritarch is a small microfossil of unknown and probably varied biological affinities with varied symmetry, shape, structure, and orientation [96]. It can originate from algae, fungal spores, organic-walled cysts from unicellular protozoa, or spaws of higher organisms. Their central cavity is closed or communicates with the exterior via pores, slitlike or irregular ruptures, or circular openings (Figures 6(g) and 6(h)).

3.2.2. Utica Shale. The measured TOC content of Utica shale TRA-10 is 4.1%. Twenty-five points of graptolite reflectance (GRo) were measured, and the mean reflectance value is 2.32%. The equivalent VRo was calculated using the same three empirical equations with Wufeng-Longmaxi shale, and the calculated values are 1.83, 2.50, and 2.41 [93–95], indicating the dry gas window. The measured helium porosity of this sample is 3.95%.

In TRA-10, the dominant maceral is graptolite, which consists of ~95% of the whole OM. Graptolites are typically oriented in a direction parallel to the bedding plane. Some occur as large pieces (~20–50 μm) in the matrix (Figures 7(a) and 7(b)), whereas others are small (a few μm or smaller) and dispersed in the matrix (Figures 7(c) and 7(f)). The spindle shape of graptolites can also be observed (Figure 7(e)). In this sample, pyrobitumen is much less common than graptolites and occurs around mineral grains in relatively small particles of <1 μm (Figures 7(c), 7(d), and 7(f)). Framboidal pyrite is common.

3.2.3. Ordos Shale. The measured TOC content of Ordos shale is 2.14%. Twenty-five points of vitrinite were measured, and the mean reflectance value is 1.88%, indicating the sample is at the overmature stage. Different from other overmature marine shales in this study, the OM in Ordos shale is composed of vitrinite and inertinite (Figures 8(a) and 8(b)). The vitrinite and inertinite pieces have no observable organic pores under a microscope.

3.2.4. Xiuwu Shale. In Xiuwu shale, the observed macerals are pyrobitumen and zooclast (Figures 8(c) and 8(d)). Pyrobitumen consists of ~95% of the whole OM. The measured TOC content is 2.84%, and the mean reflectance value from twenty-five points of pyrobitumen measurements is 3.32%. The equivalent VRo was calculated using the empirical equation proposed by Landis and Castaño [94]: VRo = (BRo + 0.41)/1.09 = 3.42%, indicating a highly overmature stage.

3.3. Organic Pores Analyzed by SEM. In Wufeng-Longmaxi shale samples, large pores (micrometer in size) were observed in pyrobitumen; they can be round, subrounded, or irregular in shape (Figures 9(a)–9(f)). The round pores have a sponge-like shape and texture (Figure 9(b)). Inside some round pores, two tail-like traces can be seen. Clay minerals generally feature a curved to highly contorted scaly and silk thread laminar structure, whereas brittle minerals had a relatively regular shape and lower brightness [58, 97, 98]. In the studied samples, relatively round and subrounded pores generally were observed in pyrobitumen surrounding brittle minerals (Figures 9(a)–9(d)). The pyrobitumens having deformed or irregular pores are usually filled inside or occurred near clay minerals having layered or deformed structures (Figures 9(e)

Geoﬂuids
Figure 4: Continued.
and 9(f)). Some pyrobitumens had irregular surfaces with abundant pores so that it was difficult to recognize them at a micrometer scale.

Pyrobitumen I has a uniform internal texture, and its pores are uniform or random (Figures 9(a)–9(f)). The pores in pyrobitumen I can be divided into two types: (1) irregular pores with spongy uniform distribution (Figure 9(b)) and (2) circular or elliptical pores (Figures 9(a) and 9(c)–9(f)). The latter has pores of different sizes that coexist. In comparison, pyrobitumen II has no observable pores within OM particles (Figures 4(g) and 4(h)). Those two types are related to hydrocarbon generation processes at the late stage. Pyrobitumen III displays a different morphology but a homogeneous internal biological structure (Figures 4(i) and 4(j)). This type of pyrobitumen consists of bacteria-like particles; the pores are significantly different from the bubble-like pores in bitumen. The pores are randomly distributed but display a homogeneous internal biological structure.

No pores could be found in graptolite or chitinozoan in the studied samples, even after enlarging images to the nanometer scale (Figures 10(a)–10(d)). It is interesting to note that SEM photomicrographs from the same Wufeng-Longmaxi shale taken on cores without any polishing (Figures 10(e)–10(h); Figure 10(f) is an amplified picture of Figure 10(e); Figure 10(h) enlarges Figure 10(g)) do show pores in graptolites at a micrometer scale. This observation is in contrast to what we observed in ion-milled samples described in this study (Figures 10(a) and 10(b)).

As described in the methods section, 60 SEM pictures were taken of each sample at different depths from Wufeng-Longmaxi shale. The studied area is the same size on each sample, which allowed us to roughly compare the different maceral contents of the samples. The OM content increases with deeper depth in the studied samples, which is also reflected by the area of dark material in the SEM images of samples (Figures 11(a)–11(h)). Pyrobitumen is
the dominant maceral in all samples, and it increases in samples from 2567 m deep and deeper. Zooclast content, including graptolite and chitinozoan, also increases with increasing pyrobitumen content.

For Utica shale, in the SEM analysis at micrometer to nanoscales, most (~95%) of the analyzed graptolites had no pores detected under SEM (Figures 12(a)–12(e)). A few pores of irregular and narrow shape were found in some graptolites (Figure 12(f)). For Xiuwu shale, pyrobitumen also is featured as structureless and filling characterization. However, different from Wufeng-Longmaxi shale, those pyrobitumen pieces have already lost abundant OM pores (Figures 8(c) and 8(d)). In addition, the inertinite and vitrinite particles in Ordos shale also featured no observable organic pores inside (Figures 8(a) and 8(b)).

3.4. Pore Characterization Based on CO₂ Adsorption and MICP in Wufeng-Longmaxi Shale. Low-pressure CO₂ adsorption was applied to characterize the micropore (pore diameter < 2 nm) distribution. CO₂ adsorption isotherms of the studied shales display similar variations and trends as type I (Figure 13), which is generally characterized by microporous solids [14]. Maximum volumes of adsorbed CO₂ range from 0.893 to 2.286 cm³/g. The volume of adsorbed CO₂ increases with TOC content (Figure 13). DFT micropore volumes range from 0.001 to 0.003 cm³/g, and DFT micropore surface areas range from 3.60 to 9.89 m²/g (Table 2).

The strongest adsorption happened in shale samples N8, N9, and N10 of the highest TOC content. Sample N5 adsorbs the least amount of CO₂, whereas samples N2 to N4 adsorb intermediate volumes. Comparing samples N2 to N5, sample N5 has relatively higher TOC content and feldspar values but relatively the least clay mineral content and quartz content.

The micropore size distribution up to 1.2 nm was calculated with the DFT model (Figure 14). Pores with diameter < 1 nm have different log differential pore volumes. There are three higher $dV/d\log D$ peaks at approximately 0.40-0.50 nm, 0.55-0.60 nm, and 0.80-0.81 nm, which indicate a high abundance of micropore distributions of those pore size

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**Figure 5:** Organic petrography photomicrographs (oil immersion, white incident light) showing typical types and morphology of organic matter in Wufeng-Longmaxi shale samples. (a, b) Graptolite fragment with biological shape and fibrous structure within its cell wall. (c) Chitinozoan fragment with a segment or scalene shape. (d) Pyrobitumen of ~40 micrometers in size filling the shale matrix.
Figure 6: Continued.
ranges. The peaks of log differential pore volume increase with increasing TOC content. Pores of diameter approximately 0.5 nm provide a significant amount of pore volume.

MICP was applied to quantify the pore structure of diameter > 5 nm, especially for macropore diameter > 50 nm. A certain pressure of mercury intrusion corresponds to a specific pore diameter. The volume of mercury intrusion under different pressures reflects pore volume within the corresponding pore size. The mercury intrusion curves exhibit two different trends in studied samples, which are presented in Figures 15(a) and 15(b). Samples N2 to N5 with relatively lower TOC content are examples of type I. The volume of mercury intrusion first increases (0.01–1 MPa) and is then kept stable (1–400 MPa) (Figure 15(a)). Samples N8 to N10 are another type of curve. The volume of mercury intrusion shows a rapid increase (0.01–1 MPa), a relatively stable phase (1–50 MPa), and a rapidly increasing phase (50–400 MPa) (Figure 15(b)). Maximum volumes of mercury intrusion, i.e., the total pore volumes, range from 0.007 to 0.020 cm\(^3\)/g, with an average of 0.011 cm\(^3\)/g. The specific surface area ranges from 1.49 to 3.83 m\(^2\)/g, with an average of 2.72 m\(^2\)/g.

Different mercury injection curves are closely correlated with TOC content and also indicate different pore size distributions. The relationship between pore size distribution and log differential pore volume is shown in Figure 16, which exhibits basically similar variations and trends in studied shales. It is obvious that the log differential pore volume featured distribution with two peaks at 3-12 nm and 900-2500 nm, which suggests that pores within these two intervals account for a major contribution to total pore volume obtained by MICP. Additionally, the inconsistency of pore size distribution in different samples indicates a strong heterogeneity of pore networks.

3.5. Pore Structure and Its Relationship with TOC and Mineral Composition in Wufeng-Longmaxi Shale. Pore structure parameters (i.e., pore volume and surface area) were obtained by CO\(_2\) gas adsorption and MICP. The cumulative micropore pore volume, micropore surface area, and macropore volume show an obvious increasing trend with TOC content that changed from ~1% to ~3%, but no such change trend in the macropore surface area. For samples with TOC contents of 0.96%-1.31%, the average micropore volume is 0.00113 cm\(^3\)/g, and the average micro pore surface area is 3.984 m\(^2\)/g. For samples with TOC contents of 2.98%-3.52%, the average value is 0.00237 cm\(^3\)/g, and the average micro pore surface area is 8.123 m\(^2\)/g.

The quartz content has a positive influence on the micropore surface area, micropore volume, and macropore volume when the quartz content is above ~40%. Clay mineral content has a negative influence on the micropore surface area, micropore volume, and macropore volume when its content is above 30%. However, when the TOC is below ~3%, the increasing clay mineral content is positively correlated to micropore and macropore volumes.

3.6. Variations in Functional Group Abundances among Maceral Groups. The purpose of using micro-FTIR analysis was to investigate whether differences between macerals are also reflected in their chemical structures and, in particular, if chemical functional groups can differentiate between zooclasts and pyrobitumen. Micro-FTIR is capable of characterizing the chemical properties of in situ particles of macerals as small as 10–30 \(\mu\)m. The main difficulty with this technique is recognizing and identifying macerals under a dry objective. Therefore, only macerals of relatively large size were analyzed by FTIR, i.e., pyrobitumen in Wufeng-Longmaxi shale and graptolite in Wufeng-Longmaxi shale and Utica shale. To facilitate maceral identification, photomicrographs under reflected light microscopy were taken prior to FTIR analysis. IR signals derived from the following functional groups were of
Figure 7: Organic petrography photomicrographs (oil immersion, white incident light) (a, c–f) and SEM images (b) showing typical maceral types (graptolite and pyrobitumen) and distributions of sample TRA-10. (a, b) The microscopy (a) and SEM (b) analysis on the same area of TRA-10. The larger rectangles in (c, d, f) are enlarged areas of the related smaller rectangles. (a, b) Typical graptolite grains occurred as large pieces and oriented in a direction parallel to the bedding plane. (c, d, f) Thinner graptolite pieces dispersed within the shale matrix. (c–f) Small pyrobitumen (less than a few micrometers) grains filled in minerals and oriented in various directions. (e) Some graptolites of a spindle or lenticular shape.
particular interest to this study: (i) aromatic CH\textsubscript{x} stretching in the 3000–3100 cm\(^{-1}\) region, (ii) aliphatic CH\textsubscript{x} stretching at 2800–3000 cm\(^{-1}\), (iii) oxygenated groups at 1650–1800 cm\(^{-1}\), and (iv) aromatic C=C ring stretching at 1550–1650 cm\(^{-1}\) [99].

The micro-FTIR spectra of pyrobitumen and graptolites in the samples studied are compared in Figure 17(a). Most analyzed particles were very small and close to the detection limits of the technique. Because of small particle sizes, the spectra are noisy; however, most functional groups were easily detectable. In this study, pyrobitumens show very weak absorbance in both aliphatic CH\textsubscript{x} stretching at 2800–3000 cm\(^{-1}\) and aromatic CH\textsubscript{x} stretching between wavenumbers 3000–3100 cm\(^{-1}\). They exhibit weak absorbance in oxygenated groups at 1650–1800 cm\(^{-1}\) and aromatic C=C ring stretching at 1550–1650 cm\(^{-1}\). In comparison, graptolites feature more distinct aliphatic CH\textsubscript{x} stretching at 2800–3000 cm\(^{-1}\) and higher absorbance of oxygenated groups at \(\sim 1710\) cm\(^{-1}\).

Previous FTIR spectra of alginite, AOM, solid bitumen, vitrinite, and inertinite studied by Wei et al. [89] on early mature Devonian New Albany Shale (marine mature shale, kerogen type II) are shown in Figure 12(b) for comparison. We note that our study used the same experimental method as Wei et al. [89]. Compared with macerals in NAS, graptolite spectra from this study are very similar to those of vitrinite and inertinite of Wei et al. [89]; they display relatively strong peaks at 2800–3000 cm\(^{-1}\) and 1710 cm\(^{-1}\). Compared to solid bitumen from NAS, the pyrobitumen of the present study has weaker absorbance of aliphatic CH\textsubscript{x} stretching and aromatic CH\textsubscript{x} stretching at 2800–3000 cm\(^{-1}\) and 3000–3100 cm\(^{-1}\) functionalities. The C=O and aromatic C=C peak intensities in pyrobitumen and solid bitumen appear similar.

4. Discussion

4.1. Compositional Controls on Porosity and Pore Structure. Previous studies have indicated that different origins of quartz could have different influences on shale porosity. Some studies proposed that the porosity increases with increasing detrital quartz content due to the compaction weakening effect and presence of intergranular pores between quartz grains [10, 100, 101]. In addition, quartz of
biogenic origins obviously plays a positive role in the porosity because of increasing TOC content [13, 102]. In comparison, the increasing biogenic quartz content could also decrease porosity due to secondary cementation of biogenic silica [103]. In our study, the quartz effect is also closely correlated to its origin. For relatively clay-poor shales (clay mineral

Figure 9: SEM images showing pyrobitumen and related pores in Wufeng-Longmaxi shale samples. (a–d) Pyrobitumen pieces with subround to round pores. Pyrobitumen is associated with minerals having a relatively regular shape and lower brightness. (b) Gas-related round pores with a tail-like structure within pyrobitumen. (e, f) Irregular or deformed pores in pyrobitumen filled with minerals of a curved to highly contorted scaly and silk thread laminar structure.
Figure 10: Continued.
content < 35%), quartz content is positively correlated with increasing TOC content, suggesting that the quartz in these shales is closely correlated with the biogenic origin, which is also indicated in previous studies [13, 102, 104]. For relatively clay-rich shales, quartz could mainly come from detrital input and has a weak correlation with the TOC content. Accordingly, different relationships between quartz and TOC content are attributed to the differences in their depositional environment and source input of quartz [65, 105]. In our study, there is also a positive correlation between TOC content and shale porosity parameters (pore volume and pore surface area). However, this relationship has a TOC content boundary. The existence of this boundary could result from different maceral types in OM, which would be discussed in Sections 4.2 and 4.3. When the TOC content in studied samples > 2%, the positive correlation is stronger than that in shale with TOC < 2%. The OM shows strong control than other factors in shales. In addition, the clay mineral content in shales is around 35% with the 2% boundary of TOC content. For clay-rich shales, OM and clay minerals together control pores in shales. The above different controls are due to the development of organic pores and also source input of quartz from detrital or biogenic origins. Content of biogenic quartz strongly correlates to OM and positively increases porosity compared to that of detrital quartz.

The OM plays a positive role in the micropore structure of Wufeng-Longmaxi shales. When the TOC content is above 1.5%, an obvious increase and strong positive relationship were found between TOC content, micropore volumes, and micropore surface areas, highlighting the large abundance of smaller pores within the organic fraction. However, the relationship between TOC content, macropore volumes, and macropore surface areas is not obvious. Clay mineral has a positive influence on macropores. The clay-rich shales usually have low TOC content, which reflects a significant contribution of clays to pore structure in organic-lean shales. Furthermore, pores in clays are usually well developed around quartz grains since rigid quartz grains can form pressure shadows that prevent pores in clays from collapsing (Yang et al. 2016).

4.2. Organic Matter Types and Transformation with Maturation. The Ordovician to Early Silurian time interval represents a period of black shale deposition under stratified and anoxic bottom-water conditions in basins of China, North Africa, the Middle East, North America, and Europe [12, 53, 106, 107]. Those organic-rich shales are the source of large amounts of hydrocarbons and therefore were the subject of intensive studies on sedimentology and source rock evaluation ([5, 7, 53, 106, 107]; Yang et al. 2016). Reported major OM in these early Paleozoic sediments include AOM, algal Tasmanites, solid bitumen, chitinozoans, and graptolites [62–64] ranging from the early mature to postmature stage. Our study analyzed maceral composition in marine Wufeng-Longmaxi shale and Utica shale deposits of Late Ordovician–Early Silurian age from China and the U.S. Those shales feature a high maturity level at the postmature stage. The majority of the original kerogen is thermally degraded, and petrographic observations show that the pyrobitumen and zooclasts (graptolites and chitinozoans) are the dominant OM components. Pyrobitumen is dominant in Wufeng-Longmaxi shale, whereas graptolites dominated OM in Utica shale samples.

Because most prolific gas-producing shales are postmature [108–110] and organic porosity provides important storage capacity for gas [3, 5, 6, 26], understanding the characterization of OM and organic pores in postmature shales is very important in evaluating shale reservoir properties. Previous studies indicate that each maceral evolves differently with maturation [27, 111]. With increasing maturity, from immature to postmature, oil-prone kerogen (AOM and alginate) first transforms to preoil bitumen and then to oil, gas, and postoil bitumen or pyrobitumen (e.g., [45]). Liu et al. [45] concluded that AOM and alginate began transforming to solid bitumen at the mature stage and that the solid bitumen network followed the original AOM network.
Figure 11: Continued.
Cardott et al. [27] also suggested that a postoil solid bitumen network could have developed along the AOM network. Mastalerz et al. [111] proposed that the 1.5% solid bitumen reflectance (equivalent VRo of approximately 1.33%, based on the empirical formula by Jacob [93]) could be considered the boundary between solid bitumen and pyrobitumen. In both Wufeng-Longmaxi shale and Utica shale, most pyrobitumen occurrences are very small (a few micrometers), scattered within the matrix, and porous. Compared to the solid bitumen reported from shales ranging from the early mature to postmature stage [45, 89, 98, 111, 112], pyrobitumen in our studied samples is smaller and more porous. We conclude that solid bitumen becomes more porous and scattered throughout the matrix as a result of secondary cracking. Researchers also suggest that with an increase in maturity to above 3.0%, OM could transform from amorphous carbon to crystalline graphite [70, 74]. When pyrobitumen loses its potential for generating hydrocarbons, no additional organic pores could be generated [74, 113, 114]. Wood et al. [115] proposed that the morphology of pyrobitumen resulted from its different origins in shales. Specifically, the curved margin of pore-filling pyrobitumen is a reflection of the original oil-water interface. The laminar structure within pyrobitumen was formed from increments of the viscous flow of oil into the original pore structure. The globular/granular texture was formed by the early precipitation of asphalt floccules from an unstable precursor oil phase in the central portions of large open pores. In our studied samples at the overmature stage (VRo = ~ 2.4%), the previously mentioned morphologies are not clearly reflected. Most pyrobitumens have a clear pore-filling structure and condensed morphology. We concluded particles except for zooclast as pyrobitumen and divided them into three types in this study. The first type is a migrated secondary product occupying interparticle space (between quartz, dolomite, K-feldspar, clay, and mica grains) and cavities. The second type occurs as isolated and condensed individual pieces occupying interparticle space (~50 μm), which might have been converted from oil-prone kerogen particles (AOM or alginite) in situ [45]. The third type of pyrobitumen particles having coarse surfaces might be an indicator of bacteria and fluid activity, which is also indicated in Wang et al. [85]. Different from the other pyrobitumen types, bacteria pellet-like pyrobitumen is isolated and might have a relatively weak correlation with hydrocarbon generation.

In comparison to alginite and AOM, vitrinite and inertinite (kerogen types III and IV) derived from terrestrial woody materials do not have a high hydrocarbon generation potential, so they do not show a significant change in morphology with increasing thermal maturity. Vitrinite and inertinite are present as distinct particles across the entire maturity range, as observed in Ordos shale and another study [45].

When the maturity reaches above 3%, the organic-rich shale loses its potential for hydrocarbon generation. In addition, as gas loss leads to pressure drop, the pores generated during the mature stage collapse and even disappear because they lack support [70, 74, 113]. A small amount of OM pores was preserved because of skeleton particle support [74], which is also indicated in Xiuwu shale in this study.

4.3. Maceral Pores and Their Relationship to Gas Storage. Organic matter-hosted pores are widely recognized as a significant component of the pore system in gas shales, including Wufeng-Longmaxi shale [55, 116, 117]. The strong correlation between TOC content and total porosity in studied Wufeng-Longmaxi samples supports the contribution of organic pores (Table 2). Among their macerals, pyrobitumen is the main component that hosts the organic pores detected by SEM. Pyrobitumen pores range from nanometer to micrometer in size. Some pyrobitumens with well-
developed nanopores were almost unidentifiable at the resolution of an optical microscope because only very thin walls remained. Subround to round pores in pyrobitumen were considered to be formed by the devolatilization of gaseous hydrocarbons from matrix-retained bitumen or oils during thermal cracking [2, 5, 48, 54]. In our study, micrometer-

**Figure 12**: SEM images showing the typical habit and internal pore structure of organic matter in sample TRA-10. (a–f) Abundant graptolites and pyrite framboids distributed within the shale matrix. (a–c, e) Dispersed graptolite pieces without pores even enlarging current magnification. (f) A few pores of irregular and narrow shape inside graptolite grains, and the existence of such pores is not common in the studied sample.
sized pore shapes depend on the degree of compaction. For example, pyrobitumen with round to subround pores frequently developed between quartz or carbonate grains, which suggests that brittle minerals can protect the micrometer-sized organic pores from compaction at the postmature stage. In turn, irregular pores in pyrobitumen are usually associated with deformed or layered clay minerals, which are ductile and easily compacted. To some extent, micrometer-sized pores resist compaction with the help of surrounding brittle minerals. In fact, some studies indicate that pore sizes < 100 nm are especially resistant to compaction [29, 118].

Zooclasts including graptolites and chitinozoan have zero to very limited pores in the studied samples, indicating that zooclasts did not undergo secondary transformation with maturation. Thus, for Utica shale and Wufeng-Longmaxi shale at the dry gas stage, the SEM-detected porosity contribution from graptolites and chitinozoan to the total porosity in shale is negligible. Ardakani et al. [43] also reported that chitinozoans had no pores visible in their wall structure in Utica shale samples from southern Quebec at the mature to postmature stage (VR ranging from ~1 to 2.1%). This could explain why the Utica shale sample with abundant zooclasts has lower porosity compared to the Wufeng-Longmaxi samples from a depth of ~2576 m that have low contributions of zooclasts and abundant pyrobitumen. In Wufeng-Longmaxi shale, owing to the relatively low abundance and limited pore network of zooclasts, the pyrobitumen network that hosts secondary organic nanopores plays a significant role in hydrocarbon storage and migration.

With increased depths in Wufeng-Longmaxi shale, the positive relationship between pyrobitumen, porosity, and gas content emphasizes the significance of pyrobitumen in this formation. Both pyrobitumen and zooclasts contribute

![Figure 13: Low-pressure CO₂ adsorption isotherms of Wufeng-Longmaxi shales. Note that the largest volumes of adsorbed CO₂ occur in samples (samples N8, N9, and N10) of the highest TOC values. The TOC content is marked near the isotherm lines. P = actual gas pressure; P₀ = vapor pressure of the adsorbing gas.](image)

| Sample ID | Total organic carbon (TOC) content (wt. %) | Pore volume (cm³/g) | Specific surface area (m²/g) |
|-----------|------------------------------------------|--------------------|----------------------------|
|           | Micropore | Macropore | Micropore | Macropore |
| N2        | 0.96      | 0.00110  | 0.0057    | 3.773  | 0.023 |
| N3        | 0.89      | 0.00114  | 0.0053    | 4.084  | 0.025 |
| N4        | 1.07      | 0.00127  | 0.0050    | 4.476  | 0.021 |
| N5        | 1.31      | 0.00101  | 0.0053    | 3.604  | 0.014 |
| N8        | 2.98      | 0.00238  | 0.0145    | 8.379  | 0.020 |
| N9        | 3.39      | 0.00285  | 0.0056    | 9.887  | 0.027 |
| N10       | 3.52      | 0.00187  | 0.0071    | 6.102  | 0.010 |
to the TOC content, but not as much as porosity. The TOC content strongly controls pore development, especially for marine shales. Therefore, among high-maturity samples with comparable amounts of TOC, those having higher proportions of pyrobitumen and lower proportions of zooclasts will likely have a greater potential for gas storage. Because pyrobitumen is the secondary product from lipid material, we can conclude that a higher input of algae can provide not only greater hydrocarbon-generating ability but also more space for hydrocarbon storage.

In contrast to our observations, some researchers found that submicron- to micron-sized pores were present in graptolite structures [55, 56]. For example, Luo et al. [55] found abundant organic pores in the nongranular graptolites in Wufeng-Longmaxi shale having equivalent VRo values ranging from 3.08 to 4.29%. They also claimed

Figure 14: Log differential pore volume derived from low-pressure CO2 adsorption for Wufeng-Longmaxi shales with samples of different total organic carbon (TOC) contents. The TOC content (wt. %) of each sample is marked in the rectangle in the third panel. The micropore size distribution up to 1.2 nm was calculated with the DFT model. Pores with diameter < 1 nm have different log differential pore volumes. There are three higher \( dV/d\log D \) peaks at approximately 0.40-0.50 nm, 0.55-0.60 nm, and 0.80-0.81 nm.
that graptolites account for 20 to 93% of the dispersed OM in the Wufeng-Longmaxi Formation [55]. However, the graptolites in our ion-milled Wufeng-longmaxi samples only accounted for a small portion of the whole OM (less than 20%) and have zero to very limited pores inside. This indicates that maturity above 3.0% may change the structure of graptolites. In addition, the SEM images on unpolished Wufeng-Longmaxi samples also show clear pores in large graptolite bodies in cores (Figures 10(e)-10(h)). One possible explanation of this discrepancy could be that the structure of graptolite is layered and soft and could be easily eroded with long-term exposure, developing a pore-like structure on the surface of unpolished cores. Ion milling removed the pore-like structure in the graptolite surface and allowed observing real internal structure in shales.

4.4. Chemical Structure of Pyrobitumen and Zooclasts. Graptolites and chitinozoans are microfossils that have thin organic walls and are common in Lower Paleozoic marine rocks [53, 62, 64, 119, 120]. Previous studies of pyrolysis-gas chromatography on chitinozoan in mature shales suggest that their composition is similar to woody material (i.e.,...
Figure 16: Log differential pore volume for Wufeng-Longmaxi shales derived from MICP. The $x$-axis marked the pore diameter in the nanometer, and the $y$-axis marked the log differential pore volume. Samples N8, N9, and N10 featured higher TOC contents than samples N2 to N8. The TOC contents of N8 to N10 are 2.98%, 3.39%, and 3.52%, respectively.
kerogen type III) and gas-prone biomacromolecules [121, 122]. Dutta et al. [123], using SEM images, suggested that chitinozoans originally are devoid of any porosity in their structure, and based on their kerogen composition, pores are not expected to develop during thermal maturation. Our FTIR analysis further suggests that the chemical composition of graptolite periderm is indeed similar to vitrinite and inertinite, which are major components of type III kerogens;

Figure 17: (a) Micro-FTIR spectra of pyrobitumen and graptolite in studied samples. The first two are of pyrobitumen, and the third and fourth show graptolite in Wufeng-Longmaxi shale and Utica shale, respectively. (b) Micro-FTIR spectra of alginite, AOM, solid bitumen, vitrinite, and inertinite from New Albany Shale samples (VR_o = 0.63%) (adapted from [89]).
i.e., they contain a large amount of oxygen-containing functional groups and aromatic groups [121]. Reyes et al. [122] suggested that chitinozoans and graptolites had limited or no contribution to overall hydrocarbon generation because morphological evidence of the thermal decomposition in the immature to gas generation window under SEM is unavailable. Our FTIR data show that at the maturity corresponding to VRo ~ 2.45%, pyrobitumen lost its hydrocarbon-generating potential and only some C=O and C=C groups are detected in the spectra.

5. Conclusions

In this study, postmature Ordovician to Early Silurian Wufeng-Longmaxi shale samples were collected from Sichuan Basin in South China to investigate OM types and their associated pore structures by correlative organic petrographic and SEM analyses and various porosimetry measurements. For comparison, organic petrographic and SEM analyses were performed on the age-equivalent Utica shale from the U.S., overmature marine shale from Xiuwu Basin, and marine-continental transitional shale from Ordos Basin in China.

Quartz content shows different relationships with TOC content in studied Wufeng-Longmaxi shales due to quartz origin difference. Quartz content is positively correlated with TOC content in clay-poor shales (clay mineral content < ~35%), indicating quartz mainly of biogenic origins, whereas it exhibits no correlation with TOC in clay-rich shales, indicating quartz mainly of detrital origins. OM is the predominant controlling factor on micropores and also controls macropore development when TOC content increased to a certain level. Clay mineral and quartz contents also make different contributions to pore development.

In both Wufeng-Longmaxi shale and Utica shale, pyrobitumen and zooclasts were the dominant OM components, but their relative proportions varied. Specifically, pyrobitumen was dominant in Wufeng-Longmaxi shale, whereas zooclasts (and graptolites, in particular) were dominant in Utica shale. Pyrobitumen in Wufeng-Longmaxi shale was classified into three types according to morphological and internal structure differences. Each type of pyrobitumen owns distinct forms, and pore development within is highly heterogeneous. Specifically, pores are universally and uniformly developed in pyrobitumen I and abundantly developed in pyrobitumen III as bacteria-like aggregates but not well developed in pyrobitumen II nor graptolites. Pores developed in pyrobitumen I were most strongly influenced by hydrocarbon generation. Pyrobitumen II is a highly condensed form resulting from high compaction and high-temperature evaporation.

At the overmature maturation level (VRo ~ 2.4%), neither graptolites nor pyrobitumens have hydrocarbon-generating potential, as indicated by their aromatic nature and almost total absence of aliphatic hydrogen functionalities.

At the scale detected by SEM, most pyrobitumens were very porous, providing space for gas storage. In contrast, zero to very limited pores were documented in zooclasts, suggesting that while they contribute to the total OM content, they do not contribute space for gas storage or migration in these rocks. The high abundance of pyrobitumen in organic matter is the main contribution to pore development. These observations suggest that the proportions of pyrobitumen to zooclasts in the total OM may play an important role in predicting organic porosity and, ultimately, storage capacity of Ordovician-Silurian shales.

The types and sources of some organic matter are indistinguishable due to overly high maturity and compaction deformation. Nevertheless, the identification of typical maceral and related pore distributions is meaningful for better understanding the generation and preservation of shale gas and pore development mechanisms.

Data Availability

The data used to support the findings of this study are available from the first author upon request.

Conflicts of Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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