Journées du GDR Hydrates de Gaz

25-27 Novembre 2025

Hôtel IBIS Styles, 22bis Rue de Trey, 25000 Besançon, France

GDR2026
Hydrates de gaz
CNRS – TotalEnergies – ENSTA - IFPEN
MINES ParisTech – BRGM – INRAE

Dear participants,

It is with great pleasure that we welcome you to the 8th annual meeting of the French Research consortium GDR2026 taking place in Besançon at Hôtel IBIS Styles, 22Bis Rue de Trey.

This event brings together leading experts in the field of Hydrate Science. Experimental, theoretical, and computational scientists will present their recent advances in Hydrate Science and their applications in the four main areas of the GDR:

- **Molecular Sciences**: to deepen our understanding of the molecular mechanisms involved in hydrates (phase equilibrium, formation/dissociation mechanisms, transport, selectivity, and molecular dynamics).
- **Process Engineering**: this theme covers technological applications such as gas storage and transport, gas or liquid effluent capture and separation, desalination and leachate treatment, as well as thermal and refrigeration applications.
- **Geosciences**: this theme addresses issues related to hydrate formation in natural sedimentary environments on continental margins and in the subsurface of polar regions.
- **Astrophysics and Planetology**: this theme focuses on the study of questions related to the formation of the primitive elements that gave rise to bodies in the solar system. It includes the study of hydrate formation from volatile compounds under extreme conditions (low temperature) and at both low and high pressures.

We express our gratitude to all the participants, speakers, and sponsors who have made this gathering possible. We wish you a pleasant stay and encourage everyone to actively engage in the discussions, explore new ideas, and forge collaborations that will drive innovation in our field.

The organizing committee:
Sylvain Picaud, Ludovic Martin-Gondre, Céline Jardin (Institut UTINAM, CNRS Université Marie et Louis Pasteur, Besançon).

The scientific committee:
Baptiste Bouillot (CNRS 5703, Mines St-Étienne), Daniel Broseta (CNRS 5150, Univ. Pau), Patrice Bordat (CNRS 5150 Univ. Pau), Livia Bove (IMPMC, UMR 7590, Sorbonne Univ.), André Burnol (BRGM, Orléans), Bertrand Chazallon (PhLAM, UMR8523, Univ. Lille), Anthony Delahaye (INRAE, Univ. Paris Saclay), Arnaud Desmedt (LLB, CEA Saclay), Olivia Fandino-Torres (Ifremer, Brest), Aurélie Guilbert-Lepoutre (Univ. Lyon 1), Jean-Michel Herri (CNRS 5703, Mines St-Étienne), Sylvain Picaud (UTINAM UMR6213, Besançon), Jeffrey Poort (UPMC Sorbonne Univ.), Anne Sinquin (IFPEN), Paolo Stringari (Mines Paris), Anh Minh Tang (ENPC, laboratoire Navier, UMR 8205), Marco Terzariol (Ifremer Brest), Gabriel Tobie (LPC, UMR 6112, Nantes).

PROGRAM – GDR Hydrates Days 2025

Tuesday 25th November 2025

14h00-14h10 Introduction

14h10-15h50: Session 1 - "Astrophysics"

14h10-14h50 – Invited Roberto BINI "The role of pressure in the reactivity of Astrochemical Ices" (Florence, Italy)

14h50-15h10 – Élodie GLOESENER "Occupancy and Density of Mixed Clathrate Hydrates in Ocean Worlds: Applications to Europa, Titan and Enceladus" (Lille, France)

15h10-15h30 – Livia Eleonora BOVE "New high density hydrates under planetary conditions" (Paris, France)

15h30-15h50 – Yevgeniy KVIRING "Glycine behavior in a cometary ice matrix" (Dijon, France)

15h50-16h00 Flash presentations for poster

16h00-16h20 Coffee break + Poster discussion

16h20-18h20: Session 2 – "Geosciences"

16h20-17h00 – Invited Andreia PLAZA-FAVEROLA "Gas Hydrate Systems on Earth: Connecting Energy, Environment, and Geosciences" (Tromsø, Norway)

17h00-17h20 – Olivia FANDINO "Mapping and Forecasting Methane Hydrate Systems in the Black Sea: Lessons to learn from the DOORS Project" (Plouzané, France)

17h20-17h40 – Art-Clarie Constant AGNISSAN "Local Geochemical Dynamics of Shallow Hydrates Bearing sediments at Active Methane Seepages in the Western Black Sea (Off Romania)" (Plouzané, France)

17h40-18h00 – Sukru MEREY "Potential of Methane Hydrates Above the Conventional Reservoir in the Sakarya Gas Field, Türkiye" (Batman, Türkiye)

18h00-18h20 – Yohan LEE "Understanding Methane Hydrate Growth in Clay Sediments" (Talence, France)

18h20-19h30: Discussion / Free time

19h30: Dinner at IBIS Styles

~21h00: Loan RENAUD's story about his Arctic adventure "Cap sur l'Arctique : 2 000 milles nautiques de recherche et d'aventure"

Wednesday 26th November 2025

9h00-10h40: Session 3 – "Molecular Sciences"

9h00-9h40 – Invited Thomas LOERTING "Amorphous Water Solutions and their Crystallization" (Innsbruck, Austria)

9h40-10h00 – Amin MOZHDEHEI "Formation and Thermodynamic Behavior of Water–THF Hydrates in Confined Mesoporous Media" (Rennes, France)

10h00-10h20 – Yuhan HUANG “Nanoscale Generation of High Pressure by TERS toward Confined Hydrate Formation” (Talence, France)

10h20-10h40 – Dounya FRAH “Hydrogen storage in mixed hydrates in porous materials: effects of perchloric acid on hydrogen incorporation” (Rueil-Malmaison, France)

10h40-11h10 Coffee break + Poster discussion

11h10-12h30: Session 4 – “Molecular Sciences (continued)”

11h10-11h30 – Victoire MEKO FOTSO “DFT Investigation of Xenon Clathrate Hydrates: structural and thermal stability” (Besançon, France)

11h30-11h50 – Sophie ESPERT “Evidence of N_2 hydrate in a filled-ice phase at high pressure combining Raman spectroscopy and DFT simulation” (Paris, France)

11h50-12h10 – Maxime LEGRAND “Accelerating molecular properties description of gas hydrates using AI-powered multi-scale simulations” (Besançon, France)

12h10-12h30 – Romane DELOFFRE “Exploring CO_2 Hydrate Molecular Dynamics with Deep Neural Network Potentials and Density Functional Theory” (Toulouse, France)

12h30-14h30: Lunch at IBIS Styles

14h30-16h10: Session 5 - “Process Engineering”

14h30-15h10 – Invited Nicolas VON SOLMS “Gas Hydrates as Energy Storage Materials and Other Applications” (Lyngby, Denmark)

15h10-15h30 – Abdelhafid AIT BLAL “A mechanistic study of CO_2 gas hydrate formation in a mesoporous zeolite” (Caen, France)

15h30-15h50 – Stefan ARZBACHER “A Low-temperature Route to Hydrate-based Carbon Capture” (Dornbirn, Austria)

15h50-16h10 – Quang-Du LE “Investigation of the Stability and Selectivity in Carbon-Based Binary Mixtures in Pure Water Clathrates and Semi-Clathrate Hydrates: Insights from In-situ Raman Spectroscopy” (Lille, France)

16h10-16h40 Coffee break + Poster discussion

16h40-18h00: Session 6 – “Geosciences (continued)”

16h40-17h00 – Peyman DEHGHANI “Influence of Injection Dynamics on Hydrate-Based CO_2 Storage in Unconsolidated Sandy Sediments” (Rueil-Malmaison, France)

17h00-17h20 – Marco TERZARIOL “Hydrate-Based CO_2 Plugging in Sandy Soils: Role of Injection Rate in Geo-Hydro-Mechanical Behavior” (Plouzané, France)

17h20-17h40 – Atanas VASILEV “Decoding Heat Flow Anomalies to Track Gas Hydrates: Danube Fan, Black Sea Case Study” (Varna, Bulgaria)

17h40-18h00 – Atousa HEIDARI “Formation Mechanisms and Thermodynamic Behavior of Complex Gas Hydrates in the Sea of Marmara via Experimental and Simulation Approaches” (Plouzané, France)

18h00-19h30: Discussion / Free time / Walk around Besançon

19h30: Dinner at IBIS Styles

Thursday 27th November 2025

9h00-10h40: Session 7 – “Molecular Sciences (continued)”

9h00-9h20 – Vincent BALLENEGGER “Free energy difference and coexistence pressure between clathrate structures II and H in methane and argon hydrates using Lattice-Switch Monte Carlo” (Besançon, France)

9h20-9h40 – Tomasz POREBA “Hydrogen storage in ice matrices at high pressure and low temperature” (Paris, France)

9h40-10h00 – Maria RESCIGNO “Giant Splitting of the Hydrogen Rotational Eigenenergies in the C_2 Filled Ice” (Rome, Italy)

10h00-10h20 – Alasdair NICHOLLS “Hydrogen Bond Symmetrisation in High-Pressure Hydrogen-Hydrate” (Paris, France)

10h20-10h40 – Loan RENAUD “Dual quantum locking: Dynamic coupling of hydrogen and water sublattices in hydrogen filled ice” (Paris, France)

10h40-11h00 Coffee break + Poster discussion

11h00-12h00: Session 7 – “Process Engineering (continued)”

11h00-11h20 – Leandro SARAIVA VALIM “Comparative Assessment of Gas Hydrate Transportability at Different Scales” (Rio de Janeiro, Brasil)

11h20-11h40 – Inès ZAIR “Microfluidic study of CO_2 hydrate crystallization: influence of wettability” (Rueil-Malmaison, France)

11h40-12h00 – Peyman DEHGHANI “CO_2 Hydrate Nucleation Study: A Novel High-Pressure Microfluidic System” (Rueil-Malmaison, France)

12h00-12h10: Concluding remarks

12h10-14h00: Lunch at IBIS Styles

END of the “GDR Hydrates” Days

List of Abstracts (Talk)

The role of pressure in the reactivity of Astrochemical Ices

D. Scelta[1,2], S. Berni[1,3], S. Romi[1,3], S. Fanetti[1,3] and R. Bini[1,2,3]

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The study of both structural properties and chemical reactivity of mixed ices plays a crucial role in astrochemistry. Interstellar and planetary ices are rarely composed of a single species; instead, they consist of complex mixtures of simple molecules such as H_2O, CO, CO_2, CH_4, CH_3OH, and NH_3. The physical structure of these mixed ices—whether amorphous or crystalline—strongly influences molecular diffusion, trapping, and the efficiency of chemical reactions triggered by photons, cosmic rays, thermal processes. Understanding how composition and morphology affect reactivity provides essential insights into the formation pathways of simple and complex organic molecules in cold astrophysical environments, shedding light on the chemical evolution of interstellar clouds and the origins of prebiotic chemistry in the early Solar System. The role of pressure in the chemistry of astronomical ices has been largely overlooked, even though it can act as a highly efficient driving force in controlling the transformation of these complex ices.

Here, we discuss two examples of pressure-driven reactivity—either induced by pressure alone or coupled with irradiation—to mimic the processes that may occur during the subduction of crustal material or when high pressure and UV irradiation act together. The formation of crystalline carbonic acid following the cold compression of CO_2 clathrate hydrate reveals unexpected intermediate steps, such as the appearance of a VHDA ice phase exhibiting remarkable thermal stability before crystallization occurs through a recently discovered metastable ice form. UV irradiation of compressed ternary mixtures containing the fundamental elements of life (C, O, H, N) has shown a rich reactivity scenario, representing far more than a merely encouraging starting point.

Occupancy and Density of Mixed Clathrate Hydrates in Ocean Worlds: Applications to Europa, Titan and Enceladus

E. Gloesener[1], M. Ciulla[2], B. Chazallon[1], M. Choukroun[3], T. H. Vu[3], A. G. Davies[3], C. Pirim[1], P. Di Profio[2], and C. Sotin[4]

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[2] *Department of Pharmacy, University "G. d'Annunzio" of Chieti and Pescara, Chieti, Italy*
[3] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States*
[4] *Université de Nantes, CNRS, UMR 6112, Laboratoire de Planétologie et Géosciences, Nantes, France*

This study examines the composition of mixed clathrate hydrates that could form in ocean worlds and assesses their potential to sink or float, contributing to the formation of a clathrate layer at the top or bottom of the internal ocean. Using a thermodynamic model based on the statistical thermodynamic approach of Van der Waals and Platteeuw [1], we evaluate the composition and density of mixed clathrate hydrates, forming in pure water systems and incorporating CH_4, CO_2 and N_2, under conditions relevant to Europa, Titan, and Enceladus. The simulations are carried out in a temperature range of 255 K to 273 K and at pressures up to several hundred MPa.

By refining constraints on the presence and composition of clathrate hydrates in ice shells, this research contributes to understanding the conditions necessary for maintaining potentially habitable subsurface liquid water reservoirs. This work provides valuable insights for interior modeling of icy bodies and supports ongoing and future missions, including JUICE, Europa Clipper, and Dragonfly.

[1] J. Van der Waals, J. Platteeuw, Adv. Chem. Phys., **2**, 1-57 (1958)

New High Density hydrates under planetary conditions

M. Rescigno[1,3], T. Poreba[1,2], A. Nicholls[1,2], L. Renaud[2], S. Espert[1,3], L. Andriambariarijaona[1], U. Ranieri[3], S. Di Cataldo[3], L. Monicelli[3], S. Berni[4], R. Bini[4], R. Gaal[2], L.E. Bove[1,2,3]
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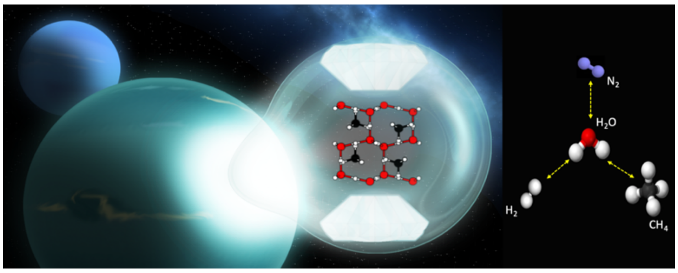
[3]Physics Department, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00196, Roma, Italy;
[4]LENS, Sesto Fiorentino, Firenze, Italy



Gas hydrates are widespread both on Earth and in extraterrestrial environments, from interstellar ices to the deep interiors of icy moons and water-rich exoplanets[1-2]. Under the p–T conditions prevailing in these bodies, clathrate hydrates progressively transform into filled-ice structures whose stability fields and properties remain largely unexplored[3-5]. Here, we present a comparative investigation of hydrogen-, methane-, and nitrogen-filled ices under extreme conditions, combining neutron and x-ray diffraction, Raman spectroscopy, and MD simulations. Our results[6-13] reveal a unified picture of the guest–host interactions governing the transitions from open clathrate frameworks to compact, hydrogen-bonded filled-ice phases, and clarify the structural relationships between the C_1–C_3 series in H_2 hydrate and the newly identified NH-V and NH-IV phases in N_2 hydrate. These findings demonstrate that simple molecular species such as H_2, CH_4, and N_2 can form stable inclusion compounds up to tens of GPa, with densities and compressibility intermediate between those of ice VII and molecular ices. The persistence of these filled-ice structures under planetary conditions has major implications for the storage and transport of volatiles in the deep interiors of icy moons and giant planets, influencing their internal stratification, and atmospheric evolution.

[1] O. Moussis et al., Space Sci Rev 174, 213 (2010); [2] I. De Paters and J.J. Lissauer, Planetary Sciences, CUP (2004) [3] L. E. Bove et al., Phil. Trans. R. Soc. A 377: 0262 (2019) ; [4] J. S. Loveday et al., Nature 410, 661 (2001) ; [5] W. L. Mao et al. Science 297, 2247 (2002) ; [6] L. Del Rosso et al., Nature Materials, 1-6 (2020) ; [7] S. Schaack et al., PNAS 116 (33) 16204-16209 (2019). [8] U. L. Ranieri, et al., PNAS 120 (52) e2312665120 (2023). [9] S. Di Cataldo, et al., PRL 133 (23), 236101 (2024). (2024). [10] L. Andriambariarijaona, et al. *Physical Review B*, 111(21), 214109 (2025). [11] L. Monacelli, et al. PRB (in press) *arXiv preprint*, arXiv:2506.13169 (2025). [12] S. Berni et al. Comm. Chemistry (submitted), arXiv:2508.09771 (2025). [13] L. Renaud et al. PNAS (submitted), arXiv:2508.09771 (2025).

Glycine behavior in a cometary ice matrix

Y. Kviring[1], J. M. Simon[1]

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The importance of comets for the origin of life on Earth has been advocated for many decades. Amino acids are key ingredients in chemistry, leading to life as we know it. The presence of volatile glycine was detected in the coma of 67P/Churyumov-Gerasimenko comet by the ROSINA mass spectrometer [1].

Here, we use molecular dynamics simulations to study the behavior of glycine molecules in a cometary ice matrix.

For our simulations, we selected crystal structures that are expected in higher layers of the comet (cubic ice, hexagonal ice, and hydrates). We present a summary of our results based on different systems: 1. Transition structure between cubic ice and hexagonal ice with and without glycine between both phases, 2. Hypothetical SII methane/glycine hydrate, with glycine located in big cages, 3. The last system consists of hexagonal ice on one side and supercooled water on the other, with and without a glycine molecule at the interface between them.

To observe the evolution of the systems, structure analysis is performed using the CHILL+ algorithm, and the Q4 parameter (in case of ice). It reveals that glycine can be trapped and diffuse in a hexagonal ice matrix by displacing water molecules in the structure, see Fig. 1. In the case of hydrates, analysis shows a weak effect of glycine on the cages. The structure is slightly deformed, but overall stable.

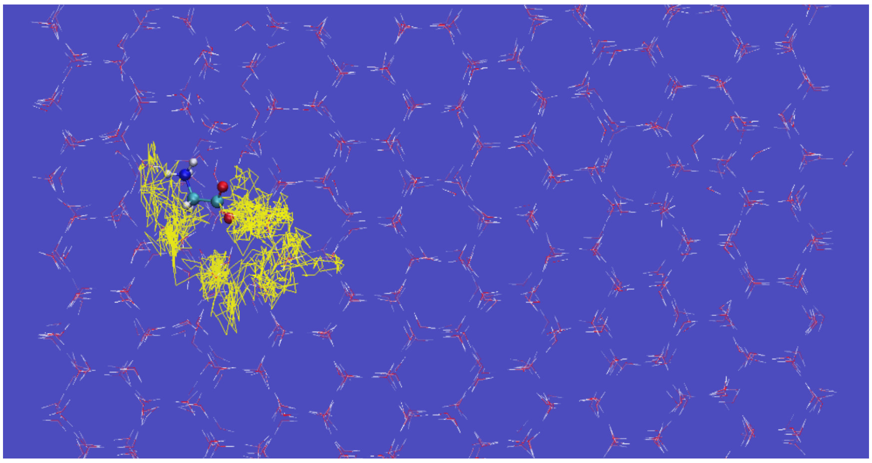

FIG. 1: Trace of glycine diffusion in the hexagonal ice matrix.

References:

[1] K. Altwegg, H. Balsiger, A. Bar-Nun, et al., Sci. Adv., 2, e1600285 (2016).

Gas Hydrate Systems on Earth: Connecting Energy, Environment, and Geosciences

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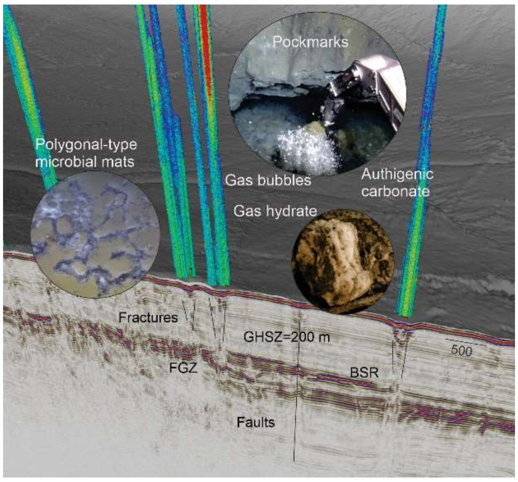
Gas hydrates were first identified in the 19th century through experimental chemistry. Nearly a century later, their presence was documented in natural gas pipelines, marking a pivotal discovery that demonstrated gas hydrates can form naturally under specific physical conditions. This finding laid the foundation for the study of gas hydrates in natural environments. Over the past century, geoscientific research has significantly advanced our understanding of the geological and physical processes that govern gas hydrate dynamics in marine environments, lakes, and permafrost regions. Today, gas hydrates have been documented across every continent, and are considered one of the largest methane reservoirs on Earth (e.g., [2] and references therein). In this talk, I will present a journey through natural gas hydrate systems, highlighting key physical and geological factors that influence their formation. Using a range of case studies, I will synthesize major geoscientific indicators of gas hydrates and discuss their implications for energy, environmental systems (ecosystems, resource management, geohazards), and climate. This comprehensive overview will provide insights into how critical gas hydrates could be to our planet's energy and environmental dynamcis. ***Figure:*** A gas hydrate system in the Fram Strait. The gas hydrate stability zone (GHSZ) is recognized by a bottom simulating reflection (BSR) and associated fee gas zone (FGZ). Pockmarks, seeps, authigenic carbonate concretions and microbial mats are all common components of a gas hydrate system in continental margins.



[1] Hammerschmidt, E., Formation of gas hydrates in natural gas transmission lines. Industrial & engineering chemistry, 1934. 26(8): p. 851-855. [2] Collett, T., et al., *Methane Hydrates in Nature, Current Knowledge and Challenges.* Journal of chemical & engineering data, 2015. **60**(2): p. 319-329.

Local Geochemical Dynamics of Shallow Hydrates-Bearing sediments at Active Methane Seepages in the Western Black Sea

C. Agnissan[1], O. Fandino[1], V. Riboulot[1], R. Haidar[2], T. Giunta[1], A. Crémière[1], B. Chazallon[2], C. Pirim[2], C. Brandily[3], J.P. Donval[1], X. Philippon[3], A. Desmedt[4], L. Ruffine[5]

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The Romanian continental margin in the western Black Sea hosts numerous active methane seepages and gas hydrate accumulations, thermodynamically stable at water depths greater than 720 m. Their occurrence has been inferred from seismic surveys [1] and directly confirmed by coring [2]. During the GHASS 2 cruise [3], several hydrate-bearing cores were recovered from two sites where faults system facilitate focused upward migration of methane-rich fluids, promoting sub-seabed hydrate formation: the Hydrate Ridge Crest (HRC)[1, 4] and a newly mapped mud volcano. In this study, we combined field observations with geochemical analyses of pore-water, sediment and hydrate samples using a large variety of instruments to characterize hydrate distribution, composition and formation dynamics. Gas hydrate appears to formed by filling subparallel fractures, as networks of interconnected veins, or agglomerated nodules, resulting from the combined effect of fine-grained sediment properties and the fractures system. At the HRC, two cores collected only ~20 m apart display contrasting chloride profiles: one showing a negative anomaly consistent with hydrate dissociation and associated pore-water freshening ; and the other exhibits a positive anomaly indicating recent or active hydrate formation, supported by *in situ* temperature and pore pressure measurements[4]. At the mud volcano site, the hydrates contain mainly CH_4 with traces of hydrogen sulfide (H_2S), suggesting interplays between hydrate formation and the anaerobic methane oxidation coupled to sulfate reduction (AOM-SR) taking place just on the top of the hydrate occurrence zone. This work demonstrates strong local spatial heterogeneity in shallow hydrate dynamics within the Romanian sector of the Black Sea, offering new valuable insights into hydrate-fluid-sediment interactions governing methane rich-seeps and hydrate systems.

1. S. Ker, Y. Thomas, V. Riboulot, N. Sultan, C. Bernard, C. Scalabrin, G. Ion and B. Marsset, Geochemistry, Geophysics, Geosystems 20 (1), 442-459 (2019).
2. B. Chazallon, C. T. Rodriguez, L. Ruffine, Y. Carpentier, J. P. Donval, S. Ker and V. Riboulot, Marine and Petroleum Geology 124, 104785 (2020).
3. V. Riboulot, S. Dupré and S. Ker, GHASS2 cruise report (2021).
4. N. Sultan, V. Riboulot, S. Dupré, S. Garziglia and S. Ker, Journal of Geophysical Research: Solid Earth 129 (11), e2024JB030253 (2024).

Mapping and Forecasting Methane Hydrate Systems in the Black Sea: Lessons to learn from the DOORS Project

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The H2020 DOORS project delivered the first integrated, cross-border assessment of methane hydrate systems in the Black Sea through a multidisciplinary approach combining geophysics, geochemistry, and microbiology. High-resolution seismic data, supported by sediment coring and pore-water analyses, revealed extensive hydrate accumulations along the continental slopes of the northwestern, central, and eastern basins—particularly offshore Romania, Bulgaria, and Turkey. These deposits are spatially associated with fault networks and focused methane fluxes, defining the most active hydrate provinces within the regional gas hydrate stability zone[1]. The total methane inventory is estimated at several gigatons of carbon, confirming the basin's major role as a natural methane reservoir[2].

A predictive susceptibility model was developed to forecast hydrate occurrence and stability under variable thermobaric regimes[3]. Integrating bathymetry, geothermal gradients, sediment porosity, and dissolved methane concentrations, the model identifies areas of maximum hydrate potential and regions most sensitive to temperature or pressure perturbations—key for evaluating climate-driven dissociation risks.

Geochemical and microbiological analyses revealed a strong coupling between hydrate dynamics and anaerobic oxidation of methane. Hydrate-bearing sediments showed pronounced sulfate and chloride anomalies, high alkalinity, and abundant ANME-1/2 archaea and sulfate-reducing bacteria, demonstrating the dual control of fluid geochemistry and microbial metabolism on methane turnover. By linking physical parameters, chemical gradients, and biological processes, the DOORS project provides a comprehensive understanding of methane storage and transformation in the Black Sea[4]. This integrated framework establishes a reference for assessing hydrate-related carbon cycling and for predicting the physico-chemical responses of hydrate systems to ongoing ocean warming and basin stratification changes.

[1] S. Ker, Y. Thomas, V. Riboulot *et al.*, Geochem. Geophys. Geosyst. **20** (1), 442 (2019).
[2] B. Kvamme and A. Vasilev, Energies **16** (3), 1223 (2023).
[3] V. Iemelianov, O. Ivanik, T. Kukovska *et al.*, Frontiers in Earth Science **Volume 13 - 2025** (2025).
[4] O. Fandino, A.C Agnissan, O. Ivanik, *et al.* First Assesment of Gas Hydrate Abundance and Slope/Seafloor Stability, Deliverable no 4.7 - DOORS project. (2025).

Potential of Methane Hydrates Above the Conventional Reservoir in the Sakarya Gas Field, Türkiye

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Methane hydrates, crystalline compounds that trap gas molecules within water-ice lattices, represent a major unconventional energy resource in both permafrost and marine environments. Over the past two decades, countries such as Japan, China, and India have advanced extensive research and pilot production programs to assess their hydrate potential. Türkiye, seeking to reduce dependence on imported natural gas and meet its growing energy demand, has focused recent exploration on the Black Sea, where conventional and unconventional gas systems coexist. Despite consuming around 50 billion m³ of natural gas annually, domestic production supplies less than one percent of demand, motivating offshore exploration initiatives led by the Turkish Petroleum Corporation (TPAO) since 2017. The Sakarya Gas Field, discovered in 2020 by the Tuna-1 well, marked a major milestone. The well encountered over 100 m of gas-bearing Pliocene–Miocene sands and additional deeper zones totaling 405 bcm of recoverable gas. Subsequent drilling, including Amasra-1, expanded the field's proven reserves to about 710 bcm—the largest offshore discovery in Türkiye. Rapid infrastructure development followed, including subsea production systems, a 169 km export pipeline, and onshore processing facilities at Filyos Port. First gas in 2023 positioned Türkiye to meet up to 30 % of its domestic demand from the Black Sea. Above these deep conventional reservoirs lies a geologic setting highly favorable for methane hydrate formation. Multiple indicators—gas seeps, mud volcanoes, bottom-simulating reflections, and recovered samples—confirm hydrate-bearing layers within the Bottom Hydrate Stability Zone extending roughly 0–500 m below the seafloor. The proximity of these hydrate zones to existing Sakarya infrastructure provides a cost-effective opportunity for future hydrate exploration and pilot production. Together, these developments establish the Sakarya region as a natural laboratory for advancing both conventional gas exploitation and methane-hydrate research, supporting Türkiye's long-term energy security and offshore resource sustainability.

Understanding Methane Hydrate Growth in Clay Sediments

Yohan Lee[1], *Constant Art-Clarie Agnissan*[2], *Antoine Patt*[3], *Yuhan Huang*[1], *Junkyu Lim*[4], *Yongwon Seo*[4,5], *Laurent Michot*[6] *and Arnaud Desmedt*[1,7]

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Methane hydrates occurring in clay-rich marine sediments are of increasing scientific and environmental interest because their distribution and formation/dissociation strongly depend on mineral-water interactions. In clay-rich systems, the presence of swelling clays introduces additional complexity, as both inter-particle and interlayer domains can host water with different activity and mobility. Smectite clays, in particular, undergo crystalline and osmotic swelling, generating interlayer space where water-gas equilibria and molecular transport may substantially deviate from those in bulk conditions. Despite extensive work on hydrate formation in sandy sediments, the mechanisms of nucleation and growth within swelling clays remain poorly understood. This study was conducted to investigate methane hydrate formation within various clay matrices under high-pressure, low-temperature conditions representative of marine environments. Raman spectroscopy and neutron scattering techniques were used to monitor structural and compositional evolution during hydrate growth. Special attention was given to how the degree of swelling and interlayer water structure influence the kinetics of hydrate formation. The observations reveal significant differences in hydrate development between kaolinite systems and Na-bentonite systems, highlighting the critical role of water migration. These experimental insights contribute to a more detailed understanding of methane hydrate behavior in clay-rich sediments and provide a foundation for interpreting natural hydrate occurrences in fine-grained, low-permeability reservoirs.

Amorphous Water Solutions and their Crystallization

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Clathrate Hydrates are often formed from the liquid solution by freezing or from crystalline ice by taking up gas from the atmosphere. In this contribution the focus is on the crystallization of clathrates from amorphous aqueous solution by heating. This encompasses the crystallization of cubic structure I and cubic structure II clathrate hydrates at 130-200 K by heating vapor-deposited amorphous ice [1-4]. Two cases are distinguished, where the amorphous solid contains irreversibly trapped guests or where pure amorphous solid water is heated in the presence of a gas atmosphere. In both cases the crystallization starts from a low-density deposit.

It further encompasses crystallization from the high-density amorphous solution, which is made by pressure-amorphization [5,6]. In this way even exotic clathrate hydrates may crystallize, for instance a monoclinic clathrate, which features a single space filling cage [7] or a chiral filled ice [8]. Finally, the impact of HDA-VHDA polyamorphism on amorphous solutions and clathrate hydrates is addressed [9].

[1] C. Mitterdorfer, M. Bauer, T. Loerting, Phys. Chem. Chem. Phys. **13**, 19765 (2011).
[2] A. Hallbrucker, E. Mayer, Icarus, **90**, 176 (1991).
[3] A. Hallbrucker, E. Mayer, J. Chem. Soc., Faraday Trans. **86,** 3785 (1990).
[4] A. Hallbrucker, E. Mayer, J. Chem. Soc., Chem. Commun. 749 (1989).
[5] M. Bauer, D. M. Többens, E. Mayer, T. Loerting, Phys. Chem. Chem. Phys. **13**, 2167 (2011).
[6] L.R. Fidler, P. Posch, J. Klocker, T. Hofer, T. Loerting, J. Chem. Phys. **160**, 194504 (2024).
[7] L.R. Fidler, M. Bauer, S. Arzbacher, T. Loerting, in preparation (2025).
[8] B. Massani, C. Mitterdorfer, T. Loerting, J. Chem. Phys. **147,** 134503 (2017).
[9] P. H. B. Brant Carvalho, T. Loerting, U. Haeussermann et al., Phys. Chem. Chem. Phys. **25,** 14981 (2023).

Formation and Thermodynamic Behavior of Water–THF Hydrates in Confined Mesoporous Media

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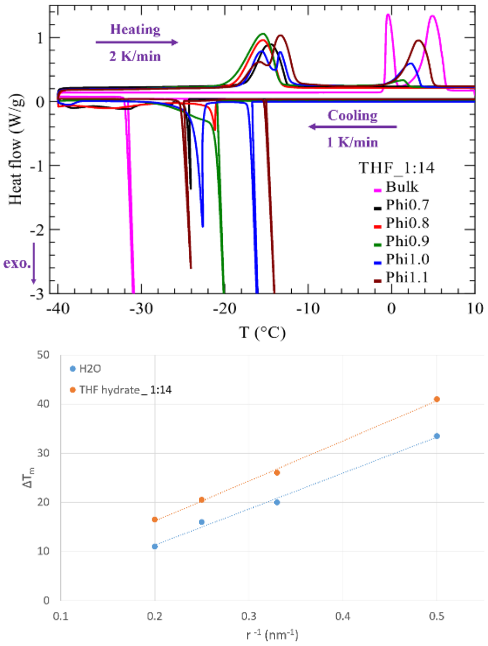
At atmospheric pressure and temperatures below 5°C, tetrahydrofuran (THF) forms a structure II hydrate, a crystalline phase analogous to natural gas hydrates that normally require high pressure. Owing to this property, THF serves as an ideal model system for studying hydrate formation and dissociation mechanisms under laboratory conditions. However, the factors influencing the initial formation of hydrates in water–THF mixtures have not yet been systematically investigated. In such systems, hydrate precursors may emerge in supercooled water–THF solutions, as suggested by cluster nucleation theory, though direct experimental confirmation remains limited. When confined within nanoporous materials, the nucleation, growth, and dissociation of hydrates can deviate markedly from bulk behavior because of capillary and interfacial effects.

This study examines the formation and thermodynamic behavior of water–THF hydrates under confinement, focusing on the influence of solution composition, cooling rate, and the presence of excess solution outside the pores on hydrate nucleation within mesoporous media. To do so, Differential Scanning Calorimetry (DSC) was used to study THF–water mixtures with molar ratios of 1:11, 1:14, 1:16, and 1:17, both in bulk and confined states. SBA-15 silica (pore radius ≈ 4 nm) served as the confinement medium. The influence of filling ratio ($\phi = 0.7–1.1\ cm^3/g$) and cooling rate (0.5 and 1 $K.min^{-1}$) was systematically examined, and melting point shifts were interpreted via the Gibbs–Thomson relation.

Top panel shows DSC thermograms highlighting the key role of filling ratio. No hydrate formed when $\phi \leq 0.9$, whereas for $\phi \geq 1.0$, a distinct dissociation peak near –13°C confirmed hydrate formation within SBA-15. Increasing THF content enhanced stability, while at 1:17, hydrates were completely absent, indicating strong dependence on local composition. Slower cooling (0.5 $K.min^{-1}$) promoted larger peak with higher enthalpy, showing more ordered hydrate structures. As shown in down panel, the melting point depression under confinement followed the Gibbs–Thomson prediction. Overall, the interplay between filling ratio, cooling rate, and THF concentration governs hydrate nucleation and dissociation, supporting the view that precursors evolve differently under confinement than in bulk systems. *(Funding: ANR project ANR-22-CE50-0002)*



(Top panel) DSC thermograms for the 1:14 THF–water mixture confined in SBA-15 mesoporous silica, showing the pronounced effect of the filling ratio (ϕ) on hydrate formation within the pores. (Down panel) Observed melting-point depression of the water and 1:14 THF–water mixture as a function of pore size, following the Gibbs–Thomson prediction.

Nanoscale Generation of High Pressure by TERS toward Confined Hydrate Formation

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Understanding how clathrate hydrates form and transform under confinement remains a major challenge, as nanoscale pressure and interfacial effects critically influence their phase stability and molecular organization [1]. Conventional high pressure methods reproduce bulk conditions but cannot directly probe or control local environments where hydrate nucleation may occur.

Tip-enhanced Raman spectroscopy (TERS) combines atomic force microscopy with optical enhancement, providing simultaneous topographic and spectroscopic information at nanoscale [2,3]. Beyond optical imaging, the TERS tip can serve as a nanoscale press, capable of generating localized pressures up to several tens of gigapascals while monitoring vibrational responses in situ.

We demonstrate this approach on suspended graphene and single-wall carbon nanotubes, showing systematic Raman redshifts with increasing tip force, allowing an estimation of the local stress generated by the tip. These results confirm that TERS enables the generation and measurement of nanoscale pressure conditions comparable to those relevant for hydrate formation, offering a new platform for probing and controlling hydrate nucleation and transformation under nanoconfinement.

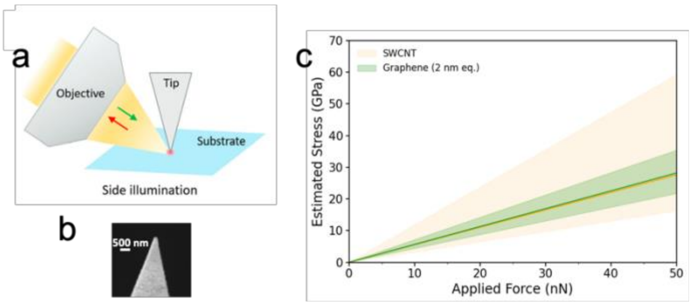

Figure 1: (a) Illustration of the TERS setup in side-illumination geometry. (b) Representative SEM image of a typical gold-coated TERS. (c) Estimated local stress as a function of applied force for suspended graphene and SWCNT.

References

[1] Both AK, Gao Y, Zeng XC, Cheung CL, Gas Hydrates in Confined Space of Nanoporous Materials: New Frontier in Gas Storage Technology, *Nanoscale* (2021); **13**, 7447–7470.

[2] Schmid T, Opilik L, Blum C, Zenobi R, Nanoscale chemical imaging using tip-enhanced Raman spectroscopy: a critical review, *Angew Chem Int Ed Engl.* (2013); **52**, 5940-5954

[3] Bonhommeau S, Cooney G S, Huang Y, Nanoscale chemical characterization of biomolecules using tip-enhanced Raman spectroscopy, *Chem. Soc. Rev.* (2022); **51**, 2416-2430

Hydrogen storage in mixed hydrates in porous materials: effects of perchloric acid on hydrogen incorporation

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Hydrogen (H_2) is gaining attention as a fuel for future heavy transport, but its storage remains challenging, especially for medium-scale facilities such as refueling stations. Its small molecular size leads to leakage, its liquefaction requires extremely low temperatures (-253 °C), and its low density necessitates compression above 500 bar, making conventional storage methods costly and limited [1].

One promising approach to facilitate H_2 use is storage in the form of hydrates. Pure H_2 hydrates are only stable at very high pressures (3000 bar, 6 °C) [2]. The addition of co-promoters such as tetrahydrofuran (THF) and acidic additives like perchloric acid ($HClO_4$) can stabilize hydrates under milder conditions (70 bar, 0 °C) [3]. $HClO_4$ promotes the incorporation of molecular H_2 into the hydrate structure and doubles the H_2 diffusion coefficient [3]. Another strategy to ease the stability conditions of mixed H_2 hydrates involves confinement within porous materials, such as activated carbon [4], which increases the interface creation.

However, calorimetric experiments have shown that $HClO_4$ provides little to no improvement, sometimes even a negative effect, on the thermodynamic stability of H_2/THF mixed hydrates (results previously presented at the GDR Hydrates 2024 days). After this thermodynamic study, the project focused on evaluating the H_2 storage capacity and conversion aspects. Since calorimetry does not provide precise information on hydrate composition, it is difficult to assess this aspect using the enthalpy changes. Therefore, we turned to another approach: Raman spectroscopy, using mapping to investigate H_2 distribution within the hydrates.

The objectives are to evaluate the role of $HClO_4$ and to investigate the combined influence of $HClO_4$ and porous silica in promoting H_2 incorporation into H_2/THF mixed hydrates. The results show that in the presence of acidic additives and porous media, $HClO_4$ mainly enhances H_2 incorporation, while silica promotes the creation of interfaces. Their combined effect leads to the highest H_2 hydrates to THF hydrates ratios.

Références
[1] N.N. Nguyen, Energy & Fuels, 37 (14) (2023), 9771-9789. [2] W.L. Mao et al., Science (80-.) 297 (2002) 2247 LP –2249. [3] T. T Nguyen et al., Frontiers in Chemistry, 8, (2020), 550862. [4] Farrando-Perez J, et al., Nature Communications. 13, (2022), 5953.

DFT Investigation of Xenon Clathrate Hydrates: structural and thermal stability

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Clathrate hydrates are a class of inclusion compounds in which guest molecules such as noble gases or small organic compounds are trapped within cages formed by a hydrogen-bonded water framework. The ability to encapsulate gases in a solid matrix makes clathrate hydrates an attractive option for hydrogen storage, especially given that water is inexpensive and abundantly available compared to other proposed storage media[1]. However, achieving efficient hydrogen storage under practical thermodynamic conditions often requires the presence of a promoter. Xenon, for instance, has been shown to significantly enhance the stability of clathrate hydrates, with experimental data indicating stability up to temperatures of approximately 65°C[2]. This makes xenon a promising candidate for hydrogen storage applications.

Density Functional Theory (DFT) simulations were performed using vdW-DF2 and revPBE-D3(0) functionals to analyze lattice dynamics and thermodynamic stability of xenon clathrate hydrates. Results showed good agreement of revPBE-D3(0) with experimental values. Preliminary simulations involving H_2 insertion within xenon-filled cages reveal pressure-dependent occupancy preferences, with certain being favored at low pressures while others are preferred under higher-pressure conditions.

[1] Gupta A., Baron G.V., Perreault P., Lenaerts S., Ciocarlan R-G, Cool P., Mileo P.G.M., Rogge S., Van Speybroeck V., Watson G., Van der Voort P., Houllebergh M., Breynaert E., Martens J., Denayer J.F.M.,. Hydrogen Clathrates: Next Generation Hydrogen Storage Materials. *Energy Storage Mat.* **41**, 69-107 (2021).
[2] Yuri A. Dyadin, Eduard G. Larionov, Tamara V. Mikina and Lyubov I. Starostina,. Clathrate formation in Kr–H_2O and Xe–H_2O systems under pressures up to 15 kbar. *Mendeleev Commun*. **7**, 74–75 (1997).

Evidence of N_2 hydrate in a filled-ice phase at high pressure combining Raman spectroscopy and DFT simulation.

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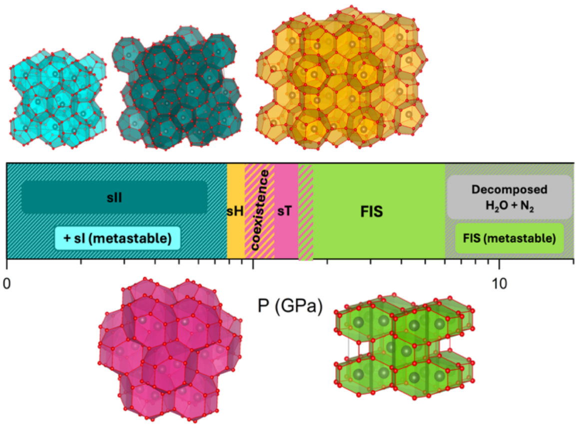

Structural transition sequence of nitrogen hydrate at ambient temperature as a function of pressure.

Gas hydrate are found in a wide range of environments on Earth and beyond – from icy-moon to exoplanet [1-4]. The pure N_2 hydrate structure has not been as extensively investigated as the methane one [5,6], especially over pressure [7]. We map the high-pressure phase diagram of nitrogen hydrate up to 16 GPa at room temperature by combining Raman spectroscopy, and crystal structure prediction using USPEX software with quantum espresso (and neutron diffraction). We reveal a rich sequence of structural transformations, from sI/sII clathrates to hexagonal (sH) and tetragonal (sT) phases, culminating in a previously unknown orthorhombic filled-ice structure above 1.8 GPa in the Pnma space group, which we designate as NH-V. This new phase cannot be indexed to any known ice frameworks such as the high-pressure methane hydrates MH-III (Imma) or MH-IV (Pmcn) [8]. Our results [9] refine the understanding of nitrogen hydrate behavior under extreme conditions and demonstrate the propensity of N_2 and H_2O to form stable filled-ice structures up to 16 GPa, with important implications for planetary science [10].

[1] O. Moussis et al., Space Sci Rev 174, 213 (2010). [2] I. De Paters and J.J. Lissauer, Planetary Sciences, CUP (2004). [3] L. E. Bove et al., Phil. Trans. R. Soc. A 377: 0262 (2019) ; [4] J. S. Loveday et al., Nature 410, 661 (2001) ; [5] S. Schaack et al., PNAS 116 (33) 16204-16209 (2019). [6] L. Andriambariarijaona, et al. *Physical Review B*, 111(21), 214109 (2025). [7] C. Petuya et al. J. Physical Chemistry C, 122, 566–573, (2018). [8] J. Loveday et al. Canadian J. Physics, 81, 1-2, 539–544, (2003). [9] S. Berni et al. Comm. Chemistry (submitted), arXiv:2508.09771 (2025). [10] G. Tobie et al. Titan: interior, surface, atmosphere, and space environment, 29 62, (2014).

Accelerating molecular properties description of gas hydrates using AI-powered multi-scale simulations

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Understanding guest diffusion and structural transitions in gas hydrates is key to assessing their potential for gas storage and separation. While Density Functional Theory (DFT) methods has become of choice, they are computationally expensive: calculating a single energy barrier encountered by a guest between two cages can take up to a week, making such methods impractical for large-scale studies, and some properties (such as guest diffusion) cannot be accessed for this reason.

A first solution involves using DFT-derived barriers in Kinetic Monte Carlo [1] (KMC) models to reach larger time and space scales, but this approach struggles with more complex compositions. A promising solution is the development of Machine Learned Interatomic Potentials [2] (MLIPs), which retain high accuracy while enabling fast, scalable simulations across a broad range of hydrate compositions.

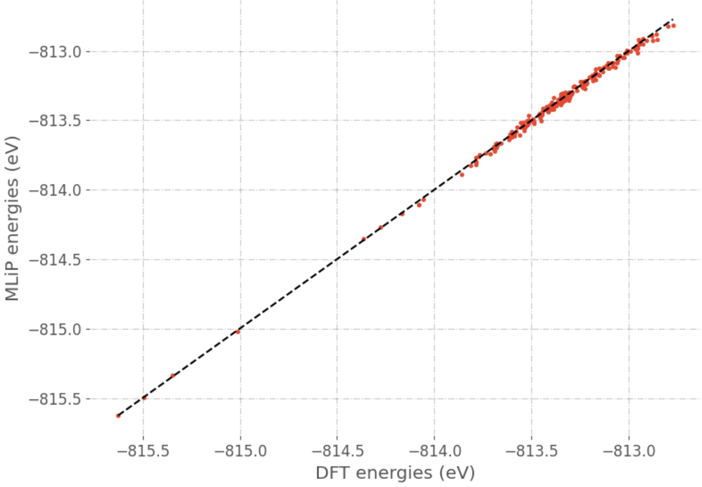

Figure 1: Comparison between DFT energies and PBE-trained MLiP predictions on a 4ns long NVT simulation of sI N_2 gas hydrate at 200K.

[1] Chu et al., Diffusion of Methane in sI Hydrates: A Kinetic Monte Carlo and Theoretical Study, J. Phys. Chem., **123**, 17 (2019)
[2] Liu et al., Phase Transitions of Zirconia: Machine-Learned Force Fields Beyond Density Functional Theory, Phys. Rev., **105**, 6 (2022)

Exploring CO_2 Hydrate Molecular Dynamics with Deep Neural Network Potentials and Density Functional Theory

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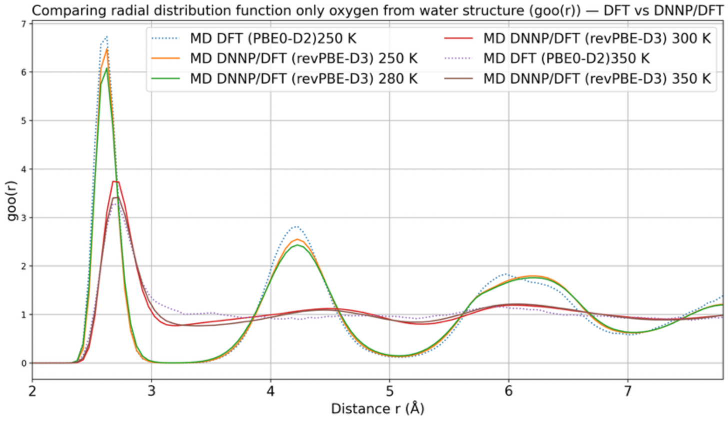

Figure 1: Radial distribution function of O–O in MD (NVT ensemble) with DNNP at the DFT level (revPBE-D3, solid lines), compared with MD-DFT (PBE0-D2, dotted lines)

Gas hydrates are of great interest to the scientific community due to their potential hazards, their energy and environmental applications. However, their study poses significant computational challenges, as these systems are large and exhibit complex behaviors under varying thermodynamic conditions. Capturing their weak intermolecular interactions with both accuracy and efficiency remains difficult. Density Functional Theory (DFT) is the most reliable method for describing their stability, but its high computational cost restricts large-scale simulations. Efforts such as the parametrization of Density-Functional based Tight Binding (DFTB) by Nicolas CINQ [1] have improved computational efficiency, though at the expense of accuracy compared to DFT. To overcome this limitation, Deep Neural Network Potentials (DNNPs) have emerged as a reliable alternative. In this work, we train a DNNP to reproduce DFT-level potential energies for CO_2 hydrates. Using the trained model, we perform molecular dynamics simulations that achieve both high accuracy and computational efficiency. These findings highlight the potential of DNNPs as a powerful tool for modeling more complex properties of gas hydrate, in particular phase diagrams, and more complex systems : multi-gas hydrates and water/hydrate interfaces, paving the way for efficient and accurate large-scale simulations.

Keywords: Gas hydrates, deep neural network potentials, molecular dynamics

References:

[1] N. Cinq, A. Simon, F. Louisnard, and J. Cuny, “Accurate SCC-DFTB Parametrization of Liquid Water with Improved Atomic Charges and Iterative Boltzmann Inversion,” *The journal of physical chemistry. B*, vol. 127, no. 35, pp. 7590–7601, (2023)

[2] Z. Jinzhe, Z. Duo, L. Denghui, M. Pinghui, L. Zyu and al « DeePMD-kit v2: A software package for deep, » *The journal of physical chemistry* vol. 159, no. 5, pp. 05480 (2023)

Gas Hydrates as Energy Storage Materials and Other Applications

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We present some of our activities in gas hydrates science and technology - most recently how gas hydrate capsules might be used for underground mechanical energy storage. We emphasize the importance of gas hydrate fundamentals - in particular gas hydrate thermodynamics - as an approach to understanding and exploiting gas hydrate properties and their potential applications.

In gas hydrate systems with potentially four phases, the underlying thermodynamic model is crucial to the accurate representation of phase equilibrium in the system. We present a cubic plus association (CPA) equation of state which can accurately model phase equilibrium in the system water-THF-cyclopentane-hydrate-nitrogen-CO_2. CPA is combined with a van der Waals-Plaatteuw model for the solid phase with parameters obtained from a Kihara potential approach.

Results for CO_2 storage and natural gas production from hydrates will also be presented

A mechanistic study of CO_2 gas hydrate formation in a mesoporous zeolite

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Carbon Capture, Utilization, and Storage (CCUS) is vital for mitigating climate change and advancing a low-carbon energy transition. Among emerging solutions, hydrate-based CO_2 sequestration (HBCS) provides a sustainable and compact route for long-term CO_2 storage.[1] However, its slow nucleation and growth kinetics remain major obstacles. In this study, we employ the first mesoporous zeolite, **ZMQ-1**,[2] featuring 2.3 nm-wide channels, as an environmentally friendly scaffold to accelerate CO_2 hydrate formation. Systematic adsorption and hydrate formation experiments were conducted on pre-humidified ZMQ-1 at **275 K** and pressures up to **3 MPa**, using both **calcined (open-pore)** and **as-synthesized (blocked-pore)** forms. Hydrate formation was confirmed through CO_2 vibrational features identified by **FTIR spectroscopy**. Remarkably, the calcined ZMQ-1 exhibited an **ultrafast induction time of only 2 minutes** at an optimal water-to-zeolite ratio (**Rw = 2**), compared to over 100 minutes for the non-calcined form. The resulting CO_2 storage capacity reached **151 wt.% (≈176 Vg/Vw)**, achieved under mild conditions (1.3 MPa, 275 K). Pressure-time and CO_2-uptake analyses further reveal that open porosity promotes efficient gas diffusion and hydrate growth at the solid–liquid interface. These findings highlight the dual role of ZMQ-1 as both a **structural template** and a **kinetic promoter**.

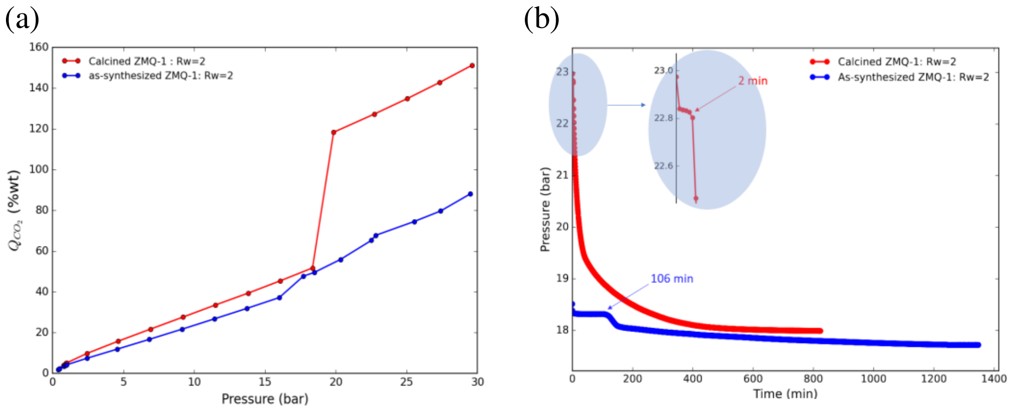

Figure 1. (a) show the CO_2 uptake isotherms of calcined and as-synthesized ZMQ-1 at Rw = 2. (b) show the Pressure–Time profiles for calcined and as-synthesized ZMQ-1 at Rw = 2.

[1] A.N. Rehman, C.B. Bavoh, R. Pendyala, Research Advances, Maturation, and Challenges of Hydrate-Based CO_2 Sequestration in Porous Media, **ACS Sustainable Chem Eng,** 2021; 9 (45),15075–15108.
[2] P. Lu, J. Xu, Y. Sun, R. Guillet-Nicolas, T. Willhammar, M. Fahda, E. Dib, B. Wang, Z. Qin, H. Xu, J. Cho, Z. Liu, H. Yu, X. Yang, Q. Lang, S. Mintova, X. Zou, V. Valtchev, A stable zeolite with atomically ordered and interconnected mesopore channel, **Nature,** 2024, 636, 368–373.

A Low-temperature Route to Hydrate-based Carbon Capture

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Hydrate-based carbon capture (HBCC) can, in principle, combine high CO_2 capacity, benign materials, and low-temperature regeneration. However, long induction times, slow growth, and demanding operating conditions have limited practical viability—typically necessitating thermodynamic or kinetic promoters. Here we present a promoter-free, low-temperature HBCC route that uses pressure swing operation in a fixed bed of ice stabilized with fumed silica [1]. The packed bed's large specific surface area provides abundant heterogeneous nucleation sites and short diffusion paths, while sub-zero operation shifts the vapor–ice–hydrate (V–I–H) equilibrium towards moderate pressures and high CO_2 selectivity. We demonstrate bench-scale performance through semi-batch, batch, and continuous experiments, and provide new equilibrium data for mixed CO_2–N_2 hydrates at 233–260 K. At 233 K and 40 bar, the outlet CO_2 mole fraction from a 15 mol% feed falls to 2.5 mol% in semi-batch operation; in continuous pressure-swing cycles at the same conditions, we achieve a split fraction of 70% with a specific energy consumption below 3.0 $GJ \cdot tCO_2^{-1}$. The process exhibits short or vanishing induction times after initial cycling (memory effect), reproducible formation rates over many cycles, and progressive improvement of kinetics at $T \leq 253$ K, consistent with a pore network that develops during repeated ice–hydrate transitions. Rate analysis shows capture scales with the difference between feed and equilibrium gas compositions and benefits from residence-time control, offering clear levers for scale-up. Despite conservative assumptions and the absence of promoters, the measured key performance indicators are comparable to state-of-the-art capture benchmarks, while preserving process simplicity and environmental compatibility. These results establish a practical, low-temperature pathway to hydrate-based carbon capture that merits accelerated pilot-scale development.

[1] E. Eder, M. Kadinger, S. Hiller, S. Arzbacher, Sep. Purif. Technol., **361**, 3 (2025)

Investigation of the Stability and Selectivity in Carbon-Based Binary Mixtures in Pure Water Clathrates and Semi-Clathrate Hydrates: Insights from In-situ Raman Spectroscopy

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The growing concern over CO_2, CO, and N_2 emissions calls for efficient post-combustion gas separation technologies. Steel industries, in particular, release large CO-, CO_2-, and N_2-rich gas volumes. Hydrate-based carbon capture and sequestration (HBCCS) offers a promising alternative by exploiting the intrinsic molecular selectivity of clathrate hydrates toward different gas species. Building on previous CO_2–N_2 studies using tetra-n-butyl ammonium bromide (TBAB) semi-clathrate hydrates [1], this work investigates CO–N_2 mixtures (10–100% CO) in canonical clathrates (pure water) to evaluate the effects of gas composition on hydrate formation and selectivity. Complementary experiments are conducted in TBAB-containing systems to assess potential promoter-induced modifications of hydrate behavior.

CO–N_2 mixtures with varying CO concentrations (10–100%) were investigated to assess selectivity in canonical clathrates (pure water) under conditions relevant for industrial applications. The gas mixtures were brought into contact with liquid water at room temperature, and hydrate formation was induced by vigorous mechanical stirring (~300 rpm) and rapid cooling within the hydrate stability field. Hydrate formation and evolution were monitored using optical visualization and in-situ micro-Raman spectroscopy. The N_2 and CO stretching modes were identified at ~2325 cm^{-1} and ~2137 cm^{-1}, respectively, with corresponding redshifts of approximately 5 cm^{-1} and 6 cm^{-1} relative to the equilibrated gas phase. The relative integrated peak areas were used to derive selectivity parameters at equilibrium.

Compared with CO_2–N_2 systems [2], the CO–N_2 hydrates showed nearly constant selectivity across concentrations, indicating limited compositional differentiation between gas and hydrate phases. This weak selectivity arises from the similar equilibrium pressures of CO and N_2 hydrates and their competitive cage occupancy. The effect of TBAB on structural stability and selectivity is analyzed and compared with CO_2–N_2–TBAB results under equivalent conditions.

References

[1]. Rodriguez, C. T., Du Le, Q., Focsa, C., Pirim, C., & Chazallon, B. (2020). Influence of crystallization parameters on guest selectivity and structures in a CO2-based separation process using TBAB semi-clathrate hydrates. Chemical Engineering Journal, 382, 122867.
[2]. Chazallon B, Pirim C. Selectivity and CO2 capture efficiency in CO2-N2 clathrate hydrates investigated by in-situ Raman spectroscopy. Chem Eng J 2018;342: 171–83. https://doi.org/10.1016/j.cej.2018.01.116.

Influence of Injection Dynamics on Hydrate-Based CO_2 Storage in Unconsolidated Sandy Sediments

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CO_2, as a major greenhouse gas, is a critical concern, and one strategy for its storage after capture is hydrate-based sequestration in marine sediments, which is currently under investigation as a promising technique. This study presents the results of an experiment conducted at IFPEN as part of the CO2BHYS project. A custom-designed cell, filled with sand to simulate realistic porosity and permeability, was used. After water saturation, CO_2 was dynamically injected into the cell. CT scanning was employed to characterise the internal state of the cell at different stages, including after sand packing, saturation, hydrate formation, and hydrate dissociation. This imaging technique reveals the distribution patterns of hydrates inside the porous medium. By correlating these CT scan results with real-time pressure and flow data, the study offers quantitative insights into hydrate distribution and preferential formation zones, highlighting differences in hydrate accumulation between the upper and lower parts of the cell. These results highlight how injection dynamics affect hydrate-based CO_2 storage and reveal key conditions for long-term stability in marine sediments.

Hydrate-Based CO_2 Plugging in Sandy Soils: Role of Injection Rate in Geo-Hydro-Mechanical Behavior

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Carbon dioxide (CO_2) is a major greenhouse gas, and hydrate-based sequestration in marine sediments offers a promising complementary storage solution due to its high density and stability. Alternatively, such a solution is also considered as a secondary carbon storage option that could mitigate potential reservoir leaks from a conventional geological storage at higher temperature in a supercritical state (*e.g.* depleted hydrocarbon reservoirs or saline aquifers). The effectiveness of this approach, however, depends on the interplay between CO_2 plume velocity and hydrate formation kinetics. In this study, we present the preliminary results of the tests performed in IFREMER as experimental part of the CO2BHYS project funded by TotalEnergies (research consortium between BRGM, IFPEN and IFREMER). We test the hypothesis that the efficiency of hydrate plug formation in sandy, uncemented sediments is controlled by the velocity of buoyancy-driven CO_2 migration. We conducted six long-term injection experiments (~140 h each) at different CO_2 flow rates while monitoring mechanical waves, flow rates, and sample volume. Following injection, we performed drained shear strength tests under triaxial conditions to assess the geomechanical behavior after plug formation. Our findings show that at low flow rates, hydrate formation was sufficiently rapid to create an effective permeability barrier. At higher flow rates, plugging required more time to develop; however, a greater quantity of CO_2 hydrate was formed, resulting in increased overall strength. These results emphasize the critical role of injection dynamics in hydrate-based CO_2 storage and provide new insights into the conditions necessary for secure, long-term containment in marine sediments.

Decoding Heat Flow Anomalies to Track Gas Hydrates: Danube Fan, Black Sea Case Study

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This study presents integrated theoretical and field-based investigations conducted under the Bulgarian Science Fund project GEOHydrate (Geothermal Evolution of Marine Gas Hydrate Deposits – Danube Paleodelta, Black Sea). The primary objective of GEOHydrate is to investigate the relationship between gas hydrate formation and in situ heat flow (HF) anomalies in seafloor sediments, particularly in the Danube Fan region of the Black Sea.

The project tests the hypothesis that gas hydrate deposits (GHDs) are associated with measurable temperature and heat flow (T&HF) anomalies at the seafloor. By characterizing these anomalies, GEOHydrate aims to reconstruct the 4D (spatiotemporal) evolution of hydrate systems.

The multidisciplinary dataset integrates 2D and 3D seismic, controlled-source electromagnetic (CSEM) surveys, in situ heat flow measurements, scientific drilling and downhole logging, and physicochemical analysis of bottom sediments and pore waters. These data originate from earlier EU and international collaborations, including BLASON, ASSEMBLAGE, GHASS, and German-led hydrate research programs SUGAR I–III, and are now further developed in the ongoing EU project DOORS.

The research employs advanced seismic interpretation, geothermal forward/inverse modeling, and basin analysis techniques. A novel geothermal workflow for hydrate detection and resource estimation is proposed, aiming to improve signal-to-noise ratios and reduce exploratory and production costs through better well targeting and strategic field development.

Outcomes contribute to three critical global challenges: climate change mitigation, clean energy development, and affordable energy access. With the Danube Fan identified as one of the most promising European gas hydrate provinces, this research is particularly relevant for the future energy security of Bulgaria and Romania.

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Formation Mechanisms and Thermodynamic Behavior of Complex Gas Hydrates in the Sea of Marmara via Experimental and Simulation Approaches

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Gas hydrate deposits in the Sea of Marmara (SoM) were discovered at ~660 m water depth on the Western High, where the seafloor temperature is ~15 °C [1, 2]. These hydrates, located along the seismically active North Anatolian Fault, contain high concentrations of non-methane hydrocarbons, particularly propane (18.6 mol%) and isobutane (9.2 mol%) [1, 3]. To understand the mechanisms controlling the formation and stability of these hydrates, we investigated the kinetic and thermodynamic behaviour of complex gas hydrates in the SoM using an integrated approach combining high-pressure experiments, molecular dynamics (MD) simulations, and thermodynamic modeling.

High-pressure stirred-cell experiments coupled with gas chromatography enabled the measurement of key kinetic parameters including induction time, formation rate constant, gas consumption, and water-to-hydrate conversion from gas mixtures with a composition similar to collected gas bubbles. Complementary MD simulations reproduced the conditions of the kinetic experiments to study how gas composition and pressure, as a driving force, influence hydrate growth. The results showed strong agreement between simulations and experiments, connecting molecular insights with laboratory observations.

This work allowed the built of a new and accurate dataset of hydrate equilibrium conditions for binary, ternary, and multicomponent gas mixtures. Comparison with the CSMGem model showed good agreement with the SoM gas mixture (3.0% deviation) but more significant deviations with the other complex mixtures. Consequently, a modified Carnot model was optimised from the available data, and this led to excellent agreement between experiments and models.

Both experimental and simulation results revealed that propane and isobutane have key roles in accelerating hydrate formation but limit the overall conversion due to their early depletion. Moreover, thermodynamic results showed that the hydrate stability zone of hydrate deposits in SoM extends up to 17.3 °C, reduced by ~1 °C under seawater salinity. These results deepen our understanding of the complex gas hydrate behavior in the Sea of Marmara.

[1] Ruffine, L., et al., Multiple gas reservoirs are responsible for the gas emissions along the Marmara fault network. Deep Sea Research Part II: Topical Studies in Oceanography, 153: p. 48-60 (2018).

[2] Bourry, C., et al., Free gas and gas hydrates from the Sea of Marmara, Turkey: Chemical and structural characterization. Chemical Geology, 264(1-4): p. 197-206 (2009).

[3] Ruffine, L., et al., Multidisciplinary investigation on cold seeps with vigorous gas emissions in the Sea of Marmara (MarsiteCruise): Strategy for site detection and sampling and first scientific outcome. Deep Sea Research Part II: Topical Studies in Oceanography, 153: p. 36-47 (2018).

[4] Ruffine, L., et al., Geochemical dynamics of the natural-gas hydrate system in the Sea of Marmara, offshore Turkey (2012).

Free energy difference and coexistence pressure between clathrate structures II and H in methane and argon hydrates using Lattice-Switch Monte Carlo

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The thermodynamic stability of a clathrate structure at given pressure, temperature, and guest composition is determined by its free energy. We investigate the free energy difference between structures II and H in methane and argon hydrates to predict the most stable structure as a function of pressure and to determine the coexistence pressure. Accurate predictions of clathrate phase stability are important in various contexts, such as evaluating gas hydrate inhibitors or identifying stable structures under the high-pressure conditions found in the interiors of icy planetary bodies [1, 2].

At fixed composition, the most stable phase is the one with the lowest Gibbs free energy G. When the gas pressure – and hence the gas chemical potential μ_g – is imposed, the number of guest molecules depends on μ_g and the host structure. In this case, the relevant thermodynamic potential is $\Gamma(N_w, \mu_g, P, T) = G - \mu_g N_g$, and the most stable phase is the one with the lowest value of Γ. We computed the free energy difference $\Delta\Gamma$ between structures II and H for methane and argon hydrates as a function of pressure using Lattice-Switch Monte Carlo (LSMC) simulations [3]. Our combined grand-canonical and LSMC approach fully accounts for the pressure dependence of cage occupancies, the volume changes driven by both changing pressure and concurrent variations in cage occupancy, and the entropy difference between the two competing clathrate phases. The LSMC method provides a more direct route to computing ΔG between crystalline phases than the thermodynamic integration technique. Here, it is applied to gas hydrates for the first time. Because LSMC requires corresponding numbers of molecules in the two phases, we first determine ΔG for identical compositions (e.g., both structures II and H with all cages singly occupied). We then relax this constraint by allowing variable occupancies, thereby transitioning from G to Γ without approximation. This second step reveals a large entropic contribution for the sH phase, which shifts the coexistence pressure between structures II and H by a significant amount.

[1] J.S. Loveday and R. J. Nelmes, Phys. Chem. Chem. Phys., 10, 937–950 (2008);
[2] S. Berni et al, arXiv:2508.09771 (2025)
[3] O. Moro, *Relative thermodynamic stability of clathrate structures from molecular simulations*, Ph.D. thesis, University of Bristol and Univ. Marie et Louis Pasteur (to be submitted)

Hydrogen storage in ice matrices at high pressure and low temperature

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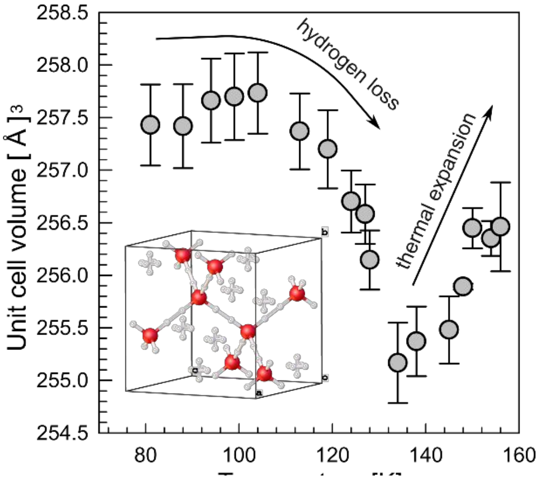

Figure 1. Unit cell volume variation during thermal decomposition of C2 hydrogen hydrate tracked with neutron powder diffraction (D20 at ILL). Inset: contents of the unit cell of C2 (oxygen in red)

Hydrogen hydrates (HH) are promising functional materials as an alternative to the current cryo-compressed hydrogen storage technology. HH clathrate sII phase transitions into to the so-called "filled ice" forms above 0.8 GPa. In filled ice, the water frame assumes one of the known ice phases, and hydrogen occupies definite positions in the ice channels. Up to ~3 GPa, five different phases have been reported, with increasing hydrogen-to-water ratio [1-2].

It has been shown that the C2-form of hydrogen hydrate ($H_2O \cdot H_2$/ $D_2O \cdot D_2$), which is constituted of cubic ice I_c skeleton, transforms into pure cubic ice I_c releasing molecular hydrogen upon decompression at 100 K [3]. However, the mechanism and kinetics of C2 hydrogen loss is not well-defined. It was suggested to progress through sample amorphization, though no evidence of an amorphous intermediate state was observed by neutron diffraction. We have recently determined, via high-pressure neutron powder diffraction experiments, that the unit cell volume of the C2 phase- produced in a Paris-Edinburgh (PE) cell at 3 GPa, and then recovered at ambient pressure and 78 K - continuously decreases upon heating above 100 K at ambient pressure. This indicates, at least partial, controlled hydrogen release without loss of crystallinity up to 130 K at ambient pressure. Additionally, we present insights into structural deformation, phase boundaries, hydrogen content and mechanisms of formation of C2 under extreme pressure and/or low-temperature conditions.

[1] Ranieri, U. et al. PNAS, 120, 52 (2023).
[2] Hirai, H. et al. Prog Earth Planet Sci 10, 3 (2023)
[3] Komatsu, K., Machida, S., Noritake, F. et al. Nat Commun 11, 464 (2020)

Giant Splitting of the Hydrogen Rotational Eigenenergies in the C_2 Filled Ice

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At pressures above 0.1 GPa and below 0.5 GPa, mixtures of water and hydrogen molecules crystallize in a nonstoichiometric clathrate compound in the sII phase. At low temperatures, the quantum motion of the “encaged” guest H2 molecules has been experimentally characterized, the anisotropy in the hydrogen-water interaction potential has been shown to be effective in splitting the quantized translational and rotational energy levels; however, such splittings are rather small, indicating a weak guest-host interaction. At pressures above 0.5 GPa, hydrogen hydrates adopt so-called “filled ice” phases, in which the water sublattice adopts the structure of one of the low pressure polymorphs of ice, stabilized at high pressure by the gas molecules. The C2 phase (stable above 2.5 GPa) is formed by two identical and interpenetrated ice-Ic-like sublattices, with a 1:1 hydrogen to water molecular ratio.

In this study we have employed a combination of computational and experimental techniques to characterize the rotational quantum dynamics of hydrogen confined in the C2 filled ice phase [1]. We solved the 3D Schrödinger’s equation for a hydrogen molecule in the effective crystal field of the C2 phase. We then employed Incoherent Inelastic Neutron Scattering at high pressures (3.4 and 6 GPa) and cryogenic temperatures, on the IN5 beamline at ILL (Grenoble).

We observed that the crystal field lifts the angular degeneracy of the rotational triplet state (l =1) with respect to the magnetic quantum number m, resulting in an experimental energy splitting of ±2.2 meV, in good agreement with the prediction of ±3.2 meV.

These findings underscore the pivotal role of hydrogen-water interactions in dictating the rotational behavior of the hydrogen molecules within the C2 phase and indicate heightened van der Waals interactions compared to other hydrogen hydrates.

[1] S. Di Cataldo, M. Rescigno, L. Monacelli , U. Ranieri, R. Gaal, S. Klotz, J. Ollivier, M. Marek Koza, C. De Michele, L.E. Bove, Phys. Rev. Lett. 133, 236101 – 2024

Hydrogen Bond Symmetrisation in High-Pressure Hydrogen-Hydrate

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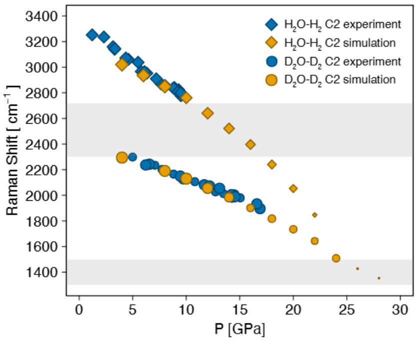

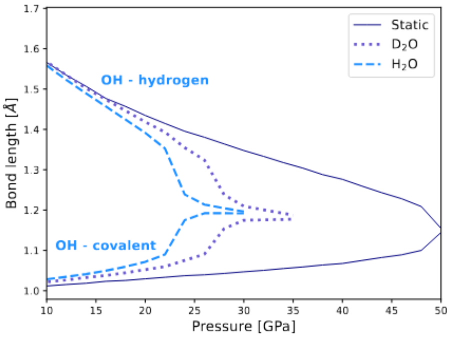

Hydrogen bond symmetrisation (HBS) is a fundamental, pressure-induced transformation in hydrogen-bond network systems, where the distinction between the donor and the acceptor sites vanishes, resulting in a symmetric hydrogen-bond. HBS has been studied extensively in the pure ice case, most notably in the high-pressure ice VII to ice X transition[1-4]. However, it remains less well characterised in the high-pressure phases of Hydrogen-Hydrate (HH). Here is presented our work on HBS in the high-pressure phases of HH, C2 and C3[5-7]. We used Raman spectroscopy as well as first-principles quantum atomistic simulations to study this effect in both hydrogenated (H_2-H_2O) and deuterated (D_2-D_2O) HH. Our results reveal that the quantum fluctuations and the interaction between the encaged H_2 molecules and the host water lattice play a crucial role in driving the symmetrisation process. We find that hydrogen bond symmetrisation occurs at a much lower pressure than in pure ice without any change in the crystal symmetry. Overall, our findings provide new insight into the complexity of hydrogen-bonded systems at high-pressures.[8]

[1] K. Aoki *et al.*, *Phys Rev B* 54, 15673-15677 (1996); [2] A. F. Goncharov *et al.*, *Science* 273 5272, 218-220 (1996) [3] P. Pruzan *et al.*, *Journal of Phys. Chem. B* 101, 6230-6233 (1997); [4] K. Komatsu *et al.*, *Nature Comm.* 15, 5100 (2024); [5] U. L. Ranieri, et al., PNAS 120 (52) e2312665120 (2023); [6] S. Di Cataldo *et al.*, PRL 133 (23), 236101 (2024); [7] K. Loshkin *et al.*, PRL 93, 125503 (2004) [8] L. Monacelli *et al.*, PRB *accepted* (2025)

Dual quantum locking: Dynamic coupling of hydrogen and water sublattices in hydrogen filled ice

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Hydrogen hydrates (HH), particularly the C2 phase, offer a rich platform to investigate the quantum coupling between hydrogen molecules and the water lattice under extreme pressures. This talk focuses on the theoretical exploration of pressure- and temperature-driven phase transitions in HH, specifically examining molecular rotation, orientational ordering, and hydrogen bond symmetrization within a quantum mechanical framework. Using a combination of computational techniques, including path-integral molecular dynamics (PIMD) and quantum embedding methods we explore the structural transformations and quantum effects at play. The results, supported by experimental data from Raman spectroscopy and synchrotron X-ray diffraction, reveal the emergence of quantum-induced ordering and a nematic phase at much lower pressures than in pure hydrogen. Our ongoing work with MLIP enables us to extend this exploration to larger and more complex systems, facilitating more accurate simulations and deeper insights into the behavior of hydrogen-rich quantum materials, particularly for hydrogen storage.

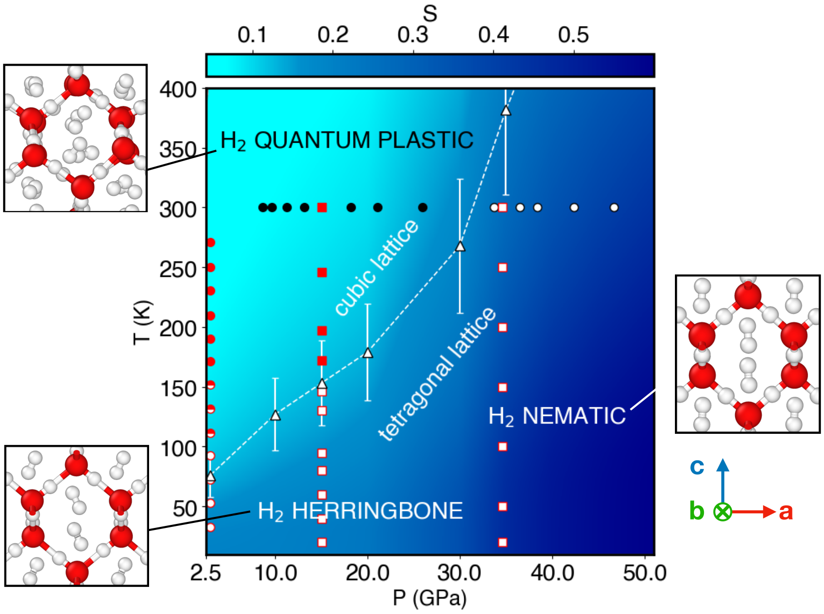

Fig 1 - Pressure-Temperature phase diagram of the C2 hydrogen hydrate, combining quantum embedded calculations and experimental data. XRD data (circles) and Raman measurements (squares) are shown, with symbols indicating cubic (filled) and tetragonal (open) phases. The background color represents the H2 orientation factor S, and white triangles with error bars correspond to simulations. Dashed lines highlight the cubic-to-tetragonal transition. Insets show DFT-optimized geometries for the quantum plastic, herringbone, and nematic phases.

[1] L. Renaud, T. Poreba et al. *Submitted paper* (2025)

Comparative Assessment of Gas Hydrate Transportability at Different Scales

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A common challenge faced by oil and gas operators is the formation of gas hydrate blockages in production lines. There is no consensus on the methodologies and apparatus used to assess gas hydrate blockage risk, and extrapolating laboratory results to field conditions remains a significant challenge. This highlights the importance of comparing different techniques and experimental scales. This study aims to investigate the influence of key variables, such as shear, gas-liquid ratio, water cut, salinity, subcooling, gas composition, and wax content, on gas hydrate transportability at different scales. From an industrial perspective, the objective is to determine the most effective technique for translating laboratory data into field-scale applications. To this end, three experimental setups are employed: a high-pressure rheometer, a rock-flow cell, and a pilot-scale flow loop.

References:

[1] Sloan E. D.; Koh, C. A. Clathrate hydrates of natural gases. Third ed. Taylor & Francis Group (2008).
[2] Cardoso, C. A., Gonçalves, M. A., & Camargo, R. M. (2015). Design options for avoiding hydrates in deep offshore production. Journal of Chemical & Engineering Data, 60(2), 330-335.
[3] Valim, L. S. Simulação fluidodinâmica da misturação de correntes líquidas aplicada à injeção de inibidores termodinâmicos de hidratos de gás, UFRJ/COPPE (2018).
[4] Kakitani et al. Measurements of Hydrate Formation Behavior in Shut-In and Restart Conditions, Energy Fuels. 33, 9457-9465 (2019).
[5] Lino, Luiz Henrique Meneghel, et al. "Transportability of hydrate slurry in the presence of wax." Chemical Engineering Science (2025): 122031.

Microfluidic study of CO_2 hydrate crystallization: influence of wettability

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Climate change, primarily driven by anthropogenic greenhouse gas (GHG), of which CO_2 constitute more than 70%, has become a central issue to the global energy policy [1]. In the context of the growing energy demand, implementing global actions to reduce emissions, such as energy transition, improving energy efficiency and developing Carbon Capture, Utilization and Storage technologies (CCUS) is essential to achieve the carbon neutrality [2] [3]. Among these solutions, carbon storage in depleted oil and gas reservoirs appears particularly promising due to the presence of naturally confining and well characterized geological structures [4].

However, the feasibility of this technology depends on the thermodynamics properties of the CO_2. During injection, the CO_2 expansion leads to a temperature drop (Joule-Thomson effect), promoting the formation of hydrates that may obstruct the rock pores and reduce permeability, thereby compromising the injectivity and the storage safety [5]. To better understand these phenomena, microfluidics offers and innovative experimental method, enabling the replication of pressure and temperature conditions at a small scale, while observing the hydrates formation and growth with a high spatial and temporal resolution [6].

This study aims to investigate CO_2 hydrate crystallization using microfluidics, comparing the formation kinetics when CO_2 is either liquid or gaseous form within hydrophilic and hydrophobic microfluidics chips. The objective is to evaluate the influence of interface wettability on nucleation and growth mechanisms, providing new insights into the risk of clogging and contributing to the safe and efficient geological storage of CO_2.

[1] J. Godin et al., Journal of Environmental Chemical Engineering, 9(4), (2021), 105644. [2] P. Jean-Baptiste et al., Comptes Rendus Géoscience, 335, (2003), 611–625. [3] H. Yang et al., Energies, 17, (2024), 5983. [4] E. Hanson et al., Results in Surfaces and Interfaces, 18, (2025), 100381. [5] C. Chesnokov et al., Advances in Water Resources, 190, (2024), 104758. [6] X. Li et al., Chemical Engineering Science, 308, (2026), 122568.

CO_2 Hydrate Nucleation Study: A Novel High-Pressure Microfluidic System

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Large-scale Carbon Dioxide (CO_2) storage in geological reservoirs (depleted oil and gas reservoirs, deep saline aquifers, and coal seams) is a promising approach for mitigating greenhouse gas emissions and addressing climate change. In the case of depleted oil and gas reservoirs, the success of such a storage will depend on various factors, among which the efficiency of CO_2 injection, particularly in the near-wellbore region, where flow rates are high. In this area, a decrease in pressure close to adiabatic conditions may lead to cooling Joule-Thomson effects and induce CO_2 hydrate formation. This hydrate formation can significantly reduce injectivity and jeopardise on-site well operations.

This work aims to investigate the likelihood of CO_2 hydrate formation during CO_2 injection into depleted reservoirs and evaluate the related kinetics. The selected approach consists of conducting laboratory-scale pore-scale experiments using a microfluidic chip to investigate hydrate nucleation in numerous CO_2 droplets/bubbles. The investigation specifically focuses on understanding the impact of different parameters, such as salinity and subcooling temperature. The pore-scale experiments employ the IFPEN® microfluidic platform to investigate the formation of CO_2 hydrates (liquid/gas) under pressure and temperature conditions relevant to the near-wellbore region during CO_2 storage in depleted reservoirs (Dehghani et al. 2025).

Dehghani, P.; Sinquin, A.; Gland, N.; Lécolier, E.; Ruffine, L.; Tang, A. M. "CO_2 Hydrate Nucleation Study: Novel High-Pressure Microfluidic Devices." Lab on a Chip, 2025, 25, 2903–2917. DOI:10.1039/D4LC01102C

List of Abstracts (Poster)

A Kinetic Description of Hydrate Systems Using Operator-Based Linearization Approach

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In this work, we extend the Delft Advanced Research Terra Simulator (open-DARTS) to include hydrate formation / dissociation modelling using the Operator-Based Linearization (OBL) approach. Hydrate-bearing porous media are modelled using a thermal–compositional–reactive formulation with governing equations for mass and energy conservation, where hydrate is represented as an immobile solid phase occupying pore space and reducing porosity and permeability. The kinetic model assumes instantaneous equilibrium between fluid phases but a non-equilibrium hydrate phase. Hydrate formation and dissociation are driven by the fugacity difference of water in fluid and hydrate phases, following an Arrhenius-type relation. The OBL method represents nonlinear physical processes via algebraic interpolation operators, precomputed in a discrete parameter space to avoid repeated flash calculations. A hybrid equation-of-state approach is used together with a modified van der Waals–Platteeuw model for hydrate, and Gibbs energy surface analysis confirms that, in the limit, kinetic and equilibrium models converge to the same thermodynamic conditions.

We applied the model at both core- and field-scale. For core-scale CH_4 hydrate formation in sand packs, the simulator reproduced spatial heterogeneity in hydrate saturation and matched experimental observations. For field-scale hydrate dissociation in a radial reservoir, we considered thermal stimulation and depressurization and reproduced characteristic dissociation behaviour. We also reproduced a core-scale CO_2 injection experiment, demonstrating flexibility beyond methane hydrates. This framework provides a tool for investigating hydrate-related risks in CO_2 sequestration operations and the feasibility of methane production from hydrate reservoirs.

Gaussian approximation potential models to predict *ab initio* quality structural and thermodynamic properties in gas hydrates

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While Density Functional Theory (DFT) is often considered the method of choice to describe molecular systems, it remains impractical for extracting long-term kinetic and thermodynamic properties. Indeed, DFT simulations are typically limited to a few picoseconds and a few hundred atoms. A common workaround is to use classical molecular dynamics, but at the cost of reduced accuracy.

A promising alternative lies in the development of Machine-Learned Interatomic Potentials (MLiPs) trained on *ab initio* data [1]. Such approaches overcome the cost–accuracy tradeoff, delivering *ab initio*-level accuracy while being nearly as fast as classical molecular dynamics. Using Gaussian Approximation Potential (GAP) models [2], it is now possible to predict structural and thermodynamic properties of gas hydrates. In this work, the model is trained on PBE data and applied to the sI N_2 gas hydrate to extract bond lengths, angles, phonon spectra, and the heat capacity at constant volume.

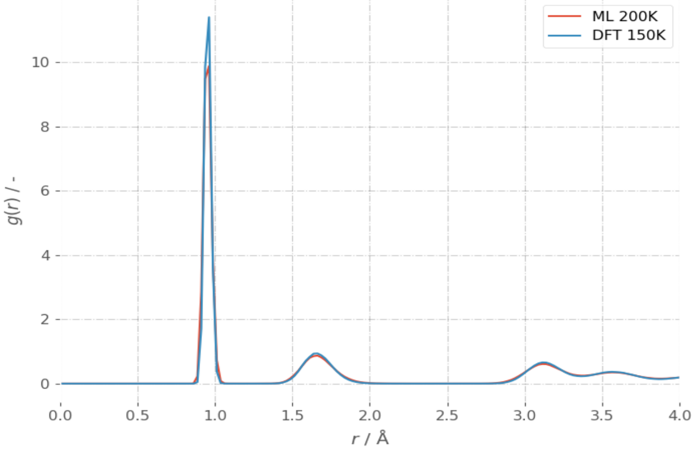

Figure 1: DFT and predicted radial distribution function (RDF) of O-H bonds within N_2 sI gas hydrate.

[1] Jinnouchi et al., On-the-fly machine learning force field generation: Application to melting points, Phys. Rev. B., **100**, 1 (2019)
[2] Bartók et al., Gaussian Approximation Potentials: The Accuracy of Quantum Mechanics, without the Electrons, Phys. Rev. Lett., **104**, 13 (2010)

Evaluation of hydrate-based gas separation by using in-situ micro-Raman imaging and optical microscopy: application to CO_2 capture from a CH_4/CO_2 mixture.

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Gas hydrates selectively enclathrate certain components of a gas mixture, opening perspectives for energy-efficient and environmentally friendly separation processes such as CO_2 capture. We present an experimental setup and procedure involving a sealed borosilicate capillary placed in the temperature-controlled stage of an optical microscope coupled with a Raman spectrometer. This configuration enables the quantitative determination of hydrate composition and water-to-hydrate conversion (or gas consumption) within a single experiment. The capillary is partially filled with water containing a small amount of a gas hydrate promoter (such as SDS) and exposed to the gas under hydrate-forming conditions, i.e. a 75/25 mol.% CH_4/CO_2 mixture at $T = 3.2$ °C and $P = 30$ bar in the chosen example. Hydrate crystallites are generated at the water/gas meniscus, grow into a slurry, and eventually form a porous hydrate phase, which can be dissociated by heating into a gas-in-water emulsion.

The results confirm a clear CO_2 selectivity: in the chosen example, hydrate compositions are enriched up to $yCO_2 = 35–45\%$ compared to 25% in the feed gas (separation factor $\alpha \approx 1.6–2.5$). Raman profiles highlight persistent spatial compositional heterogeneities of about 10% along the capillary, linked to variations in the local hydrate content. The overall conversion of water into hydrates reaches about 40%, and the rates of water conversion or gas consumption, as determined from the meniscus velocity, are significantly higher than those of pure CH_4 hydrates under similar subcooling.

This integrated methodology provides a robust framework for the thermodynamic and kinetic modelling of hydrate-based CO_2 capture, as well as for the design of other gas separation processes.

References

[1] B. Samar, S. Venet, A. Desmedt, D. Broseta, ACS Omega, 9, 31842 (2024); Energy Fuels, 39, 4880 (2025).

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