Organic Geochemistry 71 (2014) 7–16

Contents lists available at ScienceDirect

Organic Geochemistry

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

Evolution of Barnett Shale organic carbon structure and nanostructure with increasing maturation ☆

Maria-Fernanda Romero-Sarmiento [a,*], Jean-Noël Rouzaud [b], Sylvain Bernard [c], Damien Deldicque [b], Michel Thomas [d], Ralf Littke [e]

[a] IFP Énergies nouvelles (IFPEN), Direction Géosciences, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France
[b] ENS, Laboratoire de Géologie, UMR CNRS 8538, 24 rue Lhomond, 75231 Paris Cedex, France
[c] LMCM-MNHN, CNRS UMR 7202, 61 rue Buffon, 75005 Paris Cedex, France
[d] IFP Énergies nouvelles (IFPEN), Rond-point de l'échangeur de Solaize BP3, 69360 Solaize, France
[e] RWTH Aachen University, Institute of Geology and Geochemistry of Petroleum and Coal, Energy and Mineral Resources Group, Lochnerst. 4-20, 52056 Aachen, Germany

ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form 12 March 2014
Accepted 20 March 2014
Available online 31 March 2014

Keywords:
Barnett Shale
Organic porosity
Hydrocarbon retention
Raman spectroscopy
High-resolution transmission electron microscopy
Nano-scale porosity

ABSTRACT

The organic nanopore network of shales is believed to be the location of hydrocarbon trapping in source rocks. Better understanding of organic carbon structure and nanostructure constitutes a key point for estimating the oil and gas in-place at the local and basinal scale. Here we characterize, a maturation series from Mississippian Barnett Shale at multiple scales down to the nanometer scale. Organic petrography, Rock–Eval pyrolysis and Raman microspectroscopy are used to determine the organic matter properties (e.g. maturity, type, TOC content). Organic pore network attributes (e.g. pore size distribution, surface area, polyaromatic layers characteristics) are estimated using low pressure gas adsorption analyses and direct imaging by high-resolution transmission electron microscopy (HRTEM). Based on Raman data we show that Barnett Shale organic matter has only reached the level of carbonization, even within overmature samples; graphitization has not yet been triggered. Interestingly, the investigated samples exhibit an additional broad Raman band centered at about 1480 cm^{-1}, likely due to the presence of retained hydrocarbons within the organic matter nanoporosity. Low pressure gas adsorption analyses evidence a positive correlation between surface areas, mesopores (pores of about 2–50 nm of diameter) and maturity level. HRTEM images confirm Raman data: even the overmature organic matter remains disordered. Such disorientation of nanometer sized polyaromatic layers creates a nanoporosity network in organic matter that appears most developed in samples of gas window maturity. Furthermore, carbon nanoparticles of concentric nanostructures, known to result from the thermal cracking of hydrocarbons, are detected in overmature samples.

1. Introduction

Recent studies have demonstrated the presence of organic nanopores within most worldwide gas shale plays (e.g. Loucks et al., 2009, 2012; Slatt and O'Brien, 2011; Curtis et al., 2012; Chalmers et al., 2012; Bernard et al., 2012a, 2012b). This porous network within organic matter, described as organic porosity, is likely to be involved in hydrocarbon retention processes in source rocks. This retention capability has been shown to be related to total organic carbon (TOC) content, total porosity, organic matter type and chemical composition, as well as to maturity level (e.g. Ross and Bustin, 2007, 2009). Because it may strongly affect storage of hydrocarbons as well as sealing capacity, better documentation of the type, size and arrangement of organic nano-scale porosity of gas shale systems has become a goal of organic geochemical research.

It is now widely accepted that the thermal cracking of organic matter leading to the formation of hydrocarbons (oil and gas) result from complex physico-chemical processes occurring during organic matter carbonization in natural settings. During these processes, the heteroatom-rich organic precursors lose many of their oxygenated and hydrogenated chemical groups as water, carbon dioxide and liquid or gaseous hydrocarbons. Ultimately, the residual organic matter becomes enriched in nanometer sized

---

☆ This study was presented at the 26th IMOG Meeting, Tenerife, September 16–20th, 2013.

* Corresponding author. Tel.: +33 1 47 52 56 31; fax: +33 1 47 52 70 19.
E-mail address: maria-fernanda.romero-sarmiento@ifpen.fr (M.-F. Romero-Sarmiento).

http://dx.doi.org/10.1016/j.orggeochem.2014.03.008

polyaromatic layers (graphene-like) which tend to stack and form polyaromatic basic structural units [BSU] (e.g. Oberlin et al., 1980; Boulmier et al., 1982; Oberlin, 1989; Rouzaud and Oberlin, 1989). The number and diameter of stacked layers forming a basic structural unit have been documented to increase within the organic matter structure with increasing maturity level. Their local orientation controls the organic matter nanostructure and is responsible for the organic porosity. Initially randomly oriented, basic structural units become locally parallel during the oil window and start to form domains, the random orientation of which are responsible for the creation of nano-scale porosity. Such organic nanoporosity appears as a good candidate for "*in situ*" hydrocarbon trapping and can be investigated in detail using direct high resolution imaging techniques such as high resolution transmission electron microscopy (HRTEM).

Detecting hydrocarbons trapped in organic porosity and better estimating the maturity level of residual organic matter within source rocks remain difficult tasks. Raman microspectroscopy has been used to measure the degree of organization of graphitic carbon during the graphitization process, i.e. during metamorphism (e.g. Wopenka and Pasteris, 1993; Beyssac et al., 2002, 2003; Bernard et al., 2010; Rouzaud et al., 2012). In addition, this technique has recently proved valuable in providing crucial information on the maturity level of organic matter that has only experienced partial carbonization (Quirico et al., 2005; Bonal et al., 2006; Charon et al., 2014). The Raman technique may thus help to better characterize organic matter in unconventional source rocks like oil and gas shales.

Here, we report investigations conducted on ten samples from the Mississippian Lower Barnett Shale (Fort Worth Basin – USA) of various maturity levels, as estimated based on organic petrography and Rock–Eval pyrolysis experiments. Using Raman microspectroscopy data, we show that the Barnett Shale organic matter displays specific features likely related to hydrocarbons trapped in the organic porosity. In addition to low pressure gas adsorption experiments performed on isolated kerogen samples, we use HRTEM directly to image the evolution of the organic matter nanostructure as a function of maturity level.

2. Material and methods

2.1. Samples: The Mississippian Barnett Shale

The investigated samples come from the Mississippian Barnett Shale, Fort Worth Basin (Texas – USA). Our 10 shale samples are

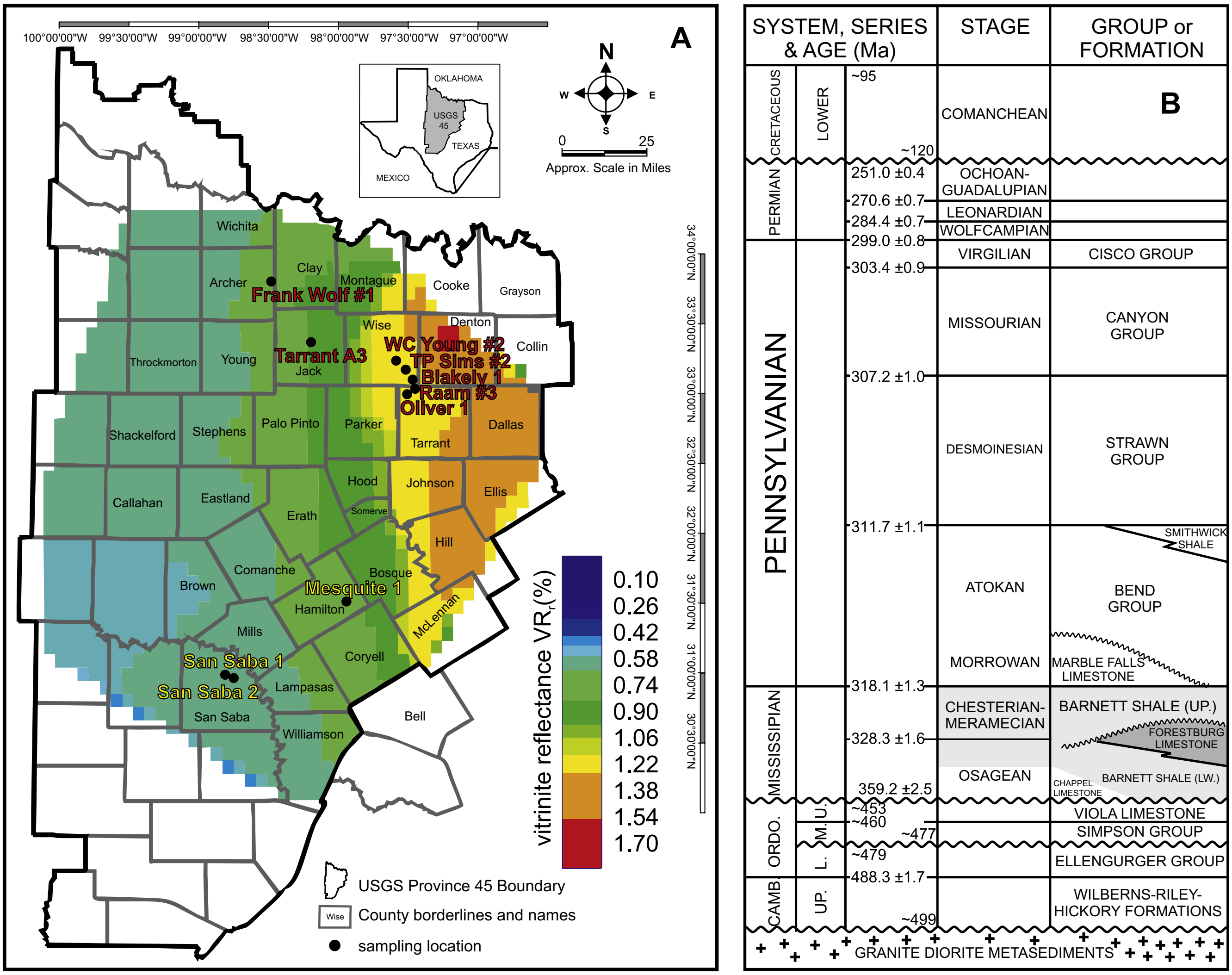

Fig. 1. (A) Computed thermal maturity map of the Lower Barnett Shale from a 3D basin model showing the location of investigated samples (modified from Romero-Sarmiento et al. (2013)). (B) Simplified stratigraphy of Fort Worth Basin, Texas (modified from Pollastro et al. (2007) and Romero-Sarmiento et al. (2013)).