Hidden periodic states in gas hydrate systems lead to spontaneous gas release without external triggers

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Hidden periodic states in gas hydrate systems lead to spontaneous gas release without external triggers

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Abstract

Gas hydrates are one of the largest marine carbon reservoirs on Earth. The conventional understanding of hydrate dynamics assumes that the system converges to a steady-state over geological time-scales, achieving fixed concentrations of gas hydrate and free gas phase. However, using a high-fidelity numerical model and consistently resolving phase states across multiple fluid-fluid and fluid-solid phase boundaries, we have identified well-defined periodic states embedded within hydrate system dynamics. These states lead to cyclic formation and dissolution of massive hydrate layers that is self-sustaining even in the absence of external triggers. This previously unresolved characteristic could manifest as spontaneous gas discharge and pressure release in, supposedly, unperturbed systems. Our findings challenge the foundational principle that the gas hydrate systems have unique steady-state solutions. Instead, existence of periodic states introduces an irreducible uncertainty in gas hydrate dynamics which puts significant error bars on previous hydrate estimates.

1 Introduction

Gas hydrates are ice-like crystalline solids formed when water molecules enclatherate methane gas molecules under specific thermodynamic (i.e. pressure-temperate-salinity) conditions [Sloan and Koh, 2007]. While uncertainty remains about their abundance in nature [Burwicz et al., 2011, Boswell and Collett, 2011, Milkov, 2004, Wallmann et al., 2012], they are commonly assumed to play an important role in Earth's carbon cycle with hydrate formation and dissociation being sources and sinks of free carbon [Wallmann et al., 2012]. The scales and impacts of methane release from natural gas hydrate deposits have been investigated for various environments, especially those that are sensitive to climate change, such as the Arctic [James et al., 2016, Kretschmer et al., 2015], the continental margins and shelves [Dickens et al., 1997, Römer et al., 2017], and the permafrost areas [Chuvilin et al., 2018, Frederick and Buffett, 2014]. Accordingly, hydrates are often interpreted in terms of steady-states on geological time-scale, perturbed only by relatively rapid environmental changes [Wallmann et al., 2012]. For instance, fluid and gas venting at the seafloor, seepage sites, and even submarine landslides are often associated with hydrate dissociation in response to an external trigger, such as warming bottom waters [Ketzer et al., 2020] or sea-level fluctuations [Cremiere et al., 2016, Wei et al., 2022]. The observations of double or multiple bottom simulating reflectors (BSRs) are also commonly attributed to the external changes in sedimentation regimes [Zander et al., 2017] rather than internal gas hydrate system dynamics. In this view, a change in hydrate distribution is the consequence of bringing a supposedly stable hydrate system into an unstable (or out-of-equilibrium) thermodynamic state. This perspective is attractive, as it allows relating direct observations like methane seeps, pockmarks, or submarine landslides to changes in current or past environmental conditions. It also attributes a modulating role to hydrates in the global carbon cycle, e.g., in the form of positive feedback mechanisms such as hydrate melting under contemporaneous global warming conditions [Biastoch et al., 2011, Ruppel and Kessler, 2017] or due to depressurization upon post-glacial rebound [Wallmann et al., 2018].

Here we explore a new complementary perspective by providing evidence for a natural, intrinsic periodicity in the gas hydrate dynamics manifested in the in-situ cyclic re-building and dissemination of massive gas hydrate and free gas volumes. Most strikingly, we show that the natural hydrate systems exhibit this rich internal dynamics under constant environmental conditions, i.e. without any external environmental triggers. We resolve this hydrate system dynamics by using complex multi-physics interactions, where the formation and dissolution of distinct gas

hydrate (GH) layers is controlled by organic matter degradation, methanogenesis, continuous burial of phases, gas migration dynamics, and GH phase change kinetics within the gas hydrate stability zone (GHSZ) [Gupta et al., 2020, Wallmann et al., 2006, 2012, Burwicz et al., 2011, Burwicz and Rupke, 2019]. Conventional understanding, cultivated through broadly used simplified mathematical models, dictates that over geological time scales these processes converge to a steady state leading to stable gas hydrate and free gas concentrations. However, our new analyses of the well-established equations describing gas hydrate systems show that the long-term stability of the gas hydrate dynamical system is not quite as straightforward. By analyzing a large spectrum of geological parameters typical for marine settings, we have discovered that for the vast majority of hydrate-bearing geological settings, the steady-state solutions of GH dynamics exhibit stable internal periodicity (i.e. periodic growth and dissolution of massive gas hydrate layers coupled with spontaneous free gas migration through the GHSZ). Most importantly, the amplitude of change between the lowest and the highest GH saturations reached within one full cycle shows a remarkable variability across geological settings, and can reach significantly large values (e.g., 30 percent of the sediment pore space in the sampled parameter space in this study). In case of the standard mathematical models that do not resolve the cyclic states, the obtained solutions (i.e. fixed-steady-state gas hydrate and free gas saturations) will be bounded within the limits of the true cyclic solution. In that sense, the cyclic states can be seen as significant 'error bars' on the fixed-steady-state solutions.

This discovery has profound implications as it challenges the conventional view that changes in hydrate distribution and the associated manifestations in observational data can only occur in response to external drivers, which implies that seafloor and sub-seafloor observations such as seafloor venting, cold seeps, pockmarks, and multiple BSRs do not need to be directly related to out-of-equilibrium subsurface conditions but could result from a self-sustaining internal cyclicity in the gas hydrate system dynamics. This discovery also points to systematic (i.e. irreducible) uncertainty embedded within high fidelity gas hydrate models, which has direct implications for the estimation of global carbon cycling, gas hydrate inventories, as well as the prediction of system responses to changing climate and environmental conditions on both short and long time scales.

2 Results

To analyse the behaviour of the GH dynamical systems, we simulated a 1D burial-driven recycling problem based on a uniform geological setting with a broad spectrum of parameters that cover majority of the gas hydrate-bearing sediments globally. The idealized 1D test setting is depicted in Fig. 1. The top-boundary is located at a depth $z = 0$, and coincides with the latest seafloor at any instant of time. Continuous sedimentation buries all phases at a rate of v_s. In general, a gas hydrate layer (e.g., pre-existing GH reservoir) remains in a stable state within the GHSZ. Under continuous sedimentation, this stable GH layer will be continuously buried with sediment grains below the base of the GHSZ, resulting in progressive hydrate dissociation and formation of a free gas phase. Buoyant gas will start to migrate upward to re-enter the GHSZ and crystallize in form of a new stable GH layer, ultimately enriching the pre-existing hydrate reservoir. This process, known as the gas hydrate re-cycling, has been previously described for natural gas hydrate systems as being characterized by high rates of sedimentation [Burwicz and Haeckel, 2020, Burwicz et al., 2017]. The computational domain parameters, initial conditions, and boundary conditions are listed in Table 1. The total depth of the sediment column within our computational domain is chosen as $z = Z_{max}$ to capture all depth zones at which methanogenesis, phase transitions, and the build-up of free gas column take place. At the start of the simulation, we assume that the sediment column is fully saturated in pore fluids of a given salinity, and no dissolved methane, free-gas, and hydrate layer are present anywhere in the column. The pore water pressure is assumed to be hydrostatic and the temperature distribution is in equilibrium with the regional thermal gradient $\Delta_z T$. At the top boundary, fixed bottom-water conditions are imposed, which translate to Dirichlet constraints for all primary variables (governed by PDEs), and at the bottom of the domain, Neumann fluxes are imposed. The growth of the sedimentary column starts with the deposition of additional sedimentary layers on top of the model domain according to the sedimentation rate defined for each modeling scenario. After deposition, the top of the sediments becomes the new seafloor and all sedimentary layers present in the model domain undergo steady-state compaction according to Berner [1980]. In our previous work [Schmidt et al., 2022], we have isolated the modeling parameters that have the largest influence on the modeling outcomes.

Overall, we ran all combinations of the parameters in the following ordered sets, resulting in a total of 297 simulation scenarios: a) Intrinsic sediment permeability $K_0 \left[\text{m}^2 \right] = \left\{ 10^{-15} , 10^{-16} , 10^{-17} \right\}$, b) reaction rate of hydrate phase-change kinetics $k_{r0} \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{Pa} \cdot \text{s}} \right] = \left\{ 10^{-17} , 10^{-18} , 10^{-19} \right\}$, and c) rate of burial $v_s \left[\frac{\text{cm}}{\text{a}} \right] = \{0.04 , 0.0405 , 0.041 , 0.0415 , 0.042 , 0.043 , 0.044 , 0.045 , 0.046 , 0.0480 , 0.05 , 0.055 , 0.06 , 0.065 , 0.07 , 0.075 , 0.08 , 0.085 , 0.09 , 0.095 , 0.1 , 0.11 , 0.12 , 0.13 , 0.14 , 0.15 , 0.16 , 0.17 , 0.18 , 0.185 , 0.19 , 0.195 , 0.2\}$.

The chosen range of intrinsic permeability ($10^{-15} \geq K_0 \left[m^2 \right] \geq 10^{-17}$) covers a wide range of values from coarse-

grained sediments to hemipelagic clay, and is representative for gas hydrate-bearing settings (Wallmann et al., 2012). Since our goal is to analyze the gas migration and GH dynamics driven by burial processes, we primarily focus on the influence of the burial rate parameter v_s on the steady-state system behaviour. There are large uncertainties associated with bulk sedimentation rates over geological times. However, to highlight the internal cyclic dynamics, we use constant burial rates over the entire simulation period (i.e., all external forcings are eliminated to highlight the self-sustaining internal cyclic states). By analyzing multiple sedimentation regimes with burial rates in the range of $0.04 \leq v_s \, [cm/a] \leq 0.2$, we explore how the sedimentation rate lying within given uncertainty bounds affects the overall behaviour of the GH dynamics.

Table 1: Initial and boundary conditions for the simulation scenarios.

Initial conditions	Boundary conditions	
$P_w\|_{t=0,\forall z} = P_w\|_{z=0} + \rho_w g z$	$P_w\|_{t>0,z=0} = P_w\|_{z=0}$	$\frac{\partial}{\partial z} P_w\|_{t>0,z=Z_{max}} = \rho_w g$
$T\|_{t=0,\forall z} = T\|_{z=0} + (\Delta_z T) z$	$T\|_{t>0,z=0} = T\|_{z=0}$	$\frac{\partial}{\partial z} T\|_{t>0,z=Z_{max}} = \Delta_z T$
$C_i\|_{t=0,\forall z} = 0 \quad \forall i \in \mathcal{S}$	$C_i\|_{t>0,z=0} = C_i\|_{z=0} \quad \forall i \in \mathcal{S}$	$\frac{\partial}{\partial z} C_i\|_{t>0,z=Z_{max}} = 0 \quad \forall i \in \mathcal{S}$
–n.a.–	–n.a.–	–n.a.–
$S_h\|_{t=0,\forall z} = 0$	–n.a.–	–n.a.–
Parameters		
Seafloor/Bottom-water conditions	$P_w\|_{z=0} = \rho_w g \mathcal{H}_w$ where, $\mathcal{H}_w = 2195$ m is height of the water column.	
	$T\|_{z=0} = 4^o$C	
	$C_{CH_4}\|_{z=0} = 0$ mM $\cdot$ $C_{SO_4^{2-}}\|_{z=0} = 30$ mM $\cdot$ $C_{CO_2}|_{z=0} = $ xxx mM $\cdot$	
	$C_{NH_4^+}\|_{z=0} = 0.003$ mM $\cdot$ $C_{OM}\|_{z=0} = 1$ wt% $\cdot$ $C_{Cl^-}\|_{z=0} = 555$ mM	
Regional thermal gradient	$\Delta_z T = 45^o$ C/km	
Total domain depth	$Z_{max} = 600$ m	

Note that boundary conditions are not specified for S_h because it is governed by an ODE (eqn.2), while both initial and boundary conditions are not specified for S_g because it is governed by an AE (eqn.4).

2.1 Periodic states

First shown by Schmidt et al. [2022], the internal periodicity in gas hydrate system is a result of the so-called "hydrate nozzle effect" where the hydrate (solid) layer acts like a converging-diverging nozzle in the path of upward migrating free gas, and the complex phase transitions between hydrate(solid) $\leftrightarrow$ dissolved-gas(fluid) $\leftrightarrow$ free-gas(fluid) and evolving pore geometry due to hydrate(solid-to-fluid) phase changes lead to a "pulsating" gas flow. This nozzle effect is not a consequence of any new model equations. Rather, our model uses the already well-established set of equations, and this effect is captured through a mathematically consistent resolution of the phase- states, leading to accurate phase transitions especially within the II-phase and III-phase zones (shown in Fig. 1).

In Fig. 2, we show the steady-state solutions for the reference scenario characterized with parameters $K_0 = 10^{-16}$ m^2, $k_{r0} = 10^{-18}$ mol/$\left(\text{m}^2 \cdot \text{Pa} \cdot \text{s}\right)$, and $v_s = 0.05$ cm/a. It is evident that under continuous burial, even without any external climate and/or environmental perturbations, the GH reservoir can exhibit a very rich dynamics localized in the vicinity of the bGHSZ. We can see that the p-T-s states show a very large amplitude of oscillation in the vicinity of the bGHSZ, but the strength of these oscillations is sharply reduced upon propagation through the overlying GH layers. Among these, the oscillation of the gas phase pressure is the most consequential because of its saw-toothed character, where the pressure builds over a long time but is released over a very short time (almost instantaneously on a geological time-scale; equivalent to an impulse loading from below as shown in Fig. 2E). This near-instantaneous pressure release could be sufficient to trigger mechanical instabilities on slopes or initiate fractures in deeper sediments.

The associated *bulk* quantities of interest (QoI), namely, 1) location of the base of the GHSZ (bGHSZ, Fig. 3A) defined as the lowest depth at which $P_g = P_e$, 2) depth-integrated volume of hydrate per squared-meter of the seafloor (V_h, Fig. 3B), and 3) peak hydrate saturation within the gas hydrate layer ($S_{h,max}$, Fig. 3C) are also plotted. These steady-state solutions and the bulk QoI show a clear periodicity over time, suggesting that under continuous burial, the GHSZ contracts and dilates and the hydrate layer builds-up and melts ad infinitum, with a change of ~60 m in the thickness of the GHSZ and ~15% in the total hydrate volume over each periodic cycle. Moreover, even though the time-period of the periodic cycles is relatively large (~220 ka), the hydrate build-up phase and the corresponding GHSZ-contraction appears to occur much faster (over a period of ~30-50

ka), compared to the hydrate-melting phase and the corresponding GHSZ-dilation (over ∼170-150 ka).

The evolution of the hydrate distribution along the sediment column is resolved over one time-period in Fig. 3F to show the hydrate build-up and melting phases more clearly. The hydrate layer obstructs upward gas migration by reducing the effective permeability, s.t., $\mathbf{v}_g \propto K := K_0 \left(1 - S_h\right)^n$. Due to the convex shape of the hydrate layer, the reduction in the gas velocity is not uniform across the whole hydrate layer. Rather, the section of the GH layer below the peak saturation decelerates the upward-migrating gas, while the section above accelerates the gas in a manner analogous to a converging-diverging mechanical nozzle. If the upward migrating gas manages to seep past the throat of this hydrate-nozzle (i.e. peak saturation) this gas is *flung* across the hydrate layer to the overlying GHSZ, where the gas quickly converts back into hydrate, building a *new layer* above the pre-existing (or old) GH layer. The continuous burial of the old layer below the GHSZ continues to supply the gas for the build-up of the new layer. Once the old layer is completely consumed, the new layer stops growing. Burial pushes this new layer towards the bGHSZ and the melting phase starts. The melting continues until enough gas has been built-up for it to escape past the peak of the GH layer, at which point a new cycle begins. The dynamics of hydrate nozzle is tightly controlled by the rate of gas supply at the base of GHSZ (proportional to the rate of hydrate dissociation) and the rate of upward gas migration (combination of upward buoyancy and deceleration from the hydrate nozzle). If the rate of dissociation is too low, the gas supply will be insufficient for its escape past the throat of the nozzle. Alternatively, if the rate of upward gas migration is too low (e.g., due to low intrinsic permeability K_0 or high exponent n or extremely high rate of hydrate formation), again the gas may not be able to escape past the throat of the nozzle. In both cases, the periodic states will not occur and the system dynamics will converge to a fixed steady state. Due to strong coupling of the hydrate ↔ dissolved-gas ↔ free-gas phase transitions with the p-T-s conditions, the cyclic building and melting of the hydrate also impacts the state of the GHSZ. The evolution of the three-phase zone (bounded from below by $\Gamma := P_g - P_e = 0$ and from above by $\Gamma_{up} := C_{CH_4}^{eq} - C_{CH_4} = 0$) is resolved in Figs.3D-E. The bGHSZ remains relatively stationary as long as the old hydrate layer is in place. When the old layer is consumed beyond a critical volume, the bGHSZ starts to shift upwards towards the base of the new GH layer. An additional point to note is that the hydrate layer enters the limit of the cyclic much faster whereas the gas saturation below the bGHSZ accumulates over multiple cycles before it converges with the true cyclic-steady-state. This is shown in Fig. 3F where the gas reservoir builds over 60 cycles. Given that the near-instantaneous pressure releases in each cycle would lead to mechanical instabilities sooner or later, it is unlikely that in nature the gas reservoir would ever build up to this theoretical steady-state gas volume.

Finally, for this reference scenario, we also show the phase plots in Fig. 4. All solutions converge on a limit cycle instead of a fixed-point, showing categorically that for this particular combination of parameters, the gas hydrate dynamical system does not reach a true steady state. Instead, it exhibits a periodic steady state. Moreover, this periodic state appears to be a stable attractor, and at least within the simulated parameter space and time range, the system does not exhibit signs of chaos. The phase plots also help in visualizing the relative changes in the system variables. For example, temperature and salinity evolve out of phase whereas temperature and pressure evolve in phase with each other. For models that do not resolve these cyclic states, we postulate that their estimations of the fixed-steady-states will lie within the limit cycles of the analogous cyclic-steady-states. In that sense, we can see these periodic solutions to set error bars over the fixed-state solutions.

2.2   Bifurcation

So far, we have looked at the solutions of one particular (i.e. reference) scenario, and established the existence of periodic states that result from rich internal dynamics (as opposed to any external forcing of perturbations of environmental conditions). In Fig. 5, we plot the maximum and the minimum values of the qoi (*quality-of-interest*) S_h^* that occur within one periodic cycle for all scenarios with $K_0 = 10^{-16}$ m^2 and $k_{r0} = 10^{-18}$ mol/ $\left(m^2 \cdot \text{Pa} \cdot s\right)$. Here, three distinct steady-state behaviors can be identified: I) No gas hydrate is formed in the domain, II) gas hydrate layer shows cyclic building, burial, and re-building, oscillating between two distinct peak values, and III) gas hydrate layer recycles continuously, reaching a fixed steady state value. The steady state behaviour shows abrupt transition from type-I to type-II to type-III back to type-I. This sudden qualitative or topological change in the behaviour of the dynamical system for a small smooth change in a parameter value is called a bifurcation.

On a process level, gas hydrate dynamics is a sum total of many competing processes. The parameter space explored here focuses on the competition between gas flow through upward migration (controlled by K_0) and burial (controlled by v_s), and flow modulation through the converging-diverging hydrate nozzle (controlled by k_{r0}). If burial velocity is too low, OM degradation remains confined to the upper sediment layers and methanogenesis does not occur. If burial velocity is too high, the dissolved methane gas is rapidly buried below the base of the GHSZ and is unable to accumulate to form a free gas phase. In both these cases, gas hydrate is not formed and the system dynamics exhibits a type-I steady state. If the burial velocity is large enough to transport OM deeper into

the sediment to promote methanogenesis, but small enough to allow the accumulation of methane into a free gas phase, gas hydrate layer will build up and undergo recycling in the vicinity of the base of the GHSZ, and the system dynamics will exhibit either a type-II or a type-III steady state, depending on how the hydrate nozzle modulates the flow of the upward migrating free gas.

In Fig. 6, the steady states of all $k_{r0} - K_0$ scenarios are plotted along the parameter dimension of burial velocity. Results highlight that the bifurcation manifold of a gas hydrate system has a highly complex shape in a high dimensional parameter space. A comparison of the steady-states suggests that high permeability and high hydrate kinetic rates promote the existence of periodic steady-states. Moreover, the shape of the bifurcation manifold in the $K_0 - v_s$ plane corresponding to $k_{r0} = 10^{-18}$ (Fig. 6B,E) is non-monotonic (i.e., the periodic-states envelope expands from $K_0 = 10^{-17}$ to $K_0 = 10^{-16}$ but contracts from $K_0 = 10^{-16}$ to $K_0 = 10^{-15}$), suggesting that in the hydrate-nozzle dynamics, the parameters k_{r0} and K_0 are not completely independent, and there likely exists an *optimal* pair with the largest range of cyclic states.

Finally, the time periods of all cyclic solutions are plotted in Fig. 6G-I. Results suggest that a combination of high permeability, low hydrate kinetic rate, and low burial velocity leads to shorter cycles. Moreover, from the limited k_{r0} samples, it appears that the time-periods are likely to converge in the K_0 dimension at high enough k_{r0}, although to prove this conclusively, a detailed mathematical analysis of the time-periodic solutions of the GH dynamics will be necessary.

The existence of bifurcations in the gas hydrate dynamics is an important discovery for many practical reasons. For example, in the parameter space sampled within this study, the periodic states do not occur everywhere. Rather, they occur only over a range of burial velocities. The amplitudes of the periodic states and their time periods also show a huge variability across the K_0 and k_{r0} dimensions. Therefore, the gas hydrate dynamics for parameters located within the bifurcation manifold will have a significant systematic (i.e., irreducible) uncertainty. This uncertainty is irreducible in the sense that it is a fundamental mathematical property of the system, unlike the other forms of parameter uncertainties (e.g. due to measurement errors or incomplete sampling, etc.) that can, at least in theory, be eliminated by improving measurements, sufficient data, etc.

3 Discussion

Commonly used multi-phase gas hydrate models are based on the same mass balance and energy equations coupled with similar reaction network including kinetically controlled in-situ POC degradation, methanogenesis, anaerobic methane oxidation (AOM), and sulfate reduction processes. To capture the internal gas hydrate system cyclicity, it is necessary to, 1) consistently resolve the phase transitions occurring simultaneously across multiple fluid-fluid and fluid-solid phase boundaries, and 2) fully resolve the fluid-sediment interactions (i.e. parametric function describing permeability evolution with hydrate saturation, necessary to simulate the nozzle effect). However, when the used formulation is mathematically or numerically smoothed or simplified, the numerical solution will not show the apparent cyclicity but will lie within the bounded limit cycles shown in Fig. 4. The internal periodicity is shown to be a self-sustaining process regardless of external forcing factors, such as anthropogenic warming, sea-level fluctuation, or large scale planetary cycles e.g. the Milankovitch cycle. However, the hydrate system response to overlapping short- and long-time scale forcing is yet to be analyzed. For instance, there is an apparent time lag in development of full system steady-state cyclicity observed in both gas hydrate and free gas phases. the gas hydrate phase reaches a full steady-state cyclicity several cycles before a steady-state free gas cyclicity. It is explained by the fact that free gas phase needs sufficient time to build up enough gas volume that allows upward migration. This is directly linked to the fact that the free gas saturation is limited by sediment permeability within the free gas zone, whereas gas hydrate peak is limited by kinetic reaction rate of phase transition. As a consequence, full steady-state system cyclicity of both gas hydrate and free gas phases can be reached faster in settings characterized by: a) high organic matter content available for efficient biodegradation, b) active fluid flow or high-permeability pathways for gas transport from below, b) additional methane sources, e.g. gas reservoirs. However, it has been shown that a steady-state gas hydrate system cyclicity can fully develop in geological settings without constant gas supply [Schmidt et al., 2022] as a result of in-situ organic matter decomposition but could be fueled by sufficient amounts of free gas present in the sediment pore space as a stationary gas pocket. We attribute this observation to the fact that gas hydrate system cyclicity by itself is a consequence of the GH-nozzle formation. However, the nozzle dynamics is modulated by the supply and connectivity of free-gas from the reservoir at its base. To this effect, biogeochemical reactions provide strong feedbacks to the GH-dynamics. Shallow hydrate systems (i.e. defined by a relatively thin GHSZ) might manifest hydrate cyclicity in features like seafloor venting of fluid and gas, slope instability, formation of pipe structures within the GHSZ, seepage sites, or moving BSRs. In a contrary, deep hydrate systems might not exhibit observable changes at the seafloor.

3.1   Global implications

The apparent existence of bifurcation manifolds and in particular, the periodic states, has profound implications as it sets hard limits on the predictability of present-day gas hydrates through steady-state analysis. What this means is, that if the parameters for a particular geological scenario lead to a cyclic (or periodic) steady-state, we cannot say with confidence which part of the cycle we are on at the present moment. However, what we can predict with some confidence is the maximum and minimum amounts of GH that can occur for the given set of parameters. This means that there is a systematic irreducible source of uncertainty embedded within the GH dynamics. Given the large variation in the GH saturation and volume occurring over one time-period of the cyclic solution, current estimates of the present-day global GH inventory may be off by several orders of magnitude.

The periodicity in the steady-state solutions of p-T-s states also means that in typical geological settings, the GH systems are highly dynamic even without any external climate and/or environmental perturbations. Especially in relatively shallow gas hydrate systems, the landslides, slope failures, pockmarks, pipes, and chimneys etc. observed on-site or in the geological records may have occurred spontaneously without any external triggers like sea level, bottom-water, sediment loading, or salinity fluctuations.

The cyclic rebuilding of GH layers occurs in phases through the hydrate nozzle mechanism, where two GH layers can coexist, one at the base of the current/latest configuration of the GHSZ and one below (corresponding to some past configuration of GHSZ). The dynamics of the cyclic states can, therefore, also explain some of the observed double (and even multiple) BSRs.

The existence of periodic states has particularly serious implications for the prediction of future climate impacts due to modern-day climate dynamics. It is likely that the anthropogenic climate perturbations (i.e., very fast changes in climate conditions) may push the formerly stable steady state of the GH reservoirs (estimated based on paleo-climate conditions) to new periodic states with large p-T-s fluctuations, thereby significantly increasing the risks of uncontrolled gas escape and geomechanical failures. The anthropogenic climate fluctuations may also push the formerly periodic states towards chaotic states, making long term predictions nearly impossible.

The discovery of the periodic states in GH dynamics has opened up multiple fundamental questions related to past, present, and future evolution of natural GH systems with profound implications for coastal dynamics, continental margins environments, and sea infrastructure. Therefore, there is a need to systematically analyze the mathematical features of this dynamics and reinterpret the role and impacts of gas hydrates within the solid Earth systems.

4   Methods

The mathematical and numerical model used in this study were developed in Gupta et al. [2020]. A detailed description of the governing equations, constitutive models, reaction network, model parameters and the numerical methodology is included in the Appendix A. Below, we briefly outline the basic premise of our GH model and give an overview of the underlying multiphysics process couplings.

On the continuum-scale, our model considers four distinct homogenized phases: free-gas (fluid), water (fluid), hydrate (solid), and sediment (solid). The sediment phase constitutes the primary matrix which is assumed to be rigid (i.e. undeformable), whereas, the hydrate and sediment phases together constitute the composite matrix. The void-spaces embedded within the primary matrix define the porosity of the medium, which remains constant over time (due to the rigidity assumption). The hydrates, however, are reactive solids that can undergo massive volume changes. Therefore, the effective porosity of the composite matrix evolves over time, depending on the progression of the hydrate phase transitions. The evolution of the effective porosity is strongly coupled with the reaction kinetics of hydrate phase change, and provides highly nonlinear and bidirectional feedbacks to fluid flow fields. The model also considers compositional flow, where gas, water, and sediment phases are composed of multiple reactive species that can interact and undergo phase transitions across the fluid-fluid and fluid-solid interfaces. However, the changes in volume of the sediment phase are assumed to be negligible compared to those of the hydrate phase, and therefore, the impacts of sediment phase transition on porosity evolution are ignored in this model.

Broadly, the model accounts for the following physical processes: 1) Advective flow of gas and water; 2) Capillary effects at the gas-water interface; 3) Burial of phases due to sediment deposition on the seafloor; 4) Hydrate phase changes across the gas-hydrate and dissolved CH_4-hydrate phase boundaries; 5) Changes in permeability due to hydrate phase changes, 6) In-situ generation of methane through organic matter (OM) degradation via sulfate reduction, methanogenesis, and anaerobic oxidation of methane (AOM); 7) Pore-water salinity, transport of dissolved salts, fresh-water recycling, and its effect on hydrate phase stability, 8) Dissolution-exsolution of methane, and model degeneracy related to the localized appearance↔disappearance of the free-gas phase; and finally, 9) Thermal effects

which arise due to the non-isothermal nature of the hydrate phase changes and the strong temperature dependence of the hydrate-gas-water phase equilibria.

Code Availability

The numerical model is implemented within version 2.8 of C++ based DUNE-PDELab framework [Bastian et al., 2010, Sander, 2020], and uses the in-built matrix assembler, linearization algorithm (Newton method with numerical Jacobian), and linear solver (parallel Algebraic Multi-Grid (AMG) solver with stabilized bi-CG preconditioner). The DUNE libraries used in this study are preserved at https://gitlab.dune-project.org/pdelab/dune-pdelab and developed openly at https://www.dune-project.org/. The source code for the model and test scenarios presented in this manuscript is publicaly archived and can be accessed as https://doi.org/10.5281/zenodo.7920830. Detailed step-by-step instructions are included in this repository (README.md) on how to install and run the code. Also included are numerical solutions for the reference scenario, along with matlab/octave based postprocessing routines to visualize these solutions.

Author contributions

The authors confirm contribution to the paper as follows: Study conception and design: S.G, E.B.-G., C.S., L.R.; data collection: E.B.-G., C.S.; model and software development: S.G.; numerical simulations: S.G., analysis and interpretation of results: S.G, E.B.-G., C.S., L.R.; draft manuscript preparation: S.G, E.B.-G., C.S., L.R., figures and movie preparation: S.G.; final manuscript preparation: S.G., E.B.-G.

Declarations

All authors declare no competing interests. All authors reviewed the results and approved the final version of the manuscript.

Supplementary Material

An animation of the numerical solutions for the reference scenario (i.e., the scenario with permeability $K_0 = 10^{-16} m^2$, kinetic rate $k_{r0} = 10^{-18} \mathrm{mol}/(m^2 \cdot \mathrm{Pa} \cdot s)$ and burial rate $v_s = 0.05$ cm/a) is included as supplementary information. The public git repository for the code includes the raw numerical solution files for this numerical simulation.

Correspondence

Enquiries regarding the mathematical and numerical model, software, and results should be directed to the corresponding author, Shubhangi Gupta, at shubhangi.gupta@um.edu.mt
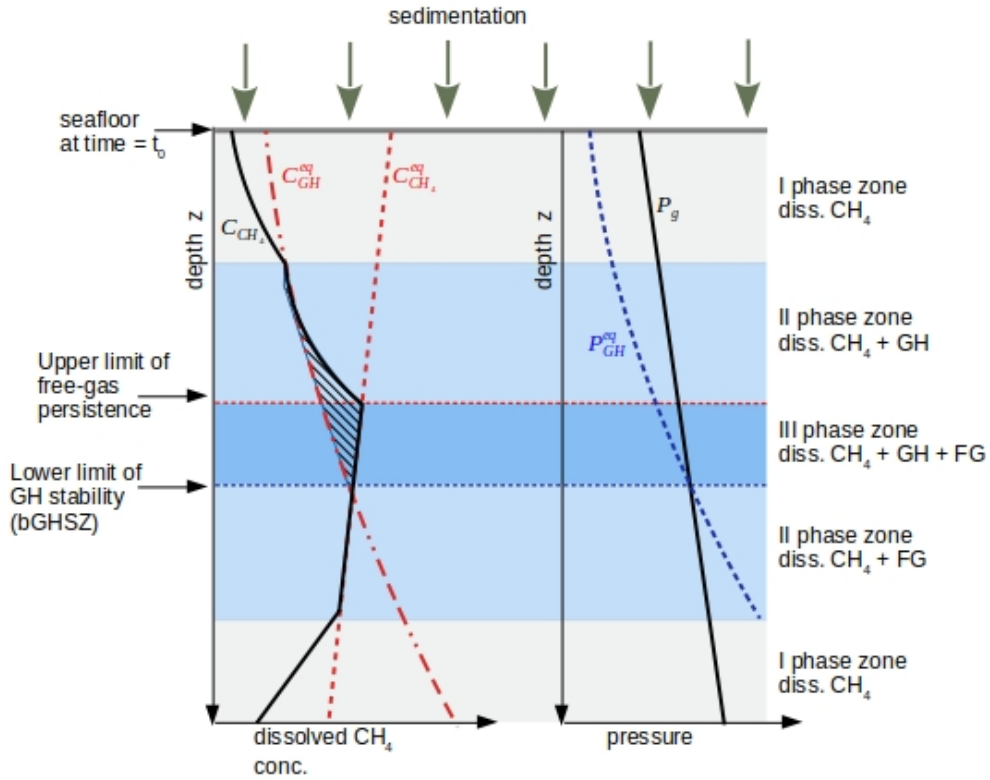
Figure 1: Schematic illustration of the multi-phase sedimentary model in this study. An example of modeling solutions showing dissolved methane concentration (C_{CH4}) and gas pressure (P_g) are depicted with solid black and blue lines, respectively. Gas hydrate and free gas solubility limits are shown with dashed red lines as C_{GH}^{eq} and $C_{CH_4}^{eq}$, respectively. Theoretical pressure marking gas hydrate phase transition (P_{GH}^{eq}) is depicted with dashed blue line. The intersection between P-T-S-dependent solubility solutions (C_{GH}^{eq} and $C_{CH_4}^{eq}$) marks the base of the theoretical gas hydrate stability zone (bGHSZ). Similarly, the intersection between the gas pressure (P_g) and the phase equilibrium curve (P_{GH}^{eq}). Three phase region where dissolved methane, gas hydrate, and free gas co-exist (given sufficient amount of dissolved CH_4) is marked as a dark blue field (i.e. III phase zone). In case there is no sufficient methane dissolved in pore fluids to overcome the free gas solubility limit, there are only two phases present in the pore space, i.e. dissolved methane fully saturating the pore fluid, and gas hydrate (light blue field and the part of the diagram marked with a crossed pattern). Consequently, in case pore fluids are not fully saturated in methane, gas hydrate and free gas phases are not stable (grey field in the plot marked as a I phase zone).
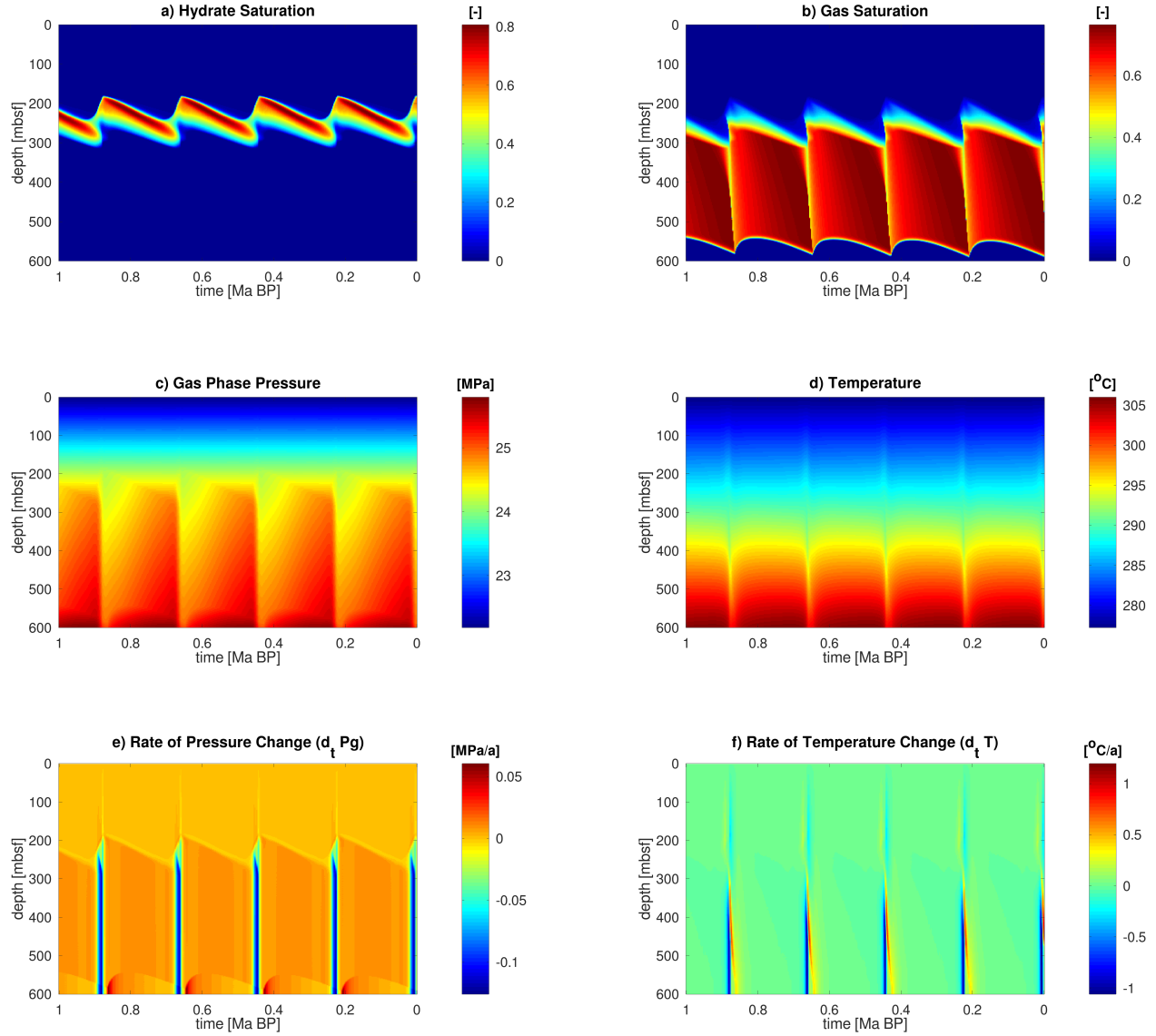
Figure 2: Depth-vs-Time solutions of selected variables at periodic steady-state for the reference scenario with $K_0 = 10^{-16}$ m^2, $k_{r0} = 10^{-18} \dfrac{\text{mol}}{m^2 \cdot \text{Pa} \cdot s}$, and $v_s = 0.05$ cm/a. Sub-figures a-b) show gas hydrate and free gas saturations, respectively, plotted against 1 Ma of simulation time to highlight the apparent periodicity of the solution. Sub-figures c-d) illustrate changes in gas phase pressure and temperature along the cycles, whereas sub-figures e-f) show the rates of significant gas pressure and temperature change, respectively.
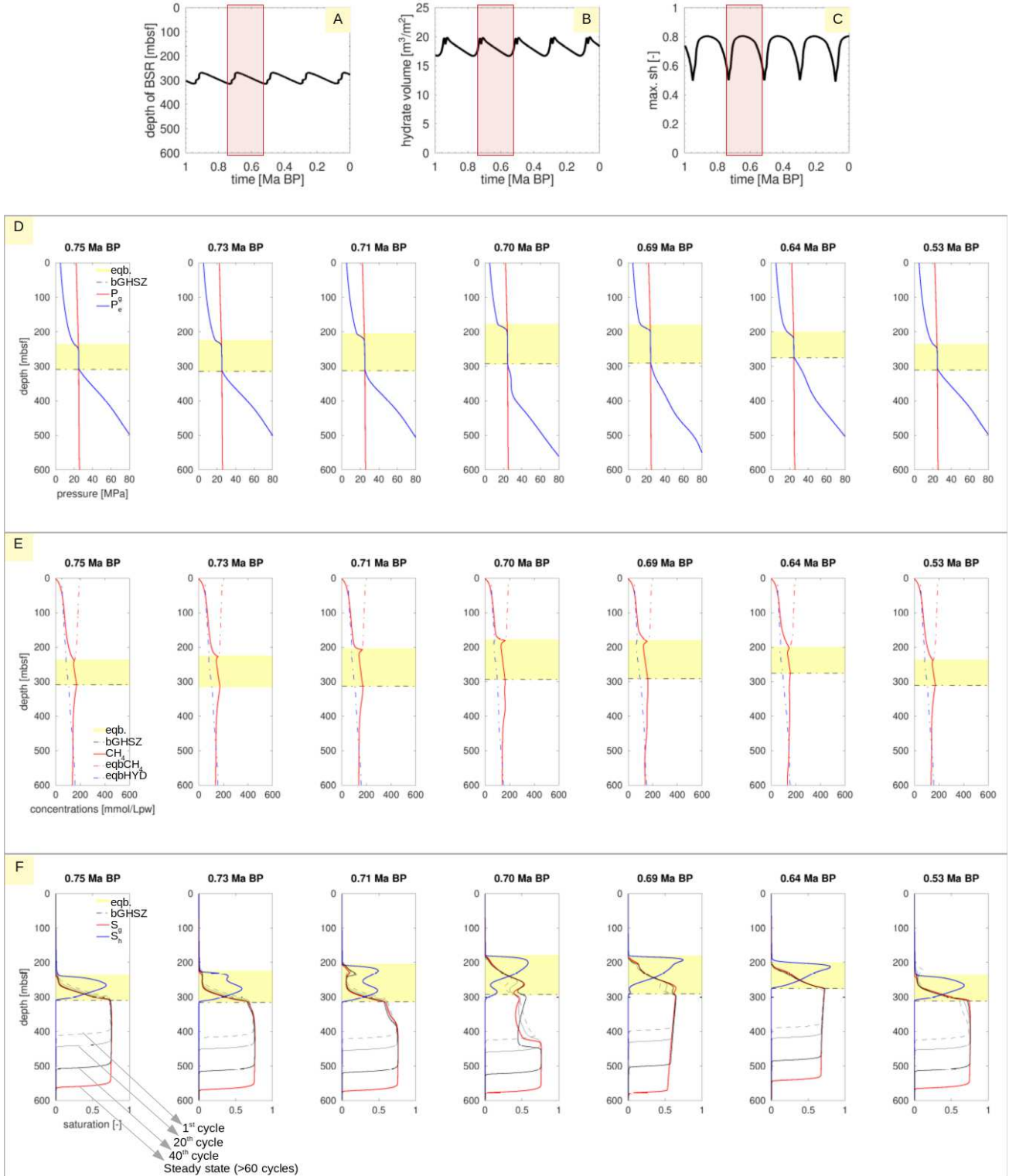
Figure 3: Cyclic gas-hydrate (GH) and free-gas (FG) flow dynamics for the reference scenario. Cyclic evolution of the bulk quantity of interest (QoI), A) base of GHSZ (bGHSZ), B) total gas hydrate volume in domain, and C) maximum hydrate saturation within the domain, is shown. Also shown is the dynamic evolution over one periodic cycle (red region in A-C) of, D) gas pressure (labelled P_g) and GH$\leftrightarrow$FG equilibrium pressure (labelled P_e), E) dissolved methane concentration (labelled CH_4) and the solubility limits of CH$_4\leftrightarrow$FG and CH$_4\leftrightarrow$GH transitions (labelled eqbCH$_4$ and eqbHYD). The III-phase zone, bounded between $(P_g - P_e) \geq 0$ and $\left(C_{CH_4}^{eq} - CH_4\right) \leq 0$, is marked in yellow. The evolution of the FG and GH saturations (labelled S_g and S_h) is shown in (F). Solutions from previous cycles are superimposed to highlight the lag between the steady-states of FG and GH.
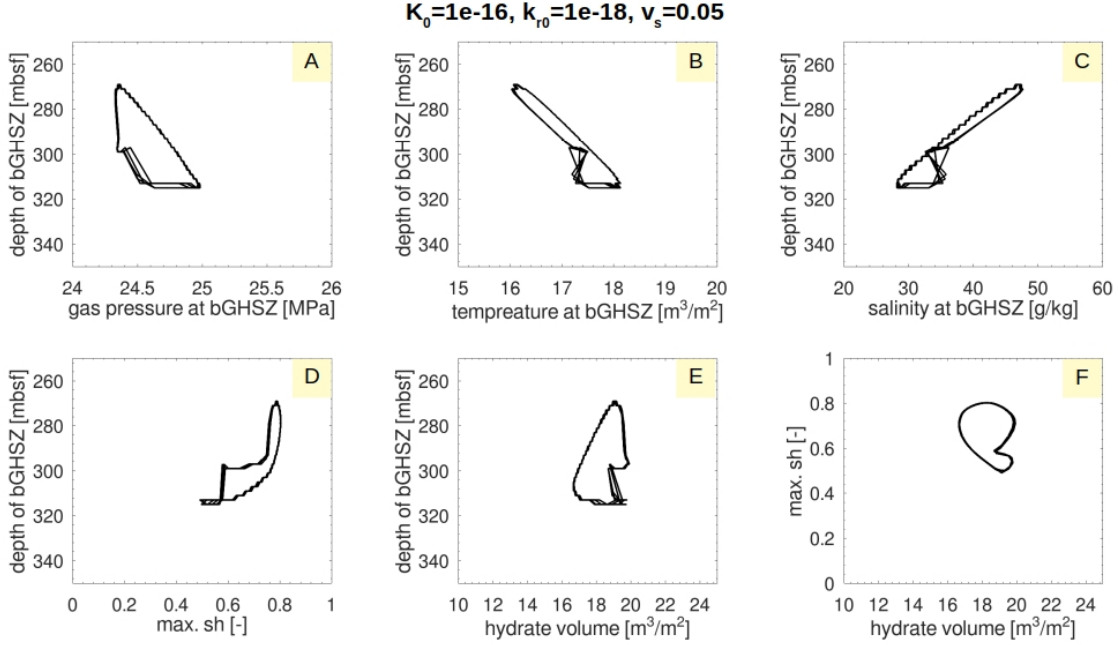
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Figure 4: Selected phase plots for the reference scenario: A) Gas pressure at bGHSZ vs depth of bGHSZ (z_{bGHSZ}), B) temperature at bGHSZ vs z_{bGHSZ}, C) salinity at bGHSZ vs z_{bGHSZ}, D) highest instantaneous hydrate saturation (S_h^*) in the domain vs z_{bGHSZ}, E) total instantaneous hydrate volume (V_h) in the domain vs z_{bGHSZ}, and F) S_h^* vs V_h. All solutions converge on a limit cycle instead of a fixed-point, showing that for this particular combination of parameters, the gas hydrate dynamical system does not and will not reach a true steady-state. Instead, it exhibits a *periodic steady-state* which would contain a simplified steady-state solution within its borders.
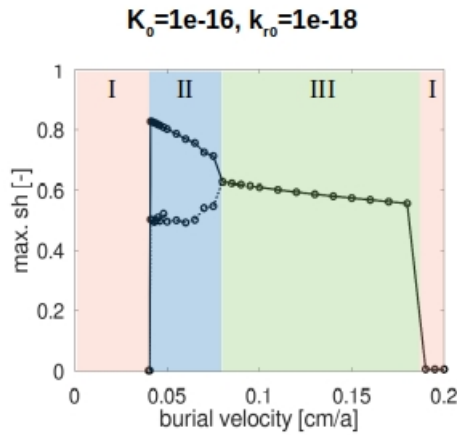

Figure 5: Bifurcation in the steady-state behaviour of the QoI S_h^* for the reference scenarios plotted along the parameter dimension of burial velocity $v_s = [0.04 ... 0.2]$ cm/a. Bifurcation is said to occur in a dynamical system when a small smooth change made to a parameter value causes a sudden qualitative or topological change in its behavior. Here, three distinct steady-state behaviors can be identified: I) No gas hydrate is formed in the domain, II) gas hydrate layer shows cyclic building, burial, and re-building, oscillating between two distinct peak values, and III) gas hydrate layer recycles continuously, reaching a fixed steady state value. The steady-state behaviour shows abrupt transition from type-I to type-II to type-III back to type-I within a rather narrow range of burial velocities, highlighting the large uncertainty embedded within the gas hydrate dynamics.
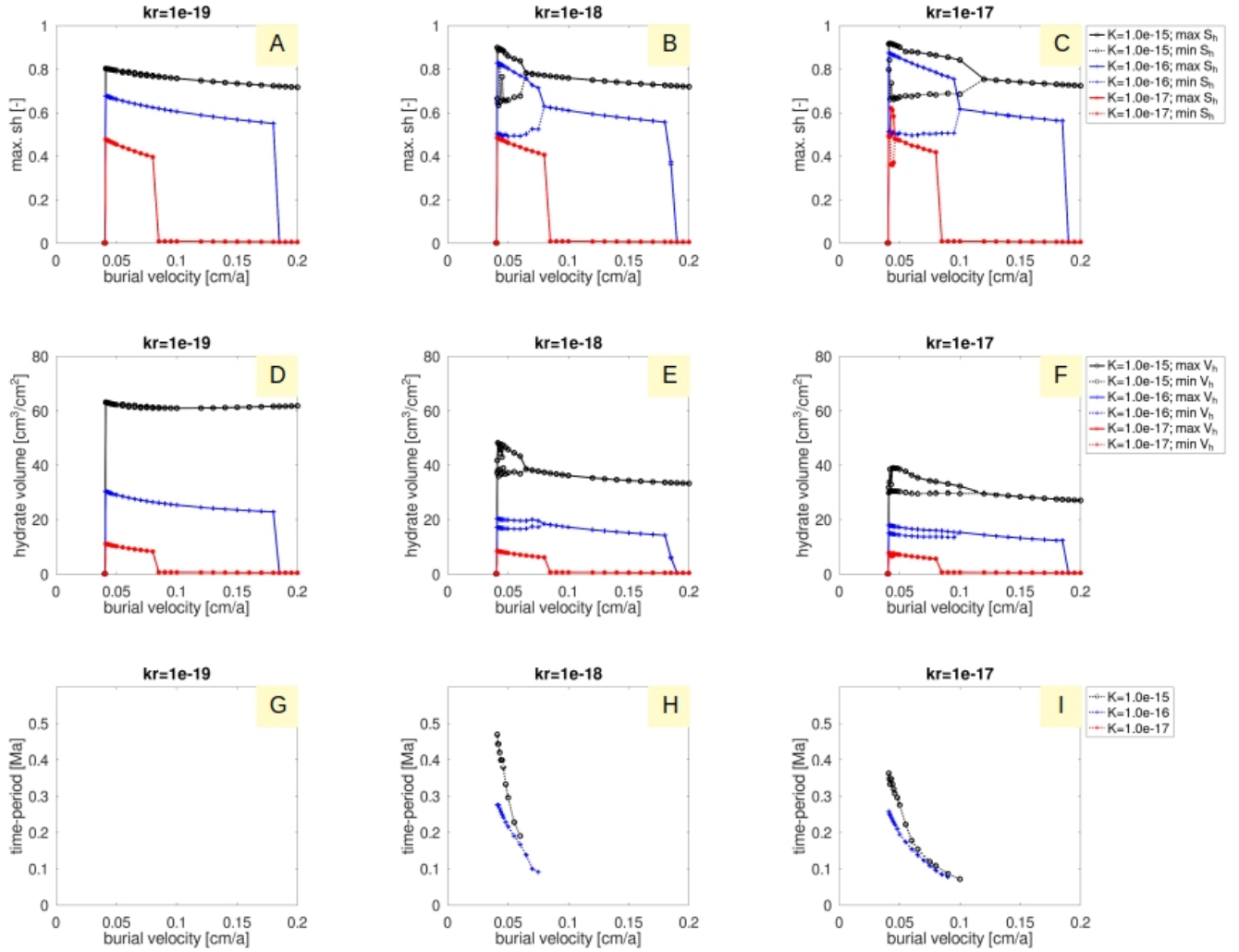
Figure 6: Bifurcation manifolds in the steady-state behaviour of all simulated scenarios plotted along the parameter dimension of burial velocity. Sub-figures A-C show the bifurcation manifolds for the QoI S_h^*, and sub-figures D-F show for the QoI V_h. Also shown, in sub-figures G-H, are the time-periods of the cyclic solutions. Gas hydrate dynamics is a sum total of many competing processes. The parameter space explored here focuses on the competition between gas flow through upward migration (controlled by K_0) and burial (controlled by v_s) and flow modulation through the converging-diverging hydrate nozzle (controlled by k_{r0}).

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A Mathematical model

Here, we present a detailed description of the governing equations, reaction network, constitutive models, and model parameters used to simulate the burial-driven gas hydrate dynamics presented in this manuscript.

A.1 Preliminaries

The continuum-scale mathematical description of the conservation laws is based on the following homogenized variables defined over an REV (representative elementary volume [Helmig, 1997]): local porosity $\phi\left(\mathbf{x}\right) := \dfrac{V_p}{V_{REV}}$ and local saturation $S_\alpha\left(\mathbf{x}, t\right) := \dfrac{V_\alpha}{V_p}$, where, $\Omega \subset \mathbb{R}^d$ is the domain of interest with $d = \{1, 2, 3\}$, $V_{REV} \subset \Omega$ is the volume of an arbitrary REV, $V_p \subset V_{REV}$ is the volume of void spaces, called pores, where the (g)as, (w)ater, and (h)ydrate phases can exist, $V_\alpha \subset V_p$ is the volume of each of the phases $\alpha = \{g, w, h\}$, and $\mathbf{x} \in \Omega$ is the position and $t \subset \mathbb{R}$ the time. Furthermore, the void spaces are fully occupied by at least one of the phases, s.t., $\sum\limits_{\alpha=g,w,h} V_\alpha = V_p$, or $\sum\limits_{\alpha=g,w,h} S_\alpha = 1$. Furthermore, the gas and water phases are mobile fluids, while the hydrate phase is an immobile solid that is chemically active, undergoing volume changes within the pores. Therefore, to describe the fluid flow through this reactive media, an effective porosity is defined, s.t., $\phi_e\left(\mathbf{x}, t\right) := \dfrac{V_w + V_g}{V_{REV}} = \phi\left(1 - S_h\right)$.

The sediment phase constitutes the primary matrix which is assumed to be rigid (i.e. undeformable), whereas, the hydrate and sediment phases together constitute the composite matrix. The void-spaces embedded within the primary matrix define the porosity of the medium, which remains constant over time (due to the rigidity assumption). The hydrates, however, are reactive solids that can undergo massive volume changes. Therefore, the *effective* porosity of the composite matrix evolves over time, depending on the progression of the hydrate phase transitions. The evolution of the effective porosity is strongly coupled with the reaction kinetics of hydrate phase change, and provides highly nonlinear and bidirectional feedbacks to fluid flow fields. The model also considers compositional flow, where gas, water, and sediment phases are composed of multiple reactive species that can interact and undergo phase transitions across the fluid-fluid and fluid-solid interfaces. However, the changes in volume of the sediment phase are assumed to be negligible compared to those of the hydrate phase, and therefore, the impacts of sediment phase transition on porosity evolution are ignored in this model.

A.2 Governing equations

Broadly, the model accounts for the following physical processes:

- Advective flow of gas and water;
- Capillary effects at the gas-water interface;
- Burial of phases due to sediment deposition on the seafloor along the continental margins;
- Hydrate phase changes due to precipitation↔dissolution of hydrates in equilibrium with dissolved methane, and formation↔melting of hydrate in equilibrium with methane in the free-gas phase;
- Changes in hydraulic properties (i.e., permeability, capillary entry pressure, specific surface area) due to evolving porosity as a result of hydrate phase changes,
- In-situ generation of methane through organic matter (OM) degradation via sulfate reduction, methanogenesis, and anaerobic oxidation of methane (AOM);
- pore-water salinity, transport of dissolved salts, fresh-water recycling, and its effect on hydrate phase stability,
- Dissolution-exsolution of methane, and model degeneracy related to the localized appearance↔disappearance of the free-gas phase; and,
- Thermal effects which arise due to the non-isothermal nature of the hydrate phase changes and the strong temperature dependence of the hydrate-gas-water phase equilibria.

The main governing equations, derived from the mass, momentum, and energy conservation principles, are briefly outlined as:

$$\partial_t \phi\left(\rho_w S_w + \rho_g S_g + \rho_h S_h\right) + \nabla \cdot \left(\rho_w \mathbf{v}_w + \rho_g \mathbf{v}_g\right) + \nabla \cdot \phi\left(\rho_w S_w + \rho_g S_g + \rho_h S_h\right) \mathbf{v}_s = 0 \tag{1}$$

$$\partial_t \rho_h \phi S_h + \nabla \cdot \rho_h \phi S_h \mathbf{v}_s = q_h^{HFD} + q_h^{HPD} \tag{2}$$

$$\partial_t \phi \left(C_{CH_4} + \frac{\rho_g}{M_{CH_4}} S_g \right) + \nabla \cdot \left(C_{CH_4} + \frac{\rho_g}{M_{CH_4}} \right) (\mathbf{v}_w + \phi S_g \mathbf{v}_s) + \nabla \cdot \phi S_w \mathbf{D}_{CH_4}^w \nabla C_{CH_4}$$

$$= \sum_{j=1}^{N_e} S_{eCH_4,j} R_{ej} + \sum_{j=1}^{N_k} S_{kCH_4,j} R_{kj} + \frac{q_g^{HFD}}{M_{CH_4}} \tag{3}$$

$$S_g \left(C_{CH_4}^{eq} - C_{CH_4} \right) = 0 \tag{4}$$

$$\partial_t \Phi_i + \nabla \cdot \mathcal{L}_i \left(C_i \right) = \sum_{j=1}^{N_e} S_{eij} R_{ej} + \sum_{j=1}^{N_k} S_{kij} R_{kj} + \sum_{j=1}^{N_o} q_{ij} \qquad \forall i \in \mathcal{S} \text{ and } i \neq CH_4 \tag{5}$$

$$\partial_t \left(\sum_{\alpha=g,w,h} \phi \rho_\alpha S_\alpha H_\alpha^v + (1-\phi) \rho_s H_s^v \right) T + \sum_{\beta=g,w} \nabla \cdot \rho_\beta H_\beta^p \left(\mathbf{v}_\beta + \phi S_\alpha \mathbf{v}_s \right) T$$

$$+ \nabla \cdot \left(\sum_{\alpha=g,w,h} \phi S_\alpha k_\alpha^{th} + (1-\phi) k_s^{th} \right) \nabla T = Q^{GDE} + Q^{HFD} + Q^{HPD} \tag{6}$$

where, eqn.1 describes the total mass balance of all pore-filling phases, i.e., gas, water, and hydrate, denoted by $\alpha := \{g, w, h\}$ respectively; eqn.2 describes the mass balance of the hydrate phase; eqn.3 describes the total mass balance of methane in both free-gas phase and the dissolved state; eqn.4 describes the Kharush-Kuhn-Tucker constraint associated with the equilibrium phase transition of methane across dissolved and free-gas states; eqn.5 describes the mass balance of all dissolved and solid species, except methane, related with the OM degradation; and finally, eqn.6 describes the total energy balance of all phases $\beta := \{g, w, h, s\}$. The variable ρ_β is the phase densities. The variables $\mathbf{v}_w$ and $\mathbf{v}_g$ are the Darcy seepage velocities of the fluid phases s.t. for each $f := \{g, w\}$,

$$\mathbf{v}_f = -K\Theta_f \left(\nabla P_f + \rho_f \mathbf{g} \right)$$

where, P_f denotes the phase pressures related through a pressure jump across the phase interface, also called the capillary pressure P_c s.t. $P_g - P_w := P_c$, $\mathbf{g}$ denotes the gravity, Θ_f the phase-wise flow-mobility, and K the absolute permeability of the composite matrix, s.t.,

$$K = K_0 \left(1 - S_h \right)^n \quad \text{with } n > 0$$

with K_0 as the absolute permeability of the primary matrix. Furthermore, the variable $\mathbf{v}_s$ denotes the burial velocity related to the rate of sediment deposition on the seafloor, s.t., the total velocity of any phase β undergoing burial is given as,

$$\mathbf{v}_\alpha^* = \mathbf{v}_\alpha + \phi S_\alpha \mathbf{v}_s \quad \text{and} \quad \mathbf{v}_s^* = (1-\phi) \mathbf{v}_s$$

where, $\mathbf{v}_g$ and $\mathbf{v}_w$ are Darcy velocities and $\mathbf{v}_h = 0$.

The terms g_α^κ denote non-linear reactive-sources for each phase α corresponding to following phase transitions: gas (methane) dissolution-exsolution ($\kappa = GDE$), hydrate formation-dissociation ($\kappa = HFD$), and hydrate precipitation-dissolution ($\kappa = HPD$).

The kinetic rate of the hydrate precipitation-dissolution transition is,

$$r^{HPD} = k^{HPD} \left(\frac{C_{CH_4}}{C_h^{eq} \left(P_w, T \right)} - 1 \right)$$

where, C_h^{eq} is the hydrate solubility, and k^{HPD} is the rate of precipitation-dissolution phase change, s.t.,

$$k^{HPD} = \begin{cases} k_+^{HPD} & \text{if } \left(\frac{C_{CH_4}}{C_h^{eq}} - 1 \right) > 0 \\ k_-^{HPD} S_h & \text{if } \left(\frac{C_{CH_4}}{C_h^{eq}} - 1 \right) \leq 0 \end{cases}$$

The related source terms are,

$$q_h^{HPD} = M_h \, r^{HPD} \quad \text{and,} \quad q_w^{HPD} = -q_h^{HPD}$$

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The kinetic rate of the hydrate formation-dissociation transitions is,

$$r^{HFD} = k^{HFD} \left(P_e(T) - P_g \right)$$

$$\text{where,} \quad k^{HFD} = \begin{cases} k_+^{HFD} A_0 S_h (1 - S_h)^{\frac{3}{2}} & \text{for } (P_e - P_g) > 0 \\ k_-^{HFD} A_0 S_g S_w (1 - S_h)^{\frac{3}{2}} & \text{for } (P_e - P_g) \leq 0 \end{cases},$$

where, P_e is the hydrate equilibrium pressure, A_0 is the surface area of the hydrate-free sediment, and k^{HFD} is the intrinsic reaction rate, with k_+^{HFD} and k_-^{HFD} as the rate constants. For simplicity of presentation in the parameter study, we have assumed that $k_+^{HFD} = k_-^{HFD} = k_{r0}$. The related source terms are,

$$q_h^{HFD} = M_h \ r^{HFD} \qquad (7)$$
$$q_g^{HFD} = M_{CH4} \ r^{HFD}$$
$$q_w^{HFD} = N_h M_{H_2O} \ r^{HFD}$$
$$\text{where,} \quad M_{CH4} + N_h M_{H_2O} = M_h$$

Note that the source term for gas dissolution-exsolution does not appear explicitly in the governing equations, because it cancels out in the total mass balance for methane in dissolved and free-gas forms.

The generalized compositional system considers N_s number of species, partitioned across the water and sediment phases. The ordered set of all species is denoted with $\mathcal{S}$ with cardinality $n(\mathcal{S}) = N_s$. The variable C_i denotes the concentration of the ith species in mmol per litre pore-water volume, where $i \in \mathcal{S}$, and Φ_i transforms the concentration of the ith species to mmol per litre total volume, s.t.,

$$\Phi_i = \mathcal{M}_{ii} \phi S_w C_i + (1 - \mathcal{M}_{ii})(1 - \phi) C_i$$

where, $[\mathcal{M}]_{N_s \times N_s}$ is a mobility matrix s.t., $\mathcal{M}_{ij} = 1$ if $i = j$ and i corresponds to an w-species, otherwise $\mathcal{M}_{ij} = 0$. $\mathcal{L}_i$ is the transport operator of the ith species describing the convective and diffusive mass fluxes, s.t.,

$$\mathcal{L}_i = \mathcal{M}_{ii} C_i \mathbf{v}_w^* + (1 - \mathcal{M}_{ii}) C_i \mathbf{v}_s^* + \left(\mathcal{M}_{ii} \phi S_w \mathbf{D}_i^w + (1 - \mathcal{M}_{ii})(1 - \phi) \mathbf{D}_i^s \right) \nabla C_i$$

where, $\mathbf{D}_i^w$ and $\mathbf{D}_i^s$ are the molecular diffusion coefficients in water and sediment phases, respectively. Furthermore, the terms $\sum_{j=1}^{N_e} S_{eij} R_{ej}$ and $\sum_{j=1}^{N_k} S_{kij} R_{kj}$ are the chemical sources where S_{eij} and S_{kij} denote the stoichiometric coefficients for the ith species in the jth equilibrium and kinetic reaction, respectively, and R_{ej} and R_{kj} denote the rates of the jth equilibrium and kinetic reaction, respectively. The equilibrium reaction rates R_{ej} are unknown and cannot be estimated apriori. We find a suitable matrix $[U]_{N_s - N_e \times N_e}$ s.t.,

$$[U]_{N_s - N_e \times N_e} \cdot [R_e]_{N_e \times 1} = 0$$

Using this matrix, we can eliminate $[R_e]_{N_e \times 1}$ from the system of governing equations and condense the compositional system described in eqn.5 from size $(N_s - 1)$ to size $(N_s - 1) - N_e$. This procedure is described in the Appendix. Finally, the term $\sum_{j=1}^{N_o} q_{ij}$ denotes sum of any other sources of the ith-species resulting from N_o processes, which can include injection/extraction, phase transitions (e.g. dissolution, exsolution, melting, precipitation), etc.

In this manuscript, the compositional system is based on the OM degradation model described by Wallmann et al. [2006]. The reaction network, consisting of the sulfate reduction, methanogenesis, and AOM reactions are summarized in Table 2. The compositional system also includes chlorinity, which is used as a proxy for pore-water salinity.

The compositional system excludes the free-gas phase because free-gas is composed of only one component, methane. Under an assumption of vapour-liquid equilibrium, if the concentration of dissolved methane remains below its solubility limit $C_{CH_4}^{eq}$ in pore-water, free-gas phase cannot exist. Methane released through methanogenesis and melting/dissolving gas hydrates dissolves into pore-water until solubility limit is reached, beyond which all excess methane is spontaneously exsolved into a newly appearing free-gas phase. Conversely, perturbation of local pressure-temperature-salinity (p-T-s) state may raise the solubility limit s.t. the methane in the free-gas phase dissolves back into pore-water, leading to locally disappearing free-gas phase. Mathematically, the transition of methane across dissolved and free-gas states can be described by the following set of inequalities,

$$C_{CH_4} = C_{CH_4}^{eq} \quad \text{if, } S_g > 0$$
$$\text{and, } C_{CH_4} < C_{CH_4}^{eq} \quad \text{if, } S_g = 0$$

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Together, these lead to the Kharush-Kuhn-Tucker (KKT) type algebraic constraint given in eqn.4. This constraint converts the model into a constrained optimization problem. Moreover, similar to the equilibrium reaction rates in the compositional system, the rate of mass-exchange across the gas-water interface due to methane dissolution-exsolution cannot be known apriori. Therefore, we eliminate these terms by summing up the respective phase-wise and component-wise mass balance equations, leading to the conservation of total methane given in eqn.3. The factor M_{CH_4} appearing in eqn.3 is the molar mass of methane, used to make the units of density and concentration consistent.

Finally, in the energy conservation eqn.6, the variable T denotes the homogenized temperature, H_β^v the phase-wise specific heat capacity at constant volume, H_f^p the specific heat capacity of fluid-phases, k_β^{th} the phase-wise thermal conductivity, and Q^κ the heat sources associated with each fluid-fluid and fluid-solid phase-transition.

Eqns.1-6 together form a strongly coupled and highly non-linear system of partial-differential-algebraic equations (PDAE), to be solved for the primary variables:

$$\mathcal{P} = \begin{bmatrix} P_w \ , \ T \ , \ S_h \ , \ S_g \ , \ C_{CH_4} \ , \ \{C_i\}_{(N_s - N_e - 1) \times 1} \end{bmatrix}^T$$

A.3 Numerical solution

The numerical scheme is based on a fully upwinded cell-centered finite volumes method for spatial discretization and an implicit Euler method for temporal discretization. The scheme is implemented in DUNE-PDELab (version 2.8) [Bastian et al., 2010] based on C++. For the linearization of the system of governing PDEs, we have implemented a semi-smooth Newton solver which can handle the gas-water phase transitions and appearing and disappearing free-gas phase in a mathematically consistent manner. A highly optimized SuperLU [Demmel et al., 1999] linear solver is used to perform 1D calculations in sequential mode. In general, the numerical implementation is capable of solving in 1D, 2D and 3D. The 2D and 3D calculations can be performed OpenMPI parallel mode using a built-in Algebraic Multi-Grid solver.

The computations for this study were performed on the high-performance computing cluster at Kiel University (CAU). Further details of our numerical scheme can be found in [Gupta et al., 2020].

Table 2: Chemical reaction network for the organic matter degradation via sulfate reduction, methanogenesis, and AOM reactions, based on the model and parameters proposed by Wallmann et al. [2006].

	Species		
number of species	$N_s = 7$		
ordered set	$\mathcal{S} = \left\{ CH_4 \;,\; SO_4^{2-} \;,\; NH_4^+ \;,\; CO_2 \;,\; Cl^- \;,\; OM \;,\; CO_3^{2-} \;,\; HCO_3^- \right\}$		

	Equilibrium reactions		
number of reactions	$N_e = 2$		
Acid-base reaction 1	$CO_2 + H_2O \xleftrightarrow{K_1} HCO_3^- + H^+$		
Acid-base reaction 2	$HCO_3^- \xleftrightarrow{K_2} CO_3^{2-} + H^+$		
Stoichiometric matrix	$[S_e]_{N_s \times N_e} = \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 1 & -1 \end{bmatrix}^T$		
Parameters	$K_1 = 1.3139 \times 10^{-6} \;,\; K_2 = 6.0940 \times 10^{-10}$		

	Kinetic reactions		
number of reactions	$N_k = 3$		
OM degradation with sulfate reduction	$(CH_2O)_a (NH_3)_b (H_3PO_4)_c + \frac{1}{2}aSO_4^{2-} \xrightarrow{R_{k1}} \left(\frac{1}{2}a + b - 2c\right) HCO_3^- + \frac{1}{2}aHS^- + bNH_4^+ + cHPO_4^{2-} + \left(\frac{1}{2}a - b + 2c\right) CO_2 + \left(\frac{1}{2}a - b + 2c\right) H_2O$		
OM degradation with methanogenesis	$(CH_2O)_a (NH_3)_b (H_3PO_4)_c + (b - 2c) H_2O \xrightarrow{R_{k2}} (b - 2c) HCO_3^- + \frac{1}{2}aCH_4 + bNH_4^+ + cHPO_4^{2-} + \left(\frac{1}{2}a - b + 2c\right) CO_2$		
AOM with sulfate	$CH_4 + SO_4^{2-} \xrightarrow{R_{k3}} HCO_3^- + HS^- + H_2O$		
Stoichiometric matrix	$[S_k]_{N_s \times N_k} =$ $\begin{bmatrix} 0 & -\frac{1}{2}a & b & \left(\frac{1}{2}a - b + 2c\right) & 0 & -1 & 0 & \left(\frac{1}{2}a + b - 2c\right) \\ \frac{1}{2}a & 0 & b & \left(\frac{1}{2}a - b + 2c\right) & 0 & -1 & 0 & (b - 2c) \\ -1 & -1 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}^T$		
Reaction rate vector	$[R_k]_{N_k \times 1} = \begin{bmatrix} \frac{1}{2}\left(\dfrac{C_{SO_4^{2-}}}{C_{SO_4^{2-}} + K_{SO_4^{2-}}} \right) R_{POC} \\ \frac{1}{2}\left(\dfrac{K_{SO_4^{2-}}}{C_{SO_4^{2-}} + K_{SO_4^{2-}}} \right) R_{POC} \\ k_{AOM} C_{SO_4^{2-}} C_{CH_4} \end{bmatrix}$		
Parameters	C:N:P ratio $\rightarrow a = 106$, $b = 16$, $c = 1$ $K_{SO_4^{2-}} = 1$ $R_{POC} = \left(\dfrac{K_C}{C_{DIC} + C_{CH_4} + K_C} \right) k_z C_{OM}$ where, $C_{DIC} = \left(C_{CO_2} + C_{CO_3^{2-}} + C_{HCO_3^-} \right)$ $\quad k_x = 0.16 \left(a_0 + \frac{z}{\omega} \right)^{-0.95}$ with $a_0 [a] = 1000$ and $\omega = \frac{v_{s,\infty}(1 - \phi_\infty)}{(1 - \phi)}$ $\quad K_C = 35$ $k_{AOM} = 0.001$		

Supplementary Files

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