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1 Probing Multiscale Structure of Mineral and
2 Nanoporous Kerogen Phase in Organic-Rich Source
3 Rocks : Quantitative comparison of Small-Angle X-ray
4 and Neutron Scattering

5 *Gaël J. Cherfallot*^{†‡*}, *Pierre E. Levitz*[†], *Pauline Michel*[‡], *Eric Kohler*[‡], *Jacques Jestin*[□] and *Loïc*
6 *Barré*^{‡*}

7 [†]Sorbonne Université, CNRS, UMR 8234, Physicochimie des Electrolytes et Nanosystèmes
8 Interfaciaux, 4 place Jussieu, F-75252 Paris, France

9 [‡]IFP Energies Nouvelles, 1 et 4 avenue du Bois-Préau, 92852 Rueil-Malmaison, France

10 [□]Laboratoire Léon Brillouin, UMR 12, CEA Saclay, 91191 Gif-sur-Yvette cedex, France

11 * Corresponding authors – Email gael.cherfallot@ifpen.fr , loic.barre@ifpen.fr

12 ABSTRACT

13 Source rocks are expected to become increasingly important in the upcoming years for oil and gas
14 production as well as for the storage of greenhouse gases. These rocks are bedded and heterogeneous
15 media, composed of minerals, kerogen and pore space. One of the most challenging issue is to better

16 define the pore space, including pore size distribution, pore volume fraction, pore connectivity and
17 pore affinity for various fluids. The aim of this study is to achieve such relevant parameters using X-
18 ray and neutron scattering techniques complementarity. Rocks thin blades cut normal to bedding plane
19 preserve sample integrity and allow their measurements on both techniques. 2D scattering patterns
20 show anisotropy, due to preferential orientation of lamellar minerals, which allows us to assess an
21 order parameter. This parameter is a valuable tool for mechanical and transport properties. A model
22 based on a three-phase system (minerals, kerogen and pores) is developed through the study of
23 scattering length density of each component within both radiations. The model allows us to fit both X-
24 ray and neutrons 1D data using the same model parameters. This later is then considered as selective.
25 It allows us to extract the kerogen mass density, the kerogen pore size distribution and its associated
26 volume fraction, and the chemical nature of kerogen pore content. This methodology has been applied
27 to a series of five source rocks of increasing maturities, from Barnett Shale Play and Montney-Doig
28 formations. Mature samples show a kerogen density of $\sim 1.6 \text{ g.cm}^{-3}$, a pore radius distribution centered
29 on $0.5 - 0.7 \text{ nm}$ accounting for a pore volume fraction of $\sim 0.01-0.04$. These kerogen nanopores are
30 filled by light condensed hydrocarbons. However, the overmature kerogen exhibit a mass density of
31 1.74 g.cm^{-3} , an additional pore radius distribution centered around 3.5 nm with a pore volume fraction
32 of 0.002 and an empty pore space. All these parameters are in agreement with Rock-Eval pyrolysis
33 measurements and literature data on similar source rocks. These results pointed out that the three-
34 phase model associated with X-ray and neutron complementarity could be applied to *in-situ* studies.

35 1. INTRODUCTION

36 Source rocks formations are one of the most widespread reservoir on earth¹ and display a high
37 potential of storage capacity.² Since recent years, gas and oil coming from organic-rich source rocks
38 systems, also known as shale gas, present an increasing interest in North American and Asian

39 countries.³⁻⁴ In the next decade, shale gas production will reach almost a fifth of the world natural gas
40 production.⁴ Thus, such geological system is expected to be intensively exploited in the upcoming
41 years.⁵ The source rocks are reported in the literature as a heterogeneous⁶ and anisotropic media⁷⁻¹⁰.
42 Shale gas are complex systems composed of several types of minerals (*i.e.* silicates, phyllosilicates,
43 tectosilicates, carbonates and iron sulfide) combined with organic matter (*i.e.* kerogen, bitumen and
44 pyrobitumen).¹¹ The rock anisotropy observed within bedding structures suggests that a preferential
45 orientation condition the fluid flows through the system.¹² The porous media are contained by both,
46 organic or inorganic phases with macropores (> 50nm) and mesopores (from 50nm to 2nm) mainly
47 located in minerals, and micropores (< 2nm)¹³ mostly encountered in the organic phases¹⁴⁻¹⁵ or in the
48 interlayer space of clay minerals. Fluids in pore space, such as gas and oil, are released by the organic
49 phase during the burial process.¹⁶ As it is also well known, this material has a low permeability (in the
50 range of nD),¹⁷ low porosity and high retention capacity through physisorption mechanism¹⁸⁻¹⁹ which
51 may vary depending on the rocks micropores content. Currently, a scientific interest on source rocks
52 transport and storage properties led to an investigation on rock porosity.^{8,20-25} Studies are focusing on
53 the improvement of nanoporous media understanding through the assessment of total porosity,^{23,26-32}
54 open versus closed pores content,^{10,33} pore size distribution,^{10,14,15,17,20-23,27,28,34-39} their
55 connectivity^{8,10,21,28,34} and the porous network tortuosity.^{34,40} Accordingly, several analytical methods
56 are employed such as gas adsorption/desorption,^{23,27-30,41} mercury injection capillary
57 pressure,^{17,21,25,28,36,42} NMR relaxometry,^{43,44,45} NMR cryoporosimetry,⁴⁶ multifrequency and
58 multidimensional NMR⁴⁷ and Small-Angle Neutron Scattering (SANS).^{6,15,20,23,27,28,34,35,39,48}
59 SANS is used to bring details on the source rocks total porosity^{28,38} and to determine their pore size
60 distribution (PSD).^{10,23,28,38} A dedicated workflow was developed from a few decades through the
61 acquisition of SANS data.^{6,15,20,23,27,28,34,35,39,48} Classically, source rocks are described as a two-phase

62 system, depending on the matrix (*i.e.* mineral and organic matter) and the pore space. Then, scattering
63 data are modeled by the polydisperse spherical pore (PDSP) model weighted by a term of contrast
64 between the sample matrix and the pores space.^{20,27,28,34,35}

65 The model describes the scattering intensity $I(Q)$ of diluted spherical pores of radius R (Equation 1)
66 as a function of the volume fraction, $\phi = \int_{R_{min}}^{R_{max}} N(R).V(R) d(R)$, of polydisperse spheres, the
67 form factor $P(Q,R)$ of spheres, and their volume, $V(R)$. Such model depend on the squared Scattering
68 Length Density (SLD) ρ difference of the considered phases, such as the matrix or the pore space, and
69 can be expressed as follows:

$$I(Q) = (\rho_{matrix} - \rho_{pores})^2 \int_{R_{min}}^{R_{max}} N(R).V^2(R).P(Q,R) d(R)$$

71 (1)

72 From these modeling a PSD is determined as well as the sample total porosity ϕ . Small-angle
73 scattering is one of the rare technique which probe the total pore space. Both SAXS and SANS
74 techniques, are based on the same principle, it is then possible in theory to obtain similar results⁴⁸.
75 However, small-angle X-ray scattering on source rocks is less investigated^{49,50} than SANS owing to
76 the presence of pyrite, with a different SLD than other minerals, introducing a supplementary phase.
77 Beam types as neutron or X-ray have a different interaction through the material which can be
78 exploited as a complementary. Indeed, the different X-ray and neutron contrast are expected to better
79 define the chemical nature of fluids in pore space.

80 Herein, this work is focused on the neutron and X-ray scattering profiles similarities and
81 complementarities. The aim is first to provide details on the minerals orientation, the kerogen mass
82 density, pore size contained in the kerogen phase and their associated volume fraction, and then to
83 assess the nature (gas or oil) of fluids in place. A multi-technical approach through the comparison of

84 X-Ray diffraction, Rock-Eval pyrolysis, Headspace gas chromatography, Field-Emission Scanning
85 Electron Microscopy and small-angle scattering techniques, is expected to bring rocks structural
86 information. For that, five source rock samples are selected based on their petrological and
87 geochemical properties to form a continuous sequence of organic matter maturity. Their X-ray and
88 neutron scattering intensities are then compared in order to get new information on (i) minerals
89 orientation relatively to the bedding plane, (ii) the maturity of kerogen, (iii) the pore size distribution
90 and the occupancy of pores in respect to gas or hydrocarbon phase.

91

92 2. MATERIALS AND METHODS

93 2.1. Source rocks.

94 Source rocks chosen and used in this study were provided by IFPEN and were collected from two
95 geological North-American Formations as part of research projects dedicated to unconventional oil
96 and gas reservoirs (GASH European program (2009-2012) and MGH IFPEN internal research
97 program). Four samples named as BSP-2, BSP-3, BSP-4 and BSP-5 come from the Mesquite 1 well of
98 the Barnett Shale Play (BSP) (Texas – United States). The BSP samples were deposited in a foreland
99 basin in the Fort Worth Basin. These rocks are fine grained laminar silicate-rich and organic-rich
100 source rocks. The last sample MT-1 originates from the Cypress field (well C-30-1 / 94-b-15) of the
101 Montney-Doig Formation (MT) (Alberta and British Columbia – Canada). This sample was deposited
102 during sediment accumulations in a foreland basin. It is a laminated coarse grained silicate-rich and
103 organic-rich rocks. In the *Table 1*, general information about the sample geological formation and the
104 depth at which they were collected, are listed.

105 **2.2. Sample preparation.**

106 For Rock-Eval pyrolysis and X-Ray Diffraction (XRD) measurements, samples were crushed into <
107 50 μm powders. Headspace Gas Chromatography (HS-GC) analysis was performed on rock sections
108 cut parallel and also cut normal to bedding. These sections were shaped into parallelepiped subsample
109 of about 1 x 2 x 0.2 cm. Field Emission Scanning Electron Microscopy (FESEM) observations and
110 scattering measurements were made on rock thin blade sections cut normal to bedding. A schematic
111 summary for sample preparation according to the technique used is illustrated *Figure 1*.

112 Source rocks are a heterogeneous systems where a representative volume is difficult to assess. In
113 addition, the comparison between Small-Angle Neutron Scattering (SANS) and Small-Angle X-ray
114 Scattering (SAXS) measurements requires to be performed on a similar probed volume as both
115 techniques have different beam sizes, classically 0.5 x 0.5 mm for SAXS and 5 x 5 mm for SANS.
116 Sample thickness optimization is also important as optical path is related both to the sample
117 transmission, different for each radiation, and to multi scattering issues.^{22,33,35,38,39,51} In the chosen
118 conditions (see below), transmission is high for SANS about 90 %, and low for SAXS, around 10 %.

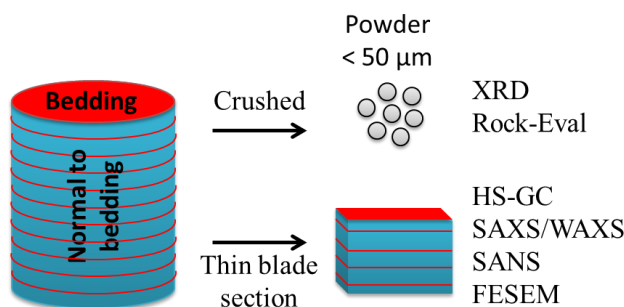
119 From these considerations and prior to this study, the sample thickness and the probed volume
120 homogeneity were assessed on a sample, called MT-2, with a low Total Organic Carbon (TOC)
121 content (1.4 %wt), extracted from the well 0/14-32-073-08W6 of the Montney-Doig formation at a
122 depth of 2070 meters. This well is located at 270 Km South-East of MT-1 sample. MT-2 was chosen
123 to evaluate the effect of mineral variability on scattering intensity, as it have a low TOC content. The
124 influence of sample thickness on SAXS data were analyzed to determine the occurrence of multiple
125 scattering effects. SAXS measurements were conducted on MT-2 normal cut to bedding thin blade
126 sections within a thickness of 100, 140 and 210 μm . Scattering intensities were normalized to the
127 sample thickness and transmission. Results (supplementary information) show that intensities in

128 absolute units are about the same according to three different sample thickness suggesting (i) no
129 multiple scattering in this Q range and (ii) measurements are performed in an almost homogeneous
130 probed volume. The multiple scattering effect was only checked on SAXS data assuming, as suggested
131 by Anovitz and Cole (2015), the fact that if the transmission is greater than 90 %, the multiple
132 scattering effects remains small.

133 To complete our view on probed volume homogeneity, SAXS measurements were performed on 9
134 and 5 random positions on the 140 μm thick MT-2 sample with a 200 x 200 μm beam size. Results
135 were decomposed as the sum of power law trends as $A.Q^{-\alpha}$. Then, the A or α parameters were used to
136 define the variability of each parameter. The α parameter vary within 1% whereas the prefactor vary
137 within less than five percent. The latter is thought to be correlated with concentration, size and contrast
138 of various scatterers. We conclude from the low dispersion of A and α parameters that with this beam
139 size, the sample phase distribution is almost constant. Moreover, the SAXS intensities measured on 9
140 or 5 random positions were averaged to get a more representative volume to be compared with neutron
141 measurements.

142 As this study is partly focused on the analysis of source rock anisotropy, the samples were cut
143 normal to bedding plane to maximize the occurrence of lamination, as shown in *Figure 1*. Rocks thin
144 blade sections with a maximum thickness of 200 μm were prepared and stuck to pierced quartz blades
145 with a pinhole of 5.5 mm diameter. This diameter allows to map and to average several SAXS
146 measurements in order to probe about the same volume as SANS ; in this way, the comparison of X-
147 ray and neutron scattering intensities are meaningful. Concerning the homogeneous probed volume of
148 samples used in this study, SAXS measurements were performed on five random location for each
149 sample. Obtained scattering intensities were checked and compared to the mean intensity. It reveals no

150 significant variation allowing us to consider that the probed volume display a constant phase
151 distribution.



152 **Figure 1.** Schematic representation of sample preparation with in blue normal to bedding plane and
153 in red the bedding.

154
155

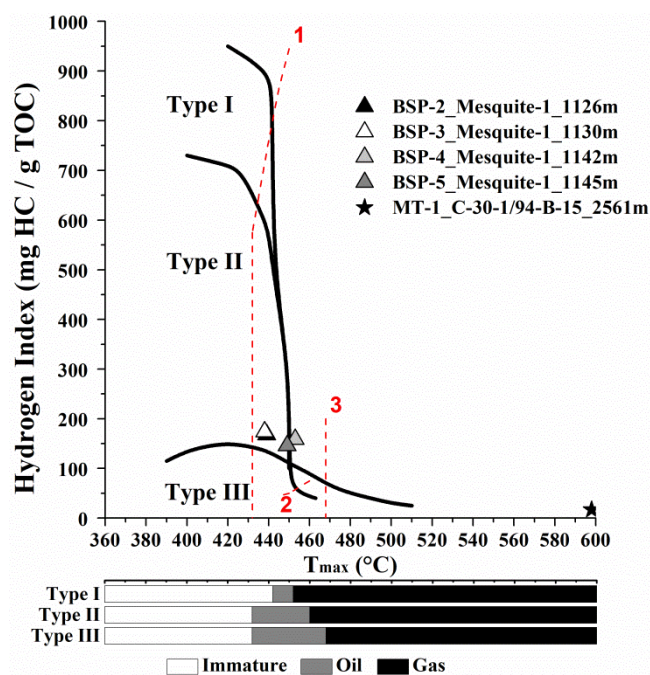
156 2.3. Rock-Eval[®] 6 pyrolysis.

157
158

158 Geochemical data on organic matter were obtained by Rock-Eval pyrolysis according to the Shale
159 Play method.^{31,52} This technique is used to define the TOC content, the organic matter type and the
160 maturity through HI vs Tmax diagram, as shown in *Table 1* and in *Figure 2*.^{11,23,24,26,28-31,34,35,53-55}
161 Analysis was performed on 60 mg of dry bulk-rock powder and standard deviation was assessed
162 through the repeatability of five measurements of each sample.

163 Samples have a TOC content ranging from 4.5 %wt (BSP-2 and BSP-3) up to 9.0 %wt (BSP-4). The
164 *Figure 2* illustrates sample measurements, all of them are consistent with a kerogen of type II.^{56,57}
165 These samples follow an increasing depositional depth from BSP-2 (1126 m) to MT-1 (2561 m). BSP
166 samples are mature, as HI range from 146 to 174 mg HC / g TOC and Tmax is close to 445°C. They
167 are in the oil window and the MT-1 sample reach the dry gas window which means that it is
168 overmature (HI = 17 mg HC / g TOC and Tmax = 598°C). As shown by Craddock and coworkers

169 (2018),¹¹ there is a strong correlation between the depositional depth and the maturity of the sample.
 170 An increase of the maturity along the depth is then expected.



171 **Figure 2.** HI as a function of Tmax diagram with delineations 1, 2 and 3 defining the limit of the oil-
 172 gas window for kerogen of type I, II and III.⁵⁴ BSP samples are represented by triangles and MT-1 is
 173 symbolized by a star.

174 **Table 1.** Rock-Eval pyrolysis data obtained within the Shale Play method on the five source rock
 175 samples. (a) Data expressed in mg HC / g rock.

| Formation | Reference | Well | Depth | Maturity | Sh0 | Sh1 | Sh2 | Tmax | HI | TOC |
|--------------------|-----------|------------|--------|----------|------|-----|------|------|---------------|------|
| | | | m | | (a) | (a) | (a) | (°C) | mg HC / g TOC | wt % |
| Barnett Shale Play | BSP-2 | Mesquite 1 | 1126.7 | Mature | 2.36 | 2.7 | 7.5 | 439 | 168 | 4.5 |
| | BSP-3 | Mesquite 1 | 1130.5 | Mature | 2.55 | 3.5 | 7.8 | 438 | 174 | 4.5 |
| | BSP-4 | Mesquite 1 | 1142.4 | Mature | 2.09 | 3.0 | 14.5 | 453 | 159 | 9.0 |
| | BSP-5 | Mesquite 1 | 1145.4 | Mature | 1.57 | 2.5 | 11.9 | 449 | 146 | 8.1 |

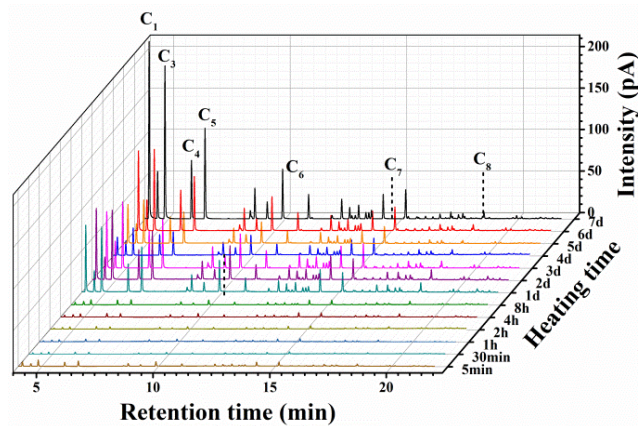
| | | | | | | | | | | |
|--------------------|------|--------------------|--------|------------|-------|-------|-------|------|------|-------|
| Montney- Doig | MT-1 | C-30-I/ 94-b-15 | 2561.8 | Overmature | 0.09 | 0.3 | 0.8 | 598 | 17 | 4.8 |
| Standard deviation | | | | | ±0.06 | ±0.02 | ±0.04 | ±0.6 | ±0.6 | ±0.01 |

176 **2.4. Headspace Gas Chromatography.**

177 To obtain detailed information on Sh0 peak and on the free hydrocarbon composition, samples are
178 characterized by HS-GC. This thermodesorption method is based on a partial pressure equilibrium
179 between the fluid in the source rocks and the vapor outside the rock generated at a given temperature.
180 For that purpose, this technique is only used as qualitative tool in this study on thin rock section
181 samples whom preparations and representations are described in section 2.2. HS-GC measurements
182 were performed on an Agilent 7890B-GC chromatograph equipped with a Headspace Sampler Agilent
183 7697A. Samples were put into a 15mL vial at 80°C between 5 minutes to 7 days. Then, a volume of
184 15 µL is taken from the vapor and injected into the chromatograph. Data on the composition between
185 C₁ and C₁₁ were acquired using a chromatographic column consisting in a fused-silica capillary coated
186 with Al₂O₃ of about 30 meters with a flow rate of 1.6.10⁻² mL.s⁻¹, an input temperature of 160°C and
187 output temperature of 210°C. Data were normalized to the sample weight and compared to a standard
188 (Supelco[®] n°21823895) for the peak indexation.

189 The distribution of *n*-alkane obtained by HS-GC as a function of heating time and retention time is
190 represented in *Figure 3* for the BSP-4 sample cut normal to bedding plan. Based on this sample study,
191 light compounds such as C₁ to C₈ are shown to be preserved during the sample preparation. Results
192 from chromatographs reveal that, at t = 4 min to 10 min, the main contribution to hydrocarbon
193 composition are ascribed to light compounds from C₁ to C₅. Over several heating times, from 5
194 minutes to 7 days, the gas distribution remains unchanged with an increasing pressure. This reveals an

195 uncompleted gas release as no partial pressure equilibrium between the vapor outside and the fluid in
196 the rock is reached. One may explain it by the rock composition which contains silicates with Si-OH
197 groups and also illite and feldspar with Al_2O_3 groups which act as retention sites. Such functional
198 groups are classically used in chromatographic fused-silica column as adsorption surfaces. Thus, a
199 chromatographic effect can be observed in the rock as adsorption/desorption can occur on functional
200 groups leading to an uncomplete desorption within the heating time used. Anyway, this suggests that
201 the diffusion through the sample is low which is consistent with a low permeability as source rocks
202 porous media display connected and disconnected pore spaces.^{7,27,34,55,58-61} Measurements on parallel
203 and normal cut to bedding plane were also performed, for heating times ranging from 5 to 480
204 minutes. Results, shown in supplementary information, reveal that desorption rate, at a given time, is
205 always lower for parallel cuts to bedding plane than for normal ones.



206 **Figure 3.** Chromatographs of the BSP-4 sample, cut normal to bedding plan, over several heating
207 times, from 5 minutes to 7 days, in an oven at 80°C.

208 2.5. XRD Measurements.

209 The mineral composition was determined using a PANalytical X'pert Pro diffractometer using a
210 detector X'celerator and equipped with a Copper X-ray tube ($Cu-K\alpha = 1.5418 \text{ \AA}$). Data were acquired
211 on disoriented powder samples and according to the following analytical conditions: 45 kV, 40 mA,

212 angular sector from 2 to 80 °2 θ . Then, minerals quantification in weight percent, was achieved by
 213 Rietveld⁶² analysis using the software X’pert High Score Plus.

214 The mineralogical composition of the five studied source rocks is given in *Table 2*. The mineral
 215 content in weight percent, is then converted in volume percent for the SLD calculation. The major
 216 mineral phase encountered in BSP and MT samples are silicates *lato sensu* with quartz as main
 217 mineral (> 30 vol %) followed by illite (4 to 20 vol %) and muscovite (15 to 28 vol%). The second
 218 contribution to mineral phase is carbonate minerals with 4 to 27 vol %. Then, pyrite content varies
 219 from almost 1 vol % to 2.5 vol %. This mineral composition agrees with other studies on the same
 220 geological formations.^{56,63}

221

222 **Table 2.** Normalized mineral compositions of BSP and MT samples converted in volume percent (vol
 223 %) using the mineral density (a) defined in the database www.webmineral.com.

| Phase | Density (g/cm ³) | BSP-2 (vol %) | BSP-3 (vol %) | BSP-4 (vol %) | BSP-5 (vol %) | MT-1 (vol %) |
|-----------|---------------------------------|------------------|------------------|------------------|------------------|-----------------|
| Quartz | 2.65 ^(a) | 41.9 | 41.7 | 30.1 | 31.6 | 36.4 |
| Albite | 2.62 ^(a) | 12.0 | 9.0 | 15.4 | 12.5 | 6.5 |
| Muscovite | 2.90 ^(a) | 15.6 | 13.7 | 28.0 | 22.5 | 17.9 |
| Illite | 2.75 ^(a) | 12.4 | 14.8 | 19.8 | 12.8 | 4.1 |
| Calcite | 2.71 ^(a) | 8.5 | 12.7 | - | 17.4 | 8.6 |
| Dolomite | 2.87 ^(a) | 8.5 | 7.1 | - | 1.4 | 18.3 |
| Apatite | 3.19 ^(a) | - | - | 4.3 | - | - |
| Pyrite | 4.93 ^(a) | 1.1 | 0.9 | 2.3 | 1.8 | 2.5 |

224

225 **2.6. Field-Emission Scanning Electron Microscopy.**

226 Visual information on phase distribution is required to determine the occurrence of scattering
227 contrast. For this reason, FESEM was used in order to acquire images on rock structures and organo-
228 mineral phases distribution at a large scale (from hundreds of microns to dozens of nanometers).
229 Observations on normal cut to bedding plane samples were made at 12 nm/pxl. Experiments were
230 carried out on a FESEM Nova NanoSEM 450 on cryogenic argon ion polished sample. Images were
231 acquired with a working distance ranging from 5.2 to 5.5 mm and a probe current of 2.5 KV.

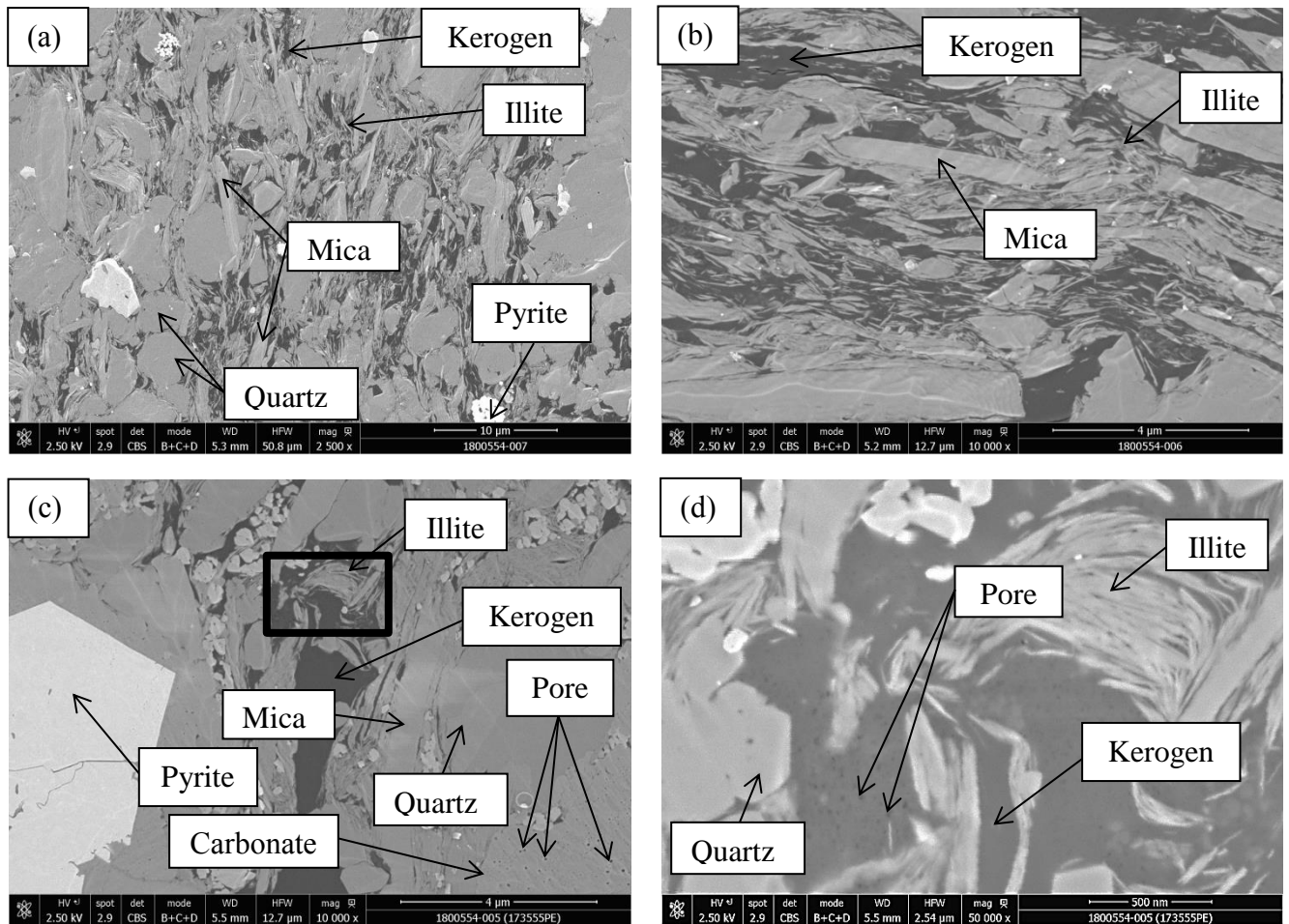
232 The FESEM images of rock structures and phase distributions are shown in *Figure 4*. Four Fields of
233 View (FOV), from 51 μm down to 2,5 μm , were observed to account for the orientation of micas and
234 clay minerals, the pores in mineral matrix and the pore within the kerogen phase. Five types of
235 structure are identified:

- 236 - Pyrite, crystallizing in a cubic system as framboidal and cubic shapes, have a high absorption
237 coefficient leading to white objects on FESEM images,
- 238 - Dark grey aggregates account for the organic matter as this material is composed of light
239 elements with a low absorption coefficient,
- 240 - Dark grey level is assigned to pores in both organic and inorganic phases,
- 241 - Subangular minerals, with a light grey level between the organic matter and pyrite minerals, are
242 attributed to quartz,
- 243 - Feldspars, with the same grey level as quartz, exhibits an angular shape allowing their
244 identifications,
- 245 - Carbonaceous minerals, similar to feldspars in shape, have a higher density. These minerals have
246 also an angular shape but some intra-granular pores can be encountered owing to liquid
247 dissolution phenomenon which is used for the identification,
- 248 - Macroscopic elongated minerals, larger than two microns, are micas,

249 - Fine elongated minerals, lower than two microns, are consistent with clayey mineral such as
250 illite.

251 *Figure 4(a), Figure 4(b) and Figure 4(c)* display macroscopic observations (FOV = 51 μm and
252 13 μm) on the BSP-4 (a and b) and BSP-5 (c) samples depicting a preferential orientation of micas
253 and clay minerals. Such features exist at a lower scale (FOV = 2,5 μm) as well as in *Figure 4(d)*
254 coming from BSP-5 sample. Moreover, *Figure 4(c)* highlights that isolated porosity exists in the
255 minerals and is mostly widespread in carbonaceous phases. Comparing *Figure 4(c)* and *Figure 4(d)*,
256 shows that pores in minerals are mainly macropores with a lower amount of mesoporosity while
257 mesopores are the major porosity in organic matter.

258

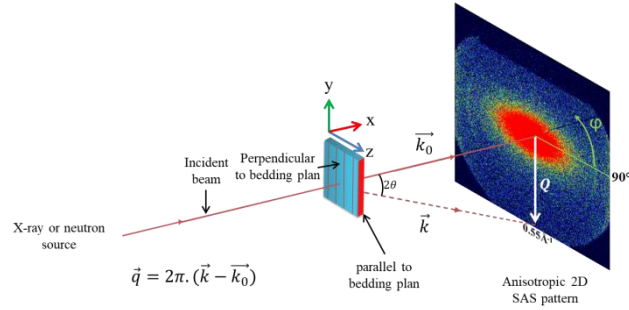


259 **Figure 4.** FESEM observations performed on BSP-4 (a and b) and BSP-5 sample (c and d) with
260 different fields of view, (a) 51 μm , (b) and (c) 13 μm and (d) 2,5 μm , to depict the phase distribution.

261 The delimited area in (c) represented the field of view observed in (d).

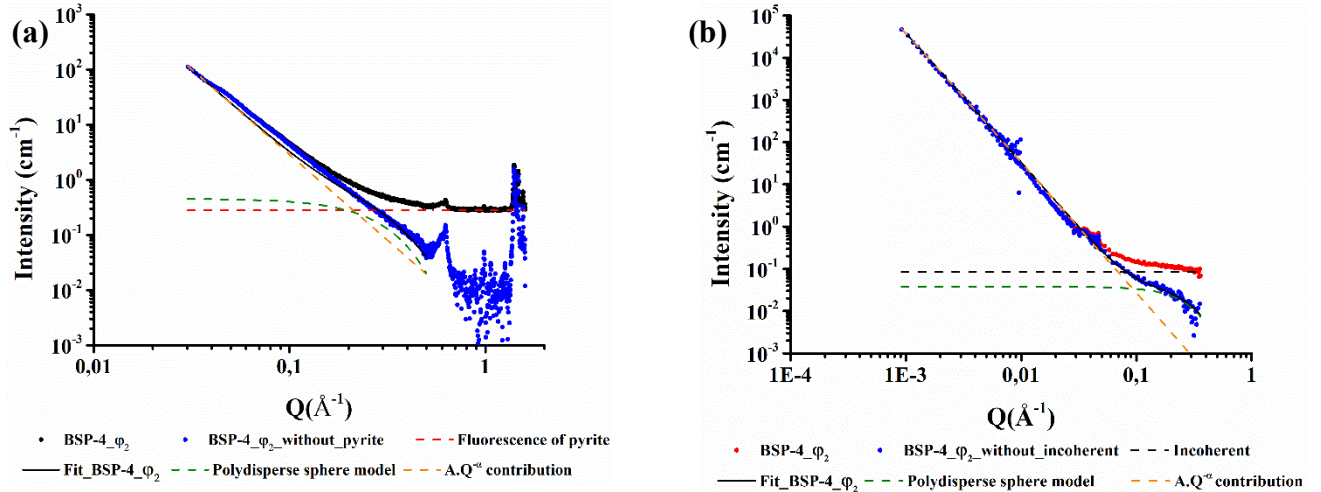
262 2.7. Scattering experiments

263 2.7.1. SAXS and WAXS measurements. SAXS instrument is equipped with a Cu rotating anode
264 (Rigaku MM07, at the wavelength of $\lambda = 1.5418 \text{ \AA}$) and a 2D detector (Rigaku). The sample to
265 detector distance is about 73.6 cm and allows the measurement of a scattering vector Q ranging from
266 0.03 \AA^{-1} up to 0.6 \AA^{-1} . The instrument is also equipped with a WAXS 2D detector and enlarges the
267 studied area until 1.6 \AA^{-1} . The experimental setup is illustrated *Figure 5*. The scattering vector Q can
268 be seen as an inverse correlated length scale in the reciprocal space and is defined as $Q = 4\pi \cdot \sin\theta/\lambda$
269 with 2θ being the scattering angle. In the case of source rocks, WAXS measurements allows the
270 identification of the 001 Bragg peaks of illite located at $d_{001} = 2\pi/Q = 10.0 \text{ \AA}$. SAXS/WAXS data
271 of each sample were corrected to their transmission, their thickness, the empty beam signal and
272 normalized to a lupolen standard. The scattering intensity obtained on WAXS data are rescaled to the
273 scattering intensity of SAXS data. Thus, the scattering intensity is expressed in absolute unit, cm^{-1} , for
274 both techniques. The presence of a continuous and flat background on WAXS data at high Q values
275 indicates the occurrence of a signal distributed over 4π which doesn't depend on Q vector. Two
276 phenomena can contribute to the background at high Q values : (i) mineral in homogeneities at sub
277 nanometer length scale giving rise to scattering intensities with small Q dependence , and (ii)
278 fluorescence, since the *Cu-K α* energy (8.04 KeV) and *Fe K-edge* energy (7.11 KeV) are close and lead
279 to a constant scattering, independent of the Q vector. As WAXS data allow to observe a very constant
280 background over high Q values, this phenomenon is attributed to the fluorescence of the iron
281 contained in pyrite which needs to be subtracted, as shown in *Figure 6(a)*.



282 **Figure 5.** Schematic representation of SAXS/WAXS configuration with respect to the laboratory frame
 283 (x,y,z) .

284 2.7.2. SANS measurements. SANS experiments were carried out on the PA20 spectrometer at
 285 Laboratoire Léon Brillouin (CEA/CNRS) at Saclay, France. Three different configurations ((i) $\lambda = 3.8$
 286 \AA /sample-to-detector distance (D) = 1.1 m, (ii) $\lambda = 6 \text{\AA}/D = 8$ m and (iii) $\lambda = 15 \text{\AA}/D = 17.5$ m), gives a
 287 total Q -range from $9.1 \cdot 10^{-4} \text{\AA}^{-1}$ to $5.1 \cdot 10^{-1} \text{\AA}^{-1}$. To be compared with SAXS/WAXS data, it is
 288 mandatory to express the SANS intensity in absolute units. For that purpose, SANS measurements of
 289 each sample were also corrected by their transmission, their thickness, the detector pixel efficiency
 290 and normalized to the incident beam. Assuming that the almost flat background at high Q values is
 291 related to the incoherent scattering of the hydrogen contained in the sample, the mean intensity value
 292 of the last Q values (0.45 to 0.51\AA^{-1}) was assessed and subtracted, as shown in *Figure 6(b)*. The
 293 validity of this assumption will be discussed in the result section.



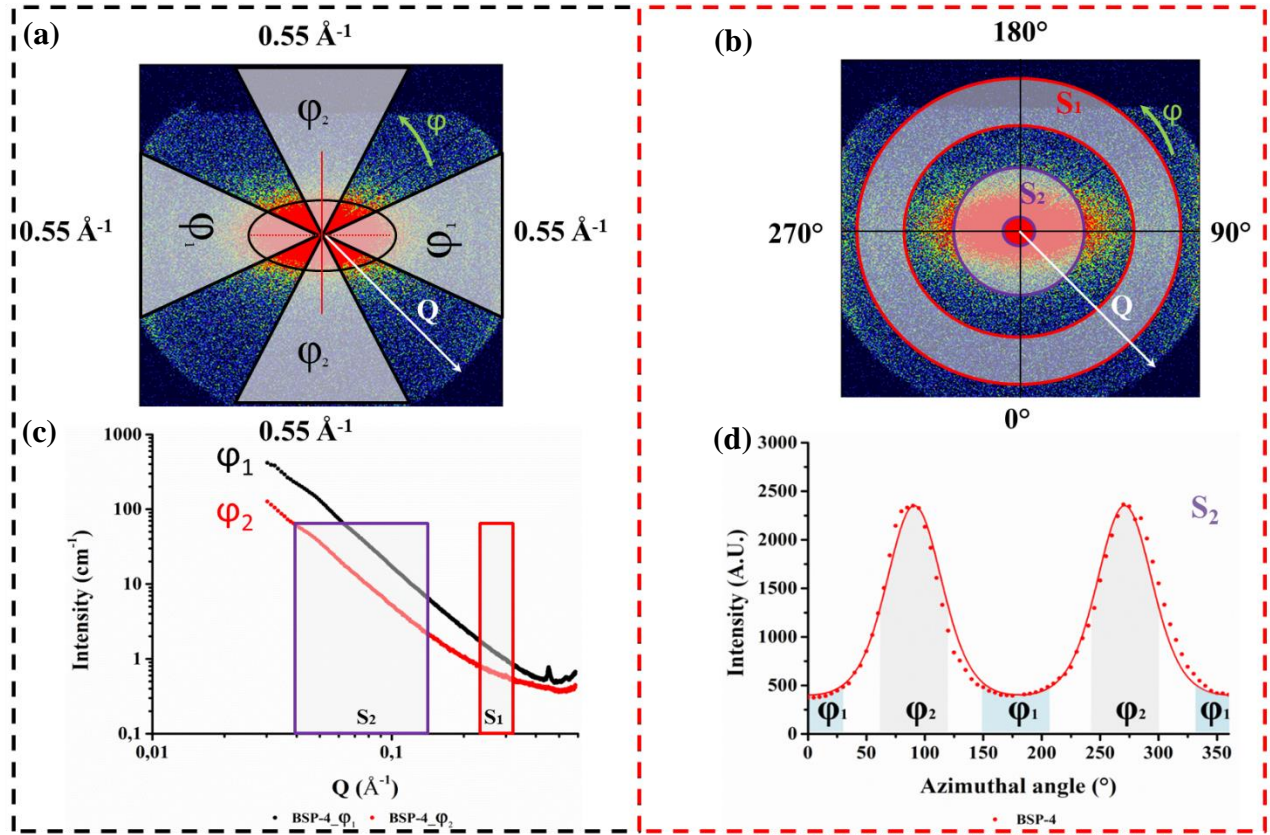
294 **Figure 6.** (a) Example of fluorescence subtraction on BSP-4_φ₂ SAXS data. (b) Example of incoherent
 295 subtraction on BSP-4_φ₂ SANS data. Both scattering profiles are displayed as a function of two
 296 contributions, log normal (dark green dash lines) and $A \cdot Q^{-\alpha}$ (orange dash lines).

297

298 **2.7.3. Initial scattering profiles treatment.** Two types of data integrations were performed on
 299 scattering 2D anisotropic pattern, as shown in *Figure 7*. As defined earlier, studied source rocks are
 300 laminated rocks. It is then possible to measure a 2D scattering pattern being anisotropic. Consequently,
 301 radial average of 2D pattern was realized using two angular sectors as illustrated in *Figure 7(a)*. The
 302 first sector φ_1 is defined by the angle $\varphi = 90^\circ$ along the elongated part of the anisotropic pattern with
 303 an aperture angle of $\Delta\varphi = 60^\circ$. The other one φ_2 is normal to the angle φ_1 as $\varphi_1 + 90^\circ$ and $\Delta\varphi = 60^\circ$.
 304 Obtained scattering curves, displayed in *Figure 7(c)*, exhibit the scattering intensity as a function of
 305 the wave vector Q .

306 The anisotropic 2D scattering patterns suggest that in the system some scatterers are preferentially
 307 oriented along one direction. Thus, scattering patterns were also azimuthally averaged according to
 308 two distinct regions, as shown in *Figure 7(b)*. The first one, S_1 , is at low Q values, $5 \cdot 10^{-2} < Q < 0.2 \text{ \AA}^{-1}$,
 309 and the second region, S_2 , is in high Q -region, $0.34 < Q < 0.5 \text{ \AA}^{-1}$. From the 1D curve, illustrated in
 310 *Figure 7(d)*, the variation of the scattering intensity is plotted as a function of the azimuthal angle φ
 311 from 0° to 360° with an aperture step angle of 5° . As particles are oriented, the scattering intensity

312 gives information on the main orientation of particles and on the sample structure. The order
 313 parameter S – denoted sometimes the Herman’s parameter - quantifies the material anisotropy and is
 314 used frequently in nematic crystal and clays domains.⁶⁴⁻⁶⁷



315 **Figure 7.** 2D pattern area of interest according to radial (a) and azimuthal (b) average and their
 316 scattering intensities (c) and (d).

317
 318 One popular way to fit anisotropic SAXS data is to use, for a small Q range, the Maier-Saupe
 319 function^{68,69} defined as :

$$f(\varphi) = A + B \cdot \exp\left(m \cdot \cos^2\left(\left(\varphi - \psi\right) * \left(\frac{\pi}{180}\right)\right)\right)$$

320 (2)

321 Where A is the flat background, B is a multiplier coefficient, m accounts for the particle orientation,
 322 φ is the azimuthal angle and ψ is the maximum of intensity. Then, the Maier-Saupe data are
 323 normalized to their area, to compare results obtained for each sample, according to :

$$A = \int_0^\pi f(\theta) \cdot \sin(\theta) d\theta \quad (3)$$

324 and

$$f(\theta)_{norm} = \frac{f(\theta)}{2\pi \cdot A} \quad (4)$$

326 With θ the normal to the angle between the particle and the laboratory frame z axis.

327 Afterward, the order parameter S is expressed as the mean of a second-order Legendre polynomial :

$$S = \left\langle \frac{3 \cdot \cos^2(\theta) - 1}{2} \right\rangle \quad (5)$$

328 And integrated over the whole solid angle $\sin(\theta) \cdot d\theta \cdot d\varphi$:

$$S = \int_0^{2\pi} d\varphi \int_0^\pi f(\theta)_{norm} \cdot \frac{3 \cdot \cos^2(\theta) - 1}{2} \cdot \sin(\theta) d\theta \quad (6)$$

331 The order parameter values range from 0, isotropic media, to 1, perfectly oriented particles as
 332 columnar or smectitic crystal-liquid phases.⁶⁶

334

335 3. RESULTS

336 **3.1. Frame of Scattering modeling**

337 Scattering intensities being related to the so called Scattering Length Densities (SLD) fluctuations,
338 we first examined what are SLD in source rocks for both neutron and X-ray and secondly how SLD
339 may be taken into account in intensities modeling.

340 *3.1.1. Scattering Length Densities*

341 The SLD of a component or a phase is related to its elemental composition and to the type of
342 radiation used. For each component, SLD is calculated according to the formula:^{20,21,27,28,70}

$$\rho = \frac{1}{V} \sum_i n_i b_i$$

343 (7)

344 Where V is a volume representative of the component, n_i the number of atoms of type i contained in
345 the volume V and b_i the atomic scattering length. The latter are tabulated for neutrons in the NIST
346 Database (<https://www.ncnr.nist.gov/resources/n-lengths/>), whereas they are estimated for X-ray
347 according to $b_i = 0.282 \cdot 10^{-12} Z_i$ (cm) where Z_i is the atomic number of atoms of type i . For a mixture of
348 components, the mean SLD, $\langle \rho \rangle$, for both radiation beam is established according to:

$$\langle \rho \rangle = \sum_j \phi_j \rho_j$$

349 (8)

350 With $\sum_j \phi_j = 1$, ϕ_j the volume fraction of the component j and ρ_j the SLD of the component j .

351 From FESEM observations, three different phases are observed : mineral, kerogen and pores.

352 ***Minerals :***

353 The SLD of the main minerals in our samples are reported on *Table 3*.

354 **Table 3.** neutron and X-Ray SLD values of minerals. (a) Data coming from the mineralogical
 355 database webmineral, on : <http://webmineral.com/>

| Phase | Chemical formula ^(a) | Density ^(a) (g/cm ³) | SLD | |
|-----------|---|--|--|--|
| | | | X-rays (x 10 ¹⁰ cm ⁻²) | Neutrons (x 10 ¹⁰ cm ⁻²) |
| Quartz | SiO ₂ | 2.65 | 22.5 | 4.2 |
| Albite | NaAlSi ₃ O ₈ | 2.62 | 22.1 | 4.0 |
| Muscovite | KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂ | 2.90 | 24.5 | 3.9 |
| Illite | K(Al,Fe,Mg) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ | 2.75 | 23.1 | 3.7 |
| Calcite | CaCO ₃ | 2.71 | 23.0 | 4.6 |
| Dolomite | CaMg(CO ₃) ₂ | 2.87 | 24.3 | 5.4 |
| Apatite | Ca ₅ (PO ₄) ₃ (OH,F,Cl) | 3.19 | 26.9 | 4.1 |
| Pyrite | FeS ₂ | 4.93 | 40.5 | 3.7 |

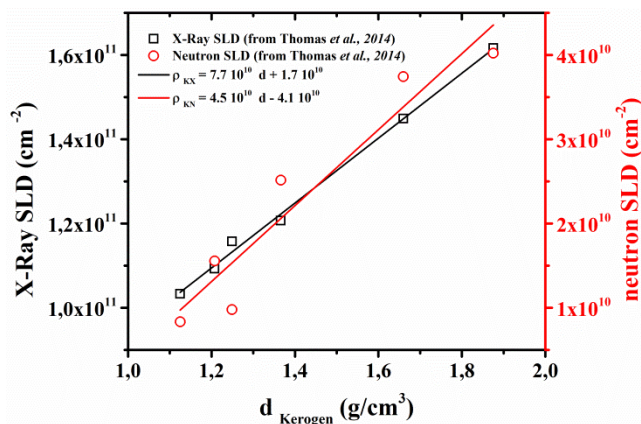
356
 357 For neutrons, minerals SLD are close to each other ($\sim 4.10^{10} \text{ cm}^{-2}$) which allows to consider
 358 minerals as a homogeneous phase. The corresponding mean value is easily assessed using Equation 8
 359 with volume fraction of each mineral determined by XRD. For X-rays, most of the minerals have a
 360 SLD value close to $24.10^{10} \text{ cm}^{-2}$, except pyrite. Thus, X-ray perceives the minerals as two distinct
 361 phases since differences in SLD give rise to a contrast.

362 ***Kerogen:***

363 Kerogen in analogous materials such as coal,⁷ is described as a homogeneous phase where its SLD
 364 is similar whatever the macerals type.

365 Since our sample selection was designed to obtain a continuous sequence of increasing maturity, it is
 366 mandatory to consider the effect of maturity on kerogen SLD. A recent study on kerogen in source
 367 rocks,⁷¹ show that neutron kerogen SLD vary from $1.10^{10} \text{ cm}^{-2}$ for immature kerogen up to $4.10^{10} \text{ cm}^{-2}$
 368 for the overmature one. Elemental compositions and densities of gas shale from various maturities and

369 after acid attack, given by Thomas and coworkers (2014),⁷¹ were used here to assess neutron and X-
 370 ray SLD as well as mass densities of kerogens. Thus, we assumed that all the Fe content in attack acid
 371 residues is only due to pyrite FeS₂. The pyrite contribution, including the sulfur one, has been
 372 subtracted to obtain elemental composition and densities of model kerogens containing C, H, O and N
 373 atoms. X-ray and neutron SLD were assessed using Equation 7. Results are plotted on *Figure 8* as a
 374 function of kerogen densities. Indeed, kerogen density vary in the same way as vitrinite reflectance
 375 and could be used as a maturity index.



376 **Figure 8.** X-ray and neutron kerogen SLD as a function of kerogen densities based on data from
 377 Thomas et al., 2014.⁷¹ X-ray linear regression (black curve) and neutron linear regression (red curve)
 378 for kerogen SLD estimations.

379 Linear regressions were performed on kerogen X-ray and neutron SLD. From these linear
 380 regressions, ρ_{KN} and ρ_{KX} can be expressed as :

$$\rho_{KN} = 4.5 \cdot 10^{10} \cdot d - 4.1 \cdot 10^{10} \tag{9}$$

382 and

$$\rho_{KX} = 7.7 \cdot 10^{10} \cdot d + 1.7 \cdot 10^{10} \tag{10}$$

383 with ρ in cm⁻² and d in g/cm³.

384

385 **Pore space :**

386 For this study, four model fluids are considered : air, methane in gaseous form, toluene and pentane.

387 SLD values are listed in *Table 4* below.

Table 4. Model Fluids SLD calculated from equation 7.

| Model fluids | Neutrons SLD (x 10 ¹⁰ cm ⁻²) | X-Ray SLD (x 10 ¹⁰ cm ⁻²) |
|------------------------|--|---|
| Toluene | 0.9 | 8.0 |
| Pentane | -0.6 | 6.2 |
| Methane _(g) | 0.0 | 0.0 |
| Air | 0.0 | 0.0 |

388

389 Pores can be fulfilled by gaseous species and/or by condensed hydrocarbons. If the pore space is
390 fulfilled by a gas, its SLD for both X-ray and neutron is close to 0. If condensed fluids are in the pore
391 space, it is then assumed that neutron SLD is almost null as condensed fluids have a SLD value
392 ranging from 1.10¹⁰ cm⁻², for aromatic fluids, to -0.5 10¹⁰ cm⁻² for aliphatic fluids. For X-ray, pore
393 space SLD will be close to 8.10¹⁰ cm⁻² for aromatics fluids and around 6.10¹⁰ cm⁻² for aliphatic fluids.

394

395 From these different SLD values, it appears that since neutron overmature kerogen and
396 minerals SLD values are close, neutron scattering acquired on overmature gas shales could be
397 interpreted in the frame of a two-phases system. As shown in *Figure 8*, for immature and mature
398 kerogen, SLD values are much lower than the SLD of the mineral phase. Consequently, the two-phase
399 system, which is classically used to described source rock scattering data, is less relevant than a three-
400 phases one. Concerning the nature of pore content, it is clear that neutron cannot distinguish gas from
401 hydrocarbons whereas X-ray can. For X-ray SLD values, four phases have different SLD : pyrite,

402 others minerals, kerogen and pore space. From XRD measurements, pyrite content is low, less than 2.5
 403 vol %, in the studied source rocks. Moreover, FESEM observations reveals that a large part of pyrite is
 404 present as grains with sizes higher than 1 μm . These grains will contribute to X-ray scattering in a Q
 405 range that is not probed by our instrument. Firstly, pyrite is therefore neglected and its contribution
 406 will be discussed after data modeling. Hence, for both types of radiation, at least three SLD values has
 407 to be considered rather than a two-phase approximation.

408
 409 *3.1.2. Scattering intensity.* As shown in FESEM observations, samples are described as a four
 410 phases system : pyrite, other minerals, kerogen and pores. Even if pyrite is discarded, we will
 411 distinguish for scattering four phases, namely minerals, kerogen, pores included in kerogen and pores
 412 in minerals. For that purpose, source rocks system can be defined as follows:

$$\sum_{i=1}^4 H_i(\vec{r}) = H_M(\vec{r}) + H_K(\vec{r}) + H_P(\vec{r}) + H_{P'}(\vec{r}) = \mathbf{1}$$

413 (11)

414 Where $H_M(\vec{r})$, $H_K(\vec{r})$, $H_P(\vec{r})$ and $H_{P'}(\vec{r})$ are respectively, the characteristic functions of the
 415 minerals, the kerogen, the pores contained in the kerogen and the pores in minerals. From previous
 416 equation, the amplitude $A(Q)$ of neutrons or X-ray can be written as :

$$A(Q) = \int_V \left[\sum_{i=1}^4 \rho_i H_i(\vec{r}) \right] e^{-iqr}$$

417 (12)

418 Since $\sum_{i=1}^4 H_i(\vec{r}) = 1$ and fluctuations of SLD occur, an arbitrary SLD reference can be chosen to
 419 determine $\rho_i H_i(\vec{r})$ in regard to the phase of interest, the kerogen, as :

$$\sum_{i=1}^4 \rho_i H_i(\vec{r}) = (\rho_M - \rho_K) H_M(\vec{r}) + (\rho_P - \rho_K) H_P(\vec{r}) + (\rho_{P'} - \rho_K) H_{P'}(\vec{r}) + \rho_K$$

420 (13)

421 $A(Q)$ can be rewritten according to the phase of interest through the Fourier transform. We note that
422 the Fourier transform of ρ_K is a dirac centered at $Q = 0$ and do not appear in the amplitude expression:

$$A(Q) = (\rho_M - \rho_K)\widetilde{H}_M(R) + (\rho_P - \rho_K)\widetilde{H}_P(R) + (\rho_{P'} - \rho_K)\widetilde{H}_{P'}(R)$$

423 (14)

424 From $A(Q)$, the scattering intensity is expressed according to $I(Q) = A(Q)A(Q)^*$.⁷⁴ The crossed
425 terms are considered negligible owing to FESEM observations revealing no correlation between the
426 kerogen and the pores contained in the mineral matrix. Arthur and Cole (2014) have shown by a
427 FESEM/FIBSEM dual beam analysis that the mesopores are mainly contained in the organic matter. In
428 addition, Bazilevskaya and coworkers (2015) demonstrated that about 50% of the porosity cannot be
429 observed by direct space analysis and may be contained in the organic matter or the interlayer of
430 clayey minerals. Thus, the scattering intensity is expressed as :

$$I(Q) = (\rho_M - \rho_K)^2\widetilde{H}_M(Q)\widetilde{H}_M^*(Q) + (\rho_{P'} - \rho_K)^2\widetilde{H}_{P'}(Q)\widetilde{H}_{P'}^*(Q) + (\rho_P - \rho_K)^2\widetilde{H}_P(Q)\widetilde{H}_P^*(Q)$$

431
432
433 (15)

434 At this point, the scattering intensity as illustrated in *Figure 6* can be described as the sum of three
435 contributions depending on a four phase system which are defined using three terms of contrast.

436 *The first contribution* is related to the contrast between mineral and kerogen phases. Based on
437 FESEM observations, kerogen is in the form of micrometric to nanometric domains and its volume
438 fraction, related to the TOC content, is few percent. A strong scattering intensity at small Q values is
439 then expected for this contribution. Indeed, at low Q values, the curve trend appears to be a power law
440 which can be expressed as $A.Q^{-\alpha}$, with α close to 3, A being a prefactor explicited later. In source and
441 sedimentary rocks studies, the α exponent is sometimes related to a surface fractal dimension D_s by
442 $\alpha = 6 - D_s$ where D_s is restricted to $2 < D_s \leq 3$.⁷⁵⁻⁷⁷ Schmidt (1982),⁷⁸ shows that the α exponent

443 could be also related to power law size distribution $f(R) \sim R^{-(1-D_s)}$. Whatever the physical meaning of
 444 power law intensity dependence, we will consider α as a fitting parameter and concentrate on the
 445 prefactor A that could be expressed as the product of squared contrast factor $(\rho_M - \rho_K)^2$ by a factor a
 446 related to the structural arrangement of kerogen in the mineral matrix. Hence, the first term of
 447 Equation 15 would be $a(\rho_M - \rho_K)^2 Q^{-\alpha}$

448 *The second contribution*, as highlighted by the FESEM characterizations, is related to pores in
 449 mineral phases, which are mainly macropores diluted within the mineral matrix. The mineral/pores
 450 interface seems to be smooth and their sizes vary from macrofractures to macropores. Consequently,
 451 their contribution likely follows a Porod behavior ($I(Q) \sim Q^{-4}$) which starts at lower Q values and
 452 strongly decreases toward higher Q values. At least, this means that this contribution to $I(Q)$ is
 453 negligible in the high Q domain probed.

454 *The last contribution* is related to the distribution of micropores in the kerogen matrix. As pores
 455 shape and size couldn't be well defined, owing to limitations (resolution and/or statistical
 456 representativeness), by direct space analysis such as FESEM or transmission electron microscopy, it is
 457 assumed that pores have a variety of shape and size as source rocks are natural materials. Both
 458 assumptions lead to a smoothing of the scattering curve compared to unique size and shape pores and
 459 make difficult to deconvolute both effects. In this study, we fixed the shape of the considered objects
 460 as spherical for sake of simplicity and assumed that size are distributed. This assumption preserve the
 461 physical meaning of the average size of the pores and it associated volume fraction. In source rocks
 462 the pore size distribution is often considered as peaked like in gas adsorption/desorption^{17,27,28,41} or
 463 NMR^{34,46} analysis. The $\widetilde{H}_p(Q)\widetilde{H}_p^*(Q)$ term is expressed as $n \int_{R_{min}}^{R_{max}} f_p(R) V_p^2(R) P(Q, R) dR$ - a diluted
 464 dispersion of pores - where n is the number density of pores, $V_p(R)$ stand for the volume of pore of size

465 R , $P(Q,R)$ is the form factor of the pores ($P(0,R) = 1$) chosen here as spherical, and $f_P(R)$ the
 466 normalized number size distribution function chosen here for convenience as log normal :

$$f_P(R) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\ln(R/\mu)^2}{2\sigma^2}\right)$$

467 (16)

468 Where μ the mean value of sphere radius and σ the size polydispersity.

469 Accordingly, for the scattering vector range measured in this study, a three-phase system with two
 470 main contributions, is defined and expressed, for X-rays (X) and neutrons (N) as :

$$I(Q)_{X,N} = a(\rho_M - \rho_K)_{X,N}^2 Q^{-\alpha} + n(\rho_P - \rho_K)_{X,N}^2 \int_{R_{min}}^{R_{max}} f_P(R) V_P^2(R) P(Q,R) dR$$

471 (18)

472 In this equation, parameters giving a direct influence on the intensity Q dependence, namely α , σ
 473 and μ , should be retrieved separately by fitting procedures. They provides details on each contribution
 474 prevailing in different Q domains. By contrast, only global prefactors $A = a(\rho_M - \rho_K)^2$ and $N =$
 475 $n(\rho_P - \rho_K)^2$ that adjust the amplitude of each Q dependence, will be extracted from the modeling.

476

477 **3.2. Anisotropy**

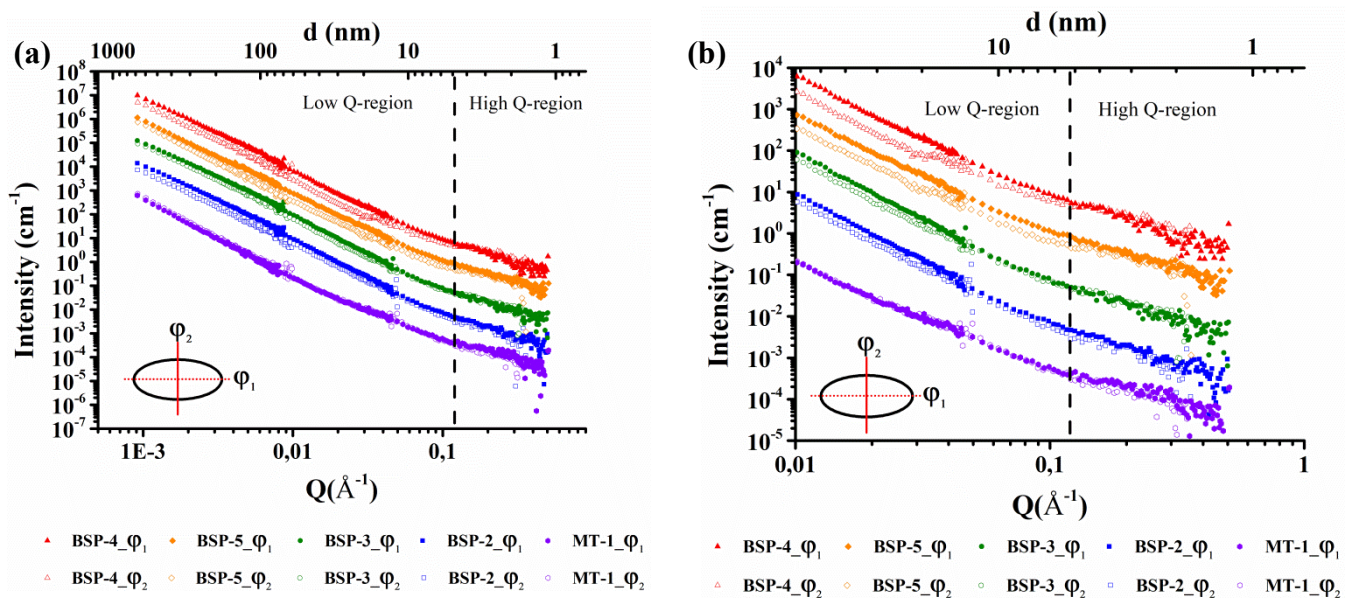
478 First, we consider the $I(Q)$ behavior for the two azimuthal sectors φ_1 and φ_2 according to *Figure*
 479 *7(a)*. Both scattering techniques results are illustrated in *Figure 9* for SANS and in *Figure 10* for
 480 SAXS/WAXS. It is noted that the MT-1 sample gives isotropic 2D pattern. As detailed in the
 481 literature, scattering data on source rocks follow at small Q values an algebraic trend assimilated to
 482 $A.Q^{-\alpha}$.^{8,20-23,27,35,71,79,80} In both techniques, the α parameter, reported in *Table 6*, have similar values
 483 close to 3 and the intensity ratio between φ_1 and φ_2 remains constant until a breakdown around 0.03 \AA^{-1}

484 $^{-1}$ in SANS and 0.1 \AA^{-1} in SAXS/WAXS. For larger Q values the scattering intensity is quite similar
 485 whatever the azimuthal sector. This behavior is ascribed to :

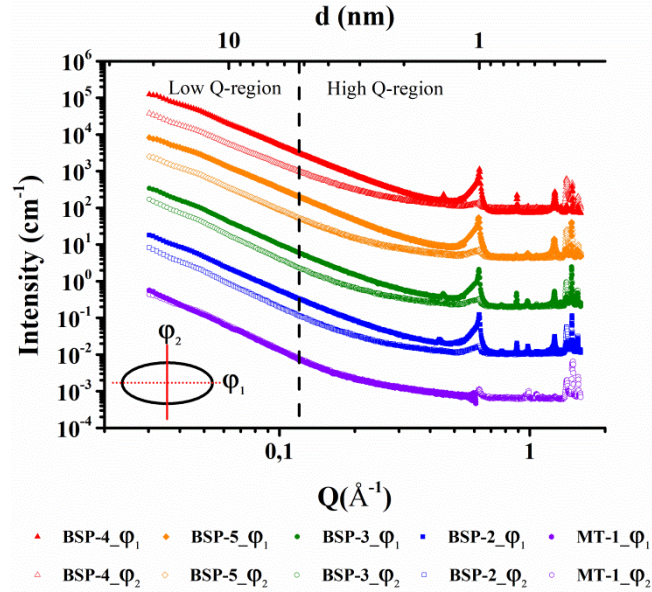
486 - anisotropic scattering at small Q values likely due to preferential orientation of low
 487 dimensionality particles such as clays and micas.

488 - isotropic scattering at large Q values reminiscent of spherical nanopores located in the kerogen

489 A further confirmation of this attribution is shown in supplementary information where the high Q
 490 intensity signal is ranked as the one of TOC content.

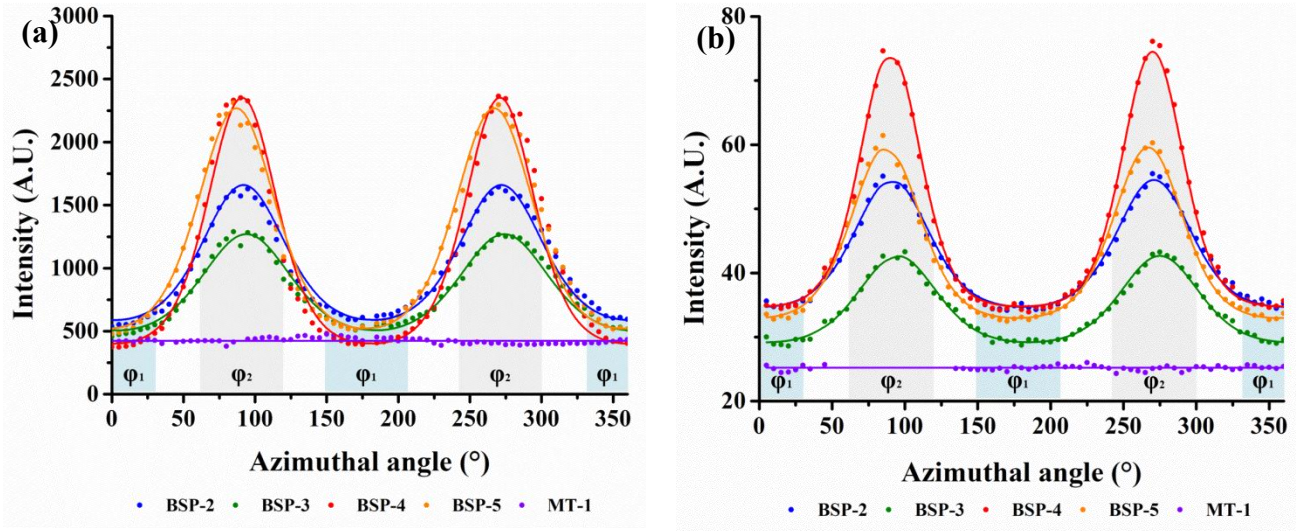


491 **Figure 9.** (a) Samples SANS profiles according to the azimuthal area of interest. Full dots represent
 492 data obtained for $\varphi_1 = 0^\circ$ and empty dots are data coming from $\varphi_2 = 90^\circ$. (b) Zoom on SANS profiles
 493 to match the Q -range of SAXS/WAXS data. In both graphs, SANS profiles of MT-1, BSP-2, BSP-5 and
 494 BSP-4 are scaled vertically according to the scale factors 0.01, 0.1, 10 and 100, respectively.



495 **Figure 10.** (a) Samples SAXS/WAXS profiles according to the azimuthal area of interest. Full dots
 496 represent data obtained for $\varphi_1 = 0^\circ$ and empty dots are data coming from $\varphi_2 = 90^\circ$. SAXS/WAXS
 497 profiles of MT-1, BSP-2, BSP-5 and BSP-4 are scaled vertically according to the scale factors 0.003,
 498 0.05, 15 and 300, respectively.

499 Secondly, we consider the $I(\varphi)$ behavior in the two Q ranges $S1$ and $S2$ according to *Figure 7(b)*.
 500 Samples data (dots) and fitting curves (lines) to the Maier-Saupe function (Equation 1) are illustrated
 501 in *Figure 11(a)* for low Q -region and *Figure 11(b)* for high Q values. At first sight, from MT-1 to
 502 BSP-4 samples an increasing intensity and sharpness of the distribution along the azimuthal angle is
 503 observed in both regions. Three groups are distinguished, the MT-1 isotropic sample with a flat
 504 intensity, the BSP-2/BSP-3 group exhibiting a broad distribution and the BSP-4/BSP-5 which have the
 505 highest and sharper distribution. In the *Figure 11(b)*, as the BSP-5 sample does not possess chlorite in
 506 SAXS profile, its intensity along the azimuthal angle is smaller than for BSP-4.



507 **Figure 11.** SAXS azimuthal integration profiles of BSP and MT samples within (a) low Q -region
 508 ($Q = 5.10^{-2}$ to 0.2 \AA^{-1}) and (b) high Q -region ($Q = 0.34$ to 0.5 \AA^{-1}). Integrated azimuthal angle regions
 509 from profiles decomposition are illustrated by the light blue and light grey areas respectively for φ_1
 510 and for φ_2 .

511 As shown in *Table 5*, it is possible from these data, to apply the Maier-Saupe fitting function to
 512 extract A , B , m and ψ parameters and then to calculate the order parameter S . Values of ψ are close to
 513 90° suggesting that anisotropic particles align preferentially with their long axis parallel to the bedding
 514 plane. Order parameters for BSP samples at low Q values are ranking from 0.13 and 0.14, for BSP-3
 515 and BSP-2, up to 0.21 and 0.26, for BSP-5 and BSP-4. Whereas, in the high Q -region, this parameter
 516 is quite low, barely reaching 0.09 at its maximum for BSP-4. BSP-2 and BSP-3 exhibit the lowest
 517 values with $S = 0.06$. Then, BSP-5 have an order parameter of 0.08. This seems to indicate that this
 518 part of the signal is less anisotropic and is dominated by an isotropic pattern. For MT-1, as its 2D
 519 scattering pattern is isotropic, S parameters for both Q regions is equal to 0.

520

521 **Table 5.** Maier-Saupe function parameters determined on SAXS profiles and their calculated S
 522 parameter for low Q -region ($Q = 5.10^{-2}$ to 0.2 \AA^{-1}) and high Q -region ($Q = 0.34$ to 0.5 \AA^{-1}).

| Reference | Low Q region : 5.10^{-2} to 0.2 \AA^{-1} | | | | | High Q region : 0.34 to 0.5 \AA^{-1} | | | | |
|-----------|--|-------|-----|--------|------|--|-----|-----|--------|------|
| | A | B | m | ψ | S | A | B | m | ψ | S |
| BSP-2 | 418.6 | 168.8 | 2.0 | 92 | 0.14 | 28.6 | 4.4 | 1.8 | 91 | 0.06 |
| BSP-3 | 324.8 | 181.1 | 1.6 | 94 | 0.13 | 22.6 | 5.6 | 1.4 | 95 | 0.06 |
| BSP-4 | 304.1 | 96.6 | 3.1 | 91 | 0.26 | 32.3 | 1.1 | 3.6 | 90 | 0.09 |
| BSP-5 | 342.1 | 177.1 | 2.4 | 87 | 0.21 | 28.9 | 2.5 | 2.5 | 87 | 0.08 |
| MT-1 | 423.4 | 0.0 | 0.0 | 0.0 | 0.0 | 24.7 | 0.0 | 0.0 | 0 | 0.0 |

523 The separation of the global signal into an anisotropic and an isotropic contribution allows to specify
 524 a more accurate expression for Q dependence of intensity :

$$526 \quad I(Q)_{X,N} = a(\varphi)(\rho_M - \rho_K)_{X,N}^2 Q^{-\alpha} + n(\rho_P - \rho_K)_{X,N}^2 \int_{R_{min}}^{R_{max}} f_P(R) V_P^2(R) P(Q, R) dR$$

527 (19)

528 where the prefactor a has been substituted by $a(\varphi)$.

529

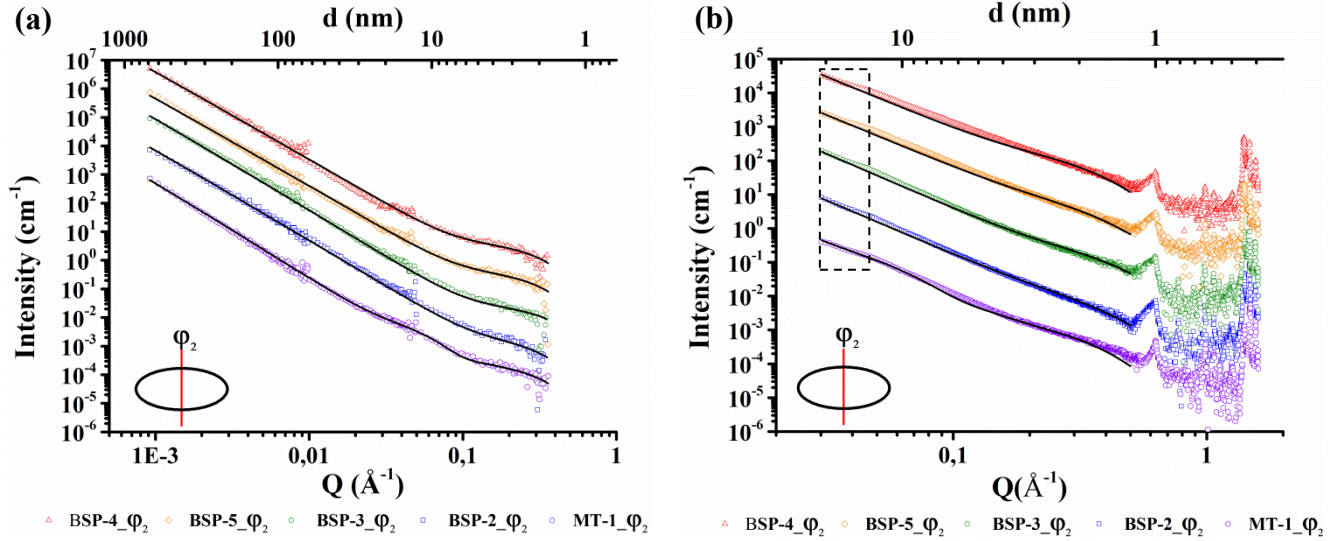
530 3.3. Multiscale structure.

531 We took advantage of anisotropic scattering to consider, in the fitting procedure based on equation
 532 19, the data acquired in azimuthal sector φ_2 . Indeed, for this sector, the scattering intensity from the
 533 first term of equation 19 is minimized and allows to better evaluate the second term contribution that
 534 remain moderate. This strategy could be optimized by considering a much smaller angular sector $\Delta\varphi_2$
 535 but it would require much larger acquisition time. Hence, SANS and SAXS/WAXS “ φ_2 ” data related
 536 to the five source rocks were fitted to equation 19 by using *SASFit* software.⁸¹ Results represented in
 537 *Figure 12(a)* for SANS data and in *Figure 12(b)* for SAXS/WAXS measurements shows a good

538 agreement between model and data for the both radiation on the whole Q range. Geometrical
539 parameters (α , μ and σ), reported in *Table 6*, are first assessed by fitting SANS data as the Q
540 dependence of these latter are more pronounced than for SAXS data. Then, modelling was performed
541 based on a simultaneous scattering fit of SAXS/SANS data to obtain the pre-factors $a(\rho_M - \rho_K)^2$ and
542 $n(\rho_P - \rho_K)^2$, containing the SLD of each phase and depending on the type of radiation.

543 Results obtained for geometrical parameters indicate that both SANS and SAXS/WAXS scattering
544 intensity can be described as the sum of two types of contributions using the same parameters giving
545 the Q dependence, namely α , μ and σ . These results also validate the SANS incoherent scattering
546 background subtraction based on mean value measured at high Q values .

547 The α parameters, that are close to each other (3.1 – 3.25) for BSP samples and slightly higher (3.4)
548 for MT1, are in the range of reported values.^{8,10,14,20,23,27,28,35,39,79} The widths σ of nanopore size
549 distributions are quite narrow, always close to 0.2 and the fitted parameters given here are obtained
550 with values of σ set to 0.2 for a better visibility. The mean radius of nanopores is close to 0.5 nm, a
551 value commonly found for this type of material.^{20,79} For the overmature sample, the curves at high Q
552 values show clearly two separate bumps assigned here to two pore size distributions. The first one has
553 a mean radius of 0.5 nm in the same range as the mature samples and the second one has much higher
554 values close to 3.5 nm. In addition, it appears that SAXS techniques can also provide information on
555 porous media in the kerogen phase as both SANS and SAXS/WAXS profiles are in good agreement
556 using pore size define from SANS modeling. From fitting data, BSP samples are described as source
557 rocks with pore radii varying from 0.5, for BSP-3, BSP-4 and BSP-5, up to 0.7 nm, for BSP-5. MT-1
558 sample displays two pore radii 0.5 nm and 3.5 nm. In addition, fit sensitivity on the pore size radius
559 was tested as shown in supplementary information. It shows that radii nanopore measurements are
560 sensitive within $\sim 1\text{-}2 \text{ \AA}$ range.



561 **Figure 12.** (a) Samples SANS and fit profiles coming from data integrated along the azimuthal angle
 562 $\varphi_2 = 90^\circ$. SANS profiles of MT-1, BSP-2, BSP-5 and BSP-4 are scaled vertically according to the scale
 563 factors 0.01, 0.1, 10 and 100, respectively. (b) Samples SAXS/WAXS and fit profiles from data
 564 acquired along the azimuthal angle $\varphi_2 = 90^\circ$. SAXS/WAXS profiles of MT-1, BSP-2, BSP-5 and BSP-4
 565 are scaled vertically according to the scale factors 0.003, 0.05, 15 and 300, respectively. In both
 566 graphs, solid lines represent the sum of $f(R)$ and $f_p(R)$ contributions determined with SASfit
 567 software.

568 **Table 6.** Fitting parameters of SANS and SAXS data obtained for the α parameter and the term of
 569 contrast $A = a(\varphi)(\rho_M - \rho_K)_N^2$ related to the $A.Q^{-\alpha}$ contribution and also the radius (μ) and the term of
 570 contrast $n(\rho_P - \rho_K)_N^2$ related to the log normal contribution.

| Reference | mu | | Neutrons | | X-rays | |
|-----------|----------|------|-----------------------------------|--------------------------|-----------------------------------|--------------------------|
| | α | (nm) | $a(\varphi)(\rho_M - \rho_K)_N^2$ | $n(\rho_P - \rho_K)_N^2$ | $a(\varphi)(\rho_M - \rho_K)_N^2$ | $n(\rho_P - \rho_K)_N^2$ |
| BSP-2 | 3.20 | 0.7 | 4.4 | 0.6 | 4.9 | 0.6 |
| BSP-3 | 3.25 | 0.5 | 3.4 | 4.4 | 4.4 | 3.5 |
| BSP-4 | 3.10 | 0.5 | 6.4 | 3.6 | 7.2 | 5.6 |
| BSP-5 | 3.10 | 0.5 | 7.6 | 6.3 | 11.0 | 5.2 |

| | | | | | | |
|------|------|-----|-----|-----|-----|-----|
| MT-1 | 3.40 | 0.5 | 0.4 | 4.0 | 1.2 | 6.2 |
| | | 3.5 | | 9.0 | | 2.9 |

571

572 Regarding the prefactors, we first consider their ratios R_A and R_N since they depend only on squared
573 contrast terms.

574

575

$$R_A = \frac{A_{\varphi,N}}{A_{\varphi,X}} = \frac{a(\varphi_2)(\rho_{MN} - \rho_{KN})_N^2}{a(\varphi_2)(\rho_{MX} - \rho_{KX})_X^2}$$

576 and

$$\sqrt{R_A} = \frac{(\rho_{MN} - \rho_{KN})_N}{(\rho_{MX} - \rho_{KX})_X}$$

577

$$R_N = \frac{N_N}{N_X} = \frac{n(\rho_{PN} - \rho_{KN})_N^2}{n(\rho_{PX} - \rho_{KX})_X^2} \quad (20a, 20b \& 21)$$

578

579 The equation 20b, together with the equations 9 and 10 relating the neutron and X-ray kerogen SLD
580 to the kerogen density d , form a system of three equations with three unknown (ρ_{KN} , ρ_{KX} and d) that
581 could be easily solved. The extracted parameters are reported on *Table 7* for samples of various
582 maturity. It appears that the extracted densities are quite similar – about 1.65 g/cm³ – for the BSP
583 samples and markedly different – 1.74 g/cm³ – for the MT1. It points out that BSP samples are mature
584 and MT1 overmature source rock as expected from Rock-Eval pyrolysis measurements (section 2.3.).
585 Regarding the neutron SLD, the one of overmature source rock – 3.7.10¹⁰ cm⁻² – is quite similar to the
586 one of mineral, suggesting that the scattering data could have been interpreted in the frame of a two-
587 phase system. Conversely, the neutron SLD differences between minerals and kerogen for the mature
588 source rocks are noticeable (0.5 – 0.7.10¹⁰ cm⁻²), justifying the three phases approximation developed
589 here. Regarding X-ray, the large differences between minerals and kerogen SLD show clearly that the
590 three-phase approximation is mandatory to interpret properly SAXS measurements.

591

592 **Table 7.** Values for ρ_{MN} and ρ_{MX} are calculated from equation 7. Kerogen densities, ρ_{KN} , ρ_{KX} and
 593 ρ_{PX} are estimated from, respectively, equation 21, 9, 10 and 22. Estimated n values for kerogen pores
 594 and the associated volume fraction.

| Sample | μ (nm) | n ($\times 10^{19} \text{ cm}^{-3}$) | Volume fraction ($\times 10^{-2}$) | Kerogen density d (g/cm^3) | ρ_{MN} ($\times 10^{10} \text{ cm}^{-2}$) | ρ_{MX} ($\times 10^{10} \text{ cm}^{-2}$) | ρ_{KN} ($\times 10^{10} \text{ cm}^{-2}$) | ρ_{KX} ($\times 10^{10} \text{ cm}^{-2}$) | ρ_{PX} ($\times 10^{10} \text{ cm}^{-2}$) |
|--------|---------------|---|--|---|---|---|---|---|---|
| BSP-2 | 0.7 | 0,5 | 1.0 | 1.66 | 4.0 | 21.3 | 3.4 | 14.5 | 4.3 |
| BSP-3 | 0.5 | 4.7 | 3.0 | 1.67 | 4.0 | 21.3 | 3.4 | 14.6 | 5.1 |
| BSP-4 | 0.5 | 6.0 | 3.8 | 1.59 | 3.7 | 20.3 | 3.0 | 14.0 | 4.4 |
| BSP-5 | 0.5 | 5.7 | 3.6 | 1.65 | 3.8 | 20.2 | 3.3 | 14.4 | 4.9 |
| MT-1 | 0.5 | 2.6 | 1.6 | 1.74 | 4.1 | 21.6 | 3.7 | 15.1 | 0 |
| MT-1 | 3.5 | 7.10^{-4} | 0.15 | - | - | - | - | - | 0 |

595
 596 Knowing kerogen SLD for both SAXS and SANS techniques, R_N ratios may provide fluids in place
 597 SLD values assuming $\rho_{PN} \sim 0$. Then, ρ_{PX} can be expressed as :

$$\rho_{PX} = \frac{-\rho_{KN} + \sqrt{R_{2N}\rho_{KX}}}{\sqrt{R_N}}$$

598 (23)

599 Calculated ρ_{PX} values are listed in *Table 7* and displayed two different values. For BSP samples, a
 600 ρ_{PX} values ranging from $4.3 \cdot 10^{10} \text{ cm}^{-2}$ up to $5 \cdot 10^{10} \text{ cm}^{-2}$ are estimated. This value can be attributed to
 601 either light condensed hydrocarbons with SLD values smaller than pentane SLD ($6.2 \cdot 10^{10} \text{ cm}^{-2}$), or to
 602 a mixture of pores fulfilled by a fluid and empty pores. For the overmature MT1 sample, a value of 0
 603 is found for the nanopores (0.5 nm) population and a value slightly negative for the mesopore (3.5 nm)
 604 population. The agreement with both a meaningful (positive) ρ_{PX} value and the best fit intensities
 605 gives a null value for mesopores SLD. Hence, for the overmature sample, nano- and meso- pores in

606 kerogen are considered as empty in full agreement with Sh0 and Sh1 values found with Rock-Eval
607 pyrolysis measurements.

608 From the prefactors $n(\rho_P - \rho_K)_{\bar{x},N}^2$ and the SLD values, the number density of pores n were easily
609 assessed and their values are reported in *Table 7*. The nanopores volume fraction ϕ can be inferred
610 from their number density n and their size distribution using $\phi = n \frac{4}{3} \pi \langle R^3 \rangle$, where $\langle R^3 \rangle$ is the
611 third moment of the size distribution that can be calculated analytically for the lognormal distribution.
612 Numerical values are reported in *Table 7*. They are in the range 1-4% and rank roughly like the TOC
613 content.

614 Concerning the pyrite influence on SAXS data, calculated intensities for BSP-4 and MT-1 samples,
615 which exhibit the highest pyrite content (2.3 and 2.5 %vol), display the higher discrepancy with
616 measured intensities in the Q range around 0.1 \AA^{-1} . This discrepancy is clearly ascribed to pyrite
617 content that gives an additional intensity contribution. If intensity modeling is still acceptable for these
618 samples, it is clear that for samples containing higher pyrite contents, the fitting procedure will give
619 meaningless parameters, especially for the mesopores SLD. Hopefully, the other estimated parameters
620 would stay unaffected by pyrite.

621

622 4. DISCUSSION

623 Source rocks is one of the most difficult material to characterize. Indeed, they are multiphase
624 systems (minerals, solid organic matter and pore space filled by various liquid or gaseous
625 hydrocarbons) and the relevant length scales extend from sub-nanometer for nanopores included in
626 kerogen up to few microns for minerals or kerogen domains. Moreover, they are natural materials with
627 inherent composition variability and laminated rocks where bedding could induce a structural
628 orientation leading to anisotropy of properties. Based on these considerations, sample preparation is

629 one of the major concern when studying such materials. Complementary scattering techniques are
630 chosen here for their ability to probe the desired length scales. Herein, an innovative methodology is
631 proposed to overcome (i) composition variability, and (ii) loose of sample integrity and orientation
632 upon grinding. Thin blade samples allows to average several random X-ray scattering measurements
633 in a surface comparable to the section the neutron beam (a 5 mm diameter circular diaphragm). A
634 sample thickness of $\sim 200 \mu\text{m}$, allow to get usable transmission for both radiation while avoiding
635 multiple scattering. Contrary to scattering measurements on powdered sample^{14,20,35,77} or on thin blade
636 section cut parallel to bedding^{10,23,27,28} that gives isotropic signal, the thin blades considered here are
637 cut normal to the bedding plane in order to get information on possible structural orientation.^{8,82}
638 Finally, this sample preparation allow to compare X-ray and neutron scattering intensities obtained on
639 the same volume and in the same orientation.

640 Quantifying this orientation has to be taken into account when considering fluid flow properties for
641 transport issues or mechanical properties. Indeed, it is well known that bedding structures modify the
642 rock permeability to fluids according to the considered orientation,^{8,12,17,83} with values ranging from
643 1.10^{-19} m^2 to 1.10^{-21} m^2 , for normal to bedding cut, and 1.10^{-21} m^2 to 1.10^{-22} m^2 , for parallel to bedding
644 cut. In soil science, recent studies evidenced the importance of preferred clay orientation on the
645 diffusional properties of water.⁸⁴ Here, order parameter vary from 0 (random orientation) up to ~ 0.3 .
646 The random orientation is associated to the coarse grained texture of Montney sample whereas
647 significant values of order parameters are found for fine grained Barnett shales. This striking
648 difference could be the result of various size ratio between low dimensionality particles such as clays
649 or micas and other minerals. Indeed, it has been shown, on model systems of particles mixture
650 (platelets and spheres), that orientation upon sedimentation depend on the diameter ratio.⁸⁵ Anisotropic
651 properties are also illustrated by the HS-GC experiment conducted on thin blade sections where the

652 concentration of thermodesorbed species in the vapor is much larger for normal cut than for parallel
653 cut to the bedding (Supplementary Data).

654 The quantitative comparisons of X-ray and neutron scattering intensities are based on contrast factor
655 specific to each radiation. The detailed examination of scattering length densities evidence that source
656 rocks could be described for both radiation with three distinct contributions : minerals, kerogen and
657 pores. For overmature kerogens, the neutron scattering could be reduced to the frequently used two
658 phase system approximation, matrix and pores.^{8,10,14,20,23,27,28,35,39,79} This two phases model, based on
659 diluted polydispersed pores, is usually applied to retrieve the pore size distribution and the total
660 porosity. Here, considering three phases allow to broaden scattering techniques to low mature
661 kerogens and to X-ray measurements. A corresponding expression of scattering intensities based on
662 two main contributions is developed. The first one is related to the dispersion of kerogen domains in
663 the mineral matrix, which prevails at low Q values, and turns out to be anisotropic. The second one
664 describes a diluted dispersion of nanopores in the kerogen, giving a dominant isotropic signal at large
665 Q values that remains moderate. We took advantage of anisotropy to consider the azimuthal direction
666 where the scattering at low Q is reduced in order to better appreciate the contribution, at large Q
667 values, of kerogen nanoporosity. The three phases model allows to fit both X-ray and neutron data
668 with the same geometric parameters which prove the selectivity of the model. Moreover, the intensity
669 ratio between X-ray and neutron prefactors for each contribution allow to retrieve valuable parameters
670 such as (i) the X-ray and neutron kerogen SLD as well as its mass density, both of them being
671 considered as a maturity index, (ii) the nanopore size distribution, the number density of nanopores
672 and their associated volume fraction, and (iii) the X-ray SLD of nanopores that gives a first
673 approximation on the nature of filling fluids. All these parameters are reachable thanks to quantitative
674 comparison of SANS and SAXS measurements, a strategy commonly applied to solve complex

675 nanostructural order.^{86,87} The pyrite has not been taken into account for SAXS modeling and we show
676 that for pyrite content above ~ 2.5 vol %, the SLD of nanopores is suspicious rendering the nature of
677 filling fluid unclear.

678 This methodology has been applied to a series of source rocks with an increasing maturity according
679 to Rock-Eval pyrolysis measurements. For mature samples, the SAXS/SANS analysis show (i) a
680 kerogen mass density of ~ 1.64 g.cm⁻³ in good agreement with geochemical estimation (ii) a nanopore
681 size radius distribution centered on 0.5-0.7 nm, in agreement with the literature,^{20,35, 79,88} with 20% of
682 polydispersity and accounting for pore volume fractions of ~ 0.01 to 0.04. When the volume fraction is
683 compared to the Rock-Eval pyrolysis TOC content (~ 4.5 to 9 % wt), the proportion of pores in
684 kerogen is about a fifth to a half of the kerogen domain. At such pore concentration, the assumption of
685 diluted pores could not always be valid and considering a structure factor $S(Q)$ in the intensities
686 modeling should be taken into account. As any peak in the high Q region, relative to a short range pore
687 ordering, has been detected, a structure factor rather based on pore aggregates should be considered. It
688 would give additional information on nanopore connectivity relevant for future studies and (iii) an X-
689 ray nanopores SLD of ~ 4 to $5 \cdot 10^{10}$ cm⁻². These values can account for either condensed (liquid) light
690 hydrocarbons or a mixture of heavier condensed hydrocarbons and empty pores. For the overmature
691 sample, the kerogen mass density is higher (1.74 g.cm⁻³) as expected, the pore size distribution is
692 bimodal with a mode close to the one of mature sample and an additional distribution of mesopores
693 (with a radius of 3.5 nm) accounting for a small pore volume fraction of ~ 0.1 -0.2 %. Both porous
694 media are found to be empty in full agreement with almost null values of free hydrocarbons as
695 measured in the Sh0 and Sh1 values using Rock-Eval pyrolysis.

696 The developed methodology of sample preparation, measurement and data modeling allow to reach
697 several valuable parameters relevant for source rocks studies. Its application seems to give satisfactory

698 results in comparison with already known parameters. The SAXS measurements could be improved
699 notably. By using shorter wavelength (e.g. molybdenum), transmission would be higher, the exposure
700 time lower and the fluorescence eliminated. If this wavelength is tuned finely around the absorption
701 edge of Fe (ASAXS), the scattering contribution of pyrite should be mitigated rendering the pore
702 content more accurate. As mentioned, data acquired with a better statistic would also allow to consider
703 a smaller azimuthal aperture and to better appreciate the moderate signal of nanopores.

704 Finally, this fine characterization of the porous media could be seen as a first step before the
705 introduction or the removal of various compounds, including hydrocarbons or CO₂, from the pores
706 space. The proposed methodology, based on contrasts, would allow to probe the affinity of a fluid to
707 pores contained in kerogen and would provide information on the pore connectivity.

708 5. CONCLUSION

709 This study was performed to better characterize source rocks for transport or mechanical issues. For
710 that, a new methodology based on SAXS/SANS complementarity is developed. The sample
711 preparation, thin blade section cut normal to bedding, allow to compare directly the anisotropic X-ray
712 and neutron patterns. From 2D scattering analysis, an order parameter likely related to the preferential
713 orientation of lamellar minerals is inferred. It represents a valuable parameter that could be used for
714 mechanical or transport properties issues. At large Q values, an additional isotropic scattering
715 contribution, ascribed to nanopores in kerogen, is evidenced and mostly apparent at specific azimuthal
716 angles. For these later, the 1D scattering profiles are modeled by two contributions related to three
717 distinct phases : minerals, kerogen and pores. These two contributions are weighted by prefactors that
718 are different for each radiation. The exploitation of both prefactor, together with the one of the
719 scattering model allow to retrieve valuables parameters such as a kerogen maturity index, number
720 density of nanopores leading to their size distribution and also their associated volume fraction. The

721 latter being related to the kerogen maximum storage capacity for gaseous species or condensed fluids.
722 Moreover, X-ray pore space SLD gives some indications about the nature of filling fluids.

723 This methodology is tested on a series of source rocks of increasing maturities. The same set of
724 geometrical parameters allow to fit both X-ray and neutron data proving the selectivity of the model.
725 The kerogen maturity index is in agreement with the Rock-Eval pyrolysis maturity approximation. The
726 nanopore sizes and their associated volume fraction are in the range of, respectively, 0.5-0.7 nm and
727 0.01-0.04 for mature source rocks. They are likely filled either by light hydrocarbons, or a mixture of
728 heavy hydrocarbons and empty pores. For the overmature one, an additional pore size of 3.5 nm,
729 accounting for a volume fraction of $\sim 0.2\%$, is evidenced. For both population, pores appears empty in
730 full agreement with Rock-Eval pyrolysis measurements.

731 This new methodology proved to be efficient and open a new way to look quantitatively at
732 nanoporous kerogen phase and its *in-situ* evolution upon treatment such as emptying or filling it with
733 various fluids.

734

735

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744

745 7. SUPPORTING INFORMATION

746 SAXS measurements on different sample thickness (100, 140 and 200 μm) are provided in
747 supplementary data as an illustration for no multiple scattering effects. Then, $I(Q)$ as a function of
748 lamellar minerals content, for X-ray or neutron radiation, and as a function of TOC content (neutron
749 radiation) are provided. For the fitting procedure, data concerning pyrite modelization on SAXS data
750 and nanopores radius sensitivity, are displayed in supporting information. Chromatograms of HS-GC
751 measurements along source rocks lamination (normal or parallel cut to bedding) are also detailed.

752

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