Organic Geochemistry 87 (2015) 119–132

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Is organic pore development in gas shales influenced by the primary porosity and structure of thermally immature organic matter?

S.C. Löhr[a,*], E.T. Baruch[b,1], P.A. Hall[b], M.J. Kennedy[a]

[a] *Department of Earth & Planetary Sciences, Macquarie University, North Ryde 2109, Australia*
[b] *Sprigg Geobiology Centre & Department of Earth Sciences, University of Adelaide, Adelaide, SA 5005, Australia*

ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form 27 July 2015
Accepted 28 July 2015
Available online 5 August 2015

Keywords:
Organic-hosted porosity
Thermal maturation
Pore characterisation
Unconventional shale reservoir
SEM
Organic matter diagenesis
Kerogen
Bitumen
Pore network

ABSTRACT

Organic matter (OM)-hosted pores, rather than mineral-hosted pores, are considered to be the dominant contributors to total porosity and hydrocarbon storage in many organic-rich unconventional reservoirs. OM-hosted pores are thought to develop during thermal maturation as generated hydrocarbons are expelled from the kerogen, leaving behind pores. However, prediction of OM-hosted pore development is hampered by the lack of a simple relationship between thermal maturity and OM-hosted porosity, with the controls on pore distribution, size and morphology remaining poorly known. In particular, the extent to which thermally immature OM hosts primary pores and the influence that these have on subsequent organic pore development remains poorly understood. Here we employ Ar ion beam polishing and high resolution scanning electron microscopy to show that primary OM-hosted pores are common in thermally immature shales of varying ages and depositional settings, where they occur in both structured and amorphous OM. We further find, utilising a thermal maturity gradient in the Devonian-Mississippian Woodford Shale, that although OM-hosted pores are common in the least mature ($<$ 0.4 %Ro) samples imaged they are not evident in examples that are mature (0.5–1.1 %Ro). However, OM-hosted pores similar to those observed in the least mature samples are present in gas-mature samples ($\geqslant$ 1.5 %Ro), where they are classified as secondary pores. Solvent extraction to remove bitumen from oil-mature samples results in an abundance of pores in samples where previously none were evident, which suggests that the absence of primary OM-hosted pores in untreated oil-mature samples is due to infilling of pores by generated and retained bitumen. The similar size and morphology of more complex secondary pores and primary pores is consistent with re-emergence of primary pores in gas-mature structured organic matter, following expulsion of infilling bitumen. Inheritance of pore structure is less evident in amorphous OM types, where secondary pores exhibit a distinctive spherical morphology that has previously been attributed to a gas bubble origin within bitumen. However, similar spherical pore morphologies are evident in immature amorphous OM, arguing against a maturation related origin, so that re-emergence of primary pores cannot be ruled out. Our findings are also relevant to models of hydrocarbon storage and migration. Given that bitumen filled organic pores are likely open in regards to hydrocarbon migration, the importance of organic pore networks for primary migration in the oil window may have been underestimated – well developed organic pore networks contributing to permeability and storage capacity are otherwise assumed to be a feature characteristic of gas-mature shale reservoirs.

1. Introduction

The study of mudrocks has long focused on their qualities as seals in conventional hydrocarbon systems or for their generative potential as source rocks. However, recent trends in shale oil and gas production have demonstrated that mudrocks can be (unconventional) hydrocarbon reservoirs in their own right. The capacity of fine grained sediments to act as economic reservoirs is largely dependent on their storage capacity, permeability and potential for fracture stimulation. The pores, along with natural fractures, form the flow path network that allows flow of oil or gas from the mudrock to induced fractures during production. Determining the type, quantity and arrangement of pores is thus of central

---

[*] Corresponding author.
E-mail address: stefan.loehr@mq.edu.au (S.C. Löhr).
[1] Current address: Origin Energy Ltd, 339 Coronation Drive, Milton, QLD 4064, Australia.

http://dx.doi.org/10.1016/j.orggeochem.2015.07.010
0146-6380/© 2015 The Authors. Published by Elsevier Ltd.

importance to any assessment of shale reservoir quality (Loucks et al., 2012; Milliken et al., 2013). In addition, the ability to predict porosity trends along thermal maturation or burial gradients is an important component of successful well placement. Prediction of porosity trends requires, in turn, a fundamental understanding of mudrock pore types and the controls on their distribution and development.

Pore networks in mudrocks are composed of nanometre- to micrometre-size pores. Three broad pore classes are recognised (Loucks et al., 2012): (1) interparticle pores, (2) mineral-hosted intraparticle pores and, (3) intraparticle, organic matter (OM)-hosted pores. Here we refer to the latter as OM-hosted pores. Mudrock porosity and pore evolution have been studied mainly through direct high resolution imaging techniques such as scanning electron microscopy (SEM; Curtis et al., 2012a; Milliken et al., 2013) or, alternatively, bulk characterisation techniques such as gas adsorption, mercury intrusion, or small-angle neutron scattering (Mastalerz et al., 2013; Bahadur et al., 2015). An advantage of the bulk pore characterisation techniques is that they provide quantitative assessments of pore volumes and pore size distribution, including < 10 nm size pores that cannot readily be imaged. However, bulk characterisation techniques cannot distinguish OM-hosted pores from mineral-hosted intra or interparticle pores, this requires high resolution imaging.

OM-hosted pores are mainly of sub-μm size, and are widely recognised as a significant component of the pore system in proven gas shales including the Barnett Shale (Loucks et al., 2009), the Woodford and Horn River shales (Curtis et al., 2012a; Loucks et al., 2012) and the Marcellus Formation (Milliken et al., 2013). Three-dimensional reconstructions of kerogen and porosity distribution using focused ion beam milling – SEM show that OM-hosted pores have the potential to form connected pore networks in organic-rich shale gas reservoirs such as the Barnett, Woodford and Horn River shales (Curtis et al., 2012b), where between 26–67% of the pore volume is connected. Although pores are typically divided into several separate pore networks, and individual pore networks rarely span the entire length of an analysed rock volume (Curtis et al., 2012b), a potentially dominant contribution of organic porosity to total porosity is indicated by the positive correlation between bulk TOC and total porosity in moderately OC rich, gas-mature mudrocks such as the Marcellus Formation (Milliken et al., 2013). These observations have resulted in the prediction that a greater potential for gas storage and gas flow exists in higher TOC mudrock intervals, depending on the abundance and connectivity of the OM-hosted pores (Loucks et al., 2012). From an unconventional reservoir perspective, therefore, it comes as no surprise that there has been a sustained effort to determine the controls on size, abundance, distribution and morphology of OM-hosted pores (Fishman et al., 2012; Mastalerz et al., 2013; Milliken et al., 2013; Valenza et al., 2013). The controls on porosity evolution and distribution with diagenesis and OM maturation, however, remain poorly known.

The common working model of organic pore genesis holds that the abundance of organic hosted pores is largely a function of thermal maturity, so that porosity increases with thermal maturity (Loucks et al., 2012). According to this model, OM-hosted pores develop due to the thermal cracking of sedimentary OM (also termed kerogen), which generates hydrocarbons that are subsequently expelled from the kerogen structure, leaving behind pores. Alternatively, the commonly bubble-like pore morphology in gas-mature samples of the Marcellus and New Albany Shales have been interpreted as evidence that these pores form as gas bubbles within quasi-solid bitumen after secondary cracking of bitumen in the gas window (Milliken et al., 2013; Schieber, 2013). The link between organic pore abundance and thermal maturity is inferred from high resolution SEM-based studies of thermal maturity gradients within proven gas shales such as the Woodford (Curtis et al., 2012a) and Barnett Shale (Bernard et al., 2012). In these studies organic pores are rarely evident in samples from the early oil window, but are more commonly observed in samples from the late oil window (> 0.9 %Ro) and are generally most abundant in gas and overmature samples, collected from deeper parts of the basin in question. In addition to direct high resolution imaging evidence, bulk porosity measurements of 30 mudrock samples from several gas shale basins across North America showed greater pore volumes and smaller mean pore diameters in more thermally mature samples relative to less thermally mature ones (Valenza et al., 2013). The authors of that study interpreted this to reflect the development of nm-size organic pores in kerogen at greater thermal maturities, although this was not confirmed directly by high resolution imaging.

There remain, however, several important gaps in the understanding of organic pore development. Organic matter pores in the Jurassic Kimmeridge Clay were found to be largely similar in terms of size, shape and abundance (Fishman et al., 2012), regardless of maturity, although there were differences between OM types at a given maturity. The SEM study by Curtis et al. (2012a) of a Woodford Shale thermal maturity gradient (samples from 8 different wells, ranging between 0.5–6.4 %Ro), on the other hand, shows that OM-hosted pores are generally more abundant in gas-mature samples compared to oil-mature ones. However, they did not observe a linear relationship between OM-hosted porosity and thermal maturity, as might be expected if maturation was the only control on pore abundance. Instead, their study revealed marked small-scale heterogeneity in distribution of OM-hosted pores, both within single OM domains where pores can cluster or be equally spaced, and between adjacent OM grains where one grain might show an abundance of pores whereas the adjacent grain has none (Curtis et al., 2012a). Similarly heterogeneous pore distribution is evident in oil and gas-mature samples of the Marcellus Formation (Milliken et al., 2013) where, additionally, organic pore abundance and size varies as a function of OM abundance rather than thermal maturity. Oil-mature samples with > 5% TOC were shown to have reduced porosities and smaller mean pore diameters compared to lower TOC samples of identical thermal maturity and from the same sedimentary sequence (Milliken et al., 2013). Overall, these observations show that: (a) potential OM-hosted porosity is strongly influenced by OM type, and (b) OM-hosted porosity varies greatly within and between samples of a given thermal maturity, even where these are from the same lithofacies and the same formation. An important role for OM type in determining OM porosity pathways is consistent with the contrasting hydrocarbon generation potential of OM types such as gas-prone woody terrigenous vs oil-prone algal marine OM (Hunt, 1996). The structured pore distribution evident in some gas-mature organic particles (Loucks et al., 2012) further suggests that organic pore morphology and distribution is influenced by OM type.

Most work to date has utilised natural thermal maturity gradients, comparing samples from the same sedimentary sequence but subject to different burial depths and temperatures. Although the presence of pores in immature sedimentary organic material has long been recognised, the great majority of studies of organic pore development have not included samples from the thermally immature end of the spectrum, with the least mature samples included in these gradients generally of early to late oil maturity (⩾ 0.5 %Ro). Yet without systematically investigating thermally immature samples the extent to which the pore system is primary, i.e. hosted within initially porous kerogen, vs secondary (i.e. later formation) cannot be assessed. Furthermore, only in thermally immature OM can those primary OM features which have the potential to influence later pore development be identified (Milliken et al., 2014);