First international inter-laboratory comparison of high-pressure CH₄, CO₂ and C₂H₆ sorption isotherms on carbonaceous shales

M. Gasparik[1a], T.F.T. Rexer[2], A.C. Aplin[3], P. Billemont[4], G. De Weireld[4], Y. Gensterblum[1b]*, M. Henry[4], B. M. Krooss[1], S. Liu[5], X. Ma[5], R. Sakurovs[6], Z. Song[7], G. Staib[6], K.M. Thomas[2], S. Wang[7], T. Zhang[8]

[1]Energy and Mineral Resources Group (EMR), Institute of Geology and Geochemistry of Petroleum and Coal, Lochnerstr. 4-20, RWTH Aachen University, 52056 Aachen, Germany

[2]School of Civil Engineering and Geosciences, and School of Chemical Engineering and Advanced Materials, Drummond Building, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom

[3]Department of Earth Sciences, Durham University, Science Laboratories, Durham DH1 3LE, United Kingdom

[4]Thermodynamics Department, Faculté Polytechnique de Mons, Université de Mons - UMONS, Place du Parc 20, 7000 MONS, Belgium

[5]Research Institute of Petroleum Exploration and Development, PetroChina, P.O.Box 910, No. 20Xueyuan Road, Haidian District, Beijing, 100083, China

[6]CSIRO Energy Technology, PO Box 330, Newcastle NSW 2300, Australia

[7]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[8]Bureau of Economic Geology, University of Texas at Austin, United States

Corresponding Author: yves.gensterblum@emr.rwth-aachen.de

Abstract

An inter-laboratory study of high-pressure gas sorption measurements on two carbonaceous shales has been conducted in order to assess the reproducibility of the sorption isotherms and identify possible sources of error. The measurements were carried out by seven international research laboratories on either in-house or commercial sorption equipment using manometric as well as gravimetric methods. Excess sorption isotherms for methane, carbon dioxide and ethane were measured at 65°C and at pressures up to 25 MPa on two organic-rich shales in the dry state. The samples were taken from the immature Posidonia shale (Germany) and from the over-mature Upper Chokier formation (Belgium). Their total organic carbon (TOC) and vitrinite reflectance (VR_r) values were 15.1% and 4.4% and 0.5% and 2.0%, respectively.

[a] Present address: GEO-Data, Carl-Zeiss-Straße 2, D-30827 Garbsen, Germany
[b] Present address: Department of Geophysics, Stanford University, 397 Panama Mall, Mitchell Bldg., Stanford, CA 94305, USA

The objective of the study was to assess the inter-laboratory reproducibility of sorption isotherms as would be expected with each laboratory following its own measurement and data reduction procedures. All labs were asked to follow a predefined sample drying procedure prior to measurement in order to minimize any effects related to moisture. The reproducibility of the methane excess sorption isotherms was better for the high-maturity shale (within $0.02 - 0.03$ mmol/g) than for the low-maturity sample (up to 0.1 mmol/g), similar to observations in earlier inter-laboratory studies on coals. The reproducibility for CO_2 and C_2H_6 sorption isotherms was satisfactory at pressures below 5 MPa, however,the results deviate considerably at higher pressures. Artefacts in the shape of the excess sorption isotherms were observed for CO_2 and C_2H_6 and these are explained as being due to a high sensitivity of gas density to temperature and pressure close to the critical point as well as from a limited measurement accuracy and possibly uncertainty in the equation of state (EoS).

The low sorption capacity of carbonaceous shales (as compared to coals and activated carbons) sets very high demands on the accuracy of pressure and temperature measurement and precise temperature control. Furthermore, the sample treatment, measurement and data reduction procedures must be optimized in order to achieve satisfactory inter-laboratory consistency and accuracy. Unknown systematic errors must be minimized first by calibrating the pressure and temperature measurement sensors to high-quality standards. Blank sorption measurements with a non-sorbing sample (e.g. steel cylinders) can be used to identify and quantitatively account for measuring artefacts resulting from unknown residual systematic errors or from the limited accuracy of the EoS. The possible sources of error causing the observed discrepancies are discussed.

1 Introduction

1.1 Motivation for inter-laboratory study of high-pressure sorption on shales

Shale Gas is gaining importance as energy resource; it is increasing its contribution to the industrial production of natural gas and lowering its cost. There is considerable research interest in sorption properties of shales, stimulated not only by their economic potential for natural gas, but also by efforts to develop approaches to mitigate climate change though capture and storage of CO_2 in geologic formations. The physical sorption of hydrocarbon gas (mostly methane) in shales provides gas storage capacity in addition to the "free gas" capacity of the pore system. While methane sorption is considered to take place predominantly in microporous organic matter (kerogen), inorganic (clay minerals) constituents may contribute a significant portion of sorption capacity in shales with low organic matter contents. Quantification of the total storage capacity, including sorbed gas and free gas is a prerequisite for estimations of resource potential and technically recoverable amounts of gas at given reservoir conditions. Due to the high variability and complex nature of the chemical composition and pore structure of these rocks, industry has to rely on experimental high-pressure/high-temperature sorption data, and these have to be reproducible among different laboratories.

Accurate measurement of high-pressure sorption isotherms on shales is challenging due to the fact that (i) the typical sorption capacity (on mass basis) of shales is only about 10% of that of coal and 1% of that of activated carbon (Figure 1) and (ii) sorption isotherms have to be measured up to high pressures (> 20 MPa) and high temperatures (> 100°C) in order to be representative of the in-situ reservoir conditions typical for shales.

The quality of gas sorption isotherms on coals and activated carbons has been assessed in various earlier inter-laboratory studies (Goodman et al. 2004, 2008; Gensterblum et al., 2009, 2010). Such comparisons have not yet been conducted or reported for gas shales. Different laboratories use different experimental techniques, instrumentation and procedures for measuring gas sorption isotherms. This makes it difficult to assess the reproducibility of sorption isotherms obtained from different laboratories. Questions arise concerning the extent to which differences in results can be attributed to sample heterogeneities, sample preparation or the measurement technique. Therefore, strict control must be exerted on experimental methodology and variables in order to obtain reproducible results. The need for inter-laboratory accuracy is well recognized by regulatory agencies and industry and is a driver for the development of standard methods. Further, the research community recognizes that several factors including the operator, the equipment, the calibration of the equipment, and the laboratory environment including temperature and humidity can influence the variability of a test result.

Here, we report the results from the first inter-laboratory reproducibility study of high-pressure gas sorption isotherms on gas shales. Excess sorption isotherms for CH_4, CO_2 and C_2H_6 were measured at 65°C and at pressures up to 25 MPa on two organic-rich shales with different Total Organic Carbon (TOC) contents and thermal maturity. Seven international research laboratories participated in this Round Robin study. These include RWTH Aachen University in Germany (RWTH), Newcastle University in the United Kingdom (WNCRL), the University of Mons in Belgium (UMONS), CSIRO Energy Technology in Australia (CSIRO), the Chinese Academy of Sciences at Guangzhou in China (GIGCAS), the University of Texas at Austin in the United States (BEG) and the Research Institute of Petroleum Exploration and Development (RIPED) in China. This study attempted to find out if, and to what extent, differences in laboratory procedures influence the results of sorption measurements and whether the qualities of published isotherms are comparable. This work will provide guidance for estimating the reproducibility that might be expected when comparing adsorption isotherms from different laboratories. The project was performed as an "open" round-robin with regular updates and exchange of results and experience among the participants. The common objective is the improvement of data quality and reliability and the refinement of experimental techniques.

1.2 Inter-laboratory studies of CO_2 sorption on coal

Two inter-laboratory comparisons on high-pressure CO_2 sorption on coal initiated by the U.S. Department of Energy, National Energy Technology Laboratory (Goodman et al. 2004, 2007) and RWTH Aachen (Gensterblum et al. 2009, 2010), respectively, have been carried out previously. In the

first round of the inter-laboratory study by Goodman et al. (2004), CO_2 sorption isotherms at 22°C and 55°C up to 7 MPa were measured on five Argonne Premium Coal samples (pre-dried at 80°C) by four independent research groups. Good agreement was found for the isotherms on high rank coals, while isotherms on mid- and low-rank coals deviated by more than 100%. The deviations were attributed to residual-moisture content caused by different procedures for removing moisture among the research institutes. In the second round of the inter-laboratory study (Goodman et al., 2007) CO_2 isotherms at 55°C and pressures up to 15 MPa were measured on three moisture-equilibrated coals by six independent research groups. A good agreement was found up to 8 MPa with the exception of those instances where the moisture content of the coal was significantly different from the as-received moisture. Above 8 MPa the reported isotherms diverged significantly.

The second inter-laboratory study initiated by RWTH Aachen University was conducted among three European research laboratories on activated carbon and coal samples. In the first round of the study (Gensterblum et al. 2009) the comparison of CO_2 sorption isotherms at 45°C and up to 16 MPa on activated carbon (Filtrasorb F400) showed an excellent agreement (deviation in sorption capacity less than 5% or 0.4 mmol/g). In the second round of this study (Gensterblum et al. 2010) three coal samples of varying rank were studied under the same experimental conditions. Differences due to sample drying were minimized by increasing the drying temperature to 105°C (as compared to 80°C in Goodman et al., 2004). Good agreement (deviations in the range of 0.02 – 0.07 mmol/g) was observed at low pressures (< 6-8 MPa) except for the lowest-rank (lignite) coal sample. However, at high pressures (> 10 MPa) the isotherms from individual laboratories diverged significantly (> 0.3 mmol/g). The authors discuss possible sources of error due to coal swelling, residual moisture, particle size and gas impurities.
In their conclusions, Gensterblum et al. (2010) emphasize the need to improve the reproducibility of high-pressure sorption measurements. This requires a thorough optimization of the instrumentation and the measuring procedures, and well-defined sample preparation procedures. This is even more crucial for sorption studies on shales given that the reservoir conditions are typically in both, high-pressure (> 20 MPa) and high-temperature (> 100°C) ranges and sorption capacities are low.

1.3 Experimental methods of high-pressure sorption measurements

Among the different methods used to study gas sorption (manometric, volumetric, gravimetric, chromatographic, temperature-programmed desorption, etc.), the two most commonly used to study gas sorption equilibria at high pressures are the manometric and the gravimetric method. The experimentally determined quantity (irrespective of the method used) is the "excess sorption" or "Gibbs surface excess" (Sircar, 1999). The uptake of gas by the sorbent sample is determined at constant temperature as a function of gas pressure (or density) giving the excess sorption isotherm. The experimental techniques make use of different physical principles to measure sorption. Comparative studies between the gravimetric and manometric methods performed with N_2 and CO_2 on activated carbons showed a very good agreement (De Weireld et al., 1999; Belmabkhout et al., 2004; Gensterblum et al., 2009, 2010). Both, the manometric and the gravimetric techniques have been used extensively in gas sorption studies on a wide variety of microporous materials (e.g. activated carbons, zeolites, metal-organic frameworks) used in gas storage, gas purification and separation processes. Recently, an increased interest in sorption studies of hydrocarbon (e.g. CH_4,

C_2H_6) and non-hydrocarbon (mainly CO_2) gases in natural materials - coals and organic-rich shales, was stimulated by technological advances in upstream hydrocarbon industry enabling the extraction of hydrocarbons from "unconventional" reservoirs (coal-bed methane, CBM and shale gas) and by their possible use for CO_2 sequestration.

1.3.1 Gravimetric method

The gravimetric method makes use of direct measurement of mass change of a sample being exposed to sorptive gas at constant temperature at varying pressures. The modern gravimetric devices utilize either a high-precision microbalance or a magnetic suspension balance for mass measurements down to sub-µg resolution. Published data utilizing the gravimetric technique were obtained almost exclusively on commercial devices (e.g. Rubotherm, Mettler-Toledo). Some laboratories use in-house modifications of these devices in order to adapt them for specific experimental conditions – e.g. high temperatures (De Weireld et al., 1999; Dreisbach et al., 2002), in-situ moisture equilibration (Billemont et al., 2011). Several studies use an in-house built gravimetric device (e.g. Day et al. 2005, 2008; Sakurovs et al. 2008, 2009). The recent availability of accurate equations of state for pure gases on-line has obviated the need for a reference cell in gravimetric systems studying single gas sorption, but this then requires more accurate temperature and pressure measurements in these systems than was hitherto necessary.

During the gravimetric sorption measurement the observed apparent mass change is a net result of mass increase due to gas molecules being sorbed on the sorbent sample at a given pressure and temperature and the buoyant force acting on the sorbent volume that displaces the sorptive gas. The "reduced mass" (Ω) is obtained from the reading of the balance corrected for the buoyancy of the sample holder (determined in a calibration test with empty sample holder). From Ω the adsorbed mass can be calculated by considering the buoyancy acting on the sorbent volume (V) (Dreisbach et al., 2002):

$$m(p,T) = \Omega(p,T) + \rho_g(p,T)V \qquad (1a)$$

Typically, the volume of the adsorbent (V) is approximated by skeletal volume measured with helium ($V_s^{He,0}$). In gravimetric method this is done by measuring the so-called "helium isotherm". The quantity thus obtained is the excess sorption (Gibbs surface excess):

$$m_{excess}(p,T) = \Omega(p,T) + \rho_g(p,T)V_s^{He,0} \qquad (1b)$$

The buoyancy correction in the gravimetric method is analogous to the void volume correction, the "non-sorption" case, in the manometric method describe in the next section. In Eq. 1b (and similarly in Eq.2) the superscript 0 in the symbol for the sample ($V_s^{He,0}$) and the void volume ($V_{void}^{He,0}$) is used to stress the fact that no corrections to the sample volume (as determined initially by the He measurement) are applied. In the literature such corrections have been used e.g. to calculate the "absolute" sorption (e.g. Dreisbach et al., 2002), or to account for sorption of helium (e.g. Sircar, 2001) or swelling effects of adsorbent sample (Ozdemir et al., 2004). The gas density ρ_g is determined by appropriate equation of state (EoS).

The advantage of the gravimetric method over the manometric is that it does not suffer from cumulative errors as is the case for the latter (see section 1.3.2). Also, the leakage does not affect the measurement accuracy as long as the pressure in the sample cell can be kept constant. On the other hand, the accuracy of the gravimetric technique on materials with relatively low sorption capacity (such as shales) is compromised at high-pressures (>10 MPa) due to a large buoyancy term, especially for devices limited to small (< 1g) sample amounts.

1.3.2   The manometric method

In the manometric method, the uptake of gas is measured by monitoring the drop in pressure in a fixed known volume containing the adsorbent sample. This technique is sometimes referred to as Sieverts method. The measuring device consists of reference (RC) and sample (SC) cells with calibrated volumes equipped with high-precision pressure sensor kept at constant temperature conditions. The experiment can be designed as constant-volume (manometric) or constant-pressure (volumetric) measurement (Mohammad et al., 2009).

The measurement is done by successively transferring the sorptive gas through the reference cell into the sample cell containing the adsorbent sample. The excess sorption is then calculated as a difference between the total amount of gas transferred (m_{total}) into the SC and the unadsorbed gas occupying the void volume of sample cell:

$$m_{excess}(p,T) = m_{total}(p,T) - \rho_g(p,T)V_{void}^{He,0} \qquad (2)$$

The void volume ($V_{void}^{He,0}$) is commonly determined by helium assuming its sorption can be neglected. Multiplied by the density of the sorptive gas $\rho_g(p,T)$, the "non-sorption" reference state is calculated. Thus, the void volume correction is analogous to the buoyancy correction in the gravimetric method. As in the gravimetric method, the gas density is determined by appropriate EoS at the experimental p, T conditions. Since m_{total} is a cumulative sum of the volume of the reference cell (V_{rc}) multiplied by the gas density difference in the reference cell before (ρ_{rc}^{j}) and after (ρ_{rc}^{j+1}) the expansion into the sample cell:

$$m_{total} = \sum_{j=1}^{n} V_{rc}(\rho_{rc}^{j} - \rho_{rc}^{j+1}) \qquad (3)$$

the measurement uncertainties in the manometric method accumulate during the isotherm determination. The uncertainty accumulation can be reduced experimentally. Mohammad et al. (2009) argue that the measurement accuracy can be significantly improved if the setup is designed as constant-pressure rather than constant-volume. There are number of other ways for reducing the accumulation of uncertainty in the manometric setup, one being optimizing the relative ratio of the void volume and the reference cell volume (i.e. the ratio of the sample cell to reference cell volume). While some authors (e.g. Belmabkhout, 2004; Gensterblum et al., 2010; Mohammad et al., 2009) provide their own estimates for the optimal volume ratio for CO_2, thorough optimization methods should be applied to determine the best strategy for dosing the sorptive gas into the sample cell.

1.3.3 Sources of uncertainty

A comprehensive review of the sources of uncertainty in measured sorption data for coals is provided in Busch and Gensterblum (2011). Additional sources of uncertainty relevant for sorption studies on shales concern the high-temperature manometric devices in which the reference and the sample cells are kept at different temperatures. If a thermal gradient exists over a part of the sample cell volume (e.g. the tubing connecting it to the rest of the apparatus) this has to be accounted for in the calculation of the excess sorption. Moreover, due to the thermal expansion of the sample cell experiencing high temperatures a careful temperature calibration needs to be performed in addition to the volume calibration.

1.4 Goals of this study

Currently there are no generally accepted standards for high-pressure (high-temperature) sorption measurements. Research laboratories and equipment manufacturers specializing on sorption use their own (commercial or in-house) equipment and apply their own set of "standard" and quality assurance procedures. The published sorption data on shales are used by various academic and industrial groups in the field of shale gas exploration and underground CO_2 storage. It is therefore crucial to assess the inter-laboratory reproducibility among different laboratories and to review the means of quantifying and reducing the uncertainty in experimental sorption data. This work follows the previous Round Robin studies on activated carbon and coals (Gensterblum et al., 2009, 2010) and intends to test the capabilities of gravimetric and manometric sorption techniques for studying the sorption behaviour of shales with relatively low sorption capacity. The aims of this study were 1) to show to what extent are the sorption data reported by different laboratories reproducible; 2) to identify the main sources of uncertainty that result in observed deviations between individual labs and 3) to suggest the necessary measures to improve the accuracy of measured sorption data on shales.

2 Methods and materials

2.1 Samples and sample characterization

Two shale samples were collected for this study. These samples include the Upper Chokier ("Namurian") shale from Belgium and the lower Toarcian ("Posidonia") shale from Holzmaden in South Germany. It was desirable to obtain samples with significant differences in Total Organic Carbon (TOC) content and thermal maturity in sufficient quantities. The basic geochemical data of the selected samples are listed in Table 1. The TOC contents of the Namurian and the Posidonia sample are 4.4 wt.% and 15.1 wt.%, respectively. The thermal maturity in terms of vitrinite reflectance is 2.0% for the Namurian, and 0.5% for the Posidonia sample.

Table 1. Basic geochemical data of the studied samples

Sample →	Namurian	Posidonia

TOC & VR$_r$	**TOC[1](wt %)**	4.4	15.1
	TOC[2](wt %)	3.8	12.3
	VR$_r$(%)	2.0	0.5
XRD	**Quartz + Feldspars (wt %)**	44.2	10.6
	Carbonates (wt %)	5.4	64.6
	Total clays (wt %)	40.3	20.3

[1]Results by RWTH
[2]Results by WNCRL

2.2 Pore characterization

To characterize the micropore and mesopore systems of the shales samples, CO_2 isotherms (at 273 K and 195 K up to 0.1 MPa) and N_2 isotherms (77 K, up to 0.096 MPa) were measured on a gravimetric sorption apparatus at the Wolfson Northern Carbon Reduction Laboratories (WNCRL) at the University of Newcastle. Details of the apparatus can be found in Rexer et al. (2013, 2014).

The equivalent surface area was determined from the N_2 isotherms using the Brunauer-Emmett-Teller (BET) equation (Brunauer et al., 1938). The ultra-micropore volumes (pore width <0.7 nm, Gregg and Sing, 1982; Cazorla-Amorós et al., 1988) were obtained from the CO_2 by the Dubinin-Radushkevich mode (Dubinin et al., 1955). The micropore size distribution was determined from the CO_2 isotherms by a non-local density functional theory (NLDFT) equilibrium model assuming slit pores (Ravikovitch et al., 1998). The Sorption Pore Volume was calculated from 195 K CO_2 isotherms according to the Gurvitsch rule (Gurvitsch, 1915; Marsh, 1987; Fletcher et al., 2005) and assuming density of CO_2 of 1.177 g/cm³. For detailed description of these methods on shale see Rexer et al. (2013, 2014).

2.3 Sample preparation

Larger chunks of rock material (> 3 kg) were crushed and milled to a powder (average particle size < 100 µm) using a laboratory disc mill (Siebtechnik GmbH) at RWTH Aachen. In order to ensure the homogeneity of the sample material distributed to different laboratories, the original parent powder sample was passed two times through the sample divider (Retsch GmbH). Individual sample aliquots were filled into glass vials in the sample divider and shipped to all participating laboratories.

2.3.1 Sample drying

In this Round Robin study the sorption isotherms were measured on dry shale samples to minimize the possible discrepancies in sorption capacity due to variable moisture contents. A drying procedure was suggested to which all the labs were asked to adhere. This two-step drying process consisted of pre-drying the sample at 110°C under vacuum for 18 hours followed by additional "in-situ" drying after the transfer of the sample into the sample cell (110°C, vacuum, 2-8 hours). It should be noted, however, that not all the labs were able to perform this second drying step under the vacuum conditions (the experimental setup of one of the participating laboratory was not equipped with a vacuum system) or at the desired temperature (the in-situ drying temperature in one of the labs was only 80°C).

2.4 Gravimetric and manometric sorption measurements

Seven international research groups have participated in this round robin study (see Introduction). The sorption equipment used by individual groups was either commercial or in-house manometric or gravimetric. In the following, descriptions of experimental parameters and sorption measurements results from individual laboratories are presented anonymously (Lab-1, Lab-2, etc.). The details of the technical parameters of the measuring devices used by each laboratory are given in Table 2.

The manometric devices used by Lab-1, Lab-3, Lab-4, Lab-5, Lab-7 have the same basic components such as reference volume, sample cell, valves, high-precision pressure and temperature sensors and temperature control units, but differ in size. At Lab-5, in addition to the manometric setup with a single temperature control unit for both, the reference and the sample cell, another setup was used that operates at two different temperatures of the reference and the sample cell. This arrangement enables measurement at high temperatures (> 150°C) of the sample cell, which is thermally isolated from the temperature sensitive parts of the setup. Two-temperature systems are also used by the Lab-3 and Lab-7 laboratory. It should be noted here that this arrangement leads to a temperature gradient along a part of the sample cell volume that spans the two temperature zones. This needs to be accounted for in the calculation of the excess sorption. At Lab-5 this was solved by a temperature calibration of the setup in combination with blank expansion tests with stainless-steel cylinder placed in the sample cell for a range of temperatures. These blank sorption isotherms were then subtracted from the measured sorption isotherms to obtain the final result. Comparison tests between the single- and two-temperature setup showed a good agreement.

Two laboratories (Lab-2 and Lab-6) use gravimetric methods. The gravimetric setup at Lab-6 is a modified Rubotherm device with magnetic suspension balance adapted for measurements at high temperatures. The gravimetric setup at Lab-2 is an in-house built device in which a larger sample cell and reference cell are suspended mechanically.

Table 2 Information on experimental parameters reported by individual laboratories

parameter ⌐ method →	Lab-1 [a] manometric	Lab-2 [b] gravimetric	Lab-3 [c] manometric	Lab-4 [d] manometric	Lab-5 [e] manometric	Lab-6 [f] gravimetric	Lab-7 [g] manometric
p_{max} [MPa]	n.a	22	20	35	30	16	15
p accuracy	n.a.	± 0.04% FS	± 1% of reading	± 0.1% FS	± 0.01% FS[1]	± 0.1% FS	± 0.05% FS
magn. susp. balance accuracy (gravimetric)	-	5 mg	-	-	-	0.01 mg	-
$V_{ref.\ cell}$ [cm³]	2.38	-	4.56	85.8 ± 0.2	1.765 / 7.318	-	6.403 ± 0.001
$V_{sample\ cell}$ [cm³]	7.15	310.23 ± 0.09	15	190.04 ± 0.07	11.666 / 51.554	6.2	16.330 ± 0.003
m_{sample} [g]	~ 6	230 - 250	~ 8	~ 140	~ 13 / 55	~ 3.5	~ 10
typical $V_{void}/V_{ref.cell}$	~ 2	~ 0.7	2-3	~ 1.23	3 - 4	-	n.a.
Temperature control							
Heating system	air-bath	air-bath	band heater	oil-bath	air-bath	air-bath	band heater
No. of heating zones	1	4	2	1	1 / 2	1	2
T accuracy [°C]	n.a.	n.a.	0.1	0.1	0.1	0.1	n.a.
T stability [°C]	n.a.	0.02	0.02 / 0.1	0.02	0.2 / 0.1	0.3	0.02 / 0.27
Gas purity							
He	n.a.	n.a.	99.999%	99.999%	99.999%	99.999%	99.9995%
CH_4	99.995%	99.995%	99.995%	99.995%	99.995%	99.995%	99.995%
CO_2	n.a.	99.995%	n.a.	99.999%	99.995%	99.996%	99.995%
C_2H_6	n.a.	n.a.	n.a.	n.a.	99.60%	99.99%	n.a.
sample treatment							
pre-drying	n.a.	yes (80°C)	yes (110°C)	yes (110°C)	yes (110°C)	yes (110°C)	yes (110°C)
in-situ drying	yes	yes	yes	yes	yes	yes	yes
$T_{in\text{-}situ\ drying}$ [°C]	110	80	110	110	110	110	110
vacuum	yes	yes	yes	no	yes	yes	yes
~ duration [h]	n.a.	48 - 96	2	2	> 8	24	~ 12
Void / sample volume measurement							
gas	He	He	He	He	He	He	He

p range [MPa]	n.a.	n.a.	1-5	1.85 - 2	1 - 15	1 - 10	0.6
$T_{sample\ cell}$ [°C]	n.a.	n.a.	65	65	65	65	65

Equation of state (EOS)

He	n.a.	n.a.	McCarty & Arp (1990)	Peng-Robinson	Kunz et al. (2007)	McCarty & Arp (1990)	McCarty & Arp (1990)
CH_4	Setzmann & Wagner (1991)[2]	Setzmann & Wagner (1991)[2]	Setzmann & Wagner (1991)	Peng-Robinson	Kunz et al. (2007)	Setzmann & Wagner (1991)	Setzmann & Wagner (1991)[2]
CO_2	Span & Wagner (1996)[2]	Span & Wagner (1996)[2]	n.a.	Peng-Robinson	Kunz et al. (2007)	Span & Wagner (1996)	Span & Wagner (1996)[2]
C_2H_6	n.a.	Friend et al. (1991)[2]	n.a.	n.a	Kunz et al. (2007)	Friend et al. (1991)[2]	n.a.

[1] = precision relative to calibration standard with 0.025% uncertainty
[2] REFPROP (NIST) database
Commercial / in-house setup:
a) In-house
b) In-house
c) Commercial - Model PCTPro by Hy-Energy Scientific Instruments, USA (now Seratam Instrumentation)
d) Commercial - Model 300 by TerraTek Systems, USA
e) In-house
f) Commercial (Rubotherm) - modified
g) Commercial - Intelligent Manometric Instrument (IMI) by Hiden Isochema, UK

2.5 Equation of state (EoS)

In mass balance calculations of the sorption measurement an equation of state (EoS) is required to calculate the density of the gas (CO_2, CH_4) at certain pressure and temperature. In specially designed gravimetric setups it is possible to directly measure the gas density with a high degree of accuracy. However, in this study each laboratory used an EoS to calculate the gas densities from the p,T data. The most commonly used and currently the most accurate EoS for CO_2 and CH_4 are those by Span and Wagner (1996) and Setzmann and Wagner (1991), respectively. These have been incorporated in the recent multi-component EoS by Kunz et al. (2007, 2012). Other, widely used EoS are cubic EoS by Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK). The two latter ones can be applied to a large suite of gas species by introducing different interaction parameters. The information (if available) about the EoS used for individual gases by each laboratory is given in Table 2. The choice of appropriate EoS for high pressure sorption studies as well as possible limitations of the currently most accurate EoS is discussed in 4.5.

3 Results

The data in this study are presented anonymously and the results from individual laboratories are labelled as "Lab-1", "Lab-2", etc. The repeated measurements of excess sorption isotherms (if reported) for a single laboratory are indicated, respectively, by different numbers (1, 2, ...) when performed as consecutive tests on the same setup (repeatability) and by different letters (A, B, ...) when performed on a modified or different setup (intra-laboratory reproducibility). All reported test results (single or repeated measurements) were labelled sequentially. Results that were known to be erroneous (e.g. calibration issues, insufficient equilibration times, etc.) from the post-analysis performed by the reporting laboratory were not considered in this study (hence, for example, Lab-5: A are not reported in Fig.5).

3.1 Pore characterization

Low-pressure pore characterization reveals a DR ultra-micropore volume (pore width < 0.7 nm) of 9.4 mm^3/g and a CO_2 sorption pore volume (SPV) of 7.8 mm^3/g for the Namurian sample. The almost identical pore volumes (the slightly lower value of the DR ultra-micropore volume compared to SPV is within the experimental error) indicate that this sample is highly microporous. A fraction of the micropores is probably generated by kerogen cracking in the oil and gas window.

The Posidonia shale sample exhibits a lower DR micropore volume (6.9 mm^3/g) which constitutes less than a half of the total sorption pore volume. Thus, it can be argued that a significant fraction of sorption sites is provided by pores larger than 2 nm.

BET surface areas are 9.5 m^2 g^{-1} and 6.6 m^2g^{-1} for the Namurian and for the Posidonia sample, respectively.

Table 3 Results of the pore size characterization by means of low-pressure CO2 (195 K and 273 K) and N2 (77 K) sorption

	DR-micropore volume [mm³/g]	Sorption pore volume [mm³/g]	BET [m²/g]
Namurian	9.4	7.8	9.5
Posidonia	6.9	15.8	6.6

Micropore size distributions of the Namurian and the Posidonia sample are shown in Figure 2a,b. In accordance with DR and SPV pore volume measurements the Namurian Shale shows an abundance of ultra-micropores (< 0.7 nm pore diameter) and little porosity above pore diameter > 0.7 nm. The portion of pore volumes in the ultra-micropore range is lower for the Posidonia shale outcrop sample.

3.2 Sample density (He-density)

The variation of the sample density determined from the void volume (manometric method) or sample volume (gravimetric method) measurements reported by individual laboratories are shown in Figure 3 for both samples. For the high-maturity Namurian sample the results from different laboratories are consistent with the exception of the Lab-1. The standard deviation (excluding the result by Lab-1) is 0.7%. For the immature Posidonia the standard deviation of the He-density is 2.8%, or respectively, 0.6%, excluding the results of Lab-5-B1 and Lab-7-A1. The observed discrepancies are due to measurement errors as well as the varying accuracy of the calibration standard. Although great care was taken with the homogenisation of the samples prior their distribution to individual laboratories some influence of sample heterogeneity (albeit a very small one) cannot be ruled out.

It should be noted that variations of He-density (i.e. sample or void volume) in the order of magnitude of > 0.6% standard deviation are sufficient to explain most of the variations in the measured excess sorption isotherms presented in 3.3. However, no correlations were found between the measured He-densities and sorption capacities for CH_4 for individual laboratories. The lack of direct correlation between the errors in He void volume and excess sorption is to some extent possible for the manometric method. While the accuracy in the He-density of the sample is directly reflecting the accuracy of calibration standard used for the volume calibration, there is some compensation of the systematic volume uncertainties in the measurement of the sorption capacity. For example, an over- / underestimation of the volume of the reference cell will lead to over- / underestimation of the amount of gas transferred into the sample cell during the sorption experiments (m_{total} in Eq.2) but also to an over- / underestimation of the void volume during the He experiment ($V_{void}^{He,0}$ in Eq.2). Since in the excess sorption is calculated as a difference between m_{total} and $\rho_g(p,T)V_{void}^{He,0}$ the systematic errors will to some extent compensate.

3.3 Excess sorption isotherms for CH_4, CO_2 and C_2H_6 at 65°C

3.3.1 Namurian shale

The CH_4 excess sorption isotherms for the highly mature (VRr = 2.0 %) Namurian shale are presented in Figure 4. Discrepancies in the high-pressure range of 0.02 to 0.03 mmol/g are observed between individual laboratories. The shapes of the isotherms do not vary significantly, except for the results from Lab-2 where a step increase in sorption capacity is observed at ~ 10 MPa. The sorption capacities measured by the Lab-5 and Lab-7 laboratories show a very good agreement and are lower than those of all other laboratories. Isotherms measured by Lab-1 and Lab-6 are also in very good agreement but are higher than those of all other labs. The results from Lab-3 are intermediate between these two groups. Interestingly, the sorption isotherm measured by Lab-2 seems to follow the first group at p < 10 MPa and the second group at p > 10 MPa. It should be noted, however, that such a step change in CH_4 excess sorption is rather unusual and physically not explainable. Hence, we consider it to be an experimental artefact.

The CO_2 sorption isotherms for the Namurian shale were only provided by three laboratories. The results show a relatively good reproducibility (within 0.05 mmol/g) up to a pressure of ~ 8 MPa , corresponding roughly to the critical pressure of CO_2 (7.374 MPa), above which the isotherms diverge significantly. The CO_2 isotherms of Lab-2 are lower than those of Lab-5 and Lab-6. At high pressures the isotherms measured at Lab-5 and Lab-6 are close to each other. However, they differ in the position of the maxima of the excess sorption.

The C_2H_6 excess sorption isotherms for the Namurian shale show a very good agreement up to 5 MPa, corresponding to the critical pressure of C_2H_6 (4.872 MPa) and deviate significantly thereafter. The Lab-6 results show the highest sorption capacity, while the results from Lab-2 show a strong decreasing trend in excess sorption above 5 MPa. The results from Lab-6 show additionally a sharp spike in the excess sorption at ~8 MPa. The results for both, CO_2 and C_2H_6, show that the rapid increase in gas density above the critical pressure significantly amplifies the differences in measured sorption among different labs.

3.3.2 Posidonia shale

The CH_4 sorption isotherms for the immature Posidonia shale are shown in Figure 5. It is observed that the scatter in the results from individual labs is higher than for the high-maturity Namurian shale. The results of the repeatability measurements reported by Lab-6 and Lab-4 are not satisfactory. The highest sorption capacities were measured by Lab-5 and Lab-6.

The CO_2 isotherms for the Posidonia sample show a good agreement between Lab-5 and Lab-6, while results for other labs deviate increasingly with increasing pressure and the measured excess sorption is systematically lower than for Lab-5 and Lab-6. The isotherms measured by Lab-4 become negative for pressures above ~ 11 MPa (shown in the inset of Figure 5b). This is considered to be a measurement artefact due to an inappropriate choice of EoS as well as due to cross-contamination of the CO_2 with residual He (due to a lack of vacuum system in the apparatus of Lab-4) as will be demonstrated below.

The results for the C_2H_6 sorption were only reported by two labs. The isotherms by Lab-2 and Lab-6 show an excellent agreement up to a pressure of 5 MPa after which they diverge somewhat. Moreover, the excess sorption isotherms by Lab-6 show a sharp spike-like maximum at ~ 8MPa and a steep decrease in excess sorption with pressure thereafter.

4 Discussion

4.1 Repeatability versus reproducibility

The results of this study show that an excellent intra-laboratory repeatability of excess sorption isotherms of hydrocarbon gases and CO_2 on shales is achievable in spite of low sorption capacities (although this was not generally the case for all labs in this study). In this context, repeatability denotes the consistency of repeated measurements performed by a single laboratory, for a given sample, on the same setup at the same conditions and by the same opetator. Thus, the random and quantifiable errors due to temperature fluctuations and measurement uncertainty (pressure, temperature, mass) do not pose a major problem for high-pressure sorption measurements with today's instrumentation. The observed discrepancies in "inter-laboratory reproducibility" hence result from the unknown systematic measurement errors and/or from differences resulting from the sample conditioning prior to the experiment. The systematic errors cannot be identified and quantified with certainty. However they can be reduced to some acceptable level experimentally and in the data reduction procedure. Strict control must be exerted on the experimental conditions and the sample treatment. In the simpler case of measurements on dry samples (this study) this means that care should be taken when drying and de-gassing the sample. While all laboratories were asked to follow a specific sample drying and degassing procedure there were some technical limitations in some of the labs. Moreover, the highly variable instrument design between individual laboratories requires that each experimentalist adapts the procedure to approach as close as possible the desired experimental conditions based on the knowledge of the instrument behaviour. In particular, the variable sizes of the sample cells, the connecting tubing system, the valves as well as highly varying heat transfer efficiencies of different temperature control systems and limits on the maximum achievable vacuum can easily lead to different levels of sample "dryness" or "activation" (de-gassing) even if the same predefined procedure is followed. Especially at low pressures (vacuum) and for large sample cells, the actual temperature of the sample in the sample cell will be influenced by heat transfer effects including heat capacity of the medium used (air- vs. liquid-baths vs. electrical resistivity heaters directly on the sample cell). One advantage of the gravimetric methods in this respect is that it allows observation of sample degassing by direct monitoring the sample mass. For optimal design of the manometric devices the temperature sensor should be directly in contact with the sample and as close as possible in the gravimetric setup. Such a design is moreover desired for

improved monitoring of the establishment of the thermodynamic equilibrium as well as for studies on uptake kinetics.

4.2 Void volume / sample volume measurements

Both, the manometric and the gravimetric techniques rely on accurate measurement of volume for the determination of the excess sorption. In the manometric method, the void volume is measured to define the quantity of unadsorbed gas ("non-sorption" reference state), whereas in the gravimetric method the sample volume, as well as the volume of the sample holder and the hangdown are required for the buoyancy correction. The measurements are performed with helium as a "reference gas" (although the issues of helium sorption and possible differences in pore-volume accessibility compared to other gases are often mentioned in the literature, they are not essential for the discussion of the inter-laboratory reproducibility).

Sakurovs et al. (2009) pointed out that inaccuracies in the void volume or the sample volume measurements are the major sources or errors in excess sorption isotherms and are mainly responsible for the observed inter-laboratory inconsistencies. The low sorption capacity of shales, as well as the high pressures that are of interest for shale gas exploration, demand high accuracies in the volume measurement and the helium density. For errors in excess sorption to be within 10%, the uncertainty in the void/sample volume should be well within 0.1%.

The buoyancy correction represents the most significant source of error in the gravimetric method and is analogous to the void volume correction in the manometric method. The buoyancy correction requires an accurate determination of the volumes of the sample, the balance pan and the hangdown as well as the gas density. For low-sorbing material such as shales the magnitude of the buoyancy term becomes very large relative to the mass increase by the uptake of gas, especially for low sample amounts.

For the evaluation of the void volume measurement with helium in the manometric method in a range of pressures, the most straightforward and unambiguous procedure is to construct the total-mass-of-transferred-helium (m_{trans}^{He}) versus the equilibrium density of helium in the sampe cell (ρ_{sc}^{He}) isotherms. Equations 4a and 4b give the m_{trans}^{He} for a single-temperature and a two-temperature (temperature gradient within the sample cell volume) manometric setup, respectively.

$$m_{trans}^{He} = V_{rc} \sum \left(\rho_{rc}^{He,i} - \rho_{rc}^{He,f} \right) \tag{4a}$$

$$m_{trans}^{He} = V_{rc} \sum \left(\rho_{rc}^{He,i} - \rho_{rc}^{He,f} \right) - V_{sc}^* \rho_{rc}^{He,f} \tag{4b}$$

In Eq. 4b, V_{sc}^* denotes the portion of the sample cell volume (tubing) which is kept at the temperature of the reference cell. An example of void volume determination using this procedure is shown in Figure 6. This procedure is preferable as (1) it does not require any subjective data point elimination or selection (e.q. outliers, data scatter as the equilibrium pressure approaches the maximum pressure value); (2) the slope is independent of the initial pressure value and (3) it mimics the evaluation of the excess isotherm in which the total amount of sorptive gas transferred into the

sample cell is measured. It is, moreover, analogous to the measurement of the "helium isotherm" in the gravimetric method to obtain the sample volume for the buoyancy correction.

4.3 Thermodynamic equilibrium

The transient processes which take place during the equilibration step include 1) temperature changes and 2) diffusion-controlled transport of the sorptive gas onto the sorption sites (or into the micropores). The temperature changes result mainly from the Joule-Thompson effect of a gas being expanded through an orifice (e.g. valve, in-line filter) into the sample cell and from the heat of sorption (although this contribution is expected to be small for shales given their low sorption capacity). These temperature effects usually happen in relatively short time interval compared to the time it takes to reach equilibrium through the slow diffusion process. However, they are very dependent on the instrument design (size of the cells, gas-dosing system, etc.), the heat transfer efficiency of the heating system and are also sample and gas-specific (Joule-Thompson coefficient, thermal conductivity, etc.). The establishment of equilibrium is inferred by monitoring the changes in pressure (manometric method) or weight (gravimetric method). There are no general criteria or recommendations with respect to the equilibration times. Insufficient equilibration times will lead to an underestimation of the sorption capacity and possibly some effect on the isotherm shape. For samples with a significant proportion of pores in the nano-scale range the equilibration process can be very lengthy and a true equilibrium may never be reached in an experiment due to kinetic restrictions. It is important, however, to define at least a "technical equilibrium" meaning that the measured pressure (or mass) changes should be on the same order of magnitude as the changes due to temperature fluctuations (resolution limit) over a sufficiently long time interval. On the other hand, substantially long equilibration times require a very good leak-tightness of the setup and/or explicit consideration of leakage in the mass balance (e.g. van Hemert et al., 2009a).

The Figure 7 shows an example of the pressure equilibration (uptake) curves of CH_4 and CO_2 during a manometric sorption experiments on the Posidonia sample performed by Lab-5. The uptake curves are plotted with a logarithmic time axis as this offers a much better visual analysis of the slow late-time uptake (van Hemert, 2009b). It is observed that for CO_2 during the first three equilibration steps the equilibrium has not been fully attained within the duration of the expansion step. It is also observed that at lower pressures (more precisely at low occupancy of the sorption sites) the equilibration process is considerably longer than at high pressures (high occupancy of the sorption sites). Accordingly, the equilibration times should be sufficiently long initially in order to approach as closely as possible the thermodynamic equilibrium while they can be reduced with the progression of the experiments (depending on the uptake kinetics) in order to minimize the effect of leakage.

In Figure 8 an example of CH_4 uptake curve is shown for which thermal effects, mainly due to Joule-Thompson effect, can be observed in the initial phase of the pressure equilibration. Such observations are typically encountered for CH_4, CO_2 and C_2H_6 in manometric setups with large sample cell volumes. Depending on the setup characteristics these effects are only observed within the first 30 – 60 seconds following the gas expansion into the sample cell.

4.4 Blank tests (Lab-5)

For sorption measurements on materials with a low sorption capacity, and especially for gases at a proximity to the critical conditions it is important to isolate the actual sorption behaviour of the sample from experimental artefacts. Blank sorption measurements using a non-sorbing sample (ideally of the same material as the sample cell, e.g. stainless steel) can be performed as a sort of device-specific diagnostic test to identify and quantitatively account for such artefacts. These can result from unknown systematic errors in pressure and temperature that propagate into the gas density calculated by the EoS; (2) the actual EoS; (3) gas impurities and/or (4) due to fundamentally different interaction of different gases (He vs. CH_4 vs. CO_2, etc.) with the inner walls of the instrument components with which they are in direct contact. These blank measurements can be performed during the setup calibration with gases and at temperatures of interest.

Blank sorption measurements have been performed systematically for the manometric setup from Lab-5. Stainless steel cylinders of different sizes were used to create a range of void volumes typically encountered in sorption tests with shale/coal samples. From the "raw" excess sorption isotherm measured on a shale sample, the "blank" excess sorption isotherm at an equivalent void volume is subtracted to obtain the final corrected excess sorption isotherm. An example of the measured ("raw") excess sorption isotherms and the blank isotherms of CH_4 and CO_2 is shown in Figure 9 for the Posidonia sample. For CH_4, the downward bending of the excess sorption isotherm following a maximum is reduced or eliminated (for immature samples such as Posidonia). For CO_2, the "concave-upward" isotherm part preceding, and the strong downward trend following the maximum in excess sorption are eliminated or reduced after the blank correction.

4.5 Equation of state (EoS)

For high-pressure sorption isotherm measurements the choice of the equation of state will have a significant influence on the calculated sorption quantity. While some modern gravimetric instruments enable direct measurements of gas density, all laboratories involved in this study relied on the EoS to calculate the gas density (or compressibility factors) from measured pressure and temperature data. Commonly used EoS include, for example, the cubic equations of Peng-Robinson (P-R) or Soave-Redlich-Kwong (SRK), which are based on critical point data and acentric factors, or the virial-type equation of Benedict-Webb-Rubin. Currently, the most accurate EoS for CH_4 and CO_2, are however, the multi-parameter wide-range EoS by Setzmann and Wagner (1991) (Se-W) and Span and Wagner (1996) (Sp-W), respectively. These EoS are based on the dimensionless Helmholtz energy and provide excellent accuracy even at the critical region. They are used for instance in the National Institute of Standards and Technology (NIST) Chemistry WebBook and in the NIST REFPROF software package. Recently, the same group introduced the GERG 2004 (Kunz et al., 2007) and the new GERG 2008 (Kunz and Wagner, 2012) EoS for multi-component mixtures for up to 21 natural gas components which will be used as an ISO standard (ISO 20765-2/3) for natural gases.

As pointed out by Mavor et al. (2004), the differences in EoS can lead to variations of up to 20% (the case for CO_2) in the calculated sorption capacities (see also van Hemert et al., 2010; Busch and Gensterblum, 2011). In this regard, the cubic EoS do not provide sufficient accuracy for application in high-pressure sorption studies and can even lead to artefact in excess sorption isotherms as we will demonstrate here. In this study, one laboratory (Lab-4) reported, using the P-R EoS for the calculations of the CH_4 and CO_2 density, while other laboratories used the Se-W and Sp-W EoS, respectively. The Figure 10 demonstrates (using the raw data of Lab-5) the difference in the calculated excess sorption for CH_4 and CO_2 using the P-R and the Se-W / Sp-W EoS. Clearly, the isotherm based on the P-R EoS deviates significantly from that based on the more accurate Se-W and Sp-W EoS and, moreover, produces artefacts that cannot be explained by thermodynamic considerations (note the shape of the CO_2 sorption isotherm).

Further, to explain the anomalous negative CO_2 isotherms reported by Lab-4 (inset in **Figure 5b**) in addition to the use of P-R EoS, residual He in the sample cell (at 1 bar) was introduced as additional source of uncertainty (this cross-contamination by residual He in expected for Lab-4 due to a lack of a vacuum system in the apparatus). These results are shown in **Figure 11**. Although different datasets are compared the trends in the isotherm shapes are similar.

4.6 Uncertainties in pressure and temperature measurements

Since measurements of pressure and temperature form the basis of the quantitative analysis in both manometric and gravimetric methods through the use of the EoS, it is imperative (especially for studies on low-sorbing materials such as shales) to use the highest current standards of accuracy and precision. Both, the pressure and the temperature sensors (including the data acquisition system) should be calibrated using certified standard procedures to minimize the systematic errors. The relative importance of the measurement uncertainties in pressure and temperature and their influence on the calculated gas density depends on the gas type and the absolute values of pressure and temperature. Figure 12 shows the uncertainty percentage contributions (UPC) (Coleman and Steele, 2009) of pressure and temperature to the density of CH_4 and CO_2 assuming expanded uncertainties (95% confidence interval) for pressure and temperature of 0.05% and 0.05 K, respectively. These uncertainty values are typical for commercial high-accuracy pressure transducers (calibrated using a standard dead weight procedure) and temperature calibration equipment based on the platinum resistance thermometers. Figure 12 shows that for CH_4, the uncertainty in the gas density resulting from the uncertainty in pressure (0.05%) is greater than the uncertainty resulting from temperature measurement. For CO_2, the uncertainty in temperature becomes more influential at pressures > 10 MPa.

Even the most accurate equations of state of Se-W and Sp-W may not provide the sufficient accuracy considering the capabilities of the current calibration standards. Figure 13 shows the overall calculated percentage uncertainty in the density of CH_4 and CO_2 due to measurement uncertainties in pressure and temperature. The shaded area in the Figure 13 represents the reported expanded uncertainty in the EoS itself. It is observed that for CH_4, the calculated uncertainty in the density resulting from uncertainties in pressure and temperature is lower than the upper bound of the EoS uncertainty reported by Setzmann and Wagner (1991). The improvement of the measurement

accuracy of pressure and temperature for density calculations is not justified without corresponding improvement in the accuracy of the EoS. The calculated uncertainty in the density of CO_2 is higher than the uncertainty interval in EoS reported by Span and Wagner (1996) for pressures below 20 MPa but lower for higher pressures. However, it should be noted that the assumed uncertainty of 0.05% and 0.05 K in pressure and temperature, respectively, are not the current highest standard. The NIST reports uncertainties of the pressure and temperature calibration standards of 40 ppm and 36 mK, respectively.

4.7 Gas impurities (moisture)

Small amounts of adsorbed water can significantly influence the sorption capacities of gases. The trace amounts of water (usually in ppm range) in high-purity gases can affect the sorption experiments on shales in sorption instruments with a large void volume relative to the sample size. This is because of relatively high absolute moisture content compared to sample mass. A set of test measurements to study this effect was performed by Lab-7 on a modified gravimetric setup for measurements of CO_2 isotherms at 273 K with and without a zeolite gas drier. The stream was passed through a zeolite cylinder bed (~ 5 x 20 cm) filled with sodium aluminium silicate (1 nm molecular sieve, 2 mm beads) from Merck KGaA. Additionally, a reactor filled the same zeolites was attached to the sample reactor. Before running isotherms the zeolite beds were dried (> 400°C) and out-gassed. The results are shown in Figure 14. The apparently higher uptake (mass increase) observed for the experiment without the gas pre-drying indicates additional sorption of water.

4.8 Other sources of uncertainty

Other sources of uncertainty in high-pressure sorption measurements not discussed here in detail can be found in the literature on sorption in coals (Krooss et al. 2002; Gensterblum et al. 2009, 2010; Sakurovs et al. 2009; van Hemert et al. 2009; Busch and Gensterblum, 2011). These comprise errors due to leakage, sample compression and swelling, gas impurities or due to solvent properties of the supercritical CO_2. Of these, leakage is the most significant as high leakage rates during the sorption experiment may overestimate the sorption capacity, or even give unrealistic results. Each experimentalist should take all necessary measures to minimize the leakage and to ensure that its effect on the sorption measurements (and for specific applications) is acceptable. A detailed analysis considering the influence of leakage on the mass balance of the sorption experiments was provided by van Hemert et al. (2009). Gas impurities (e.g. residual helium in sample cell / gas supply tubing) can result from insufficient evacuation of the sample cell or insufficient purging of the gas supply tubes and will compromise the mass balance. Gensterblum et al. (2010) discuss the effects of gas impurities for CO_2 sorption measurements on coals. For sorption studies on shales, if the sorption device is equipped with a vacuum system (10^{-2} Pa and lower) with proper purging and sample cell evacuation these effects will be insignificant.

5 Recommendations for optimizing high-pressure sorption measurements on shales and for data reporting

The discrepancies in high-pressure sorption measurements on shales reported in this study indicate that the current quality standards in measurement procedures need to be improved. The identification of the different types of errors (procedural, calibration, errors due to poor equipment design) is not possible from the reported results and equipment specifications alone. Therefore, tentative recommendations are proposed here for the optimization of sorption measurement and for data reporting. These recommendations were adapted from Zlotea et al. (2009):

(1) Methodology.
In general, both methods, manometric and gravimetric provide consistent results and from the data reported here no systematic discrepancies between the two methods (beyond those for a single method) are observed. Both methods have advantages and disadvantages. The drawback of the manometric method is the accumulation of errors for multi-point sorption isotherm. A thorough optimization of the procedure of successive gas transfer into the sample cell is anything but trivial. The estimates for an optimal ratio of reference cell volume to void volume vary in the literature from 2 to 10 and optimal dosing might require variable volume of the reference cell for controlled ratios of the initial and equilibrium density (depending on the proximity to the critical point). On the other hand, the magnitude of the buoyancy term and temperature fluctuations relative to the mass increase due to gas uptake, decreases significantly the sensitivity in the gravimetric method for low-sorbing shales.

(2) Volume calibration.
The volume calibration of the reference and sample cells (manometric) and the buoyancy correction of the empty sample pan (gravimetric) require very accurate volume measurements (<< 0.1% standard error). Certified volume standards (e.g. precision balls and electro-polished steel cylinders) should be used and thermal expansion coefficients have to be known and considered in the volume calibration. For the manometric instrument, at least a three-point calibration (empty sample cell + two measurements with calibration standards of different volumes) should be performed. The calibration should be repeated in regular intervals and always after modifications on the device.

(3) Calibration of pressure and temperature sensors and of magnetic balance.
The calibration of the individual components is necessary to reduce the unknown systematic errors, which may affect the gas densities calculated for the EoS and the mass readings in the gravimetric setups. The entire measuring loop (sensor + data acquisition system) should be calibrated at the experimental conditions of interest (the temperature compensation limits for many high-accuracy pressure transducers are limited to $40 - 50°C$).

(4) Pressure measurements.
Pressure measurements should be performed using the highest available standards in terms of accuracy. For optimal measurements over an extended range of pressures two (or more) pressure transducers with different full-scale range can be used. In the manometric method, the pressure data are sometimes obtained by separate pressure transducers attached to the reference and the sample cell. In this, as well as in the previous case, it is important that the

different pressure transducers are carefully cross-calibrated so as to not introduce additional errors into the mass balance.

(5) Temperature control and measurements.

The temperature of the thermostated parts should be stable within <0.1 K. In manometric setups the temperature stability can be further increased e.g. by aluminium or steel blocks with high thermal mass around the reference and the sample cell. Temperature measurements should be performed with high-accuracy platinum resistivity thermometers-(Pt-100) and these should be calibrated by standard procedures (commercial calibration equipment provides accuracy level of 0.01 K). Temperature probes should be placed directly inside the reference cell and the sample cell (in contact with sample) if possible. Otherwise, the spatial and temporal variations in temperature should be considered in the error analysis. The equipment should be placed within the thermostated volume experiencing the lowest thermal gradients.

(6) Temperature gradient.

For manometric sorption instruments with separate heating zones for the reference and the sample cell (allowing high temperatures in the reference cell), the thermal gradient existing in part of the sample cell volume (usually tubing connecting it to the reference cell) has to be quantified and accounted for in the mass balance calculation. A temperature calibration with an empty sample cell and/or with non-sorbing (steel) material with known thermal expansion properties can be performed to quantify the thermal boundary and determine the thermal expansion of the sample cell (this is necessary for measurements at high temperatures). Care should be taken when performing measurements on moist samples on instruments with thermal gradients, as the moisture can condense in the cold spots and introduce errors in the calibration volume and the gas density.

(7) Blank tests.

These tests are carried out with non-sorbing material (ideally the same material as that of the sample cell) in the pressure and temperature ranges of interest to verify the measurements and identify experimental artefacts. The blank tests can be performed as part of the volume calibration and should be carried out with at least two non-sorbing sample calibration standards so as to cover the typical range of void volumes occurring in the measurement.

(8) Leakage rate.

The leakage rate should be determined prior to each experiment, ideally using helium at a representative pressure. Within the experimental possibilities the leakage should be reduced so that no corrections in mass balance are necessary (e.g. by reducing the amount of tube connections). The cumulative leaked amount of gas (considering the equilibration times) should be kept below the acceptable error margin with respect to the total excess sorbed amount. Corrections for the leakage in mass balance can be performed (see for example van Hemert et al., 2009a), however it is preferable to reduce the leakage by improved setup design. The leakage is not critical for the gravimetric method as long as the pressure can be kept constant.

(9) Void volume/sample volume measurement.

The void volume and sample volume measurements with helium should ideally be performed for a range of pressures to check the consistency of void volume with pressure. For samples containing volatile compounds (e.g. moisture, low molecular-weight

hydrocarbons), measurements should be performed before and after the sorption experiment. For manometric setup a recommended data evaluation technique for multiple-point void volume measurement was presented in part 4.2.

(10) Gas purity.

The trace impurities in high-purity / research grade gases do not pose any detectable influence on the measurement accuracy. However, it is very important to avoid any cross-contamination of the measurement gas due to insufficient purging and/or evacuation. Moreover, when measuring isotherms on dry samples removal of moisture from the gas supply should be considered especially if the sample cell volume is very large relative to the sample amount.

(11) Sample out-gassing.

Sample out-gassing can be performed at different conditions depending on the application (dry versus moist samples, temperature sensitive materials, etc.). It is important, however, to consider the specific instrument design, especially the size of the sample cell, the heat transfer characteristics (gas versus liquid circulation versus electrical mantle heating) in order to adjust the out-gassing time. Temperature sensors in direct contact with the sample will enable to verify that the sample has reached the desired temperature at high vacuum conditions.

For reporting the data the following relevant information should be included:

(1) Sample information:

All available geologic and geochemical sample information (e.g. TOC, RockEval, vitrinite reflectance, XRD, etc.). These analyses should be performed on an aliquot of the same sample as that used for sorption measurements.

(2) Sample treatment:

Crushing and sieving (particle/mesh size), sample homogenization, pre-drying (temperature, pressure), moisture adsorption procedure and moisture content.

(3) Experimental details:

Pressure range and temperature of the measurement; type of instrument (manometric, gravimetric, other); accuracy specifications and information on the calibration of pressure and temperature sensors, and magnetic balance; volume calibration of the reference/sample cells, buoyancy correction; temperature gradient corrections; experimental parameters (equilibration time or criteria), equations of state. We also recommend to report the sample mass, the ratio of void volume/dead space volume to sample mass, as well as the values and standard deviations for volumes of the sample and reference cell (as these data will be helpful for statistical evaluation of the measuring performance).

(4) Analysis gas:

Purity, filtration (pre-drying) for each gas used in the experiment.

(5) Repeatability of sorption measurement:

Were measurements repeated for the same/different sample aliquots and conditions and on the same/different instrument?

(6) Evaluation of data:

Data reduction equations for calculating void volume and excess sorption, mathematical treatment of the temperature gradient, special consideration in the mass balance, etc.

6 Conclusions

An inter-laboratory study was performed to assess the reproducibility of high-pressure sorption isotherms on shales. These are of interest for shale gas exploration and exploitation and for the assessment of the viability of CO_2 storage and enhanced methane production from shale. Seven international laboratories specialized on high-pressure gas sorption experiments have joined this "open round robin". Excess sorption isotherms of CH_4, CO_2 and C_2H_6 on two shales with high and low thermal maturity were determined at 65°C and at specified drying conditions.

The inter-laboratory reproducibility study was carried out at predefined experimental conditions but with each laboratory following its own measurement and data reduction procedures. The observed discrepancies in the measured sorption isotherms between individual laboratories are significant considering the sorption capacity of shales. The reproducibility of excess sorption isotherms for CH_4, was better for the high-maturity sample (within 0.02 – 0.03 mmol/g) than for the low-maturity sample (up to 0.1 mmol/g), similar to comparable round robin studies on coals. The reproducibility for CO_2 and C_2H_6 sorption isotherms was satisfactory at pressures below 5 MPa but at high pressures the individual results deviate considerably. Given, that for the applications in shale gas exploration, the knowledge of sorption behaviour of shales at high pressures (and high temperatures) is of prime interest, the currently observed discrepancies between the individual laboratories call for further quality improvement and standardized methods. Since intra-laboratory consistency tests (though, not all) show that a high degree of repeatability is achievable, more attention should be paid to identifying and eliminating the unknown systematic errors through the usage of the highest-quality measuring instrumentation, calibration standards and optimization of operator-defined experimental parameters. A suitable benchmark test material (in sufficient quantity and representative of shales) may prove useful for future studies.

7 Acknowledgements

8 References

Belmabkhout, Y., Frère, M., De Weireld, G. High-pressure adsorption measurements. A comparative study of the volumetric and gravimetric methods. Meas. Sci. Technol. 2004, 15(5), 848–858.

Billemont, P., Coasne, B., and De Weireld, G. An experimental and molecular simulation study of the adsorption of carbon dioxide and methane in nanoporous carbons in the presence of water. Langmuir 2011, 27(3), 1015–1024.

Brunauer, S.; Emmett, P. H.; Teller, E. Journal of the American Chemical Society 1938, 60, 309.

Busch, A., Gensterblum, Y. CBM and CO2-ECBM related sorption processes in coal: A review. Int. J. Coal Geol. 2011, 87(2), 49–71.

Cazorla-Amorós , D., Alcañiz-Monge , J., de la Casa-Lillo, M. A., Linares-Solano, A. CO_2 As an Adsorptive To Characterize Carbon Molecular Sieves and Activated Carbons, Langmuir, 1998, 14 (16), 4589–4596

Coleman, W.H., Steele, W.G. Experimentation, Validation, and Uncertainty Analysis for Engineers. John Wiley & Sons, New Jersey (2009), p.88

S.J. Day, G.J. Duffy, A. Saghafi and R. Sakurovs, Factors controlling CO2 absorption in Australian coals. Greenhouse Gas Control Technologies, 7. Elsevier Science Ltd, Oxford, 2005, 2221-2224.

Day, S., Sakurovs, R., Weir, S. Supercritical gas sorption on moist coals. Int. J. Coal Geol. 2008, 74(3-4), 203–214.

De Weireld, G., Frère, M., Jadot, R. Automated determination of high-temperature and high-pressure gas adsorption isotherms using a magnetic suspension balance. Meas. Sci. Technol. 1999, 10(2), 117–126.

Dreisbach, F., Lösch, H.W., Harting, P. Highest Pressure Adsorption Equilibria Data: Measurement with Magnetic Suspension Balance and Analysis with a New Adsorbent/Adsorbate-Volume. Adsorption 2002, 8, 95–109.

Dubinin, M. M.; Zaverina, E. D.; Serpinsky, V. V. Journal of the Chemical Society (Resumed) 1955, 1760.

Fletcher, A. J., Thomas, K. M., Rosseinsky, M. J. Journal of Solid State Chemistry 2005, 178, 2491.

Friend, D.G., Ingham, H., Ely, J.F. Thermophysical Properties of Ethane. J. Phys. Chem. Ref. Data 1991, 20(2), 275–347.

Gensterblum, Y., van Hemert, P., Billemont, P., Busch, A., Charriére, D., Li, D., Krooss, B. M., de Weireld, G., Prinz, D., Wolf, K.H.A.A European inter-laboratory comparison of high pressure CO2 sorption isotherms. I: Activated carbon. Carbon2009, 47, 2958–2969.

Gensterblum, Y., van Hemert, P., Billemont, P., Battistutta, E., Busch, A., Krooss, B. M., De Weireld, G., Wolf, K.-H.A.A. European inter-laboratory comparison of high pressure CO2 sorption isotherms. II: natural coals. Int. J. Coal Geol.2010, 84, 115–124.

Goodman, A. L., Busch, A., Duffy, G. J., Fitzgerald, J. E., Gasem, K. A. M., Gensterblum, Y., Krooss, B. M., Levy, J., Ozdemir, E., Pan, Z., Robinson, R. L., Schroeder, K., Sudibandriyo, M., White, C. M. Energy Fuels 2004, 18, 1175.

Goodman, A. L., Busch, A., Bustin, R. M., Chikatamarla, L., Day, S., Duffy, G. J., Fitzgerald, J. E., Gasern, K. A. M., Gensterblum, Y., Hartman, C., Jing, C., Krooss, B. M., Mohammed, S., Pratt, T., Robinson, R. L., Romanov, V., Sakurovs, R., Schroeder, K., White, C. M. Int. J. Coal Geol. 2007, 72, 153.

Gregg, S. J., Sing, K.S.W. Adsorption, Surface Area and Porosity, Academic Press, London 1982.

Gurvitch, L. J. Phys. Chem. Soc. Russ. 1915, 47, 805.

Krooss, B. M., van Bergen, F., Gensterblum, Y., Siemons, N., Pagnier, H. J. M., David, P. High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. Int. J. Coal. Geol. 2002, 51, 69–92.

Kunz, O., Wagner, W., Jaeschke, M. The GERG-2004 wide-range reference equation of state for natural gases. GERG Technical Monograph 15 Fortschritts-Berichte Verein Deutscher Ingenieue (VDI), 2007, 6. VDI-Verlag, Düsseldorf.

Kunz, O., Wagner, W. The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004. *J. Chem. Eng. Data* **2012** *57* (11), 3032-3091.

Marsh, H. Carbon 1987, 25, 49.

Mavor, M. J., Owen, L. B., and Pratt, T. J. Measurement and Evaluation of Coal Sorption Isotherm Data. Soc. Petr. Eng. 1990, SPE 20728.

McCarty, R.D., Arp, V.D. A new wide range equation of state for helium. Advances in Cryogenic Engineering 35, 1465–1475.

Mohammad, S., Fitzgerald, J., Robinson, R. L., Gasem, K. A. M. Experimental Uncertainties in Volumetric Methods for Measuring Equilibrium Adsorption. Energy Fuels 2009, 23(5), 2810–2820.

Ravikovitch, P. I., Haller, G. L., Neimark, A. V. Advances in Colloid and Interface Science 1998, 76–77, 203.

Rexer, T. F. T., Benham, M. J., Aplin, A. C., Thomas, K. M. Methane Adsorption on Shale under Simulated Geological Temperature and Pressure Conditions. *Energy Fuels* **2013,** *27* (6), 3099-3109.

Rexer, T. F., Mathia, E.J., Aplin, A.C., Thomas, K.M. High-Pressure Methane Adsorption and Characterization of Pores in Posidonia Shales and Isolated Kerogens. Energy Fuels 2014, dx.doi.org/10.1021/ef402466m.

Sakurovs, R., Day, S., Weir, S., Duffy, G. Temperature dependence of sorption of gases by coals and charcoals. Int. J. Coal Geol. 2009, 77(1-2), 16–22.

Sakurovs, R., Day, S., Weir, S., Causes and consequences of errors in determining sorption capacity of coals for carbon dioxide at high pressure. Int. J. Coal Geol. 2008, 73(3-4), 250–258.

Setzmann, U., Wagner, W., Pruss, A. A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at Pressures up to 1000 MPa. J. Phys. Chem. Ref. Data 1991, 20 (6), 1061–1151.

Sircar, S. Gibbsian Surface Excess for Gas Adsorption - Revisited. Ind. Eng. Chem. Res. 1999, 38, 3670–3682.

Sircar, S. Measurement of gibbsian surface excess. AIChE J. 2001, 47, 1169–1176.

Span, R., Wagner, W., A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. J. Phys. Chem. Ref. Data 1996, 25 (6), 1509–1596.

van Hemert, P., Bruining, H., Rudolph, E. S. J., Wolf, K.-H.A.A., and Maas, J. G. Improved manometric setup for the accurate determination of supercritical carbon dioxide sorption. Rev. Sci. Instrum. 2009a, 80, 035103.

van Hemert, P. Manometric determination of supercritical gas sorption in coal, PhD Dissertation, Delft University of Technology, 2009b, p.112.

Zhang, T., Ellis, G. S., Ruppel, S. C., Milliken, K., Yang, R. Effect of organic-matter type and thermal maturity on methane adsorption in shale-gas systems. Org. Geochem. 2012, 47(0), 120–131.

Zlotea,C., Moretto,P., Steriotis, T. (2009)A Round Robin characterization of the hydrogen sorption properties of a carbon based material. Int. J. Hydrogen Energy34, 3044-3057.

Figure captions:

Figure 1. Typical sorption capacities for methane on three different carbonaceous materials - activated carbon, high-rank coal and shales measured at RWTH Aachen laboratory.

Figure 2. Micropore size distribution of the a) Namurian and the b) Posidonia shale sample showing the cumulative (V) and differential (dV(w)) pore volume. The pore size distribution was determined by fitting the CO_2 isotherm at 273 K to a slit pore nonlocal density functional theory (NLDFT) model.

Figure 3. Comparison of the helium densities determined by individual laboratories.

Figure 4. Comparison of the CH_4, CO_2 and C_2H_6 excess sorption isotherms at 65°C for the Namurian shale.

Figure 5. Comparison of CH_4, CO_2 and C_2H_6 excess sorption isotherms at 65°C for the Posidonia shale.

Figure 6. Example of proposed void volume determination in a manometric device. The total amount of helium transferred successively into the sample cell is plotted against helium density. The slope of this "helium isotherm" is equal to the void volume. The data represent two repeated measurement on the Namurian sample on a two-temperature manometric sorption device and Eq. 4b was used to calculate m^{He}_{trans}.

Figure 7. Examples of the uptake curves of the CH_4 and CO_2 during the manometric sorption experiment on the Posidonia shale sample from Lab-5. The time axis is in logarithmic form (as recommended by van Hemert et al. 2009b). The uptake curves for CO_2 for the first three equilibration steps indicate that the equilibrium has not been fully attained within duration of the expansion step. For the later equilibration steps for CO_2 (8.– 10.) and for all equilibration steps for CH_4 the pressure data at the end of the equilibration step show only fluctuations due to temperature variations.

Figure 8. Example of uptake curve of the CH_4 during the manometric sorption experiment showing initially (first 30 seconds) thermal effects (Joule-Thompson effect). Such a situation is typically observed for large sample cells (the sample cell volume in this example was ~ 55 cm³).

Figure 9. CH_4 and CO_2 excess sorption isotherms for the Posidonia sample measured at Lab-5. The excess mass (in grams) is plotted along with the "blank" sorption isotherm obtained from a measurement with a stainless steel cylinder placed in the sample cell. The void volumes in the sorption and in the blank experiment were roughly equal.

Figure 10. Comparison of the raw CH_4 and CO_2 excess sorption isotherms for the Posidonia shale calculated using the equations of state (EoS) of Setzmann and Wagner (Se-W) and
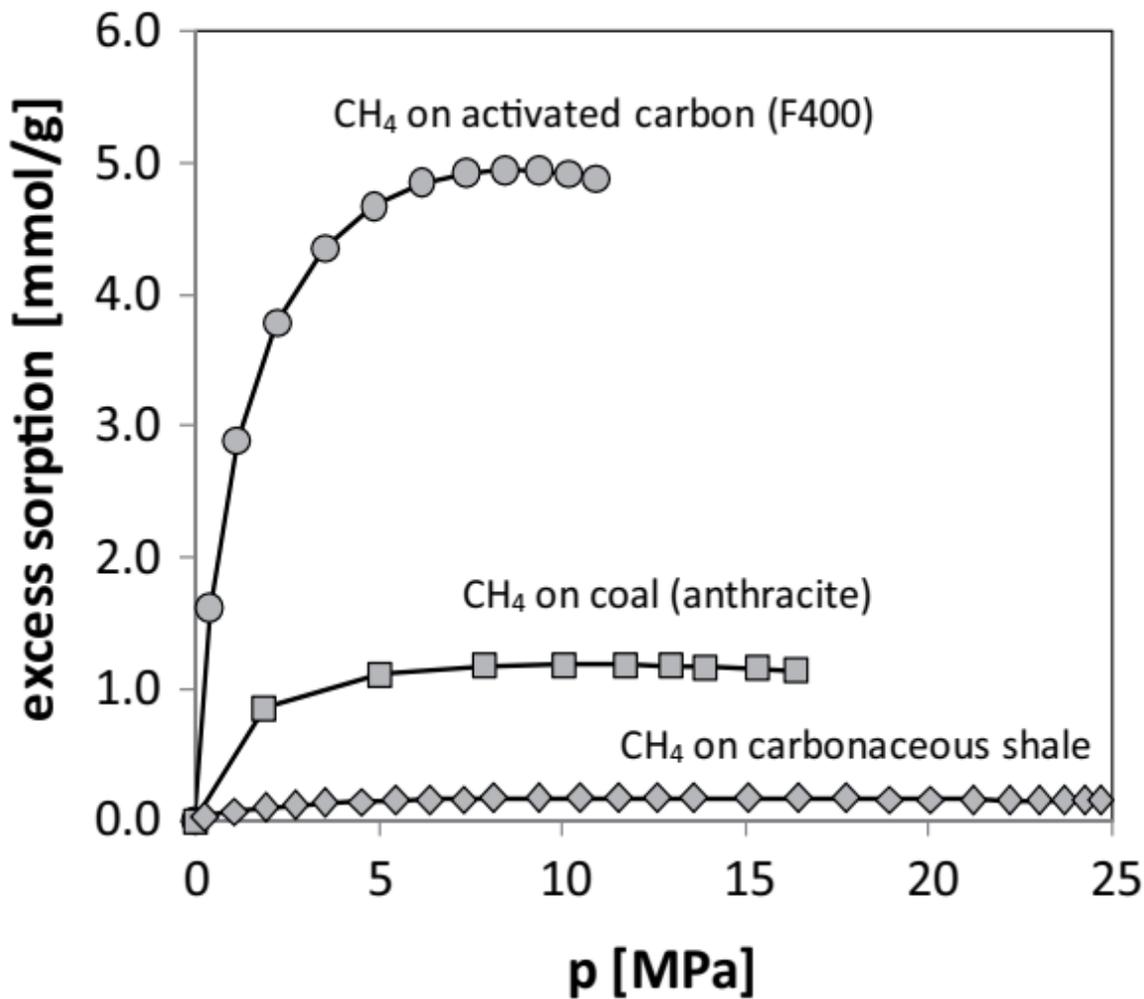
Span and Wagner (Sp-W) for CH_4 and CO_2, respectively, with those based on the Peng-Robinson (P-R) EoS.
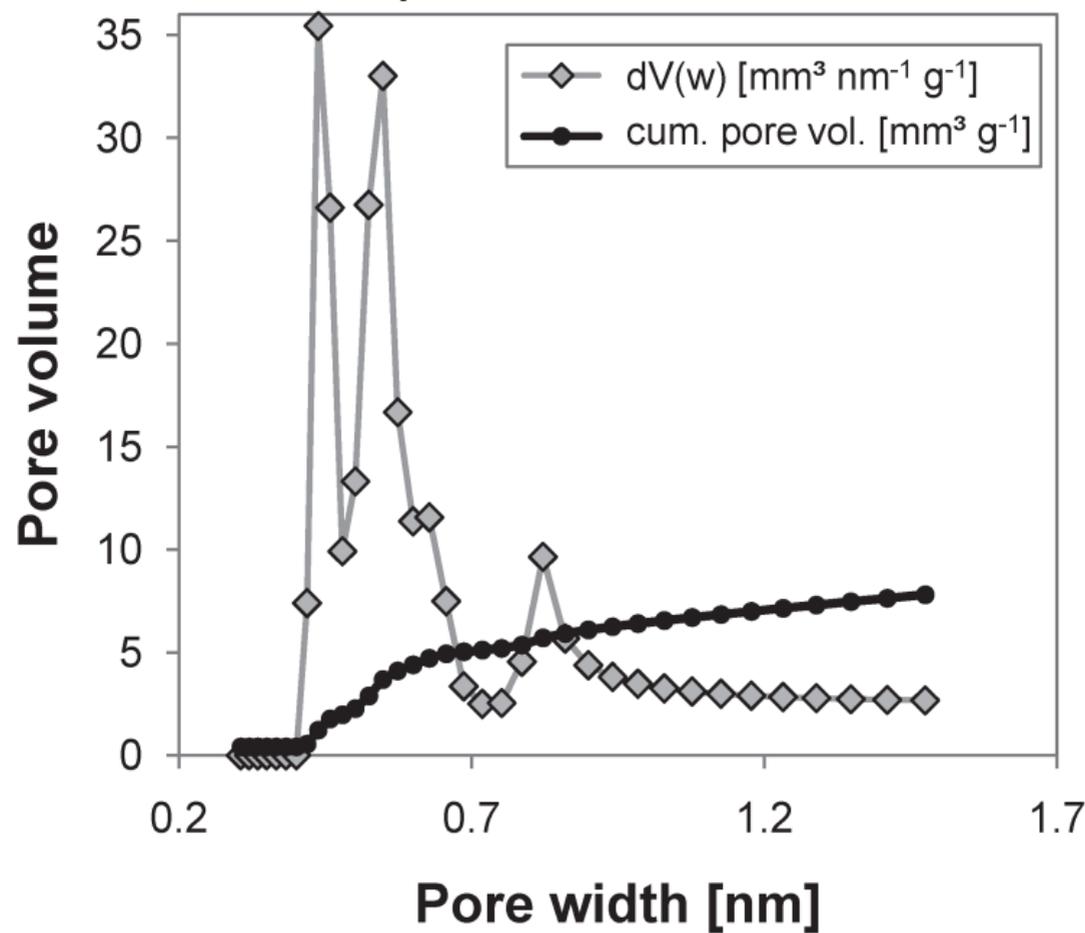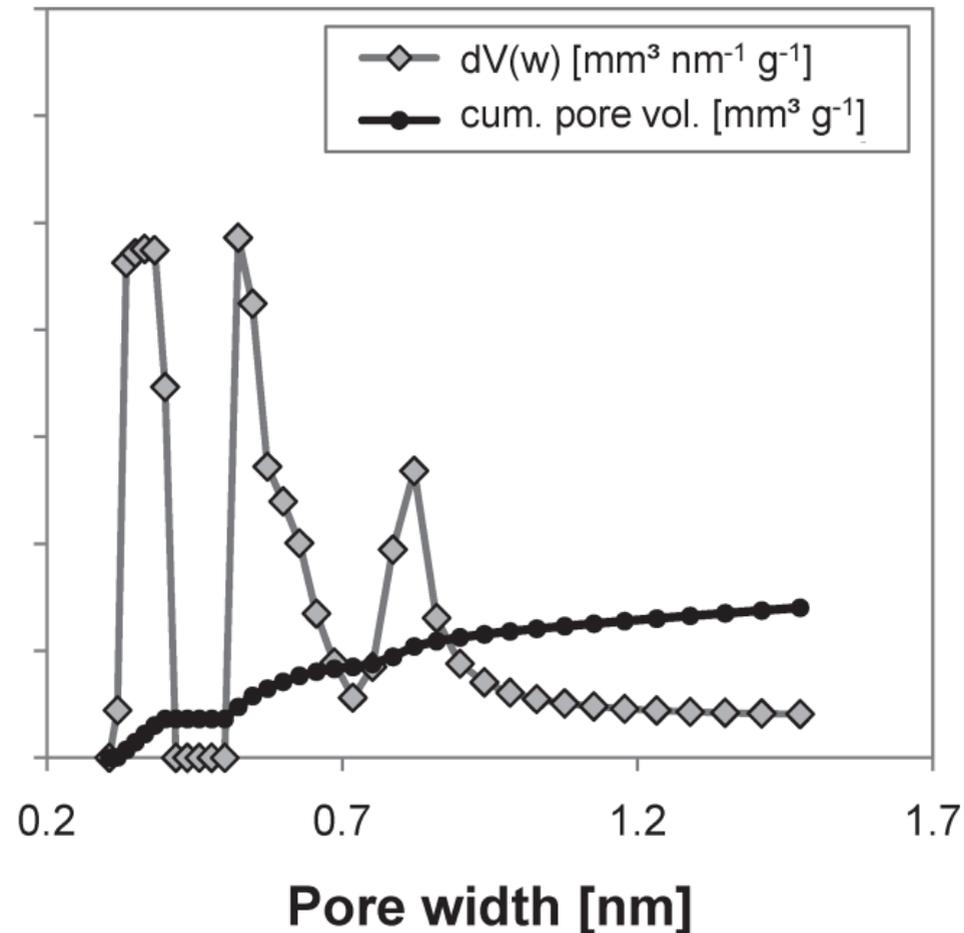
Figure 11. Comparison of the CO_2 sorption isotherms on Posidonia sample by Lab-4 (P-R EoS, no vacuum system) with the raw isotherms by Lab-5 recalculated using the P-R EoS and introducing an error due to residual He in the sample cell (1 bar).

Figure 12. Uncertainty percentage contribution of pressure (UPC_p) and temperature (UPC_T) to the overall uncertainty in the gas density for CH_4 and CO_2 based on the EoS of Setzmann and Wagner (1991) and Span and Wagner (1996), respectively($T = 338$ K). For the measurement uncertainties in pressure and temperature, values of 0.05% and 0.05 K (95% confidence interval) were assumed, which reflect the current accuracy standards for laboratory applications.

Figure 13. Overall uncertainty (at 95 % confidence interval) in the density of CH_4 and CO_2 resulting from measurement uncertainties in pressure and temperature of 0.05 % and 0.05 K, respectively. The uncertainty was calculated based on the Setzmann and Wagner equation of state (EoS) for CH_4 (Se-W) and Span and Wagner EoS for CO_2 (Sp-W). The shaded areas represent the reported uncertainty (at the same confidence interval) of the EoS itself. The assumed measurement uncertainties in pressure and temperature represent rather conservative estimates with respect to current calibration standards.
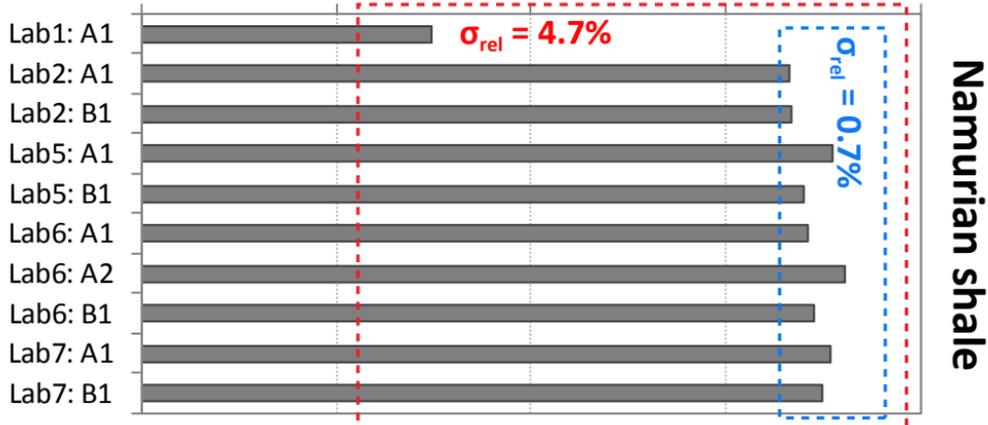
Figure 14 CO_2 sorption isotherms at 273 K on shale measured with a modified gravimetric setup with and without gas pre-drying. Trace moisture contents present in high-purity gases can affect sorption measurements on devices with large void volumes relative to sample mass.
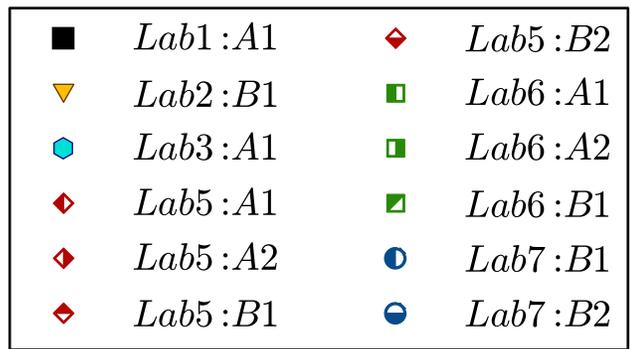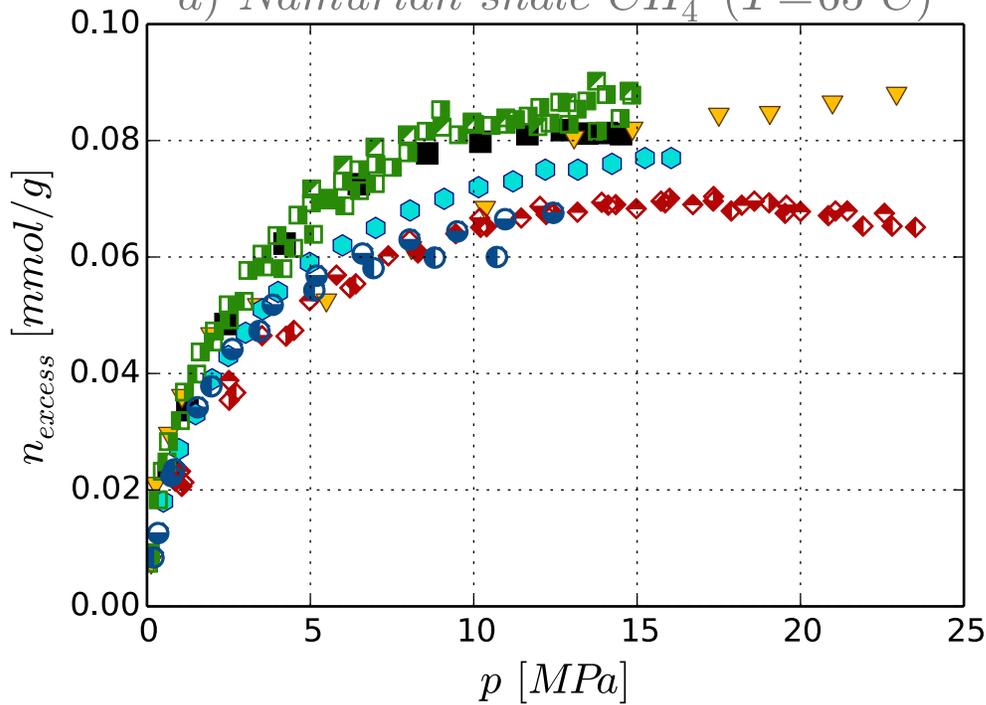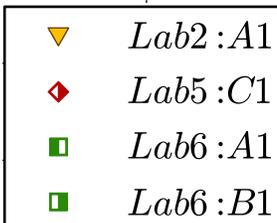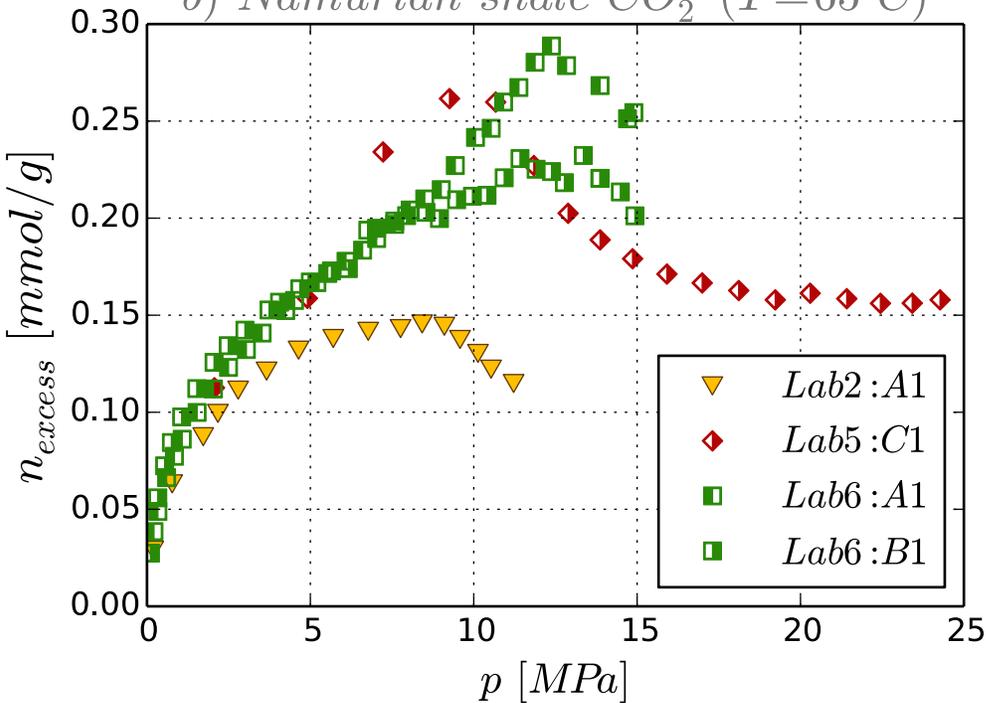
a) Namurian Shale

b) Posidonia shale

Legend (both plots):
- dV(w) [mm³ nm⁻¹ g⁻¹]
- cum. pore vol. [mm³ g⁻¹]

Y-axis: Pore volume

X-axis: Pore width [nm]

He-density [g/cm³]

Namurian shale

Lab1: A1	
Lab2: A1	
Lab2: B1	
Lab5: A1	
Lab5: B1	
Lab6: A1	
Lab6: A2	
Lab6: B1	
Lab7: A1	
Lab7: B1	

$\sigma_{rel} = 4.7\%$
$\sigma_{rel} = 0.7\%$

Posidonia shale

Lab2: A1	
Lab4: A1	
Lab4: A2	
Lab4: B1	
Lab4: B2	
Lab5: A1	
Lab5: B1	
Lab6: A1	
Lab6: B1	
Lab7: A1	

$\sigma_{rel} = 0.6\%$
$\sigma_{rel} = 2.8\%$
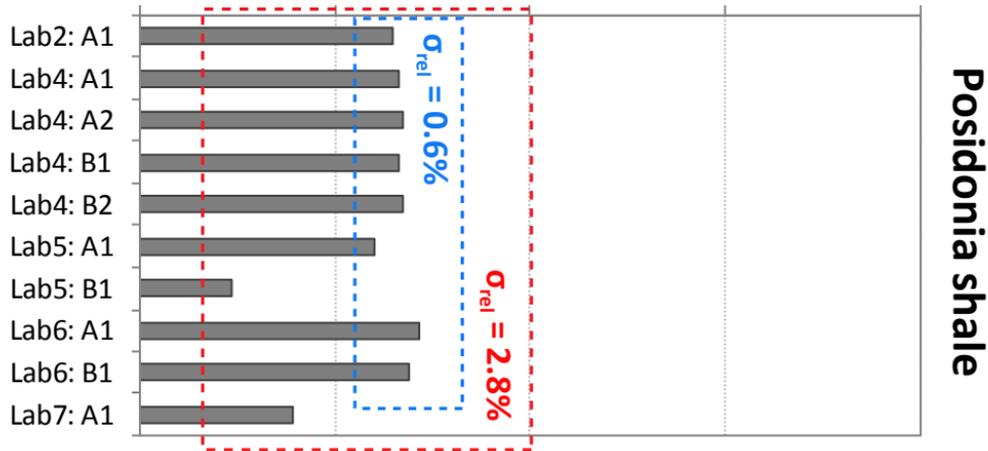
a) *Namurian shale* CH_4 ($T=65\,°C$)

Legend:
- *Lab1:A1*
- *Lab2:B1*
- *Lab3:A1*
- *Lab5:A1*
- *Lab5:A2*
- *Lab5:B1*
- *Lab5:B2*
- *Lab6:A1*
- *Lab6:A2*
- *Lab6:B1*
- *Lab7:B1*
- *Lab7:B2*

b) *Namurian shale* CO_2 ($T=65\,°C$)

Legend:
- *Lab2:A1*
- *Lab5:C1*
- *Lab6:A1*
- *Lab6:B1*

c) *Namurian shale* C_2H_6 ($T=65\,°C$)

Legend:
- *Lab2:A1*
- *Lab5:B1*
- *Lab5:B2*
- *Lab6:A1*

Axes: n_{excess} [$mmol/g$] versus p [MPa]
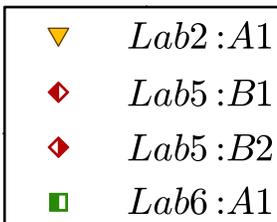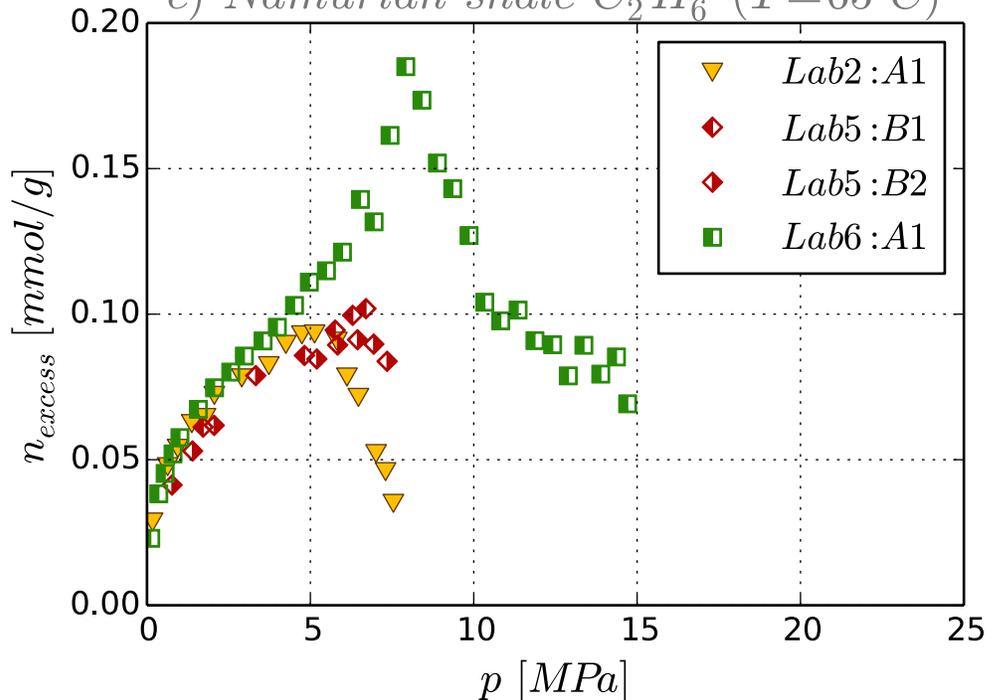
a) *Posidonia shale* CH_4 $(T=65\,℃)$

Legend:
- $Lab2:A1$
- $Lab4:A1$
- $Lab4:A2$
- $Lab4:B1$
- $Lab4:B2$
- $Lab5:B1$
- $Lab6:A1$
- $Lab6:B1$
- $Lab7:A1$
- $Lab7:A2$
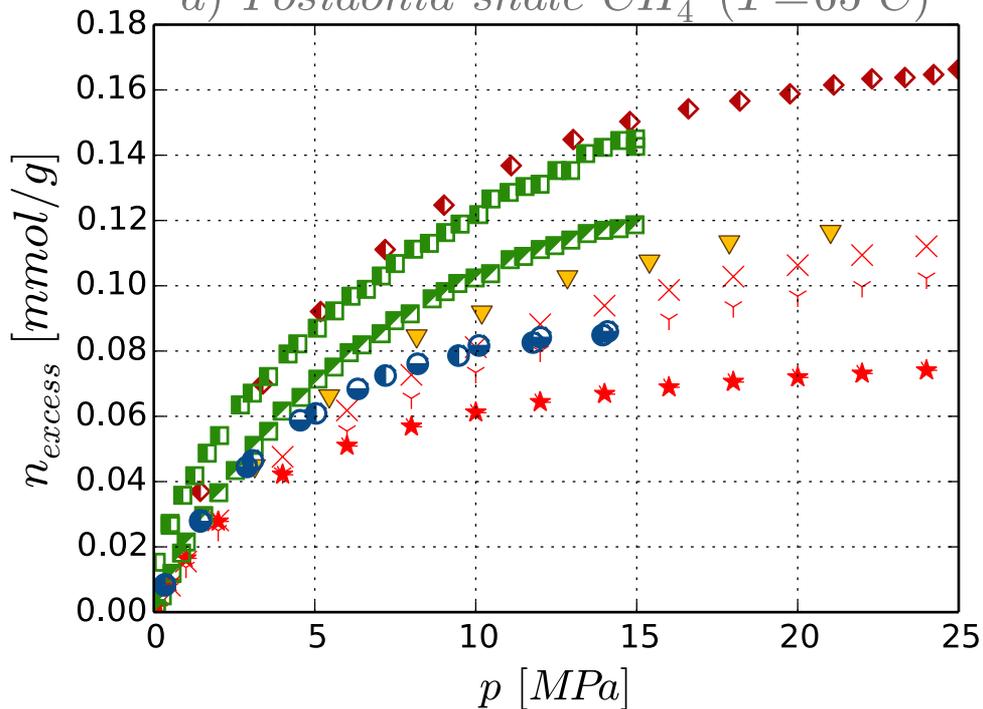
b) *Posidonia shale* CO_2 $(T=65\,℃)$

Legend:
- $Lab2:A1$
- $Lab4:A1$
- $Lab4:A2$
- $Lab5:B1$
- $Lab6:A1$
- $Lab6:B1$
- $Lab7:A1(61\,℃)$
- $Lab7:A2(61\,℃)$

Inset legend:
- $Lab4:A1$
- $Lab4:A2$
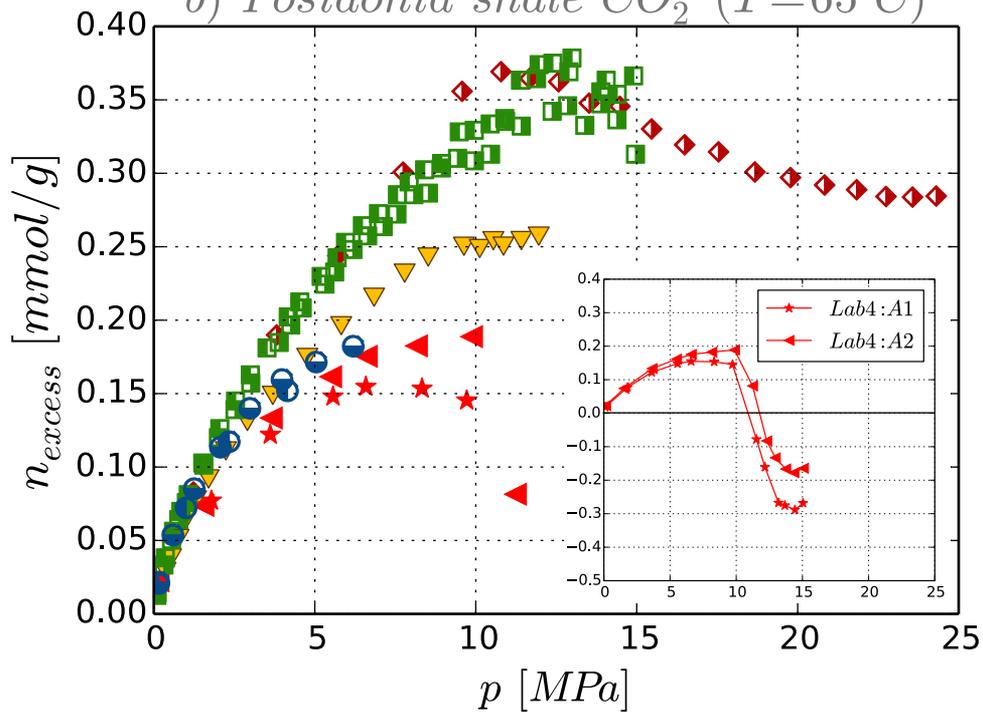
c) *Posidonia shale* C_2H_6 $(T=65\,℃)$

Legend:
- $Lab2:A1$
- $Lab6:A1$
- $Lab6:B1$

Axis labels: n_{excess} $[mmol/g]$ versus p $[MPa]$

Plot legend: ----□---- He in sample cell

$y = 3.169680E\text{-}05x - 1.223199E\text{-}07$

$R^2 = 9.999996E\text{-}01$

$\underline{\text{slope}} = V_{void}^{He} = (31.697 \pm 0.004) \times 10^{-6} \text{ m}^3$

Y-axis: $m_{trans}^{He} \times 10^4$ [kg]

X-axis: ρ_{SC}^{He} [kg/m³]