



Full Length Article

The promoting effect of natural sand on methane hydrate formation: Grain sizes and mineral composition



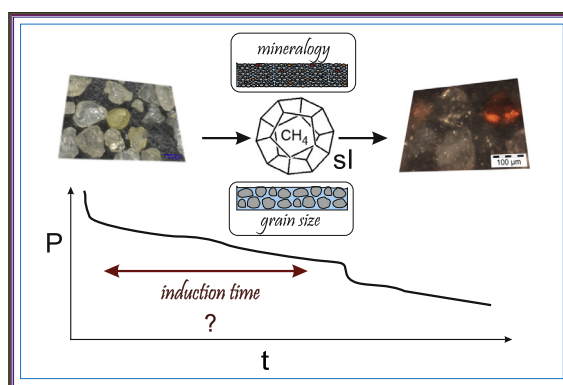
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HIGHLIGHTS

- Strong variations in the promotion of methane hydrate formation in natural sand.
- Surface and mineralogical changes such as iron-oxy-hydroxide coating affect formation.
- Involved processes include accelerated hydrate nucleation, changes in dissolution rates or bulk water volume.

GRAPHICAL ABSTRACT



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ABSTRACT

Investigations regarding the effects of particle size on gas hydrate growth are commonly carried out using glass beads, silica powder, and various clay minerals. Comparisons of different grain sizes of sands are less common as are natural samples. Since the highest gas hydrate saturations and possible energy resource targets are associated with natural sandy sediments, the presented experiments address the possible effects of different grain sizes from a natural sand sample on methane hydrate formation. Influences on the kinetics of hydrate formation in natural deposits are of particular interest in hydrate production or carbon dioxide sequestration in methane hydrates. In both cases an undesired secondary hydrate formation may occur on short time scales, usually under non-equilibrium conditions.

The static small-volume experiments are carried out far within the methane hydrate stability field (7 MPa/274 K) using five different grain size classes of a natural quartz sand: <125 μm , < 250 μm , 250–500 μm , 500–1000 μm , and 1000–2000 μm . A constant volume of water or salt water is added to saturate the sediment sample and pressure is built up using methane gas. Pressure and temperature are continuously recorded and a glass window allows for microscopic observation and Raman spectroscopy to verify methane hydrate formation.

For the chosen experimental set-up there is a strong particle size effect on the kinetics of methane hydrate formation. A high concentration of fine sands with a grain size <125 μm led to explicitly faster gas hydrate formation compared to coarser sand or a small fraction of fine particles diluted in a sample of coarser sand grains. Our article discusses possible causes in conjunction with changes of the mineral surface. These include accelerated hydrate nucleation or growth due to the surface area (1) or mineral composition (2) and changes in dissolution kinetics (3) caused by enhanced dissolution rates or changes in the ratio of bound to bulk water volumes. The addition of salt significantly increased induction times but did not supplant the particle size effect.

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1. Introduction

Natural gas hydrates are considered to represent the Earth's largest reservoir of hydrocarbons and a possible energy resource for the next decades [1,2]. To allow for an economic gas production from this reservoir detailed knowledge on the distribution of gas hydrates is as crucial as is the possibility to predict their behavior during production, which can lead to dissociation as well as re-formation. Commonly the occurrences and formation of natural gas hydrates are described by temperature, pressure, salinity, and gas concentrations. In his conceptual model, Clennell et al. [3] discuss the influence of the host sediments caused by hydrophilic mineral surfaces and capillary pressure. The model is inclined to help explain the growth, highly inhomogeneous distribution, and morphology of gas hydrates in the sediments, which also relates but is not limited to the methane (CH_4) supply [e.g., [4]].

A number of experiments regarding the potential control of host sediments on thermodynamic properties of gas hydrates have been performed over the last decades [5–11], whereas similar effects on the kinetics of gas hydrate formation experienced considerably less attention [5,12,13]. This particularly applies to experiments using different sand grain ranges rather than clay [8,14], despite the fact that it is the sandy sediment that holds a higher saturation of gas hydrates in natural occurrences [1]. These sediments also hold the higher permeability allowing for a larger and faster non-focused gas supply to generate gas hydrates and for a sufficient gas production from gas hydrates, respectively. While a focus has already been placed on the physical properties of sands containing gas hydrate during dissociation [e.g., [15,16]], the kinetics of secondary hydrate formation in sands and the sediments' influence has been given little attention so far. However, this could be of importance for methane production from gas hydrates and/or CO_2 sequestration and the related scale-up models.

There is a consensus in literature that small pore sizes combined with large mineral surfaces increase capillary inhibition effects and decrease water activity [e.g., [3]]. In his model, Clennell et al. [3] attribute the occurrence of free gas slightly above the calculated depth of gas hydrate stability in marine sediment columns to these inhibition effects. This is supported by various experiments [e.g., [5–11]] showing a shift of gas hydrate equilibrium toward lower temperature and higher pressure in the presence of small particles. The driving forces for gas hydrate formation are reduced. In experiments small pore sizes and large mineral surfaces are commonly represented by different clay minerals or artificial equivalents such as glass beads ($<20\ \mu\text{m}$), whereas the grain sizes of the opposing large particles usually vary rather arbitrarily between $63\ \mu\text{m}$ and $500\ \mu\text{m}$ (fine – medium sand). In a recent paper, Sun et al. [14] have now pointed out that the effect of fine silica sand on the pressure–temperature trace (p–T trace) of gas hydrate formation is similar to that of even finer particles in that it decreases the hydrate stability field compared to coarse sands. The authors state that effects of coarse sand on the stability field of gas hydrate is negligible. Higher gas hydrate saturations were reported to occur in coarse sands [17].

Studies on the kinetic effects of particles on gas hydrate formation are rarer and more inconsistent possibly owing to the stochastic nature of gas hydrate formation and the interrelation with experimental set-ups [18]. The authors agree that the presence of particles/surfactants generally promotes hydrate formation and shortens the induction time due to enhanced gas hydrate nucleation [e.g., [10,19]]. However, the effect of the particle sizes is still controversial. Kang et al. [12] conclude that the kinetically promoting effect they observe is not related to the influence of pore sizes when using silica gels with pore sizes $6\text{--}100\ \text{nm}$ but to higher driving forces, in this case higher pressure. Sun et al. [14] focus

on temperature depressions of the gas hydrate stability field by fine sand compared to coarse sand but do not mention kinetic behavior. They refer to experiments by Tohidi et al. [20] who observed that hydrates first form in large pores but start to dissociate in fine pores in their glass micromodels, which underlines the temperature depressions in fine sands. To the best of our knowledge, the kinetic effects of different sized sand grains are rather unknown as also mentioned by Ruffine [21] who focusses on the kinetic patterns related to methane influx in sandy sediment cores ($180\text{--}500\ \mu\text{m}$).

Is there actually a grain size effect on kinetics and what would be the major driver in natural samples? According to Kang et al. [12] there should be an optimum point of particle diameter for the rate of hydrate formation. This would be the grain size with the largest positive effect on gas hydrate formation kinetics – providing different effects exist – without significantly restricting diffusion.

Apart from the variable particle sizes, natural samples are not mono-mineralic. What is the effect of mineral surface chemistry in natural samples on hydrate nucleation and growth? It may be viewed as being of minor importance compared to the grain size effects; however, experiments are extremely rare. In one of the few publications, Riestenberg et al. [10] mention that compounds which render water structures more favorable for hydrate crystal growth could lower the overpressure needed for gas hydrate formation, as already mentioned in a publication by Cha et al. [5].

The main emphasis of this paper is to discuss the kinetic effect of different sized sand grains of a natural quartz sand on methane hydrate formation. For this purpose we separated and characterized a natural sand into five grain size ranges and observed when and if gas hydrate formed in a system of sand – methane gas – liquid phase at conditions far within the stability field. In the presented experiments the fine fraction clearly promoted the kinetics of gas hydrate formation. The paper discusses (a) the processes promoted by the smallest grain size range, namely the nucleation and growth of gas hydrates or/and the dissolution of methane, and (b) the effects of changes in mineral surface chemistry that accompany grain size changes.

2. Method

To study the potential impact of the grain size distribution on gas hydrate formation a natural sand was separated into five different fractions. One subsample at a time was transferred into a cooled pressure cell together with ultrapure water or IAPSO seawater standard (Fig. 1, Table 1). After closure and pressurization of the cell with methane the valves were closed and pressure changes recorded. Optical measurements included Raman spectroscopy and microscopic observations.

2.1. Samples and sample preparation

The light natural sand was chosen due to its very high quartz content ($\sim 98\ \text{wt.}\%$) and its lack of organic matter. Not only would the properties of organic matter alter the experimental conditions they would also disturb the Raman-spectroscopic measurements due to its fluorescent nature. The sand was ultrasonically cleaned before being separated into five grain size fractions by sieving: $<125\ \mu\text{m}$, $<250\ \mu\text{m}$, $250\text{--}500\ \mu\text{m}$, $500\text{--}1000\ \mu\text{m}$, and $1000\text{--}2000\ \mu\text{m}$. The group $<250\ \mu\text{m}$ contains a small fraction ($<10\%$) off group $<125\ \mu\text{m}$. The amount of grains $1000\text{--}2000\ \mu\text{m}$ was insufficient for repeated measurements.

On average the pore space and effective porosity of non-consolidated and well sorted sands is in the same range for coarse

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