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Pore-types and pore-network evolution in Upper Devonian-Lower Mississippian Woodford and Mississippian Barnett mudstones: Insights from laboratory thermal maturation and organic petrology

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ABSTRACT

Pore-evolution models from immature organic-matter (OM) -rich Barnett (0.42%R_o) and Woodford (0.49%R_o) mudstones were compared with models previously developed from low-maturity OM-lean Boquillas (Eagle Ford-equivalent) mudstones to investigate whether (1) different mineralogy (siliceous vs. calcareous) exerts different catalytic and sorption effects and influences OM-pore origin and evolution; and (2) different types of macerals show different OM pore evolution history. Laboratory gold-tube pyrolysis, scanning electron microscopy (SEM) and thin-section petrography, organic petrography, and geochemical characterization were used to investigate the role of bulk mineralogy, maceral type, and thermal maturation on OM-pore evolution. Results suggest that mineralogy has little impact on OM-pore development and evolution. Macerals, identified using both SEM (platy OM, particulate OM, organic–mineral admixtures, *Tasmanites*) and organic petrology (vitrinite, inertinite, amorphous organic matter [AOM]/bituminite, telalginite [*Leiosphaeridia*, *Tasmanites*]), do affect the origin and evolution of OM pores owing to differences in chemical compositions, generation kinetics, and activation-energy distributions between *Tasmanites*, matrix bituminite, and other types of macerals. *Leiosphaeridia* and *Tasmanites* in Woodford mudstone samples exhibit a delay in onset and a shorter period of petroleum generation and pore development compared to the matrix bituminite in the Barnett and Woodford mudstone samples. Pre-oil solid bitumen was observed to have migrated into initial primary mineral pore networks at the bitumen generation stage in both Barnett and Woodford samples. At higher levels of thermal maturation, the volume of primary mineral pores decreases and the pore volume composed of modified mineral pores and OM pores becomes greater. Pore evolution and pore-type heterogeneity in these mudstones is a function of the initial mineral pore network, types of kerogen and macerals, and generation kinetics of individual macerals upon thermal maturation.

1. Introduction

It has been well documented that the formation of organic matter (OM) pores in mudstones is predominantly affected by thermal maturation processes (e.g., Bernard and Horsfield, 2014; Bernard et al., 2012a,b; Bohacs et al., 2013; Curtis et al., 2012; Ko et al., 2016; Loucks et al., 2009; Mastalerz et al., 2013; Milliken et al., 2013; Pommer and Milliken, 2015; Zargari et al., 2015). The change in size and shape of OM pores is related to continuous transformation of OM and can be associated with generated bitumen, pre-oil solid bitumen, oil, gas, pyrobitumen, and char (e.g., Bernard et al., 2012a; Cardott et al., 2015; Curiale, 1986; Jacob, 1989; Ko et al., 2016; Landis and Castaño, 1995; Löhr et al., 2015; Loucks and Reed, 2014; Mastalerz and Glikson, 2000; Wood et al., 2015).

The effect of mineralogy (clay mineralogy in particular) on the composition and yield of generated petroleum—with variations caused by differences in mineral adsorption and catalytic capacities—has been known for decades (e.g., Goldstein, 1983; Hetényi, 1995; Huizinga et al., 1987a,b; Johns, 1979; Pan et al., 2010; Tannenbaum et al., 1986; Tannenbaum and Kaplan, 1985; Wei et al., 2006a,b). Catalytic cracking

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of kerogen and/or bitumen by interaction of minerals with OM has been proposed by many previous studies (Espitalié et al., 1980, 1984; Hetényi, 1995; Horsfield and Douglas, 1980; Johns, 1979; Tannenbaum et al., 1986; Tannenbaum and Kaplan, 1985). Minerals in rocks can catalyze chemical reactions (i.e., C—C bond cleavage, defunctionalization, condensation, oxidation, and reduction) occurring during the maturation of kerogen. Much effort has been made to investigate the role of minerals in petroleum composition during the thermal maturation, specifically in regard to the presence or absence of minerals such as calcite, pyrite, quartz, calcium sulfate, illite, kaolinite, and montmorillonite (i.e. smectite). For example, montmorillonite shows a pronounced catalytic effect, significantly changing the chemical composition and yield of oil from kerogen, whereas other minerals such as calcite, pyrite, quartz, and calcium sulfate show weaker or no effect (e.g., Lao et al., 1989; Tannenbaum et al., 1986). These effects are related to montmorillonite having a high surface area and exposed cations on its surface (Johns, 1979); most importantly, montmorillonite contains sites where organic reactions can be catalyzed (Johns, 1979; Wei et al., 2006a,b). Both montmorillonite and illite can alter bitumen composition by adsorbing a considerable amount of asphaltene and polar compounds, whereas calcite and other non-clay minerals show little or no adsorption (Huizinga et al., 1987a,b; Tannenbaum and Kaplan, 1985). Although these studies have shown the effects of mineralogy on petroleum composition, the role of bulk mineralogy on pore development in unconventional reservoirs during maturation has received comparatively little investigation.

The process by which pores evolve within different macerals during thermal maturation also remains unclear. Curtis et al. (2012), Loucks et al. (2012), Milliken et al. (2013), and Schieber (2010) have suggested that the type of kerogen (i.e., Type I, II, III, IV) might play a role in the formation of pores during thermal maturation. Variations in the relative proportion of macerals can affect geochemical properties of bulk OM and petroleum-generating potential (e.g., Horsfield et al., 1988; Schenk et al., 1990; Mastalerz et al., 2012). Only in the last several years, has the idea been introduced that OM pores may vary as a function of maceral type and the importance of integrating optical organic petrology with SEM petrography to distinguish different OM types (solid bitumen vs. different types of maceral) in which porosity is developed been recognized (Cardott et al., 2015; Cardott and Curtis, 2017; Fishman et al., 2012; Hackley and Cardott, 2016; Mastalerz et al., 2013).

To investigate if bulk mineralogy, kerogen and maceral types, and thermal maturation change the shape and size of OM pores and the evolution of OM-pore and mineral-pore networks, we applied laboratory gold-tube pyrolysis, mineralogical and geochemical characterization, organic petrology, and SEM petrography methods. This study compares the pore-evolution model developed by Ko et al. (2016, 2017) for OM-lean Upper Cretaceous Eagle Ford mudstones to pore evolution in the Woodford and Barnett mudstones analyzed here. Specific research questions examined include the following: (1) Do differences in maceral type affect OM pore development and evolution? (2) Does bulk mineralogy, especially clay mineralogy, affect the timing of OM transformation and pore evolution?

2. Geologic setting

2.1. Woodford mudstones

Upper Devonian–Lower Mississippian Woodford mudstones in southern Oklahoma were deposited in an epicontinental sea during global sea-level transgression, within a failed aulacogen structure (Blakey, 2009; Cardott and Chaplin, 1993; Ham, 1973; Lambert, 1993; Nicholas and Rozendal, 1975). From the Cambrian through Permian, the basin was primarily filled with carbonates and marine mudstones. The Woodford marine mudstone was deposited in a deeper-water euxinic environment and is siliceous, containing chert and subordinate amounts of greenish gray mudstone, sandstone, dolostone, phosphate nodules, and pyrite (Cardott and Chaplin, 1993; Comer, 2007). In general, chert, composed of radiolarian remains and diagenetic silica, is more abundant in distal parts of the basin; mudstone, siltstone, and sandstone are more abundant in proximal areas.

Siliceous mudstones and chert, composed primarily of microcrystalline, cryptocrystalline, and microfibrous quartz, are the two main lithofacies in the Woodford Formation at the study location. Woodford Formation rocks are, in general, stratigraphically age-equivalent to other OM-rich mudstone deposits, including the Chattanooga Shale in the Black Warrior Basin, the Antrim Shale in the Michigan Basin, the New Albany Shale in the Illinois Basin, the Marcellus Shale in the Appalachian Basin, and the Bakken Formation in the Williston Basin (Blakey, 2009; Meissner, 1978). The Woodford Shale, long known as the source rock for most of Oklahoma's petroleum reserves, has become an active target for shale-gas and shale-oil development in the Anadarko, Arkoma, and Marietta-Ardmore Basins (Cardott, 2011). In the area of investigation, Woodford mudstone is conformably overlain by the Mississippian Sycamore Formation, which is composed of silty limestone interbedded with dark shale and unconformably overlies the Silurian and Lower Devonian Hunton Group (Fishman et al., 2013; Ham, 1973).

2.2. Barnett mudstones

Mississippian Barnett siliciclastic mudstones were deposited in a deeper-water foreland basin, the Fort Worth Basin (FWB), during the late Paleozoic Ouachita orogeny as the Gondwana plate approached the Laurussia craton (Loucks and Ruppel, 2007; Meckel et al., 1992). Barnett mudstones reach a maximum thickness of about 1000 ft. (304.8 m) in the northeast near the Muenster Arch and thin to the west and south (Montgomery et al., 2005; Pollastro et al., 2007). The Ouachita thrust–fold belt bounds the FWB to the east. The Muenster, Red River, Bend, and Lampasas Arches, as well as the Llano Uplift bound the FWB on the west and north (Montgomery et al., 2005; Pollastro et al., 2007).

The Barnett Shale is composed of a mixture of siliceous mudstone, calcareous siliceous mudstone, argillaceous limestone, skeletal packstone, and phosphatic packstone to grainstone facies (Hickey and Henk, 2007; Loucks and Ruppel, 2007; Redmond, 2016). The Barnett Shale in the northern FWB has been studied extensively and developed as a general gas-shale reservoir model based on many pioneering studies (Bowker, 2007; Han et al., 2015; Jarvie et al., 2007; Loucks and Ruppel, 2007; Milliken et al., 2007; Milliken et al., 2012; Montgomery et al., 2005; Pollastro et al., 2007). Natural gas was first produced from Barnett strata starting in 1981 (Bowker, 2007). The Forestburg limestone subdivides the Barnett in the northern FWB into upper and lower units but is absent in the southern FWB (Loucks and Ruppel, 2007; Montgomery et al., 2005; Pollastro et al., 2007). The Barnett Formation unconformably overlies the Ordovician Ellenburger, Simpson, and Viola shelf carbonates and is directly overlain by the phosphatic glauconitic lime packstone unit and Pennsylvanian Marble Falls Group carbonates (Montgomery et al., 2005; Wood, 2013). In the southern FWB, the Barnett has been shown to unconformably overly the Mississippian Whites Crossing unit, the Devonian Houy Formation, or the Lower Ordovician Ellenburger Group (Redmond, 2016).

3. Samples and methods

3.1. Core and outcrop samples

The Devonian–Mississippian Woodford mudstone samples used in this study were collected by Dr. Geoffrey S. Ellis of the U.S. Geological Survey (Denver, Colo.) from a well-studied (e.g., Aufill, 2007; Ham, 1973; Kirkland et al., 1992; Krystyniak, 2005; Paxton and Cardott, 2008) road cut along Interstate 35 on the south flank of the Arbuckle Anticline in Carter County, Oklahoma, USA (Fig. 1). The outcrop has