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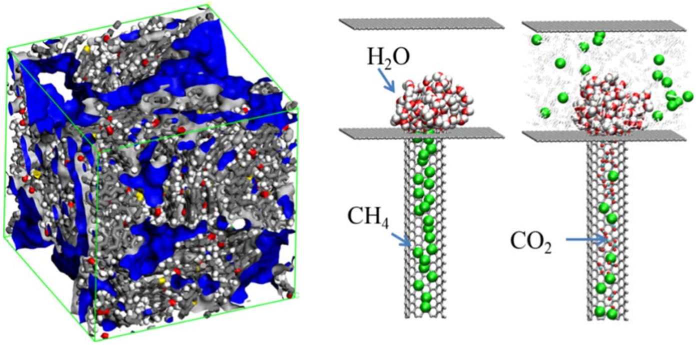
# Differential retention and release of $CO_2$ and $CH_4$ in kerogen nanopores: Implications for gas extraction and carbon sequestration

Tuan Anh Ho[a,*], Yifeng Wang[b], Yongliang Xiong[c], Louise J. Criscenti[a,*]

[a] Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185, USA
[b] Nuclear Waste Disposal Research and Analysis Department, Sandia National Laboratories, Albuquerque, NM 87185, USA
[c] Repository Performance Department, Sandia National Laboratories, Carlsbad, NM 88220, USA

## GRAPHICAL ABSTRACT



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## ABSTRACT

Methane ($CH_4$) and carbon dioxide ($CO_2$), the two major components generated from kerogen maturation, are stored dominantly in nanometer-sized pores in shale matrix as (1) a compressed gas, (2) an adsorbed surface species and/or (3) a species dissolved in pore water ($H_2O$). In addition, supercritical $CO_2$ has been proposed as a fracturing fluid for simultaneous enhanced oil/gas recovery (EOR) and carbon sequestration. A mechanistic understanding of $CH_4$-$CO_2$-$H_2O$ interactions in shale nanopores is critical for designing effective operational processes. Using molecular simulations, we show that kerogen preferentially retains $CO_2$ over $CH_4$ and that the majority of $CO_2$ either generated during kerogen maturation or injected in EOR will remain trapped in the kerogen matrix. The trapped $CO_2$ may be released only if the reservoir pressure drops below the supercritical $CO_2$ pressure. When water is present in the kerogen matrix, it may block $CH_4$ release. However, the addition of $CO_2$ may enhance $CH_4$ release because $CO_2$ can diffuse through water and exchange for adsorbed methane in the kerogen nanopores.

## 1. Introduction

Shale gas production starts with creating a fracture network by injecting a pressurized fluid in a wellbore. The induced fractures are then held open by proppant particles. During production, gas is released from the shale matrix, migrates to nearby fractures, and ultimately reaches a production wellbore [1,2]. At present, water is the most commonly used fracturing fluid. However, other fluids have also been suggested [3,4]. Carbon dioxide is of particular interest, because it would tend to adsorb to the shale matrix and displace $CH_4$. The

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[*] Corresponding authors.
*E-mail addresses:* taho@sandia.gov (T.A. Ho), ljcrisc@sandia.gov (L.J. Criscenti).

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adsorbed $CO_2$ would remain locked underground, thus curtailing greenhouse gas emissions [3]. It has been suggested that fracturing with supercritical $CO_2$ may spur the development of large-scale carbon sequestration [5]. Unlike a conventional water-based fracturing fluid, $CO_2$ may not form a trapped liquid phase around a wellbore that could potentially hinder gas production. Furthermore, because of its lower viscosity, supercritical $CO_2$ may help stimulate more complex fracture patterns, thus enhancing shale gas exploitation.

Carbon dioxide is also a major component generated during kerogen maturation in shale diagenesis [6]. Although the behavior of $CH_4$-$CO_2$-$H_2O$ in a bulk system (i.e., an unconfined system) is relatively well understood [7], much remains unknown regarding the interactions of these fluid components in nanoconfinement, as we know that shale is characterized by the predominant presence of nanometer-sized pores [8]. Here, we focus on a molecular-level understanding of $CH_4$-$CO_2$-$H_2O$ interactions in kerogen nanopores. We present molecular simulation results on the differential retention and release of $CO_2$ and $CH_4$ in heterogeneous and complex over-mature kerogen nanostructures as well as $CH_4$ displacement by $CO_2$ in single nanopores of controlled size and shape. We also investigate the impact of water on methane release with the presence or absence of $CO_2$.

## 2. Molecular modeling methods

Two approaches were used to study the interactions of $CH_4$-$CO_2$-$H_2O$ in kerogen nanopores. Monte Carlo (MC) simulations were used to study gas adsorption onto a complex kerogen structure, and molecular dynamics (MD) simulations were performed to study $CH_4$ displacement by $CO_2$ in carbon nanopores. Fig. 1A shows a simulation snapshot of the heterogeneous, complex nanoporous kerogen structure (box size of $43.5 \times 43.7 \times 44.2$ Å$^3$) that we used to study kerogen-$CH_4$ interactions in a previous paper [9,10] and also in this work. The kerogen molecules in this structure each possess the analytically-determined elemental and functional data of kerogen including the H/C, O/C, N/C, and S/C ratios, the average aromaticity, and the average size of the aromatic unit [11,12]. They are simulated using the CVFF force field [13] (a LAMMPS [14] data file containing all force field parameters for the kerogen molecule is provided in the Supplementary Material (SM)). The calculated kerogen density (1.17 g/cm$^3$), pore size distribution (4–15 Å), and methane excess adsorption are in good agreement with experimental data [9].

Grand Canonical Monte Carlo (GCMC) molecular simulations were conducted using the TOWHEE simulation package [15] to study $CH_4$ and $CO_2$ adsorption in the kerogen structure shown in Fig. 1A. Two gas adsorption scenarios were investigated: (1) adsorption of either pure $CH_4$ or $CO_2$ to determine the storage capacity of kerogen for each gas, and (2) adsorption of a 1:1 binary mixture of $CH_4$ and $CO_2$ to investigate competitive adsorption. These simulations were conducted for 8 million steps and the last 4 million steps were used to calculate the gas adsorption data reported in this work. The $CH_4$ and $CO_2$ molecules were simulated using the TRaPPE force field parameter sets [16]. In the TRaPPE force field, $CH_4$ molecules are described as united atoms and $CO_2$ is modeled as a 3-site rigid molecule. These models can reproduce the densities and the diffusion coefficients of $CH_4$ and $CO_2$ in bulk phases at the conditions simulated in this work (i.e., temperature is 338 K and pressure is up to 300 atm). In GCMC simulations, chemical potentials are required as input. Table S1 in the SM provides the chemical potentials for pure $CO_2$ and $CH_4$ at 338 K used in the Scenario 1 simulations. Table S2 in the SM provides pairs of $CO_2/CH_4$ chemical potentials that yield a 1:1 binary gas reservoir for Scenario 2. These chemical potential pairs were determined by running simulations of 1:1 binary gas using the NVT (constant number of particles, volume, and temperature) ensemble simulations using TOWHEE [15].

In the second approach, we implemented molecular dynamics (MD) simulations with the NVT (constant number of particles, volume, and temperature) ensemble using LAMMPS [14] to investigate the impact of pore size and shape on the migration of fluids from an external reservoir into and out of the kerogen pores modeled by carbon nanotubes and graphene slit pores (see Fig. 1B, C). The simulated systems consist of a reservoir connected to a carbon nanotube (CNT) (Fig. 1B) or a graphene slit-pore (Fig. 1C). The simulation box size was $41.75 \times 42.54 \times 82.34$ Å$^3$. Carbon atoms in the CNT and graphene sheet were kept rigid and simulated using the parameters proposed by Cheng and Steele [17]. The carbon atoms at the CNT opening were terminated with 6 and 8 hydroxyl (–OH) groups uniformly distributed around the rim of 0.814 and 1.085 nm CNTs, respectively. For the graphene sheet that forms the slit-pore, 9 hydroxyl groups were attached to every other carbon atom along the graphene sheet rim. These hydroxyl groups were simulated using parameters from Konatham et al.'s work [18].

These simple systems were designed because kerogen pores are irregular and bubble-like with elliptical cross sections, ranging between 5 and 500 nm in length in thermally mature shales [19]. The pore sizes (0.814 and 1.085 nm) used in these systems are within the range of the pore size distribution in kerogen determined from $CO_2$ adsorption experiments [20–22]. Although these configurations may not reflect the full chemistry of actual kerogen, they are a good approximation to kerogen nanopores since actual kerogen is also a hydrophobic material

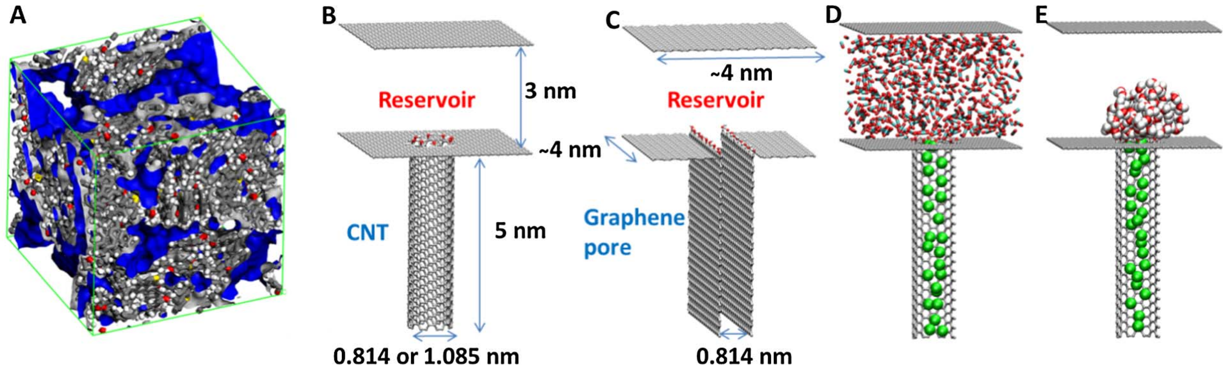

**Fig. 1.** (A) Over-mature nanoporous kerogen structure. Red, blue, yellow, gray, and white spheres represent oxygen, nitrogen, sulfur, carbon, and hydrogen atoms, respectively. Pore-volume and kerogen interface is outlined in blue (i.e., surface side facing the pore volume) and in gray (i.e., surface side facing the kerogen atoms). (B) Cylindrical carbon nanotube (CNT) connecting with a reservoir defined in between two flat graphene sheets. The pore size effect was investigated by changing CNT diameter from 0.814 nm to 1.085 nm. (C) Graphene slit-pore connecting with a reservoir. The pore shape effect was studied by comparing the results obtained for cylindrical pore (0.814 nm CNT – Fig. 1B) and for 0.814 nm graphene slit-pore (Fig. 1C). (D) Initial configuration to study the invasion of $CO_2$ (cyan-red) into the methane (green)-filled CNT. (E) Simulation snapshot represents the water (red-white spheres) blocking at the opening of CNT filled with methane molecules (green spheres). The temperature is 338 K for all simulations. Note that half of the CNT is removed to visualize the methane molecules inside. See SM for more simulation details regarding the number of molecules simulated and force field implemented. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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