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Identification and nanoporosity of macerals in coal by scanning electron microscopy

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ABSTRACT

Recent applications of scanning electron microscopy (SEM) to shale resource plays at magnifications of < 500– > 80,000 × have reported nanoporosity in organic matter with limited interpretations of organic matter type. Macerals, inclusive of kerogen and solid bitumen, are recognized and distinguished in reflected white and epifluorescent light in coal and shale samples at magnifications of 200–750 ×. The objectives of this study are to identify macerals by SEM and evaluate which macerals contain primary and secondary nanoporosity. Since coals are organic rich with a better chance of identifying adjacent maceral types than when dispersed in shales, broad ion beam milled samples of humic and sapropelic (boghead and cannel) coals ranging in rank from peat to semianthracite were examined in backscattered electron (BSE) mode at low magnification (≤ 2,500 ×) to identify maceral type. Once identified, macerals were examined at higher magnifications of 1200–75,000 × to assess maceral nanoporosity.

Manipulation of the accelerating voltage to 10 kV in BSE mode of a high volatile bituminous humic coal durain lithotype sample revealed a contrast between maceral groups (vitrinite, inertinite, liptinite), with limited identification of individual maceral types. Vitrinite maceral subgroups telovitrinite and detrovitrinite are distinguished based on their relative gray scale appearance compared to other macerals and occurrence as bands or groundmass, respectively. The liptinite macerals alginite, sporinite and cutinite are distinguished based on dark relative gray level and their shape. The liptinite maceral bituminite/amorphinite was recognized by dark relative gray level and occurrence as groundmass in a boghead coal. The inertinite macerals fusinite and semifusinite are recognized by light gray level appearance compared to other macerals and bogen structure but are not distinguishable separately. Macerals dispersed in shale, lacking the subtle contrast of adjacent macerals, are much more difficult to identify.

Even though porosity is revealed at high magnification in BSE mode, too high of a magnification (> 15,000 ×) prohibits identification of maceral types. The best approach is to examine samples at a lower magnification (e.g., 650 ×) at 10 kV accelerating voltage in BSE mode to identify the maceral type and then go to a higher magnification at 1–2 kV accelerating voltage to observe nanoporosity.

Primary nanoporosity is observed within coal macerals at low rank (peat and subbituminous), but decreases in amount with increasing rank. Primary microporosity occurs as woody cell lumens in semifusinite and fusinite macerals. Secondary nanoporosity develops in post-oil solid bitumen in shale beginning below the peak of the oil window with a lack of nanoporosity at lower thermal maturity. Compared to the abundant nanoporosity of post-oil solid bitumen in shale, only trace amounts of nanoporosity is observed in other macerals in coals of high volatile bituminous rank and higher under the SEM.

The emphasis of this study was the identification and nanoporosity of macerals in coal by SEM. The same results may extend to the same macerals in shale. Knowledge of organic matter porosity distribution by maceral type and development by thermal maturity provides insight for coalbed methane, shale gas and tight oil production potential.

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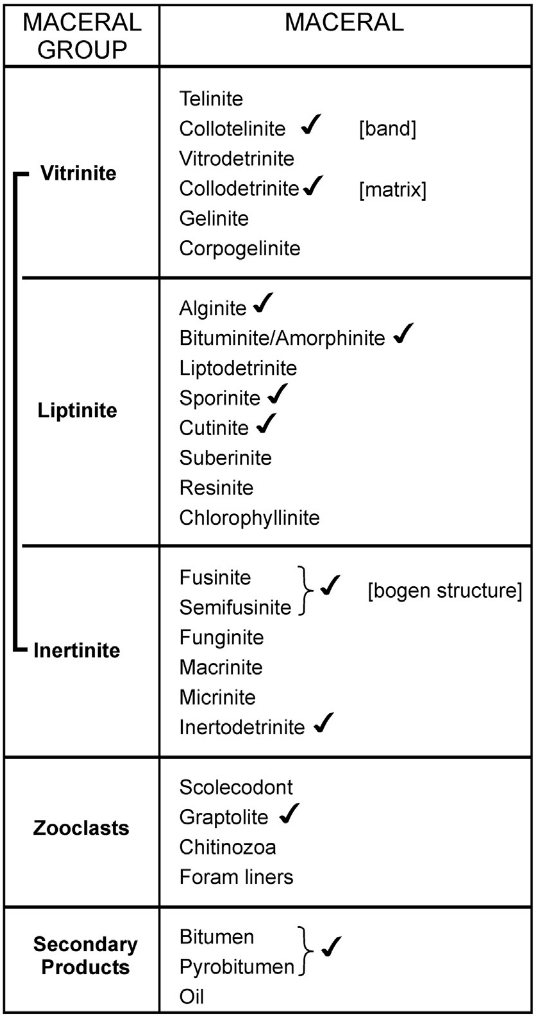
1. Introduction

The production of natural gas from coal (i.e., coalbed methane) and natural gas and oil from shale (i.e., shale gas and tight oil) has revolutionized the U.S. petroleum industry in recent years. All hydrocarbon reservoirs require porosity and permeability to store and produce oil and gas. In unconventional resource plays (coal and shale), where the hydrocarbon source rock also is the reservoir, porosity is most prevalent in the organic matter in organic-rich, siliceous shales (Loucks et al., 2012; Dong et al., 2017). Scanning electron microscope (SEM) studies have demonstrated that some organic matter is porous while others are nonporous at the same thermal maturity (Curtis et al., 2012). The difficulty in recognizing organic matter types in the SEM limits the understanding of which types are porous or nonporous (Hackley and Cardott, 2016).

Organic matter is complex and its classification depends on the sample type and how it is observed. Organic matter composition varies by rock type (e.g., coal and shale), depositional environment (e.g., humic coal vs. sapropelic coal; marine vs. nonmarine shale), and rank, among other variables. Taylor et al. (1998, p. 242–243) discussed several petrographic classifications for organic matter in rocks under reflected and transmitted light, including the categories of maceral, kerogen, phytoclast, organoclast, and palynofacies. The maceral classification was developed for coal and applied later to dispersed organic matter in shales which contain additional macerals not found in humic coal (e.g., amorphous organic matter/bituminite/amorphinite, solid bitumen, alginite, zooclasts). The maceral classification of coal, primary dispersed organic matter, and solid bitumens in Potter et al. (1998, their tables 2 and 4) was used in this study. A condensed version of the maceral classification, modified from Stasiuk et al. (2002), is in Table 1.

Table 1
Classification of macerals in sedimentary rocks (modified from Stasiuk et al., 2002). Check mark indicates maceral is identifiable in SEM.



MACERAL GROUP	MACERAL
Vitrinite	Telinite Collotelinite ✓ [band] Vitrodetrinite Collodetrinite ✓ [matrix] Gelinite Corpogelinite
Liptinite	Alginite ✓ Bituminite/Amorphinite ✓ Liptodetrinite Sporinite ✓ Cutinite ✓ Suberinite Resinite Chlorophyllinite
Inertinite	Fusinite } ✓ [bogen structure] Semifusinite } Funginite Macrinite Micrinite Inertodetrinite ✓
Zooclasts	Scolecodont Graptolite ✓ Chitinozoa Foram liners
Secondary Products	Bitumen } ✓ Pyrobitumen } Oil

All petrographic methods of organic matter observation have limitations. Different sample preparation methods limit maceral identification in coal and shale samples under the light microscope. For example, polished whole rock coal and shale samples are routinely viewed in reflected white and epifluorescent light to identify vitrinite, liptinite, and inertinite macerals, but limit the identification of amorphous organic matter (AOM). Shale strew slides viewed in transmitted white and epifluorescent light are optimum to observe AOM and liptinite macerals, but lack a polished surface to identify opaque vitrinite and inertinite macerals. Similarly, the SEM has limitations in the extent that macerals may be recognized.

Macerals (i.e., all solid organic matter inclusive of kerogen and solid bitumen) are recognized and distinguished in reflected white and epifluorescent light at magnifications of 200–750 × using 20–50 × oil immersion objectives and 10-15 × oculars (ASTM, 2016). Recent applications of SEM to shale resource plays at magnifications of < 500 × to > 80,000 × have reported nanoporosity in organic matter, with limited interpretations of organic matter type (e.g., Sondergeld et al., 2013; Milliken et al., 2014; Chen and Jiang, 2016). Pore development by maceral type and thermal maturity is important in evaluating shale reservoirs for oil and gas (Milliken et al., 2013, 2014). The objectives of this study are to evaluate the extent to which macerals may be recognized in SEM, which macerals contain primary and secondary porosity, and at what thermal maturity levels secondary porosity develops.

2. Previous literature

Early applications of the transmission electron microscope to specialized ultrathin sections of coal distinguished vitrinite, liptinite (e.g., sporinite, resinite), and inertinite (e.g., micrinite, semifusinite) macerals at high magnification (1400–122,500 ×) in appearance much different than in the optical microscope (McCartney et al., 1966; Taylor, 1966). Based on atomic number contrast, a relative comparison of materials can be made in which carbon-rich organic matter appears dark gray while mineral matter displays lighter gray levels under backscattered electron (BSE) microscopy. Stanton and Finkelman (1979) correlated macerals identified in an optical photomap with identical fields in secondary electron (SE) and BSE images. While macerals could not be distinguished in SE images, exinite macerals appeared darker than vitrinite and mineral-filled cell lumens distinguished fusinite from vitrinite in BSE images. Davis et al. (1986) examined maceral concentrates of collinite (vitrain), sporinite (durain), and fusinite (fusain) in SE images with limited interpretations of maceral types. Lallier-Verges et al. (1991) recognized collotelinite in vitrites and collodetrinite in bi- and trimaceral microlithotypes in ultrathin sections of two high volatile C bituminous humic coals by SEM and TEM.

Terminologies used for organic matter in shales under SEM include the general term “organic matter” (Loucks et al., 2009, 2010, 2012; Curtis et al., 2013; Camp and Wawak, 2013; Er et al., 2016; Zhou et al., 2016), kerogen and solid bitumen (Bernard et al., 2012, 2013; Chalmers et al., 2012; Milliken et al., 2013; Cardott et al., 2015; Li et al., 2016) and the related yet different terms “detrital organic matter”, “secondary organic matter”, “depositional organic matter”, and “migrated organic