Experimental Investigation of the Dependence of Accessible Porosity and Methane Sorption Capacity of Carbonaceous Shales on Particle Size

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Crushing and grinding of carbonaceous shale samples is likely to enhance the accessibility of pores and embedded organic matter as compared to the intact rock. This may lead to an overestimation of the total (volume and sorptive) gas storage capacity. In order to investigate the importance of these effects we have measured unconfined apparent grain densities (helium pycnometry) and methane sorption capacities (high-pressure methane excess sorption) of four carbonaceous shales (Cambro-Ordovician Alum Shale, Jurassic Kimmeridge Clay, Jurassic/Cretaceous Bazhenov Shale, and Late Cretaceous Eagle Ford Shale) as a function of particle size. Measurements were first conducted on 38 mm diameter core plugs, which then were crushed and milled to successively smaller particle sizes (<10 mm, <2 mm, <64 μm, and <1 μm). Apparent grain densities of the smallest particle fractions of the Alum, Bazhenov and Kimmeridge samples were consistently higher by 0.5 to 1% than apparent grain densities of the original sample plugs. Methane excess sorption capacity increased significantly for particle sizes <64 μm for the Alum and <1 μm for the Bazhenov and Kimmeridge samples while no significant changes upon grinding were observed for the Eagle Ford Shale. For the Bazhenov Shale, the apparent grain density increased slightly from 2.446 g/cm³ to 2.450 g/cm³ upon particle size reduction from <64 μm to <1 μm while the maximum sorption capacity (“Langmuir volume”) increased substantially from 0.11 mmol/g to 0.19 mmol/g. Similarly, for the Kimmeridge Clay and Alum Shale, a slight increase of the apparent grain density from 1.546 g/cm³ to 1.552 g/cm³ and from 2.362 g/cm³ to 2.385 g/cm³, respectively, was accompanied by increases in sorption capacity from 0.37 mmol/g to 0.45 mmol/g and from 0.14 mmol/g to 0.185 mmol/g, respectively. The increase in sorption capacity indicates an opening of a considerable amount of micropores with large internal surface area upon physical disruption of the rock fabric and/or removal of included fluids. It may also be due to increased swelling abilities of clay minerals and organic matter upon destruction of the stabilizing rock fabric with decreasing particle size. Grain density and sorption isotherms measured on small particle sizes are likely to overestimate the gas storage capacities and the amounts of producible gas-in-place since under field conditions (largely undisrupted rock fabric), significant portions of this storage capacity are essentially inaccessible. Poor interconnectivity of the pore system and slow, diffusion-controlled transport will massively retard gas production. Based on these findings, particle sizes >64 μm should be used for porosity and sorption measurements because they are more likely to retain the properties of the rock fabric in terms of accessible pore volume and sorptive storage capacity.
The characterization of the pore systems of shales still constitutes a major challenge although substantial effort has been dedicated to this research (e.g. [1–8]), and some progress has been made in recent years. However, there are still major uncertainties regarding pore interconnectivity, accessibility, contribution of “closed” pores to the total pore volume, and upscaling of laboratory data.

From a petrophysical and economical point of view, the effective or “open” (accessible; inter-connected) porosity is of prime interest. It can be subdivided into the transport porosity constituting the main interconnected fluid transport pathways and the storage porosity (e.g. dead-end pores) branching off from the main interconnected fluid transport pathways. Rocks may also possess certain amounts of pores with restricted access. These become accessible only upon destruction of the rock fabric by grinding or milling. Figure 1 schematically shows that a clear and unambiguous determination of “pore volume” is not possible for shales. Pore volumes and grain densities measured in the laboratory depend on the method used and on the particle size of the samples. We therefore use the term “apparent grain density” for the density measured by helium pycnometry on intact “bulk” samples where the original rock fabric is largely preserved. In combination with the “bulk density” of the rock sample, the “apparent pore volume” fraction can be determined. Both, apparent grain and apparent pore volume, are not intrinsic properties and can change upon particle size reduction. They also may vary depending on equilibration time, utilization of different gases, and sample pretreatment (e.g. drying procedure and solvent extraction). The “true grain volume” is an intrinsic rock property and is defined as the volume (of the mineral and organic matter) after removal of all enclosed pores and fluids. This is typically achieved by grinding to very small particle sizes.

Disruption or destruction of the rock fabric by grinding/milling will make an increasing percentage of pore volume accessible by physically opening isolated pores. Additionally, diffusion lengths, e.g. in organic matter, are reduced so that gas uptake during sorption measurements proceeds faster and becomes measurable on the laboratory timescale.

The proportions of pore volume with restricted access can be estimated by determining changes in apparent grain density with decreasing particle size. Such particle size dependence was investigated in several studies by means of helium pycnometry [9–11]. In all studies, apparent grain densities/porosities increased significantly upon particle size reduction with the largest increase reported by Klaja et al. [10] from 2.671 g/cm³ to 2.758 g/cm³ upon particle size reduction from plug to <0.5 mm. Fu et al. [9] did not report apparent grain densities but expressed this change in percentage of nonconnected pores with the largest increase being from 3.57% to 5.98% porosity (40% nonconnected pores) upon particle size reduction from plug to 0.25-0.15 mm. Sondergeld et al. [11] report a porosity increase of approximately a factor two upon crushing and grinding plugs to a “smaller” (unspecified) particle size.

Small angle neutron scattering (SANS; [12–14]) or scanning electron microscopy (SEM; [15]) have been used for porosity assessment, and the results have been compared with those obtained by He pycnometry or a combination of He pycnometry and low-pressure N₂ adsorption to calculate inaccessible porosities in shales. Typically, these results show significant discrepancies. Ideally, porous media with complex mineralogy and/or pore size distribution without inaccessible pores should first be utilized to investigate whether different methods give reasonable and comparable results. Presently, the difference between SANS- and He pycnometry-derived porosity is interpreted as the proportion of inaccessible porosity (also denoted as closed porosity, nonconnected porosity, isolated porosity, or ineffective porosity) without verifying whether these methods give similar results for porous media containing only accessible pores. Proportions of “inaccessible porosity” were estimated to be as high as 37% (He pycnometry: 3.0%, SANS: 4.8%) in a Cretaceous shale from Canada [12], up to 42.6% for a Longmaxi shale [14], up to 34% (He pycnometry: 3.03%, SANS: 4.57%) for samples from the Niutitang shale [13], and 13% (He pycnometry: 3.14%, BIB-SEM: 3.62%) with an imaging approach for the Longmaxi shale [15]. Busch et al. [2] discussed in some detail the uncertainties of different methods used for porosity estimation (including SANS, FIB-SEM, and He pycnometry). None of the abovementioned studies provides information on the uptake kinetics (rate and duration) of
helium in the pycnometry measurements. Therefore, one major uncertainty could also be related to incomplete pressure equilibration during the measurements.

The effect of particle size of shale samples on gas sorption capacity has so far only been investigated rarely as well. However, some useful information has already been obtained from the analysis of high-pressure methane sorption isotherms on different particle size fractions of shales [16–19]. Generally, both gas uptake rate and excess sorption capacity increase with decreasing particle size. Ji et al. [17] found an increase in sorption capacity from 0.02 mmol/g to 0.056 mmol/g (n_{ex} = ~11 MPa) and from 0.265 mmol/g to 0.305 mmol/g (n_{ex} = ~11 MPa) for a chlorite-rich and montmorillonite-rich shale, respectively, upon particle size reduction from 270-830 μm to <53 μm. Gasparik et al. [16] found that the methane sorption capacity increased from 0.09 mmol/g to 0.11 mmol/g (n_{ex} = ~25 MPa) and 0.13 mmol/g to 0.15 mmol/g (n_{ex} = ~25 MPa) upon particle size reduction from 0.5-1.0 mm to <80 μm for samples from the Lower Jurassic (Toarcian Lias e) Posidonia Shale of Northern Germany and the Cambrian/Ordovician Alum Shale of Bornholm, Denmark, respectively. For the same particle size reduction for another sample from the Cambrian/Ordovician Alum Shale, no change was observed. An increase from 0.34 mmol/g (n_{ex} = ~25 MPa) to 0.40 mmol/g (n_{ex} = ~25 MPa) for a particle size reduction from 2.36-4 mm to <0.1 mm for the Kimmeridge Clay was reported in Li & Krooss [18]. Lutynski & González [19] measured an increase in CO₂ sorption capacity from 0.08 mmol/g (n_{ex} = ~5 MPa) to 0.16 mmol/g (n_{ex} = ~5 MPa) upon particle size reduction from 1-2 mm to <0.1 mm on a Silurian gas shale.

A common assumption as to why porosity and sorption capacity increase with decreasing particle size is that the “closed” porosity of certain pore fractions is opened up and becomes accessible upon grinding (e.g. [16]). However, comparisons of measurements on intact cores (plugs) and crushed samples are rare. Hence, possible effects of the rock fabric on the pore interconnectivity and accessibility are commonly ignored. In most studies, only a few particle size fractions were used, which possibly did not sample the entire pore size ranges of the shale samples, and/or particle size fractions are mostly prepared with an upper and lower boundary, thus entailing possible fractionation by sample milling and sieving (enrichment or depletion of organic matter and/or clay minerals), which may have an effect on experimental investigations of porosity and especially sorption capacity.

The main aim of this study was to investigate whether successive reduction of the particle size from plug (~38 mm diameter) to <1 μm diameter affects the apparent grain density and methane excess sorption capacity of shales. The entire amount of the original samples was used in all measurements by merely reducing the upper boundary of particle sizes. Only minor losses occurred during the preparation process. This procedure provides valuable information on the particle size dependence of methane sorption capacity and the potential contribution of pores with restricted access to the pore volume.

2. Experimental Setup and Measuring Procedure

Gas expansion tests with helium and methane were performed in a calibrated manometric setup consisting of a stainless steel sample cell, two high-pressure shutoff valves, and a high-precision pressure transducer (Keller AG, Series 33X) connected by 1/16” stainless steel capillaries (Figure 2). The combined volumes of the pressure transducer, the capillaries between the high-pressure shutoff valves, and an additional stainless steel cell are used as the reference volume. Temperatures within the setup are kept constant at 30°C ± 0.3°C and recorded continuously.

The tests were first performed with helium and then methane at pore pressures up to 20 MPa. A detailed description of these measurements is given in Gasparik [20]. In the present study, larger sample cells were used in order to accommodate core plugs of 38 mm diameter and up to 40 mm length. After conducting the uptake measurements...
on the whole plugs, these were broken/crushed to >10 mm fragments. Subsequently, particles <2 mm, <64 μm, and <1 μm were used. In order to avoid fractionation of the sample material by the sieving process, the entire sample material was always reused. Therefore, each particle size fraction also includes all smaller particle sizes. One exception is the >10 mm fraction which consisted of rock fragments and did not contain any fines. In order to reliably reach a particle size of <1 μm, an XRD-Mill (McCrone, 20 minutes per milling procedure) was utilized with ethanol as a cooling fluid. This last milling process may have caused some degree of extraction of soluble organic matter.

2.1. Determination of Apparent Grain Density. The apparent grain volume of the rock samples \( V_{gr,apparent} \) (m\(^3\)) is typically determined by helium expansion from a calibrated reference volume into a sample cell of known volume under isothermal conditions. Here, any pores with restricted access form part of the apparent grain volume and will thus lead to an underestimation of the grain density. The mass balance equation yields the following expression for \( V_{gr,apparent} \):

\[
V_{gr,apparent} = V_{sc} - V_{rc} \left( \frac{\rho_{rc} - \rho_{eq}}{\rho_{eq} - \rho_{sc}} \right)
\]

\( V_{rc} \) and \( V_{sc} \) are the volumes of the reference cell and the sample cell (m\(^3\)), respectively, \( \rho_{rc} \) and \( \rho_{sc} \) are the gas densities in the corresponding cells prior to expansion, and \( \rho_{eq} \) is the gas density after pressure equilibration between the two volumes (kg m\(^{-3}\)). From the results of these measurements, the apparent grain density can be calculated:

\[
\rho_{gr,apparent} = \frac{m}{V_{gr,apparent}}.
\]

2.2. Determination of Bulk Density and Porosity. Various methods are available to determine the bulk density of rock samples. For an overview of methods for volume and density determination, see Webb [21]. For samples with geometrical shapes (e.g., cylinders or cubes), the bulk volume \( V_b \) can be determined by caliper measurements. The bulk volumes of samples with irregular shapes can be obtained from buoyancy measurements (Archimedes principle) or from mercury intrusion porosimetry (MIP; “envelope volume”).

The bulk density is then given by

\[
\rho_b = \frac{m}{V_b}.
\]

The porosity can then be calculated as

\[
\phi = 1 - \frac{\rho_b}{\rho_{gr,apparent}}.
\]

2.3. Methane Excess Sorption Capacity. The methane excess sorption \( m_{excess} \) of dry cylindrical plugs was determined using the following mass balance equations:

\[
m_{excess} = m_{trans} - \rho_{CH_4} (P_{eq,T}^T) \ast V_{Void},
\]

\[
m_{trans} = \left( \rho_{CH_4} (P_{eq,T}) - \rho_{CH_4} (P_{eq,T}^T) \right) \ast V_{rc}.
\]

They are defined as the difference between the cumulative mass of methane transferred from \( V_{rc} \) into \( V_{Void} \) \( (m_{trans}) \) and the mass of the free “unadsorbed” methane occupying \( V_{Void} \) under the respective equilibrium pressures and temperatures. Methane densities were calculated using the GERP-2004 software [22]. Sorption isotherms measured in this study were parameterized using

\[
n_{sorption}(P, T) = n_L \frac{P}{P + P_L(T)}.
\]

Here, \( n_{sorption} \) (mol kg\(^{-1}\)) denotes the amount of methane sorbed at the respective equilibrium pressures and temperatures \((P \text{ and } T)\), \( P_L \) (MPa) is the Langmuir pressure (the pressure at which half the sorption sites are occupied), and \( n_L \) (mol kg\(^{-1}\)) is the maximum Langmuir capacity (the sorbed amount when all sorption sites are occupied).

Equation (7) describes the absolute isotherm and represents the limiting case where the density of the sorbed phase is “infinite” or much higher than the density of the free gas phase so that the volume of the sorbed phase is negligible. In those cases where the measured excess sorption isotherm exhibits a maximum, this assumption cannot be maintained. However, since sorption isotherms obtained in this study do not exhibit maxima, it was possible to utilize Equation (7) to parameterize these isotherms for the pressure range used in this study (0.1–20 MPa).

3. Samples

Four carbonaceous shales with different mineralogical compositions (quartz+feldspar: 10–66 wt.%, clay: 8–46 wt.%, carbonate: 0.1–62 wt.%) and a wide range of total organic carbon contents (TOC: 4.5–45 wt.%) were selected for this study (Table 1). The thermal maturities ranged from the immature stage (Alum, Kimmeridge shales) and oil window stage (Eagle Ford Shale) to the dry gas stage (Bazhenov Shale). Before the experiments, all sample plugs (38 or 30 mm diameter and 20–40 mm length) were vacuum-dried at 105°C until weight constancy was reached but at least for 24 hours. The Eagle Ford and Kimmeridge samples were taken from outcrops and therefore may have undergone some degree of weathering.

4. Results

4.1. Apparent Grain Density as a Function of Particle Size. Figure 3 displays the apparent grain density values determined by helium pycnometry for all samples and particle size fractions. While all particle size fractions of the Eagle Ford
Table 1: Porosity, total organic carbon content (TOC), vitrinite reflectance (VRr), and mineral composition (XRD meas.) for the samples used in this study.

| Sample      | Porosity (%)*1 | TOC (wt.%) | VRr (%) | Q+F (wt.%) | Clays (wt.% of mineral phases) | XCO$_3$ (wt.%) | Other |
|-------------|----------------|------------|---------|------------|-------------------------------|----------------|-------|
| Alum        | 14.5           | 8.2        | 0.5     | 57.2       | 32.7                          | 0.2            | 9.9   |
| Bazhenov    | 7.3            | 6.0        | 1.5     | 65.5       | 29.0                          | 2.5            | 3.0   |
| Eagle Ford  | 11.7           | 4.5        | 0.9     | 26.3       | 8.1                           | 62.3           | 3.3   |
| Kimmeridge  | 6.9            | 45.0       | 0.5     | 9.6        | 45.5                          | 12.1           | 32.8*2|

*1 Measured by He pycnometry on unconfined sample plugs. *2[32.8]: 11.17 wt.% pyrite, 10.67 wt.% anhydrite, and 10.92 wt.% gypsum. Geochemical and mineralogical data from 1Ghanizadeh et al. [23] and 2Gasparik et al. [24]. Q+F: quartz+feldspar; clays: kaolinite, mixed layered I/S; XCO$_3$: mostly calcite, minor contributions of dolomite or siderite; other: mostly pyrite, minor contributions of gypsum and anhydrite.

Figure 3: Apparent grain density of plugs and different particle sizes for shales from (a) Alum, (b) Bazhenov, (c) Eagle Ford, and (d) Kimmeridge formations.
Shale (Figure 3(c)) had essentially the same grain density of 2.431 g/cm³, the apparent grain densities of the <1 μm fractions of all other samples were consistently higher than apparent grain densities of the plugs. The following sample-specific trends were observed:

1. The apparent grain densities of the Alum Shale (Figure 3(a)) do not show a noticeable trend for the three largest particle sizes (plug, >10 mm and <2 mm), but they subsequently increase from 2.362 g/cm³ (<2 mm) to 2.385 g/cm³ (<64 μm).

2. For the Bazhenov Shale (Figure 3(b)), apparent grain densities increase from 2.435 g/cm³ (plug) to 2.447 g/cm³ (<2 mm), do not show any significant change at particle sizes <2 mm and <64 μm, and increase for particle size <1 μm (2.450 g/cm³).

3. For the Kimmeridge Clay (Figure 3(d)), a minor increase in apparent grain density is observed from the plug to the <64 μm particle size, but this change is within the standard deviation of the values for each individual particle size. A stronger increase from 1.546 g/cm³ for the <64 μm fraction to 1.552 g/cm³ for the <1 μm fraction was observed.

4.2. Methane Sorption Capacity as a Function of Particle Size. Methane excess sorption isotherms were measured at 30°C ± 0.3°C on the same particle size fractions as for determination of apparent grain densities (Figure 3). The results show large differences in the maximum methane excess sorption capacity varying from 0.03 to 0.4 mmol/g for all samples. Methane excess sorption capacities are in the order of Kimmeridge > Alum > Bazhenov > Eagle Ford for the plug samples. All measured excess sorption isotherms are similar in shape and do not exhibit maxima. Therefore, the Langmuir function (Equation (7)) was used to fit the experimental isotherms. Fitted parameters for all isotherms are listed in Table 2. The $n_L$ and $P_L$ values range between 0.043 and 0.45 mmol/g and 2.2 and 5.0 MPa, respectively.

No change in methane excess sorption capacity with particle size was observed for the Eagle Ford Shale (Figure 4(c)). All other samples exhibit specific particle size dependencies: (1) methane sorption isotherms of the three largest particle size fractions of the Alum Shale (Figure 4(a)) are similar and exhibit higher values for particle sizes <64 μm; (2) the methane sorption capacity of the Bazhenov Shale (Figure 4(b)) first increases from plug size to <2 mm particle size, stays constant between <2 mm and <64 μm, and strongly increases from <64 μm to <1 μm particle size; (3) the methane sorption capacity for the Kimmeridge Clay (Figure 4(d)) exhibits a minor increase from plug size to <64 μm particle size and strongly increases from <64 μm to <1 μm particle size. In total, the

| Sample                  | Particle size | $n_{ex,10\text{MPa}}$ (mmol g⁻¹) | $n_L$ (mmol g⁻¹) | $P_L$ (MPa) |
|-------------------------|---------------|---------------------------------|-----------------|-------------|
| Alum Shale (8.2% TOC)   | Plug          | 0.105                           | 0.145           | 3.87        |
|                         | >10           | 0.103                           | 0.141           | 3.70        |
|                         | <2            | 0.104                           | 0.139           | 3.27        |
|                         | <0.063        | 0.131                           | 0.185           | 4.13        |
|                         | <0.001        | 0.150                           | 0.182           | 2.18        |
| Bazhenov (6.0% TOC)     | Plug          | 0.058                           | 0.076           | 3.16        |
|                         | >10           | 0.071                           | 0.095           | 3.44        |
|                         | <2            | 0.077                           | 0.105           | 3.73        |
|                         | <0.063        | 0.078                           | 0.111           | 4.22        |
|                         | <0.001        | 0.131                           | 0.193           | 4.69        |
| Eagle Ford (4.5% TOC)   | Plug          | 0.035                           | 0.052           | 4.99        |
|                         | >10           | 0.030                           | 0.043           | 4.52        |
|                         | <2            | 0.034                           | 0.048           | 4.23        |
|                         | <0.063        | 0.030                           | 0.036           | 1.98        |
|                         | <0.001        | 0.030                           | 0.038           | 2.54        |
| Kimmeridge (45% TOC)    | Plug          | 0.281                           | 0.355           | 2.63        |
|                         | >10           | 0.282                           | 0.357           | 2.63        |
|                         | <2            | 0.287                           | 0.350           | 2.20        |
|                         | <0.063        | 0.287                           | 0.368           | 2.80        |
|                         | <0.001        | 0.355                           | 0.448           | 2.61        |
maximum Langmuir capacities increased by 28% (from 0.145 mmol/g to 0.182 mmol/g), 152% (0.076 mmol/g to 0.193 mmol/g), and 26% (from 0.355 mmol/g to 0.448 mmol/g) for the Alum, Bazhenov, and Kimmeridge samples, respectively, upon size reduction from plug size to particle sizes <1 μm.

5. Discussion: Particle Size Dependence of Porosity and Methane Sorption Capacity

As shown in Section 4.1, the experimentally measured apparent grain density often displays a distinct dependence upon particle size. Although this dependence shows sample-specific variations, the apparent grain density of plug samples was generally lower than that of the smallest particle size analyzed in this study. This change in apparent grain density can be expressed in terms of porosity by assuming that the bulk density of the intact cores determined by caliper measurements is the same for all particle sizes. Porosities computed by this procedure increased from 0.145 (plug) to 0.153 (<1 μm) for the Alum, from 0.073 to 0.079 for the Bazhenov, and from 0.069 to 0.074 for the Kimmeridge (Table 3).

Possible reasons for changes in the porosity upon particle size reduction could be (1) incomplete pressure equilibration (especially for larger particle sizes), (2) changes in the fluid (water or hydrocarbon) content, and (3) mechanical opening of isolated pores due to grinding/crushing.

(1) Pressure equilibration was closely monitored during this study, which is displayed in Figure 5 for intact rocks utilized in this study and some additional samples in terms of porosity change as a function of time.
Equilibration times varied from nearly instantaneous (e.g. Ziegelschiefer Frm.) to >225 minutes (e.g. Niutitang Frm. and Prince Albert Frm.) and do not strictly correlate with porosity amount. This clearly demonstrates the importance of pressure decay monitoring for porosity determination. Setting too short equilibration times would sometimes result in strongly underestimated porosity values. Since equilibration times will be shorter for crushed particle sizes, setting the same equilibration times will invariably result in higher porosity values. These differences in porosity might be wrongly assigned to “closed” porosity, albeit being a function of the equilibration time only. For the samples utilized in this study, equilibration times were adjusted as such that misinterpretations could be ruled out.

If (1) and (2) can be excluded, then mechanical opening of fully enclosed pores due to grinding/crushing is likely to be the main reason for porosity changes upon particle size reduction.

Grain densities were also calculated from volumetric fractions of mineral and organic phases (Table 3) from XRD and TOC analyses. These should reflect grain densities excluding pores with restricted access. Grain densities from mineral phases were taken from Anthony et al. [26], and organic matter density was estimated as 1.15 g/cm³ [27]. With these assumptions, the calculated grain densities for the Alum, Bazhenov, and Eagle Ford shales are larger than those obtained from pycnometry measurements of the smallest particle sizes, whereas grain densities are lower for the Kimmeridge Clay. However, since the volume fraction of

| Sample    | Particle size (mm) | Bulk density (g cm⁻³) | Apparent grain density (g cm⁻³) | Porosity (%) |
|-----------|--------------------|-----------------------|---------------------------------|--------------|
| Alum      | Plug*¹              | 2.021                 | 2.363                           | 0.145        |
|           | >10                 |                       | 2.360                           | 0.143        |
|           | <2                  |                       | 2.362                           | 0.144        |
|           | <0.063              |                       | 2.385                           | 0.152        |
|           | <0.001              |                       | 2.387                           | 0.153        |
|           | <0.001              |                       | 2.421*³                         | 0.165*³      |
| Bazhenov  | Plug*²              | 2.257                 | 2.435                           | 0.073        |
|           | >10                 |                       | 2.442                           | 0.076        |
|           | <2                  |                       | 2.447                           | 0.077        |
|           | <0.063              |                       | 2.446                           | 0.077        |
|           | <0.001              |                       | 2.450                           | 0.079        |
|           | <0.001              |                       | 2.467*³                         | 0.085*³      |
| Eagle Ford| Plug*¹              | 2.148                 | 2.433                           | 0.117        |
|           | >10                 |                       | 2.426                           | 0.115        |
|           | <2                  |                       | 2.433                           | 0.117        |
|           | <0.063              |                       | 2.431                           | 0.116        |
|           | <0.001              |                       | 2.431                           | 0.116        |
|           | <0.001              |                       | 2.494*³                         | 0.139*³      |
| Kimmeridge| Plug*¹              | 1.437                 | 1.544                           | 0.070        |
|           | >10                 |                       | 1.544                           | 0.070        |
|           | <2                  |                       | 1.546                           | 0.070        |
|           | <0.063              |                       | 1.546                           | 0.071        |
|           | <0.001              |                       | 1.552                           | 0.074        |
|           | <0.001              |                       | 1.533*³                         | 0.062*³      |

*¹Plug with 38 mm diameter. *²Plug with 30 mm diameter. *¹Grain densities and porosities calculated from XRD data with assumed org. matter wt.% = 1.3
*²TOC wt.% and organic matter density: 1.15 g cm⁻³.

Equilibration times varied from nearly instantaneous (e.g. Ziegelschiefer Frm.) to >225 minutes (e.g. Niutitang Frm. and Prince Albert Frm.) and do not strictly correlate with porosity amount. This clearly demonstrates the importance of pressure decay monitoring for porosity determination. Setting too short equilibration times would sometimes result in strongly underestimated porosity values. Since equilibration times will be shorter for crushed particle sizes, setting the same equilibration times will invariably result in higher porosity values. These differences in porosity might be wrongly assigned to “closed” porosity, albeit being a function of the equilibration time only. For the samples utilized in this study, equilibration times were adjusted as such that misinterpretations could be ruled out.
organic matter in the Kimmeridge Clay is 0.79, by merely changing the assumed organic matter density from 1.15 to 1.17 g/cm³, grain densities from XRD and TOC analyses are in a good agreement with pycnometry-derived grain densities. XRD, TOC, and He pycnometry data on particle sizes <1 μm therefore provide first estimates for organic matter densities. For the Eagle Ford Shale, an unusually low organic matter density of 0.97 g/cm³ would be required in order to match the grain densities derived from XRD/TOC analyses and He pycnometry. This could indicate that low-density bitumen contributes significantly to the TOC, which is reasonable because the Eagle Ford Shale is within the oil window. For the Bazhenov Shale, which is in the gas window (VR = 1.5%), organic matter densities would be expected to be higher than 1.15 g/cm³ (~1.3 g/cm³ according to [27]), and therefore, its relatively low organic matter density can also be attributed to the presence of low-density bitumen. Another explanation could be that the smallest particle size fractions still contain a considerable amount of isolated pores or pores with restricted access.

Previous studies using He pycnometry to assess the particle size dependence of apparent grain density/porosity in shales report that apparent grain densities increased significantly upon particle size reduction ([10]: up to 0.1 g/cm³ upon particle size reduction from plug to <0.5 mm; [9]: up to 40.3% nonconnected porosity upon particle size reduction from plug to 0.25-0.15 mm). It is questionable whether such high numbers for an unconnected porosity/increase in apparent grain density as reported in Klaja et al. [10] and Fu et al. [9] can be justified. This would imply that a substantial proportion of the porosity cannot be accessed by helium. Since both studies utilize commercial porosimeters and do not provide information on uptake rates and pressure equilibration criteria, an explanation could be that a certain fraction of pores has not been filled with gas within the timescale of the measurement or the equilibrium criteria set by these commercial instruments. This could also partly explain differences obtained in porosities utilizing SANS or FIB-SEM in comparison to He pycnometry [12–15]. It is important to realize that equilibration times may vary by several orders of magnitude for different particle sizes and rock types (e.g. low-permeable shale and sandstone). This is supported by our own measurements conducted with a customized pycnometer with full control over timescale and equilibrium criteria (Figure 5). We find that the maximum
The present study, to the best of our knowledge, presents for the first time sorption capacity data of shales for particle size ranges from plug to <1 μm and can therefore be regarded as an extension of the end members in terms of particle sizes. The results documented here agree well with previously reported data [16–19]. It can generally be stated that methane sorption capacity increases with decreasing particle size (Figure 4). However, we found that the methane sorption capacity mostly does not change dramatically unless samples are crushed to particle sizes <64 μm (Alum Shale) or <1 μm (Bazhenov and Kimmeridge samples). There are also instances where no particle size dependence is observed (Eagle Ford Shale).

Gas uptake rates of shales are mostly determined on cuttings or powders to reduce the measuring time. A major disadvantage of these measurements is that information on the transport properties of flow pathways in the original rock fabric is lost. In order to illustrate this, experiments presented here document the uptake and sorption characteristics as a function of particle size. Figure 6(a) shows CH₄ uptake rates for all samples (plugs) at constant mean pore pressure (0.1 MPa). At these conditions, equilibration times differ by three orders of magnitude as a consequence of different permeability coefficients of the specimens and are in the order of Kimmeridge > Alum = Bazhenov > Eagle Ford. The influence of particle size (at constant mean pore pressures) on methane uptake rates is shown in Figure 6(b) for the Kimmeridge sample. Here, equilibration times may differ by three orders of magnitude as well, which is attributed to changes in interconnectivity and accessibility of the pore space. For the smallest particle sizes, pressure equilibration is almost instantaneous, indicating that due to the destruction of the original rock fabric, no information on permeability coefficients can be derived. Uptake rates are consistently lower for methane than for helium as evidenced for the Alum Shale (Figure 6(c)). This can be partly related to the lower molecular mobility of heavier molecules (Graham’s law), but it is also related to the tendency of methane to adsorb on organic matter as compared to helium. Equilibration times do not show a consistent trend with increasing mean pore pressures as evidenced by the methane uptake curves for a plug of the Bazhenov Shale (Figure 6(d)).

The increase in methane sorption capacity with decreasing particle size corresponds to changes in apparent grain density/porosity data obtained by helium pycnometry (Figures 3 and 4). Sample-specific trends are similar for both porosity and methane sorption capacity, but the relative increases do not necessarily correlate. Whereas porosity and methane sorption capacity show a strong simultaneous increase for the Alum and Kimmeridge shales for a particle size <64 μm and <1 μm, respectively, this does not hold for the Bazhenov Shale where the largest increase in porosity is apparent upon reduction from plug to >10 mm particle size and the largest increase in methane sorption capacity is apparent upon particle size reduction from <64 μm to <1 μm. For the Bazhenov Shale, an increase of apparent grain density from 2.446 g/cm³ to 2.450 g/cm³ (equivalent to a porosity increase from 0.077 to 0.079) by particle size reduction of <64 μm to <1 μm corresponds to an increase of the maximum Langmuir capacity from 0.11 mmol/g to 0.19 mmol/g. Similarly, for the Kimmeridge Clay and Alum Shale, an increase from 1.456 g/cm³ to 1.552 g/cm³ and 2.362 g/cm³ to 2.385 g/cm³ corresponds to an increase of the maximum Langmuir capacity from 0.37 mmol/g to 0.45 mmol/g and from 0.14 mmol/g to 0.185 mmol/g, respectively. This can either be attributed to the accession of a considerable proportion of pores with large internal surface area (e.g., micropores), to the physical opening of these pores or fluid removal from these pores that most likely reside within organic matter or clay minerals, or to the increased swelling abilities of clay minerals and especially organic matter upon removal of the stabilizing rock fabric with decreasing particle size.

By utilizing high-resolution interferometry measurements of shale topographies (mm-sized samples) during CO₂ injection, Pluymakers et al. [28] demonstrated that heterogeneous swelling in shales occurs and also localized it to patches of organic matter within the shales. Swelling of organic matter was quantified to be up to 250 nm in 4 hours and 850 μm in 20 hours for the Pomeranian and Green River shales in vertical direction into free space, respectively. Such an effect can also be expected for methane, albeit to a lesser extent. Within plugs, clay minerals and organic matter will be surrounded by an intact rock fabric inhibiting the swelling potential. However, this may change upon crushing and grinding (especially for the smallest particle sizes analyzed in this study), which will lead to the creation of void space around particles with a large proportion of organic matter and/or clay minerals. This void space would act as accommodation space for swelling, accompanied by an increase in sorption capacity.

For reasonable estimations of volumetric and sorptive storage with respect to rock fabric and pore accessibility, based on data obtained in this study, it is recommended to use particle sizes >64 μm and to closely monitor pressure decay to ensure that pressure equilibration was achieved. It should be noted that a more reasonable approach would be to utilize plugs within triaxial flow cells in order to account for lithostatic stress effects on the intact rock fabric and free as well as sorptive gas storage capacity. In a recent study Fu et al. [9] suggested that closed porosity could contribute to gas storage capacity in gas shales and that these pores could be made accessible by hydrofracturing. Our data shows that these pores, if at all existent (see Eagle Ford Shale), can only be made accessible by milling the samples down to a particle size <64 μm (Alum shale) or <1 μm (Bazhenov & Kimmeridge shales), and therefore, the contention of Fu et al. [9] is highly optimistic because it is unlikely that significant volumes of the rock fabric can be damaged by hydrofracturing to such an extent and gas trapped in such pores cannot be produced.

6. Conclusions

In this experimental study, we have investigated the effect of sample/particle size on porosity and methane sorption...
capacity of shales. Sample sizes ranged from plug (38 mm diameter, 40 mm length) to <1 μm, which to our knowledge is the largest measured range studied thus far. Contrary to numerous published studies, we could demonstrate that porosity with restricted access (“closed” porosity) is <10% of the absolute measureable porosity. Only a minor increase in porosity upon crushing or grinding can, however, lead to a strong increase in the maximum Langmuir capacity (up to 74% for the Bazhenov Shale (0.111 mmol/g to 0.193 mmol/g)). Grain density and sorption isotherms measured on small particle sizes are likely to overestimate the gas storage capacities and the amounts of producible gas-in-place since under field conditions (largely intact/undisrupted rock fabric), significant portions of this storage

Figure 6: (a) Comparison of fractional methane uptake for all samples investigated in this study at constant mean pore pressure, (b) fractional methane uptake for Kimmeridge Clay at constant mean pore pressure and varying particle sizes, (c) comparison of helium and methane uptakes for the Alum Shale at constant mean pore pressures, and (d) fractional methane uptake with increasing mean pore pressure for the Bazhenov Shale.
capacity are essentially inaccessible. Poor interconnectivity of the pore system and slow, diffusion-controlled transport will massively reduce gas production rates.

Data Availability

Data will be made available upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

[1] P. Bertier, K. Schweinar, H. Stanjek et al., “On the use and abuse of N2 physisorption for the characterization of the pore structure of shales,” in Filling the gaps - from microscopic pore structures to transport properties in shales, vol. 21 of CMS Workshop Lectures, pp. 151–161, The Clay Minerals Society, 2016.

[2] A. Busch, K. Schweinar, N. Kampman et al., “Determining the porosity of mudrocks using methodological pluralism,” Geological Society, London, Special Publications, vol. 454, no. 1, pp. 15–38, 2017.

[3] C. R. Clarkson, N. Solano, R. M. Bustin et al., “Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion,” Fuel, vol. 103, pp. 606–616, 2013.

[4] R. Fink, B. M. Krooss, and A. Amann-Hildenbrand, “Stress-dependence of porosity and permeability of the Upper Jurassic Bossier shale: an experimental study,” Geologic Society, London, Special Publications, vol. 454, no. 1, pp. 107–130, 2017.

[5] R. G. Loucks, R. M. Reed, S. C. Ruppel, and U. Hammes, “Spectrum of pore types and networks in mudrocks and a descriptive classification for matrix-related mudrock pores,” AAPG Bulletin, vol. 96, no. 6, pp. 1071–1098, 2012.

[6] J. Klaver, G. Desbois, R. Litthee, and J. L. Urai, “BIB-SEM characterization of pore space morphology and distribution in postmature to overmature samples from the Haynesville and Bossier Shales,” Marine and Petroleum Geology, vol. 59, pp. 451–466, 2015.

[7] J. Klaver, S. Hemes, M. Houben, G. Desbois, Z. Radi, and J. L. Urai, “The connectivity of pore space in mudstones: insights from high-pressure Wood’s metal injection, BIB-SEM imaging, and mercury intrusion porosimetry,” Geofluids, vol. 15, no. 4, pp. 577–591, 2015.

[8] M. Mastalerz, L. He, Y. B. Melnichenko, and J. A. Rupp, “Porosity of coal and shale: insights from gas adsorption and SANS/USANS techniques,” Energy & Fuels, vol. 26, no. 8, pp. 5109–5120, 2012.

[9] Y. Fu, Y. Jiang, Z. Wang et al., “Non-connected pores of the Longmaxi shale in southern Sichuan Basin of China,” Marine and Petroleum Geology, vol. 110, pp. 420–433, 2019.

[10] J. Klaja, G. Lykowska, and A. Przelaskowska, “Helium porosity measurements for rocks from unconventional reservoirs performed on crushed samples,” Nafta-Gaz, vol. 71, no. 11, pp. 856–863, 2015.

[11] C. H. Sondergeld, K. E. Newsham, J. T. Comisky, M. C. Rice, and C. S. Rai, “ Petrophysical considerations in evaluating and producing shale gas resources,” in SPE Unconventional Gas Conference, pp. 1–34, Pittsburgh, PA, USA, 2010.

[12] J. Bahadur, Y. B. Melnichenko, M. Mastalerz, A. Furmann, and C. R. Clarkson, “Hierarchical pore morphology of Cretaceous shale: a small-angle neutron scattering and ultrasmall-angle neutron scattering study,” Energy & Fuels, vol. 28, no. 10, pp. 6336–6344, 2014.

[13] M. Sun, B. Yu, Q. Hu et al., “Pore structure characterization of organic-rich Niutitang shale from China: Small angle neutron scattering (SANS) study,” International Journal of Coal Geology, vol. 186, pp. 115–125, 2018.

[14] M. Sun, B. Yu, Q. Hu et al., “Pore characteristics of Longmaxi shale gas reservoir in the northwest of Guizhou, China: investigations using small-angle neutron scattering (SANS), helium pycnometry, and gas sorption isotherm,” International Journal of Coal Geology, vol. 171, pp. 61–68, 2017.

[15] S. Zhou, G. Yan, H. Xue, W. Guo, and X. Li, “2D and 3D nanopore characterization of gas shale in Longmaxi formation based on FIB-SEM,” Marine and Petroleum Geology, vol. 73, pp. 174–180, 2016.

[16] M. Gasparik, P. Bertier, Y. Gensterblum, A. Ghanizadeh, B. M. Krooss, and R. Litthee, “Geochemical controls on the methane storage capacity in organic-rich shales,” International Journal of Coal Geology, vol. 123, pp. 34–51, 2014.

[17] L. Ji, T. Zhang, K. L. Milliken, J. Qu, and X. Zhang, “Experimental investigation of main controls to methane adsorption in clay-rich rocks,” Applied Geochemistry, vol. 27, no. 12, pp. 2533–2545, 2012.

[18] X. Li and B. M. Krooss, “Influence of grain size and moisture content on the high-pressure methane sorption capacity of Kimeridge Clay,” Energy & Fuels, vol. 31, no. 11, pp. 11548–11557, 2017.

[19] M. Lutyński and M. Á. González González, “Characteristics of carbon dioxide sorption in coal and gas shale – The effect of particle size,” Journal of Natural Gas Science and Engineering, vol. 28, pp. 558–565, 2016.

[20] M. S. Gasparik, Experimental Investigation of Gas Storage Properties of Black Shales, [Ph.D. thesis], RWTH Aachen University, 2013, November 2019, https://publications.rwth-aachen.de/record/228638.

[21] P. A. Webb, “Volume and density determinations for particle technologists. Micromeritics Instrument Corp,” 2001, September 2019, https://www.micromeritics.com/Repository/Files/Volume_and_Density_determinations_for_Particle_Technologists_0.pdf.

[22] O. Kunz, R. Klimke, W. Wagner, and M. Jaeschke, Wide Range Equation of State for Natural Gases and Other Mixtures GERG TM15 2007, Verlag Deutscher Ingenieure, Düsseldorf, Germany, 2007.

[23] A. Ghanizadeh, M. Gasparik, A. Amann-Hildenbrand, Y. Gensterblum, and B. M. Krooss, “Experimental study of fluid transport processes in the matrix system of the European organic-rich shales: I. Scandinavian Alum Shale,” Marine and Petroleum Geology, vol. 51, pp. 79–99, 2014.

[24] M. Gasparik, A. Ghanizadeh, Y. Gensterblum, and B. M. Krooss, “Multi-temperature method for high-pressure sorption measurements on moist shales,” Review of Scientific Instruments, vol. 84, no. 8, article 085116, 2013.

[25] M. Sadeghiamirshahi and S. J. Vitton, “Analysis of drying and saturating natural gypsum samples for mechanical testing,” Journal of Rock Mechanics and Geotechnical Engineering, vol. 11, no. 2, pp. 219–227, 2019.
[26] J. W. Anthony, R. A. Bideaux, K. W. Bladh, and M. C. Nichols, 
*Handbook of Mineralogy*, Mineralogical Society of America, 
Chantilly, VA, USA, 2001.

[27] P. Ungerer, E. Behar, and D. Discamps, “Tentative calculation 
of the overall volume expansion of organic matter during 
hydrocarbon genesis from geochemistry data: Implications 
for primary migration,” in *Advances in Organic Geochemistry*, 
M. Bjorøy, Ed., pp. 129–135, Wiley, Chichester, UK, 1981.

[28] A. Pluymakers, J. Liu, F. Kohler, F. Renard, and D. Dysthe, “A 
high resolution interferometric method to measure local 
swelling due to CO₂ exposure in coal and shale,” *International Journal of Coal Geology*, vol. 187, pp. 131–142, 2018.