[PS]State-of-the-Art Ion Milling Ablation Applied to Shale Gas Sample Preparation*

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Abstract

Gas shales are a promising unconventional source of hydrocarbons to meet the increasing demand of energy. However, our scientific understanding of shales is still limited. In the literature, many studies suggest that porosity in shale gas rocks is mainly related to intercrystalline matrix, intraparticles and organic matter with pores dimensions in the range of nanometers. Thus, it is necessary the application of high resolution microscopy techniques as FIB-SEM or FESEM, where sample preparation is critical due to: (i) increase the shale rock sample polishing quality in order to be able to visualize clean nanoporosity; (ii) to avoid generation of artificial pores during grinding, and (iii) to preserve the original microstructure of the shale rock sample.

The ion milling technique consists in Ar+ bombardment onto the rock surface to remove material at the atom level. As a test, several shale gas rock samples were selected and prepared using a LEICA EM TIC 3X with triple ion beam available at the Repsol Technology Centre facilities (Mostoles, Spain). The use of a triple ion beam considerably reduces cost, milling time, and artifacts generated when using a single ion beam. Once prepared, the selected samples were studied using a FEI ESEM Quanta FEG 650, focusing on the observation of the general abundance of organic matter in the silty mudstone/shale. Organic matter components typically present abundant porosity ranging from 5 to 1000 nanometers, which are especially important because they can absorb gases and store free gases.

Total organic matter pore volume can be calculated from individually-calculated porosity in macerals and total organic carbon (TOC). Considering this, average porosity from the sample image area can be calculated and then it can transformed TOC values from weight percent to volume percent, thus allowing the porosity value to be applied to the total organic matter in the sample.

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Loucks, R.G., R.M. Reed, S.C. Ruppel, and D.M. Jarvie, 2009, Morphology, Genesis, and Distribution of Nanometer-Scale Pores in Siliceous Mudstones of the Mississippian Barnett Shale: Journal of Sedimentary Research, v. 79/12, p. 848–861.

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State-of-the-Art ion milling ablation applied to shale gas sample preparation

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Introduction

Porosity in shale gas rocks is mainly related to intercrystalline matrix, intraparticles and organic matter with pores dimensions in the range of nanometers. Organic matter pores adsorb hydrocarbons and store free hydrocarbons.

It is necessary the application of high resolution microscopy techniques as FIB-SEM or FESEM, where sample preparation is critical due to: (i) increase the shale rock sample polishing quality in order to be able to visualize clean nanoporosity, (ii) to avoid generation of artificial pores during grinding, and (iii) to preserve the original microstructure of the shale rock sample

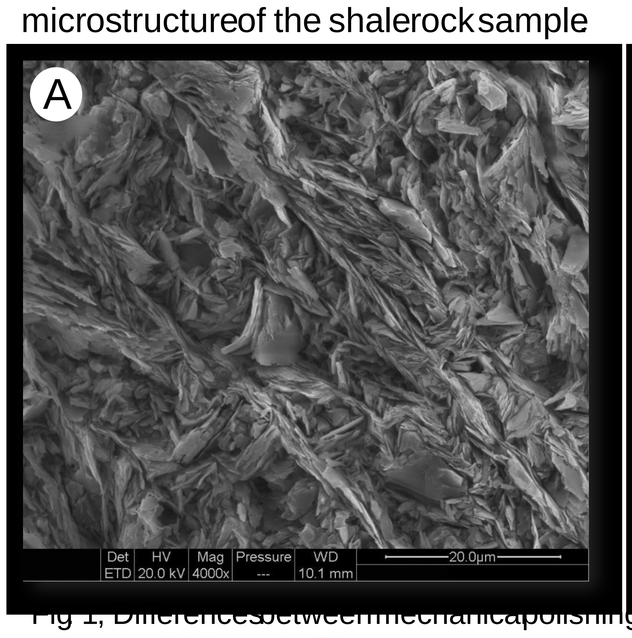

Fig 1, Differences between mechanical polishing sample (A) and Argon ion milled surface from a sample of this study (B).

Methodology

The ion milling technique consists in Ar^+ bombardment onto the rock surface to remove material at the atom level. Shale gas rock samples were selected and prepared using a LEICA EM TIC3X with triple ion beam.

The image resolution necessary to delineate the smallest pores 5 nm) was achieve using a field-emission-gun FEI ESEM Quanta FEG650 equipped with an Oxford Q-MAX (50 mm^2 window) EDS. The samples were examined using both secondary electron (SE) and backscattered electron (BSE) imaging.

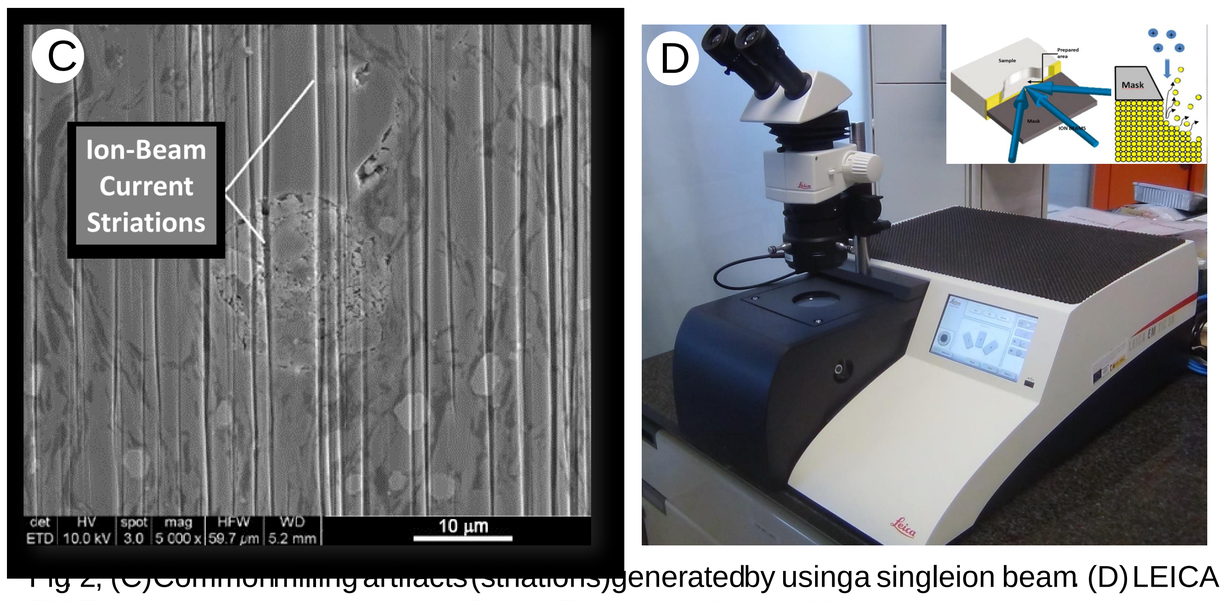

Fig 2, (C) Common milling artifacts (striations) generated by using a single ion beam. (D) LEICA EM TIC3X with triple ion beam at Repsol Technology Centre (Mostoles, Spain) which reduces cost, milling time and artifacts generated when using a single ion beam.

Results

Intraparticle pores within organic matter are related to thermal maturation of organic matter and are the result of hydrocarbon generation (Loucks et al., 2009, 2010). Organic-matter nanopores most commonly have irregular ellipsoidal shapes. A single piece of organic matter can contain hundreds of pores with diameter ranging from 5 to 1000 nm.

Measurements of porosity were made from SEM micro-photographs on pores observed in the organic matter from shale samples. Porosity percentage in the grains of organic matter was determined by using computer software JMicrovison (Roduit, 2008) to measure all individual pores in an area of interest.

Conclusions

SEM-based characterization of shale nanopores is a critical first step in better understanding of the distribution and causes of pore development in shale-gas systems.

The triple ion-milling technique optimizes the cross-section quality and reduces working time with its ability to cut broad and deep at high speeds, revealing the internal structures of the sample with scarcely any deformation or damage. Another advantage is that reduces and eliminates a common milling artifact in the milled surface which is produced by systems provided with single ion beam.

Future developments are oriented to quantify total maceral porosity, pore-throat sizes and their relationship between organic porosity, organic matter type, and thermal maturity.

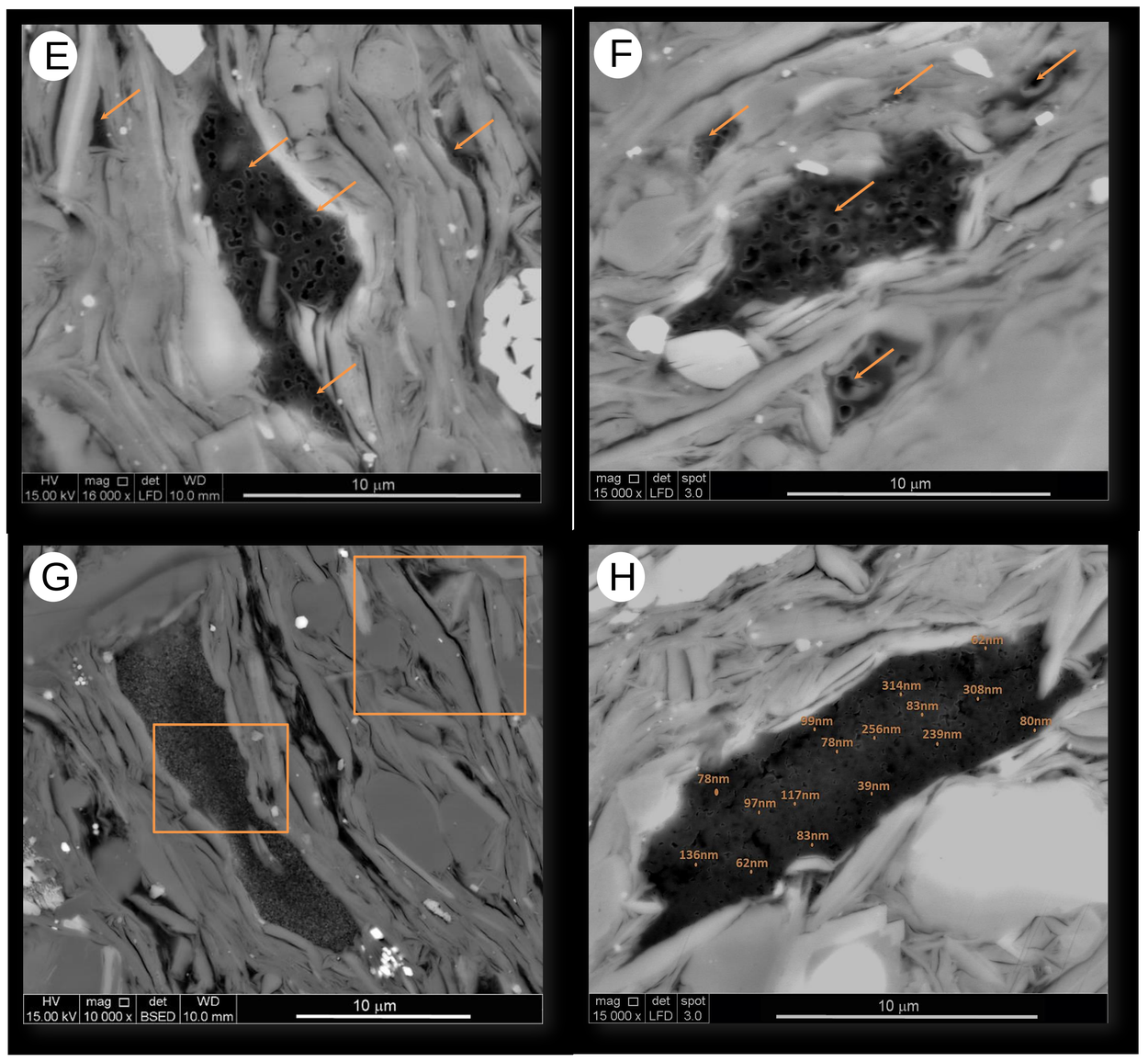

Fig 3, (E&F) BSE images showing microporous organic matter fragment (see arrows). (G) BSE image showing elongate microporous organic fragment. The rectangle indicates a detailed area. (H) SE image shows organic pores range from < 40 nm to 315 nm in diameter. (I) Quantified porosity (in orange) using the image processing software Jmicrovision.

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Loucks, R. G., Reed, R. M., Ruppel, S. C., Jarvie, D. M., 2009, Morphology, Genesis, and Distribution of Nanometer-Scale Pores in Siliceous Mudstones of the Mississippian Barnett Shale. Journal of Sedimentary Research, 79(12), 848 861.

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