Methane and carbon dioxide adsorption in kerogen models using molecular simulations

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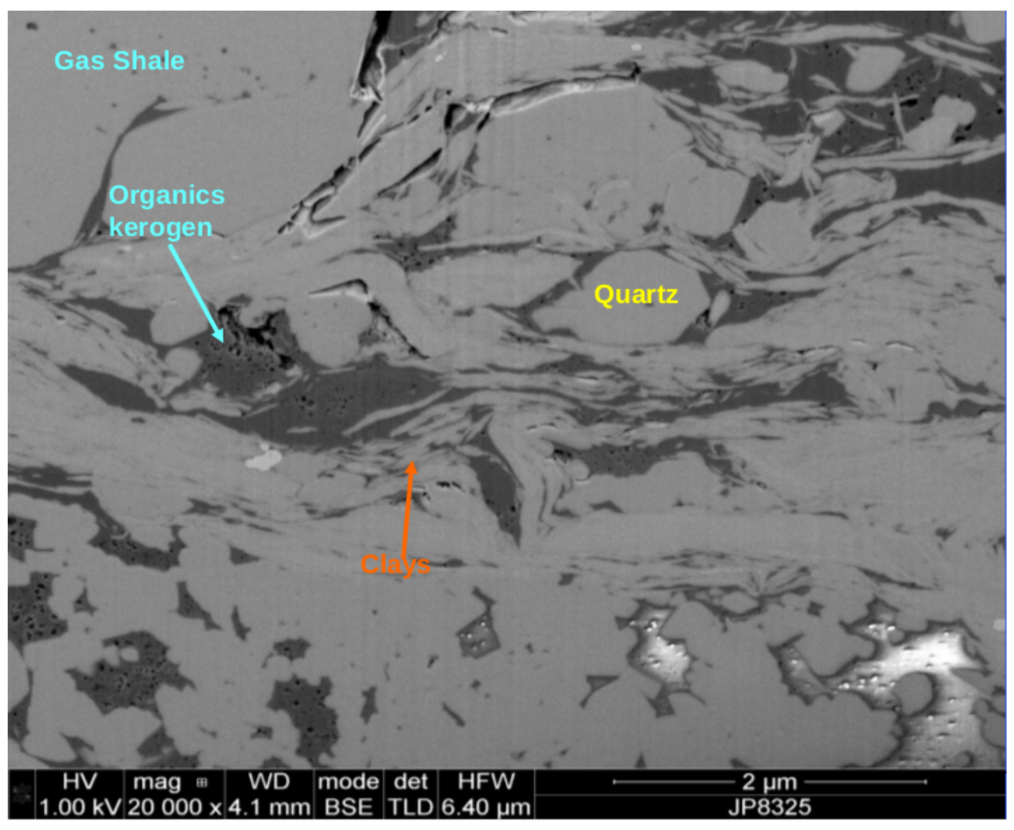
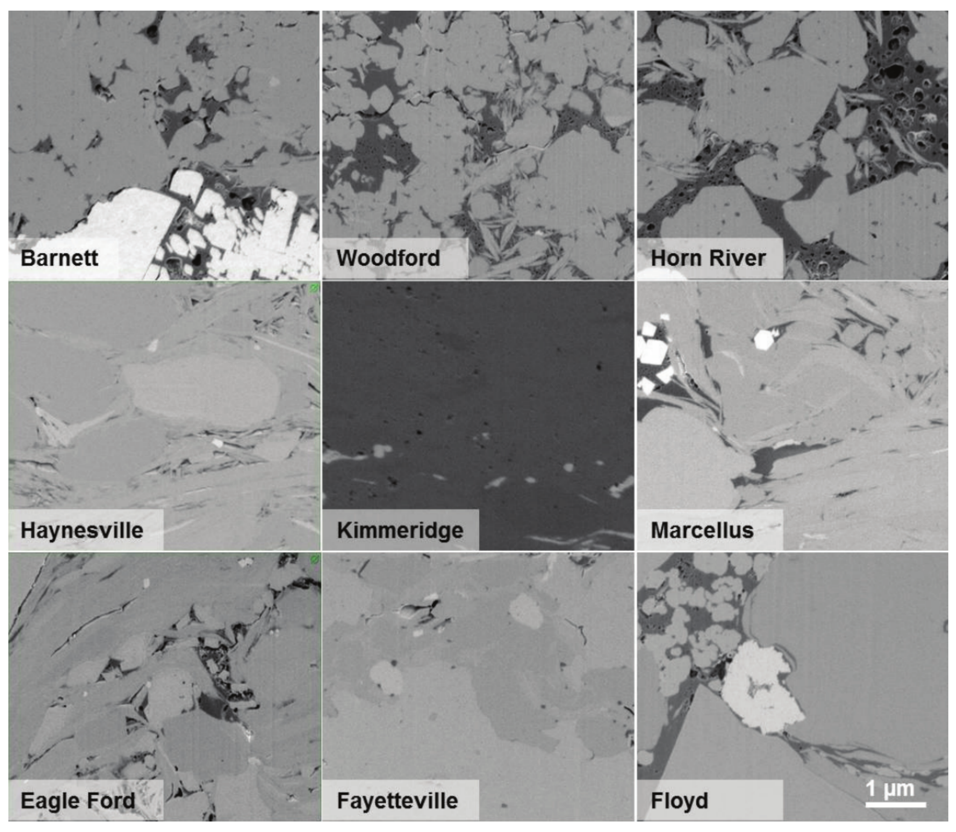
1. Introduction

- Shales are sedimentary rocks composed of (1) a mineral matrix and (2) organic matter. Both media may contribute to the storage of hydrocarbons and non-hydrocarbon species in unconventional reservoirs.
- Kerogen is a mixture of organic chemical compounds that make up a portion of the organic matter in shales.
- Realistic kerogen models were constructed implementing a molecular dynamics simulated annealing process.
- Adsorption experiments were simulated using grand canonical Monte Carlo for methane, and configurational biased/continuous fractional component for carbon dioxide.

2. Shales

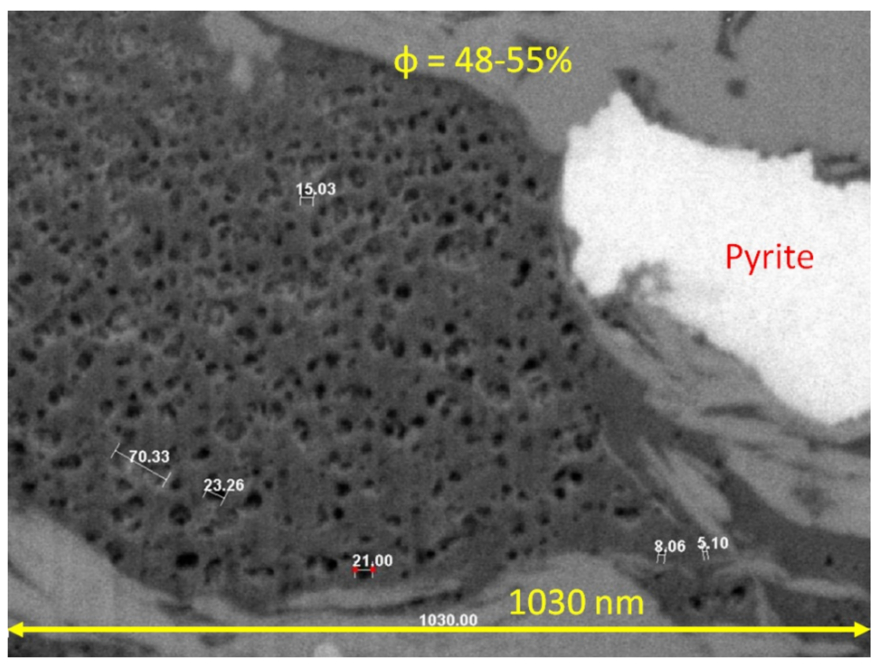


SEM image of an ion-milled Barnett shale sample. Modified from reference [1].



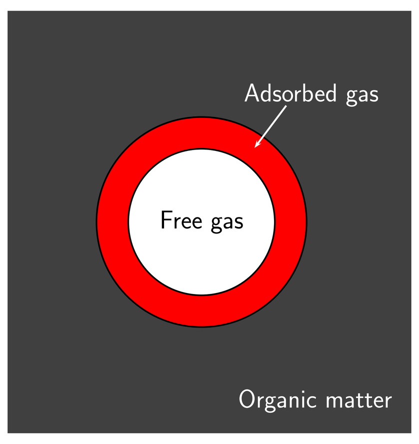
BSE images of nine different shales [2].

3. Organic pores



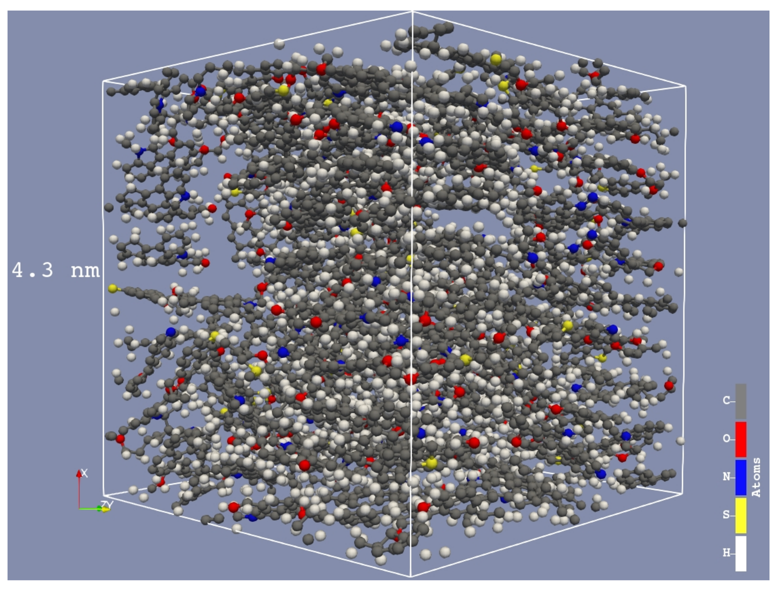
Porosity may be found within the organic matter, the inorganic matrix, or both. SEM image of a kerogen body showing porosity. Modified from reference [1].

4. Adsorption



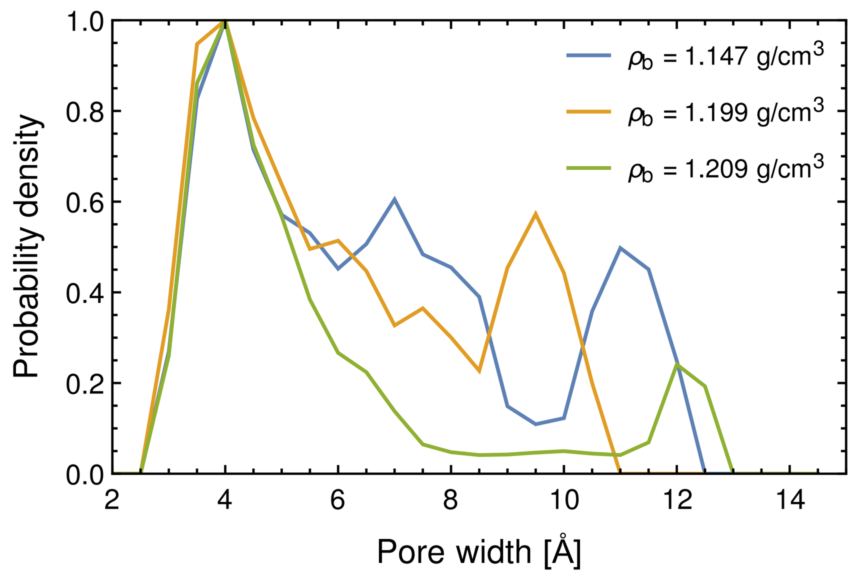
Confinement enhances the interaction energy between the rock surface and gas, resulting in an overall increase in attraction relative to a free surface. The density of the adsorbed phase is higher than that of the free phase.

5. Kerogen molecular models



Kerogen structures constructed using basic models of kerogen type II-D in reference [3], which reproduce the elemental and functional analysis data reported in reference [4].

6. Characterization



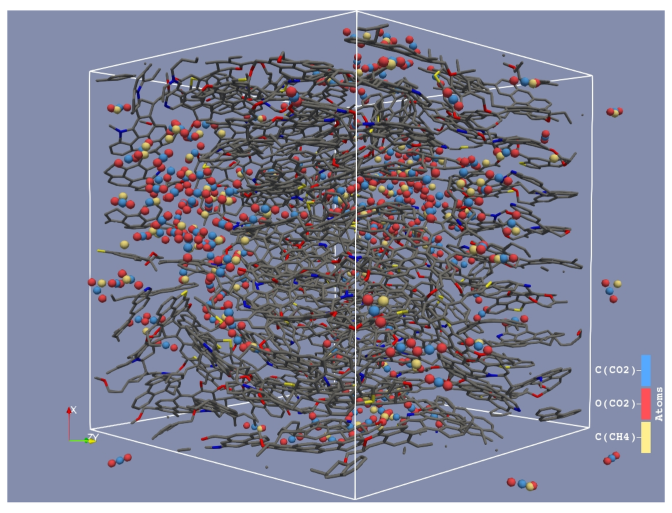
Pore size distribution using a He probe.

	Model		
	1	2	3
Bulk density [g/cm^3]	1.147	1.199	1.209
Porosity^a [%]	24	19	19
Surface area^b [m^2/g]	399	279	207
Kerogen density [g/cm^3]	1.514	1.482	1.493

^{a} He probe.
^{b} N_2 probe.

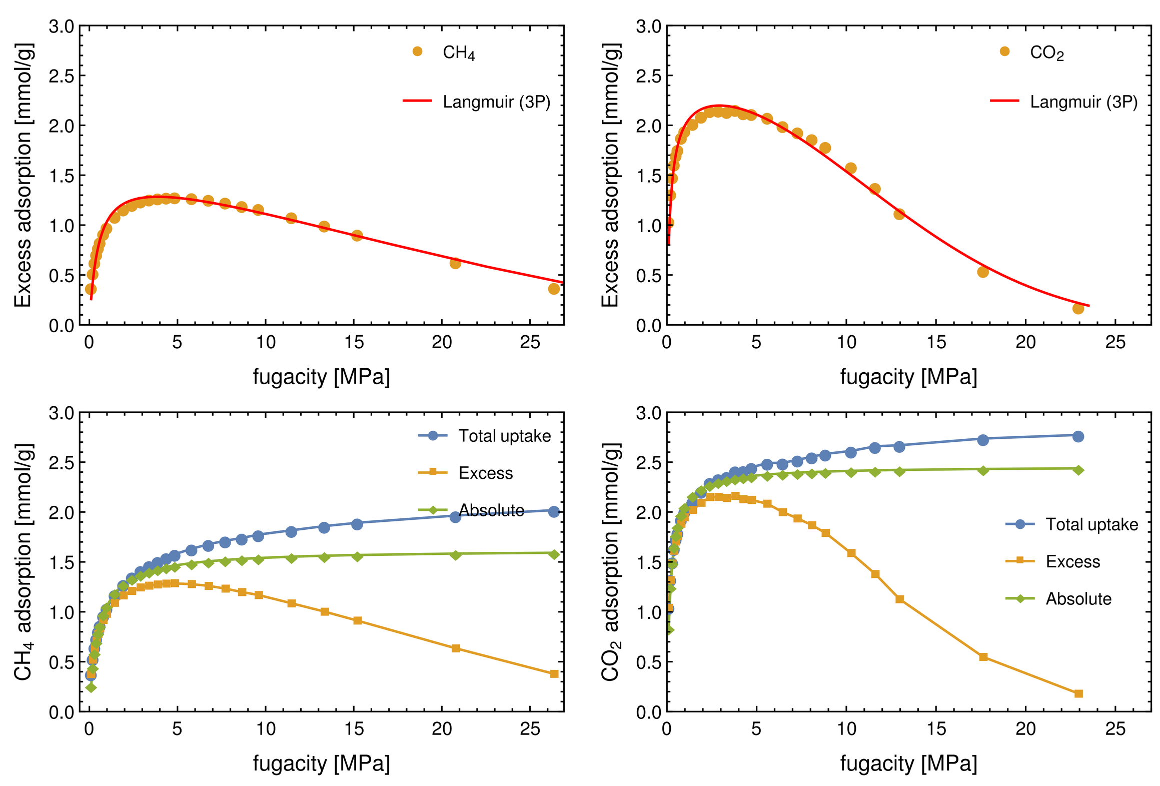
Properties usually determined experimentally in laboratory. In this work, MC simulations were carried out to mimic such experiments.

7. Uptake of CH_4 and CO_2



Comparison between methane and carbon dioxide present in kerogen at same conditions. Both gases remain in the pore space of the models, which suggests no diffusion of gas into kerogen structure. The larger uptake of carbon dioxide compared to that of methane is due to the higher density of CO_2 at those conditions and also to its larger adsorptive capacity, which would indicate the viability of CO_2 enhanced gas recovery and carbon sequestration in depleted gas shale reservoirs.

8. Results

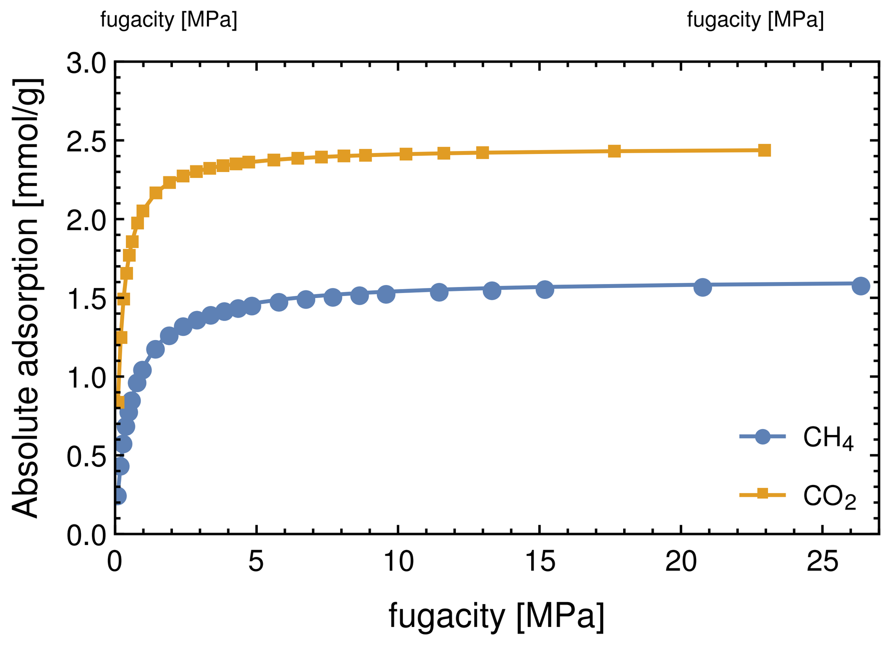


Excess adsorption curves were fitted using a modified-Langmuir model [5],

$$n_{\text{excess}} = n_L \frac{p}{p_L + p}\left[1 - \frac{\rho_b(p,T)}{\rho_{\text{ads}}}\right],$$

where n_L, p_L, and ρ_{ads} are the Langmuir volume, the Langmuir pressure, and the density of the adsorbed gas, respectively.

Gas	n_L [mmol/g]	p_L [MPa]	ρ_{ads} [g/cm^3]
CH_4	1.624	0.526	0.228
CO_2	2.444	0.189	0.792



The figure on the left is a comparison between the absolute adsorption of methane and carbon dioxide. At fugacity values above 5 MPa, carbon dioxide has approximately 1.5 times the adsorptive capacity of methane in overmature kerogen. It corresponds to the ratio of the Langmuir volumes of both gases.

9. Conclusions

This work estimates that carbon dioxide has approximately 1.5 times the adsorptive capacity of methane in overmature kerogen. Two implications might be the viability of CO_2 enhanced gas recovery and carbon sequestration in depleted gas shale reservoirs. Some additional benefits from this work are:

- the creation of realistic kerogen models using MD simulations; and
- the methodological study of a system that is difficult to isolate in laboratory.

References

[1] C. H. Sondergeld, R. J. Ambrose, C. S. Rai, and J. Moncrieff, "Micro-structural studies of gas shales," in *SPE Unconventional Gas Conference*. Society of Petroleum Engineers, 2010.

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[3] P. Ungerer, J. Collell, and M. Yiannourakou, "Molecular modeling of the volumetric and thermodynamic properties of kerogen: Influence of organic type and maturity," *Energy and Fuels*, vol. 29, pp. 91–105, 2015.

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