

Gas hydrate growth and dissociation in narrow pore networks: capillary inhibition and hysteresis phenomena

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Abstract: Marine sediments hosting gas hydrates are commonly fine-grained (silts, muds, clays) with very narrow mean pore diameters ($\sim 0.1 \mu\text{m}$). This has led to speculation that capillary phenomena could play an important role in controlling hydrate distribution in the seafloor, and may be in part responsible for discrepancies between observed and predicted (from bulk phase equilibria) hydrate stability zone (HSZ) thicknesses. Numerous recent laboratory studies have confirmed a close relationship between hydrate inhibition and pore size, stability being reduced in narrow pores; however, to date the focus has been hydrate *dissociation* conditions in porous media, with capillary controls on the equally important process of hydrate *growth* being largely neglected. Here, we present experimental methane hydrate growth and dissociation conditions for synthetic mesoporous silicas over a range of pressure–temperature (*PT*) conditions (273–293 K, to 20 MPa) and pore size distributions. Results demonstrate that hydrate formation and decomposition in narrow pore networks is characterized by a distinct hysteresis: solid growth occurs at significantly lower temperatures (or higher pressures) than dissociation. Hysteresis takes the form of repeatable, irreversible closed primary growth and dissociation *PT* loops, within which various characteristic secondary ‘scanning’ curve pathways may be followed. Similar behaviour has recently been observed for ice–water systems in porous media, and is characteristic of liquid–vapour transitions in mesoporous materials. The causes of such hysteresis are still not fully understood; our results suggest pore blocking during hydrate growth as a primary cause.

Naturally occurring gas hydrates (or clathrate hydrates) in sediments may pose a hazard to deepwater drilling and production operations (Kvenvolden 1999; Milkov *et al.* 2000), have potential as a strategic low-carbon energy reserve (Kvenvolden 1999; Lee & Holder 2001), could provide a means for deep ocean CO₂ disposal through sequestration/storage (Hunter 1999; Brewer *et al.* 1999), and have long-term significance with respect to ocean margin stability, methane release to the atmosphere and global climate changes (Kvenvolden, 1999; Dickens, 2003).

Although our understanding of sediment-hosted gas hydrates has grown considerably in recent years, we still lack fundamental knowledge concerning the mechanisms of hydrate growth, accumulation and distribution within the subsurface. Clathrates have been recovered in shallow ocean floor sediment cores from numerous sites around the world (e.g. Ocean Drilling Program (ODP) Leg 164, Blake Ridge, offshore South Carolina (Paull *et al.* 2000), and Leg 204, Cascadia Margin, offshore Oregon (Tréhu & Shipboard Scientific Party 2003)). Sediments hosting gas hydrates are generally characterized by organic matter-rich fine-grained silts, muds and clays, with lesser

coarser sandy layers present at some sites. Hydrates commonly display a wide range of growth habits, and are often patchily distributed within the host sediment according to texture (Booth *et al.* 1996). In fine-grained strata, hydrates are generally found in the form of segregated nodules, lenses, pellets or sheets. In contrast, where coarser layers are present, clathrates often form an interstitial pore fill between sediment grains. This variation in growth patterns according to sediment type suggests that host sediment properties may play an important role in controlling hydrate morphology and distribution within the subsurface (Clennell *et al.* 1999; Henry *et al.* 1999).

Further evidence for potential host sediment controls on hydrate equilibria comes from the predicted depth of the Base of the Hydrate Stability Zone (BHSZ) in seafloor sediments. While ODP coring has confirmed that the BHSZ commonly lies close to pressure and temperature conditions calculated from bulk (unconfined) phase equilibria, there are a number of sites where the thickness is notably less than predicted (e.g. Blake Ridge (Paull *et al.* 2000), and Cascadia Margin (Tréhu & Shipboard Scientific Party 2003)). The depth of the BHSZ is dependent on various factors, including

59 gas concentration (gas concentration must exceed
60 aqueous equilibrium solubility in the presence of
61 hydrate), composition (the addition of CO₂, H₂S
62 and higher thermogenic hydrocarbons such as
63 ethane/propane increases hydrate stability), pore
64 water salinity (dissolved salt reduces stability) and
65 the local geothermal gradient. However, where
66 these are relatively well established from drilling/
67 coring (such as at the Blake Ridge and Cascadia
68 Margin), additional factors must be sought to
69 explain predicted/actual BHSZ discrepancies. One
70 potential influence may be the host sediments them-
71 selves. The mechanisms by which sediment proper-
72 ties could alter hydrate stability and/or influence
73 distribution are still relatively poorly understood
74 (Max 2000); however, one potentially important
75 factor which has received considerable attention in
76 recent years is capillary inhibition (Clennell *et al.*
77 1999; Henry *et al.* 1999).

80 Phase behaviour in confined geometries

81 It is well established that the pressure–temperature
82 (*PT*) conditions of first-order phase transitions
83 (e.g. solid–liquid, liquid–vapour) may be signifi-
84 cantly altered in confined geometries. In narrow
85 pores, high-curvature phase interfaces can induce
86 strong differential capillary pressures, altering the
87 chemical potential of components relative to bulk
88 (unconfined) conditions. For solid–liquid transi-
89 tions, where pore sizes are sufficient for phases to
90 retain the structural and physical properties of the
91 bulk phase, solid melting temperatures are generally
92 depressed as a function of pore radius in accordance
93 with the Gibbs–Thomson equation (the constant
94 pressure analogue of the constant temperature
95 Kelvin equation for vapour pressure in mesoporous
96 media; (Enüstün *et al.* 1978; Christensen 2001). For
97 simple, single-component systems (e.g. ice–water),
98 the common form of the equation relates the pore
99 solid melting point depression, ΔT_p , from the bulk
100 (unconfined) melting temperature, T_b , to the pore
101 radius, r , through:

$$102 \Delta T_p = T_b \cdot \frac{F \gamma_{sl} \cos \theta}{r \rho_l \Delta H_{sl}} \quad (1)$$

103 where γ_{sl} is the solid–liquid interfacial free energy
104 (often referred to as the surface or interfacial
105 tension), F the shape factor of the interface (depend-
106 ent on interface curvature), ρ_l the density of the
107 liquid phase, ΔH_{sl} the latent heat (enthalpy) of
108 fusion, and θ the contact angle between the solid
109 phase and the pore wall (180° measured inside the
110 solid phase if an unfrozen liquid layer is assumed,
111 thus $\cos \theta = -1$). Where γ_{sl} and ΔH_{sl} are rela-
112 tively constant over the *PT* conditions of interest,
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equation (1) dictates a linear relationship between
 $\Delta T_p/T_b$ and reciprocal pore radius, as confirmed
experimentally for many organic and inorganic
liquids (Rennie & Clifford 1977; Jackson &
McKenna 1990, 1996; Christensen 2001). It should
be noted that equation (1) assumes that the solid
phase pressure (P_s) is equal to the bulk pressure
(P_b), that is, $P_l < P_s = P_b$. Where the liquid phase
(P_l) is at bulk pressure ($P_s > P_l = P_b$), the value ρ_l
should be replaced by ρ_s , the density of the solid
phase (Enüstün *et al.* 1978).

Although the thermodynamics of solid–liquid
equilibria in small pores (particularly ice–water
equilibria) has been the subject of investigation for
over 100 years (Christensen 2001), only relatively
recently did Handa & Stupin (1992) demonstrate
that methane hydrate dissociation temperatures
are depressed in narrow pores. Seafloor sediments
hosting gas hydrates are commonly fine-grained
(silts, muds, clays), with narrow mean pore dia-
meters ($\sim 0.1 \mu\text{m}$; Griffiths & Joshi 1989; Clennell
et al. 1999). In light of this, it has previously been
speculated that capillary phenomena could play an
important role in controlling hydrate stability and
distribution within sediments, and may be partly
responsible for observed discrepancies between pre-
dicted and actual BHSZs (Ruppel 1997; Clennell
et al. 1999; Henry *et al.* 1999).

In the most extensive theoretical analyses to
date, Clennell *et al.* (1999) & Henry *et al.* (1999)
(companion papers) developed a capillary-thermo-
dynamic model for hydrate formation in the seafloor
which attempted to account for the effect of pore
size on equilibrium conditions. From model predic-
tions, the authors could not confirm that capillary
inhibition alone was responsible for observed dis-
crepancies between predicted and actual BHSZs,
although it was concluded that capillary pheno-
mena did most likely play an important role in con-
trolling hydrate phase behaviour and distribution,
particularly in segregation and lens/nodule/layer
formation. A lack of firm conclusions concerning
the extent to which pore size affects the HSZ
could in part be attributable to a lack of available
values for hydrate–liquid (water) interfacial free
energy (the authors used a value for ice–water inter-
facial free energy), and, significantly, an absence of
reliable data relating pore size/geometry to hydrate
growth/dissociation conditions with which to
validate model predictions.

The potential role capillary effects may have
in controlling hydrate growth and accumulation
within sediments has led to considerable experimen-
tal and theoretical research into the phenomenon
over the past 8 years. Work has focused primarily
on (relatively) well characterized porous silicas
(Uchida *et al.* 1999, 2002; Seshadri *et al.* 2001;
Wilder *et al.* 2001a, b; Seo *et al.* 2002; Smith

117 *et al.* 2002a, b, 2004; Wilder & Smith 2002; Zhang
 118 *et al.* 2002, 2003; Seo & Lee, 2003; Aladko *et al.*
 119 2004; Dicharry *et al.* 2005), and more recently on
 120 natural sands and clays (Uchida *et al.* 2004).
 121 Although there are a number of discrepancies
 122 between studies, particularly regarding experimen-
 123 tal data interpretation (as discussed by Anderson
 124 *et al.* 2003a), the overall conclusion is that narrow
 125 pores have a significant and consistent inhibiting
 126 effect on hydrate stability. However, phase behav-
 127 iour in porous media is highly complex, and
 128 there are many potentially important factors that
 129 have not yet been addressed. One significant, and
 130 particularly relevant, issue is that the focus to date
 131 has been the measurement and prediction of hydrate
 132 dissociation conditions in porous media, with
 133 the equally, if not more important process of
 134 hydrate growth being largely overlooked.

135 As suggested by Clennell *et al.* (1999), capillary
 136 theory predicts a considerable hysteresis may exist
 137 between solid growth and melting conditions in
 138 narrow pores. The hysteresis loops commonly
 139 associated with gas (e.g. nitrogen) adsorption/
 140 desorption in mesoporous materials and hydro-
 141 carbon reservoir rock drainage/imbibition curves
 142 are testament to the fact that such behaviour is a
 143 common characteristic of capillary pressure con-
 144 trolled phase transitions and fluid flow within
 145 porous media.

146 In Anderson *et al.* (2003b), we reported exper-
 147 imental CH₄, CO₂ and CH₄-CO₂ clathrate hydrate
 148 dissociation and ice melting data for mesoporous
 149 silica glasses. This data was used to estimate values
 150 for ice-water and hydrate-liquid (water) interfacial
 151 free energies through a modified version of equation
 152 (1), and subsequently employed to validate a capil-
 153 lary corrective function for hydrate thermodynamic
 154 models which allows the prediction of hydrate
 155 dissociation conditions for narrow cylindrical- or

spherical-like pores (Llamedo *et al.* 2004). The
 added effect of pore water salinity was also investi-
 gated (Østergaard *et al.* 2002). Here, we report
 the results of a detailed experimental investigation of
 methane hydrate growth and dissociation conditions
 in synthetic mesoporous silica glasses. Data reveal
 an equilibrium hysteretic hydrate formation/
 decomposition behaviour not previously observed
 for clathrates in porous media. Through an analysis
 of experimental data, we will assess potential
 origins of the observed hysteresis phenomena, and
 then comment briefly on potential implications for
 seafloor hydrate systems.

Experimental equipment and methods

A specifically designed high-pressure (max.
 41 MPa) set-up was used in experiments. The set-
 up, shown in Figure 1, consists of an equilibrium
 cell (75 cm³ volume) with removable sample cup,
 central PRT (platinum resistance thermometer),
 inlet/outlet valve, Quartzdyne pressure transducer
 and insulated coolant jacket.

The PRT was calibrated with a Prima 3040
 precision thermometer, and measures cell temper-
 ature to ± 0.01 K with an estimated accuracy
 of ± 0.1 K. The transducer, via a computer inter-
 face, can measure system pressure to within
 $\pm 6.9 \times 10^{-6}$ MPa, and has a quoted accuracy of
 ± 0.008 MPa for the complete operating range of
 0–138 MPa. System temperature was controlled
 by circulating fluid from a programmable cryostat
 (253–373 K) through the cell jacket, and could
 be kept stable to within ± 0.02 K. Cell temperature
 and pressure were continuously monitored and
 recorded using a computer.

Double-distilled water was used in all exper-
 iments. High-purity methane (99.995 mol%) was

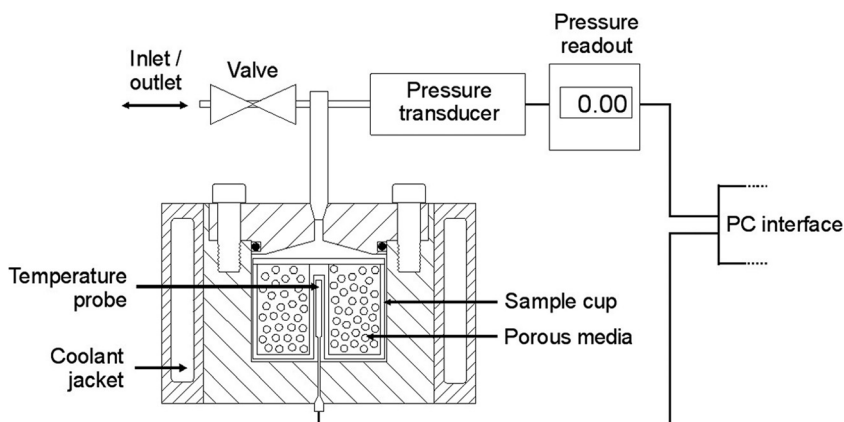


Fig. 1. Schematic illustration of the high-pressure set-up used in experiments.

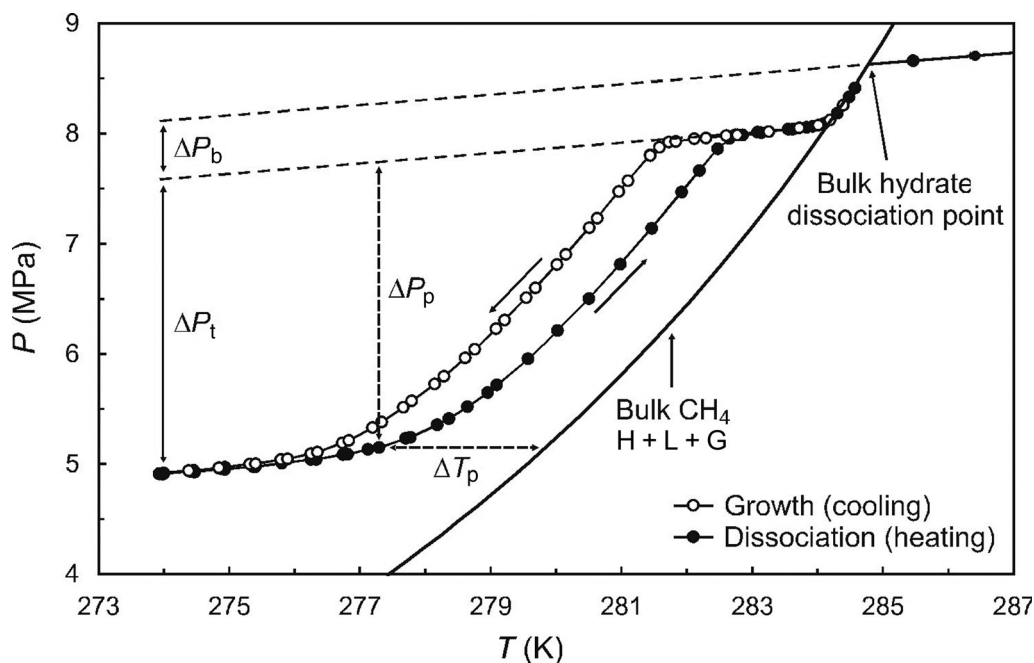
175 supplied by Air Products. Porous silica samples,
 176 known as Controlled Pore Glass (CPG), were pur-
 177 chased from CPG Inc., USA (now Millipore,
 178 USA), and consist of 37–74 μm porous silica
 179 shards. Three samples, of 30.6, 15.8 and 9.2 nm
 180 nominal pore diameters, were used for experiments.
 181 Sample pore size distributions were previously
 182 characterized independently by NMR (nuclear mag-
 183 netic resonance) cryoporometry (Anderson *et al.*
 184 2003b; Dore *et al.* 2004).

185 Test procedures were as follows. CPG silicas
 186 were dried overnight in an oven, then saturated
 187 (water volume, $V_w >$ pore volume, V_p) with a mea-
 188 sured volume of distilled water. Prepared samples
 189 were placed in the cell, the cell cooled and water
 190 frozen (to minimize evaporation), then air evacu-
 191 ated. Temperature was subsequently raised again
 192 to the desired starting temperature (generally outside
 193 the bulk hydrate stability zone) before methane was
 194 injected to the initial starting pressure. To form
 195 hydrates in the first instance, the cell was cooled
 196 rapidly until growth commenced, as indicated by
 197 pressure–temperature relations. Subsequent to
 198 this, hydrate growth and dissociation *PT* pathways
 199 for sample hysteresis regions were determined by
 200

a stepped temperature cycling method based on
 the approach of Tohidi *et al.* (2000) & Anderson
et al. (2003b). The method involves heating/
 cooling of the cell in steps (generally 0.2–0.5 K),
 with sufficient time being given (in this case
 8–24 h) for the system to reach equilibrium (as
 indicated by stable pressure) following each step,
 which results in very reliable and highly repeatable
 (to within ± 0.1 K) measurements.

Results and discussion

Equilibrium methane hydrate growth and disso-
 ciation conditions were determined at various pres-
 sures for the three different CPG silica samples
 (30.6, 15.8 and 9.2 mean pore diameters). Figure 2
 shows an example of typically observed clathrate
 growth and dissociation pressure–temperature
 pathways, in this case for the 30.6 nm sample. As
 system water volume exceeds CPG pore volume,
 gas hydrates form both within and outside the pore
 network; hydrates outwith the pores dissociate at
 the bulk (unconfined) methane hydrate + liquid +
 gas (H + L + G) phase boundary, with both pore



227
 228 **Fig. 2.** Plot of primary growth and dissociation *PT* data for the 30.6 nm mean pore diameter CPG silica saturated with
 229 water. ΔP_t and ΔP_b are the total change in pressure associated with hydrate formation in the pores and the bulk
 230 respectively. ΔT_p and ΔP_p are the temperature depression of pore hydrate/growth dissociation conditions (from the bulk
 231 methane H + L + G phase boundary) and change in pressure associated with pore hydrate formation at any given
 232 recorded equilibrium *PT* condition on the heating/cooling curves respectively. Bulk CH_4 data: polynomial fit to Deaton
 & Frost (1946), McLeod & Campbell (1961).

hydrate growth and dissociation conditions being depressed to significantly lower temperatures. The hysteresis between pore clathrate growth and dissociation conditions is distinct – hydrate formation occurs at temperatures significantly lower than decomposition, with irreversible (unidirectional) *PT* pathways forming a complete closed hysteresis loop. To our knowledge, this clear, repeatable (in the same closed system over 6 months), equilibrium *PT* hysteresis between growth and dissociation has not previously been reported for clathrate hydrates in porous media. Similar (although not so consistently repeatable) equilibrium hysteretic behaviour has been described for ice–water transitions in hardened cement pastes (Schulson *et al.* 2000; Swainson & Schulson 2001), however it is generally not reported in most literature studies of solid–liquid transitions in mesoporous materials.

In contrast to the repeatable, equilibrium hysteresis observed here, significant differences between measured freezing and melting temperatures due to stochastic heterogeneous nucleation phenomena have been reported for fluids confined to porous materials (Faivre *et al.* 1999; Morishige & Kawano 1999). In this case, hysteresis can be attributed to kinetic issues arising as a result of the supercooling generally required to initiate solid nucleation in the absence of a pre-existing crystalline phase. Here, we

have eliminated the need for nucleation by ensuring clathrate is present in the bulk (outside the pores) when cooling to initiate pore hydrate growth. Theoretically, this means only progressive solid growth front propagation into media on cooling is required.

Characteristics of hysteresis loops

From Figures 2 and 3, we see that primary pore hydrate dissociation and growth patterns are characterized by a sigmoidal (with respect to linear liquid + gas only *PT* relationships) curves indicative of formation/decomposition across a Gaussian-like distribution of pores typical of Controlled Pore Glasses (Anderson *et al.* 2003a, b; Østergaard *et al.* 2002). Partial or complete dissociation curves for various synthetic (Vycor and sol–gel) mesoporous silicas have been reported previously by other workers (Uchida *et al.* 1999, 2002; Seshadri *et al.* 2001; Wilder *et al.* 2001a, b; Seo *et al.* 2002; Smith *et al.* 2002a, b, 2004; Wilder & Smith 2002; Zhang *et al.* 2002, 2003; Seo & Lee 2003; Dicharry *et al.* 2005), and show very similar characteristics.

For the purposes of interpretation, we can re-plot heating curve data in terms of the volume of pore hydrate formed relative to growth/dissociation temperature depression. Figure 4 shows a plot of

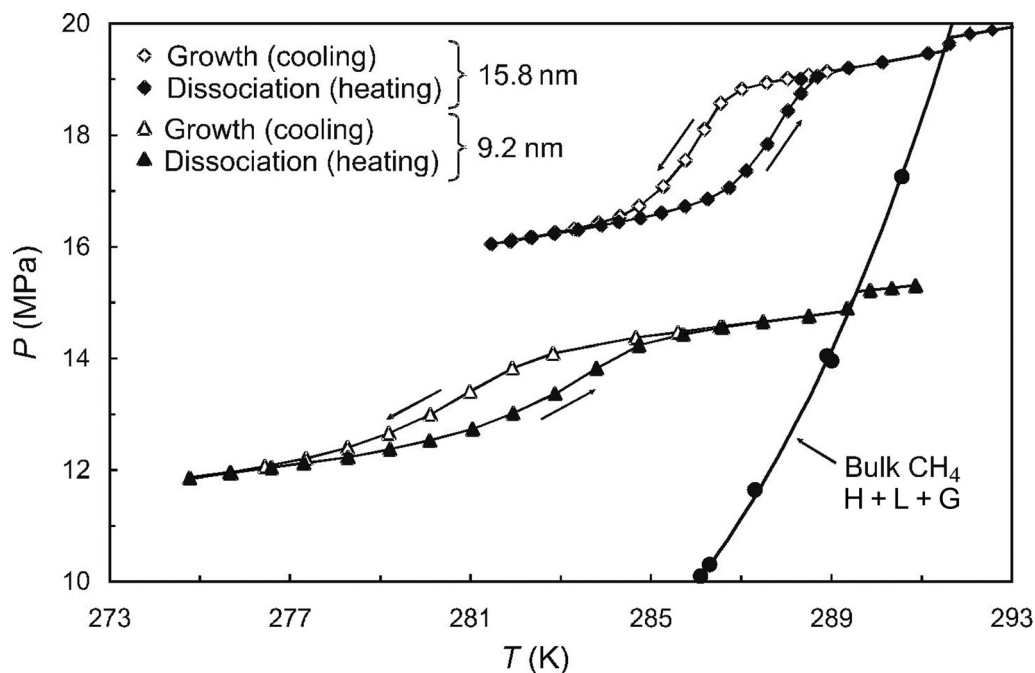


Fig. 3. Examples of primary methane hydrate growth and dissociation loop *PT* data for the 9.2 nm and 15.8 nm pore diameter CPG silicas. Bulk CH_4 data: polynomial fit to Deaton & Frost (1946), McLeod & Campbell (1961).

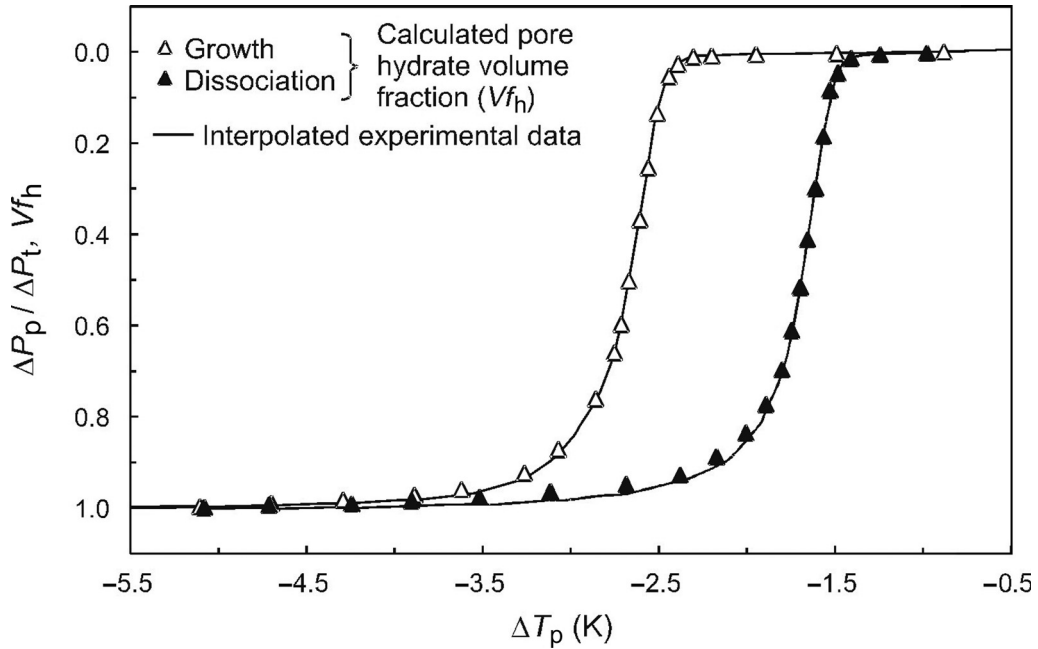


Fig. 4. Plot of ΔT_p v. $\Delta P_p/\Delta P_t$ (experimental data) and calculated volume fraction of pore hydrate (V_{f_h}) present for selected experimental points (30.6 nm sample). The fraction of total pressure change associated with pore hydrates essentially equals the volume fraction of pore hydrate formed at any point.

ΔT_p v. $\Delta P_p/\Delta P_t$ for the 30.6 nm sample where, as illustrated in Figure 2, ΔT_p is the temperature depression of hydrate growth/dissociation conditions from the bulk methane hydrate phase boundary, ΔP_p is the change in pressure associated with pore hydrate formation at any point and ΔP_t is the total change in pressure associated with pore hydrate formation. Also plotted for comparison is the calculated volume fraction of pore gas hydrate (V_{f_h}) present at each point. Hydrate volume fractions were calculated by standard iterative mass balance/volume methods assuming a methane hydration ratio of 1 : 6 (Handa 1986; Lievois *et al.* 1990; Ciscone *et al.* 2005). As can be seen, the fraction (of total) pressure change associated with pore hydrates for each point is essentially equal to the volume fraction of pore hydrate present at that condition. Thus, in further analyses, we can consider that as a good approximation, $\Delta P_p/\Delta P_t = V_{f_h}$.

As our interest lies in the relationship between pore radius and hydrate growth/dissociation conditions, we could theoretically use equation (1) to convert ΔT_p to equivalent r , allowing the examination of data in terms of V_{f_h} v. r . However, this would require the assumption of specific pore/solid–solid interface shapes for both solid formation and melting conditions, as defined by the shape factor, F , in equation (1). To avoid this

assumption, we can compare growth and dissociation in terms of acting capillary pressure, P_c , at ΔT_p . P_c can be calculated by substituting the right hand side of the Young–Laplace equation:

$$P_c = P_s - P_l = \frac{F\gamma_{sl} \cos \theta}{r} \quad (2)$$

where P_s is the pressure of the solid (hydrate) phase and P_l the pressure of the liquid phase, into equation (1) and rearranging to yield:

$$P_c = \frac{\Delta T_p}{T_b} \cdot \rho_l \Delta H_{sl} \quad (3)$$

Figure 5 presents pore hydrate volume fractions as a function of calculated capillary pressure during growth and dissociation for all the three CPG silicas. As can be seen, hysteresis loops for all samples show very similar characteristics, with primary growth (increasing P_c) and dissociation (decreasing P_c) PT pathways being of sigmoidal form, consistent with Gaussian-like pore size distributions. As would be expected, capillary pressures increase as a function of pore diameter, the 9.2 nm mean pore diameter sample having the highest capillary pressure range/greatest degree of hydrate inhibition.

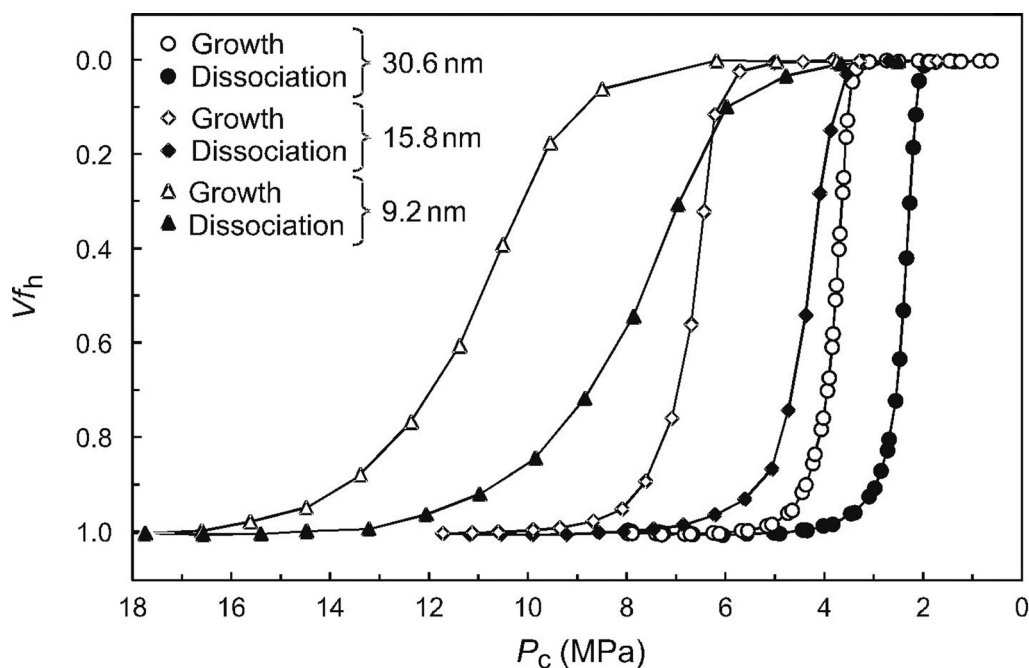


Fig. 5. Volume fraction pore hydrate versus capillary pressure for primary growth and dissociation loop data for all CPG silica samples studied.

By initiating cooling from any point on the primary dissociation curve, or conversely, by heating from any point on the primary growth curve, a variety of secondary characteristic ‘scanning’ growth/dissociation PT pathways may be followed, as illustrated in Figures 6 and 7 for the 30.6 nm sample. We adopt the term ‘scanning’ because it is generally used to describe similar curves in gas adsorption/desorption studies of mesoporous materials (Mason 1982, 1988). As for primary growth/dissociation pathways, scanning curves are irreversible, leading to an infinite number of possible, but consistent and repeatable PT pathways within the primary loop, depending on initial conditions. This behaviour, although often not investigated (primary loops only being reported), has been studied in detail for gas adsorption/desorption (Mason 1988). However, as far as we are aware, there is little (if any) comparable data for solid–liquid equilibria available.

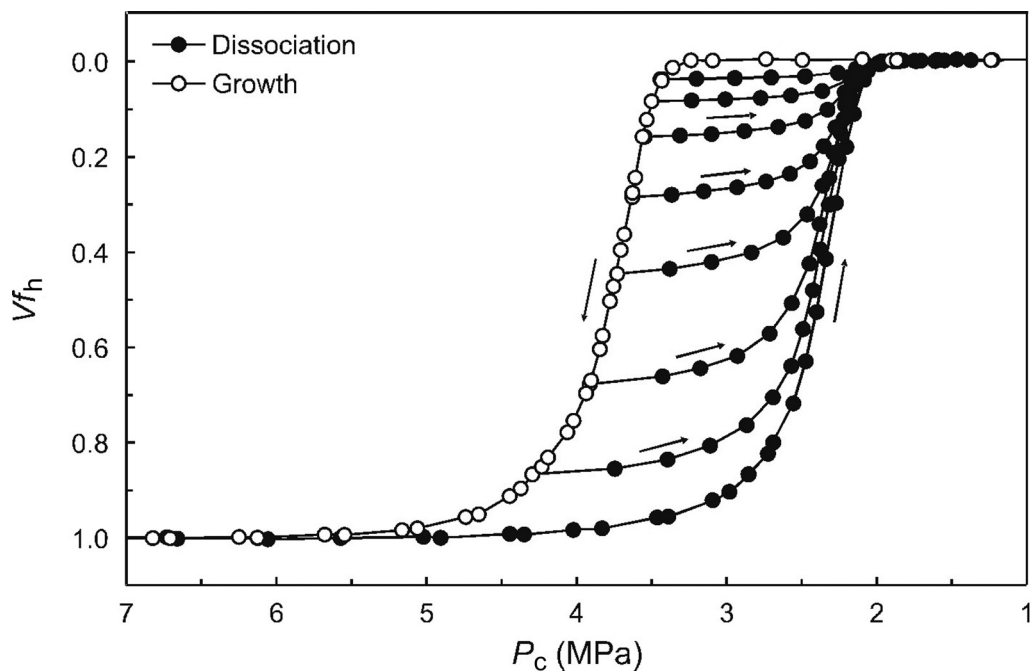
Origins of hysteresis

We have shown previously (Anderson *et al.* 2003*b*) that, in agreement with the Gibbs–Thomson equation (1), mean pore diameter CH_4 , CO_2 and CH_4 – CO_2 clathrate hydrate dissociation (and ice melting data) for CPG samples shows a linear correlation between $\Delta T_p/T_b$ and $1/r$, giving a consistent

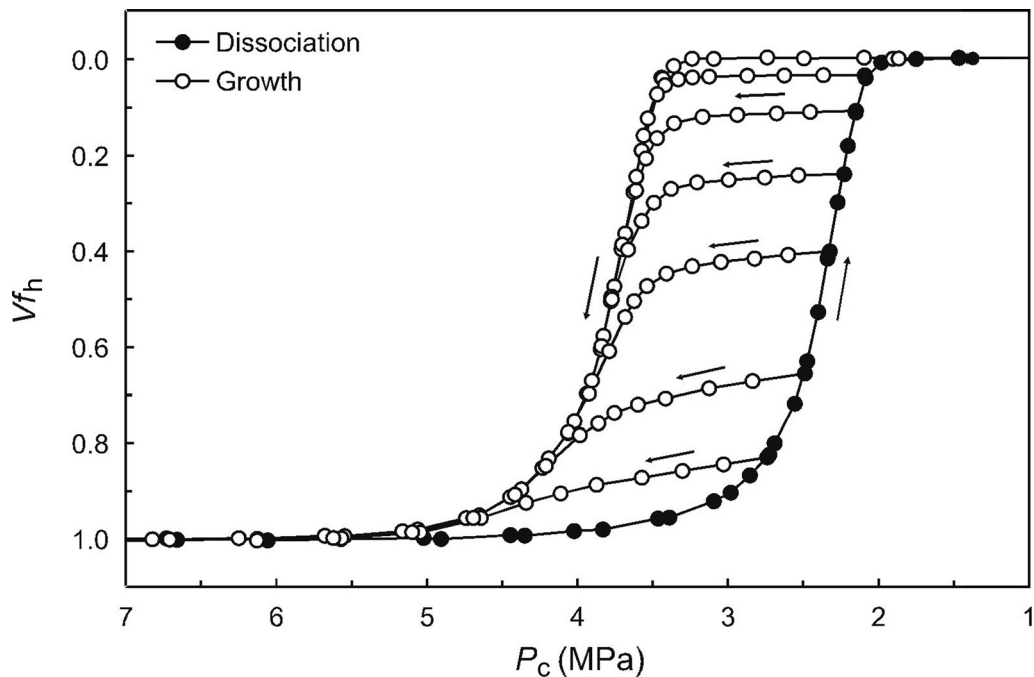
and thermodynamically predictable relationship between hydrate dissociation conditions and pore size (Llamedo *et al.* 2004). However, data presented here show that hydrate growth conditions are depressed to significantly lower temperatures compared with dissociation, resulting in a distinct PT hysteresis between opposing transitions. To predict this behaviour, and assess its potential implications for hydrates in the seafloor environment, then it is first necessary to establish its origins.

The causes of hysteresis in porous media are still poorly understood (Everett 1954; Mason 1982, 1988; Christensen 2001; Ravikovitch & Neimark 2002). A significant part of the problem lies in the complexity of pore structures, which may comprise various heterogeneous (at the pore scale) pore geometries, a wide range of pore diameters and varying degrees of interconnectivity. To precisely predict hysteresis behaviour for a particular medium, we can imagine that it might be necessary to have an intimate knowledge of the pore space in terms of all these factors. A detailed analysis of CPG pore structures is beyond the scope of this paper; however we can speculate as to the origins of the observed hysteresis patterns based on accepted capillary theory.

The most basic pore model assumes single, simple pore shapes, such as spheres or cylinders. To introduce pore interconnectivity as a factor, it



433 **Fig. 6.** Volume fraction pore hydrate versus calculated capillary pressure for secondary scanning dissociation curves
434 originating from the primary growth curve (30.6 nm mean pore diameter CPG sample).
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463 **Fig. 7.** Volume fraction hydrate versus capillary pressure for secondary scanning growth curves originating from the
464 primary dissociation curve (30.6 nm mean pore diameter CPG sample).

is common to consider a matrix of spherical-like nodes connected by cylindrical-like bonds (Mason 1988; Vidales *et al.* 1995). Based on scanning electron microscopy (SEM) images and molecular dynamics simulations (Gelb & Gubbins 1998), this type of model might give a reasonable representation of controlled pore glasses. In such a media, we can consider two particular factors which may contribute to hysteresis: (1) pore geometry, and (2) pore blocking.

Influence of pore geometry

The geometry of a pore will have a major influence on the interface curvatures of confined phases, thus capillary pressures. For a media containing a notable component of cylindrical-like capillaries, hysteresis could potentially arise due to differences in solid–liquid interface curvatures during crystallisation and melting (Brun *et al.* 1977; Jallut *et al.* 1992; Faivre *et al.* 1999). The interface shape factor F in equations (1) and (2) is defined by the solid–liquid interfacial curvature, κ , in terms of the pore radius by:

$$F = \kappa r \quad (4)$$

with κ being defined by:

$$\kappa = \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (5)$$

where r_1 and r_2 are the two orthogonal radii that describe the interface at any point. For solid–liquid transitions in a spherical pore, r_1 and r_2 are equal during both solid growth and melting, thus mean curvature is $2/r$ for both cases. In contrast, as shown in Figure 6, for solid growth in cylindrical pores, if the solid–liquid interface is considered a hemispherical cap, then r_1 and r_2 are equal, giving a mean curvature of $2/r$. However, for melting, although r_1 remains constant, r_2 is infinite ($1/r_2 \rightarrow 0$), thus total curvature is $1/r$. A curvature of $1/r$ implies that the solid–liquid interface should not retreat through a pore upon melting, but rather the solid cylinder should instantaneously melt along its length when stability conditions for the appropriate pore radius are surpassed. This concept is analogous to gas/oil phase ‘snap-off’ in (water-wet) cylindrical pores of reservoir rocks as hydrocarbon saturation is reduced (Blunt 1997; Hui & Blunt 2000). We can account for this geometrical control in equations (1) and (2) by modifying appropriately; $F = 2$ for growth and 1 for dissociation.

Based on the above, we can envisage that a media containing a notable proportion of cylindrical-like capillaries should display a temperature (or pressure) hysteresis between solid-phase crystallization and

decomposition. Applying this to the results for CPG detailed here, then, if cylindrical pores are the cause of the observed hysteresis, we might expect to observe that for an appropriate volume of fraction of pore hydrate, V_{fh} , capillary pressure during hydrate growth, $P_{c,g}$, should be around double that for dissociation, $P_{c,d}$. From examination of the data presented in Figures 5–7, this is clearly not the case: capillary pressures during hydrate growth are considerably less than double that for dissociation, with $P_{c,g}$ to $P_{c,d}$ ratios decreasing with decreasing sample mean pore diameter.

Figure 8 shows a plot of $P_{c,g}$ v. $P_{c,d}$ for equal pore volume fractions of clathrate present. As can be seen, rather than $P_{c,g}$ being a multiple of $P_{c,d}$ (e.g. $P_{c,g} = 2P_{c,d}$) the relationship appears to be additive, that is, $P_{c,g} = P_{c,d} + x$, where x is relatively constant for a specific CPG sample, but variable between samples, and decreases with mean pore diameter. Furthermore, if CPG is composed primarily of cylindrical-like capillaries, then we might expect that, upon heating from the primary growth curve, dissociation would begin only when the primary dissociation curve was reached, that is, hydrate which had grown into progressively smaller cylindrical pores to radius r at $P_{c,g}(r)$ would only melt on heating when $P_{c,d}(r)$ was reached, with $P_{c,g} = XP_{c,d}$ (X being 2 for an ideal cylinder as detailed). However, Figure 6 shows that hydrate dissociation begins in earnest almost immediately on heating from the primary growth curve, suggesting the presence of a significant proportion of pores with interface curvatures which are approximately equal on growth and dissociation, that is, spherical-like rather than cylindrical.

Data thus suggest that differences in interface curvature for growth and dissociation in cylindrical capillaries is not the sole mechanism responsible for the observed hysteresis. However, results do not preclude this as being at least partly responsible for the phenomena. For any given point on the primary growth curve, the capillary pressure is at least double that for the associated point of complete pore hydrate dissociation achieved on heating, as can be seen in Figures 6 and 9. As shown in Figure 9, data suggest that $P_{c,g}$ is close to $2P_{c,d}$ at the points of initial hydrate growth (on the primary growth curve) and final hydrate dissociation, respectively (although determining these conditions exactly is problematic as the amount of hydrate present in the pores becomes infinitesimally small and within the error in measured pressure change).

As noted, the fact that dissociation begins almost immediately on heating from the primary growth curve suggests hydrate in pores with mean interface curvatures (thus capillary pressures) which are similar on growth and dissociation,

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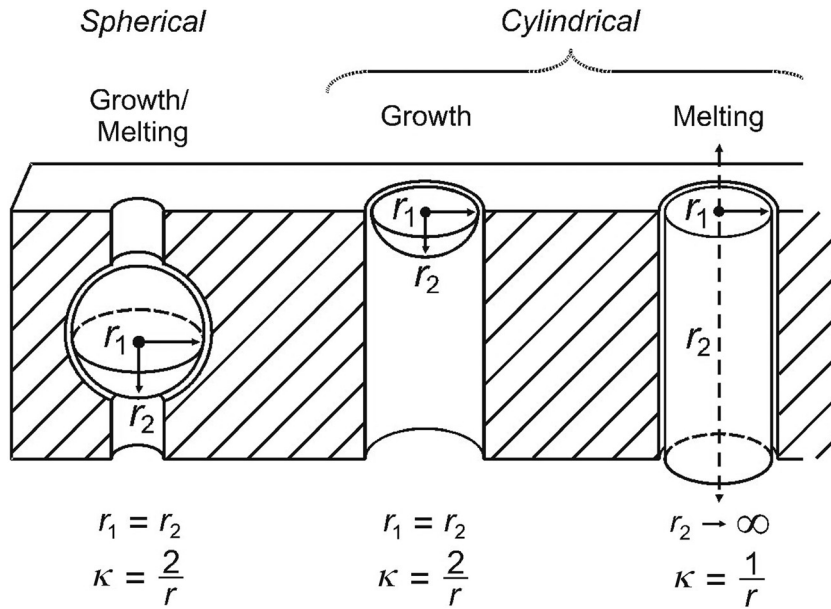


Fig. 8. Illustration of the difference in interface curvatures for hydrate growth and dissociation in ideal spherical and cylindrical pores.

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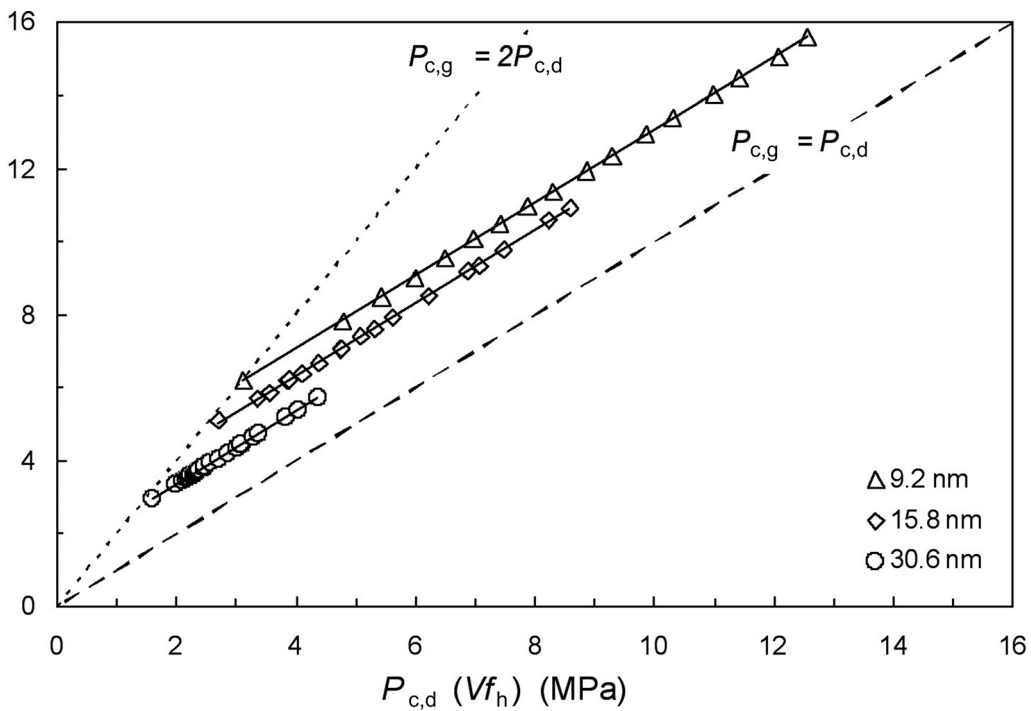


Fig. 9. Plot of capillary pressure during hydrate ($P_{c,g}$) growth v. that for dissociation ($P_{c,d}$) for equal volume fractions (V_{f_h}) of pore hydrate present. At the points corresponding to initial growth/final dissociation ($P_{c,g}$ and $P_{c,d}$ minima), $P_{c,g}$ approaches $2P_{c,d}$.

580

that is, spherical-like pores. Hydrate in these pores should theoretically grow and melt at the same capillary pressure condition (or ΔT_p). However, data in Figure 6 shows that this is not the case as P_c at conditions for growth is much higher than that for dissociation for the same volume of hydrate present. In light of this, it is necessary to consider mechanisms which could cause the observed hysteresis that are not primarily related to the interface curvature/geometry of individual pores. A potential candidate for this is 'pore blocking'.

Pore blocking effects

Pore blocking has been proposed by a number of authors as a primary cause of the hysteresis commonly observed for liquid–vapour phase transitions in porous media (Mason 1988; Ravikovitch & Neimark 2002). The classic example of pore blocking is that for 'ink-bottle' pores (large pores with narrow necks) which cannot drain (desorb) until the capillary pressure reaches that needed for vapour phase entry into the narrow pore neck. We can apply this same theory to solid–liquid transitions if we consider the solid hydrate phase penetrating liquid-filled pores as analogous to vapour phase penetration during desorption.

Figure 10 shows a simple illustration of the mechanisms by which pore blocking could be envisaged to occur in a hydrate–liquid system.

If we consider a large pore of radius r_a accessible to the bulk only via smaller pores of $r < r_a$, then, in the absence of heterogeneous nucleation within the pore space, hydrate growth conditions for the large pore will be determined by the capillary entry pressure required for clathrate penetration of the smallest access pore throat, in this case of radius r_d . This means that hydrate growth in the large pore will take place at a temperature much lower than its 'unblocked' equilibrium freezing/melting temperature, as predicted by equation (1). On heating, however, equilibrium dissociation conditions of hydrate in the large pore will depend on its own radius, r_a . If we consider this blocking mechanism acting in a porous medium with a wide distribution of interconnected pores of different radii, it can be envisaged that many pores of large radius may only be accessible to growth fronts propagating from the bulk by means of narrower pore throats. In this case, it would be expected that a significant hysteresis would develop between solid growth and melting temperatures.

In Figure 11, data for selected individual secondary dissociation (scanning) curves for the 30.6 nm

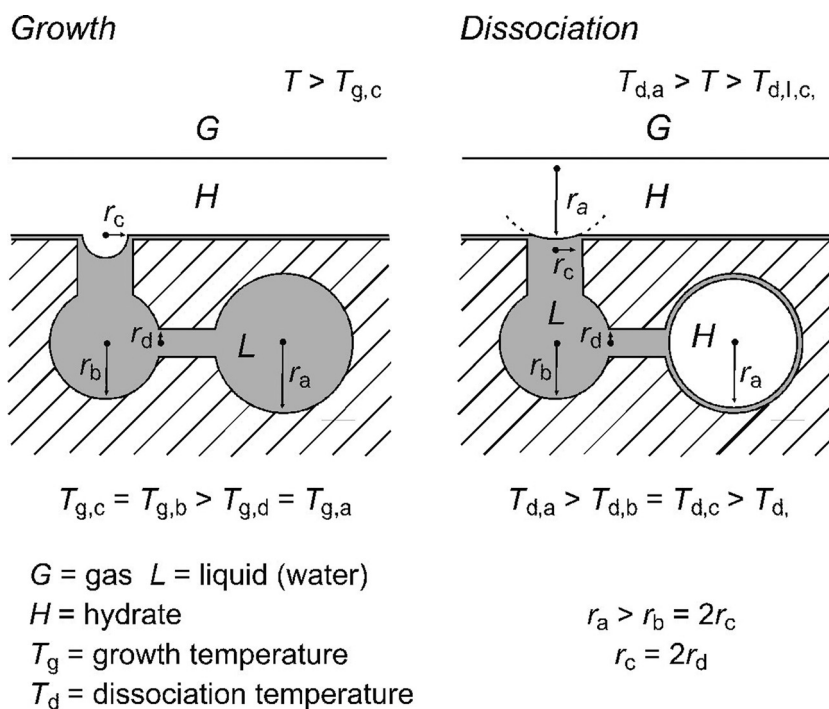


Fig. 10. Illustration of pore blocking effects in interconnected pores of different radii and geometry (cylindrical or spherical). See text for discussion.

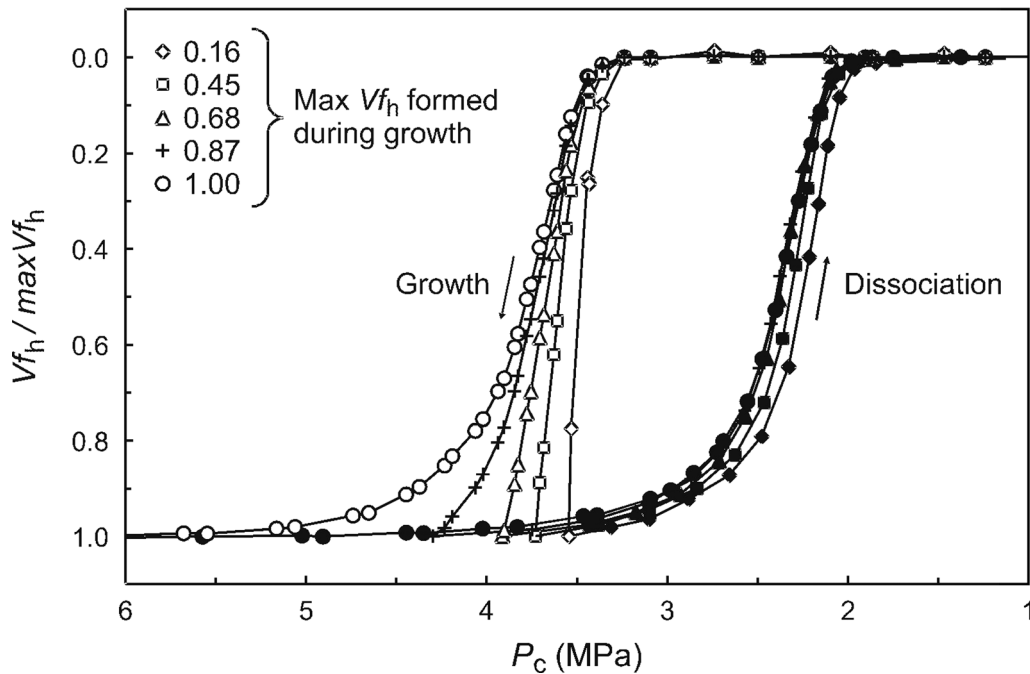


Fig. 11. Normalized volume fractions of pore hydrate versus capillary pressure for selected secondary scanning dissociation curves originating on the primary growth curve. Plotted V_{fh} data are normalized individually based on maximum pore volume fraction of hydrate ($\max V_{fh}$) formed during growth (open symbols) on the primary growth curve before dissociation was initiated along a scanning curve (solid symbols).

sample have been normalized with respect to appropriate maximum volume fraction of hydrate formed on the primary growth curve in each case. Also shown are associated primary growth curve data for each. Heating curves essentially represent dissociation across the cumulative pore size/volume distributions (PSD) for pores in which hydrates have formed during cooling along the primary growth curve to the starting P_c condition. We can see from Figure 11 that, irrespective of initial starting conditions on the primary growth curve, dissociation curves are strikingly similar, suggesting that, in each case, hydrate decomposition takes place across a PSD closely representative of the media as a whole. As the P_c (thus ΔT_p) reached during primary growth is increased, so a larger volume of hydrate formed in pores of smaller radii (increased capillary pressure) is added to the total hydrate volume, as evidenced by associated secondary scanning dissociation curves shifting to higher capillary pressures. This pattern strongly supports pore blocking as a cause of the observed hysteresis.

Based on the above, we can envisage that the primary growth curve represents hydrate penetration into the media as a function of the pore throat entry radius distribution and associated accessible, 'freezable' volume (i.e. pore volume of water which

can be converted to gas hydrate). As the system is cooled, the capillary entry pressure for progressively smaller 'access' pore throats is achieved, allowing the growth front to penetrate further from the bulk into the media, converting an additional fraction of the pore volume to hydrate at each stage, with each volume fraction converted being closely representative of the pore size distribution as a whole.

Secondary growth scanning curves originating on the primary dissociation curve add support to a pore blocking model (Fig. 7). It can be envisaged that, during dissociation, hydrate in some large pores (dissociation temperatures not yet reached) should become isolated (e.g. consider the large pore of radius, r_a in Fig. 10). On cooling, hydrate in these large pores will act as secondary sites for initiation of the hydrate growth front as it starts to penetrate back into the media. For many regions of the pore network, this may mean that the capillary pressure, thus ΔT_p required to initiate hydrate growth, is considerably less than that which would normally be required for conditions where the front penetrates from the bulk alone (i.e. primary growth curve conditions). As such, re-growth on secondary scanning curves should be more pronounced and occur at lower $P_{c,g}$ than for the

697 primary growth curve. This behaviour is observed in
698 Figure 7; for secondary scanning growth curves
699 initiated on the primary dissociation curve, hydrate
700 formation (increasing V_{f_h}) at lower P_c becomes
701 increasingly pronounced as starting P_c is reduced
702 (i.e. less hydrate dissociated before regrowth
703 initiated), with the 'knees' which represent break-
704 through pressures becoming increasingly flattened.

706 Significance for seafloor hydrate systems

707 It is beyond the scope of this paper to investigate in
708 detail the potential effects of the observed hysteresis
709 on gas hydrate growth/dissociation conditions in the
710 natural sedimentary environment. However, some
711 preliminary comments can be made based on the
712 results presented here.

713 Fine-grained silts, muds and clays which commonly
714 host gas hydrates can have quite narrow mean pore
715 diameters (0.1 μm) (Griffiths & Joshi 1989; Clennell
716 *et al.* 1999). For curvatures of $2/r$ (spherical) and
717 $1/r$ (cylindrical), our results suggest that pore
718 diameters of 0.1 μm could reduce hydrate stability
719 (dissociation) by 15 m (c. 0.5 °C) and 30 m (c. 0.9
720 °C) respectively in areas of moderate geothermal
721 gradient (30 °C/km). This is a significant potential
722 displacement. Depending on the extent to which pore
723 blocking (and the locus of hydrate formation within
724 pore space) plays a role, then temperature restrictions
725 for hydrate growth could be notably greater.

726 Results strongly suggest that hydrate formation in
727 narrow pores is characterized by progressive solid
728 growth front penetration from the bulk or larger
729 voids into the media. Front progression (as temperature
730 is decreased or pressure increased) will be dependent
731 upon the distribution of narrow pore throats relative
732 to associated accessible voids. One would imagine
733 these factors to be quite media-specific. This, and the
734 fact that pore hydrate dissociation conditions are
735 independent of interconnectivity, suggests the pore
736 space of natural sediments must be characterized in
737 terms of both pore throat entry radius distribution
738 and specific pore radius/volume distribution if we
739 are to accurately predict both hydrate growth and
740 dissociation conditions for a particular media.

741 Regarding the proposed pore blocking phenomena,
742 it should be noted that the process requires nucleation
743 to be restricted within pores. For the mesoporous
744 materials examined here (maximum pore diameters
745 of 0.05 μm or 50 nm), it seems that growth front
746 propagation is favoured over nucleation, although it
747 might be expected that, in much larger pores/
748 voids, heterogeneous nucleation may be the preferred
749 mechanism for hydrate crystallization.

Conclusions

We have reported the results of a detailed experimental investigation of methane hydrate growth and dissociation conditions in synthetic mesoporous silica glasses. Data demonstrates that hydrate formation and decomposition in narrow pore networks are characterized by a distinct hysteresis between opposing transitions—hydrate growth taking place at temperatures considerably lower (or pressures higher) than those of dissociation. The hysteresis is an equilibrium phenomenon, and takes the form of irreversible, repeatable closed primary bounding growth/dissociation PT loops within which various characteristic secondary growth and dissociation specific 'scanning' PT pathways may be followed, depending on initial conditions. Similar hysteretic phenomena have been reported for ice growth and melting in the pores of cement pastes, and the behaviour appears to be closely analogous to that commonly observed for liquid–vapour transitions (gas adsorption–desorption) in mesoporous materials.

A detailed experimental analysis suggests that hysteresis arises primarily as a result of pore blocking during hydrate growth, although differences in interface curvatures during solid growth and decomposition resulting from pore geometry constraints (e.g. cylindrical pores) are likely to also contribute.

Results show that hydrate growth is characterized by capillary pressure-controlled progressive solid growth penetration from the bulk (or larger pores/voids) into the pore network as a function of decreasing temperature (increasing capillary pressure) with heterogeneous nucleation in pores not being favoured. In contrast, pore hydrate dissociation conditions appear to be principally controlled by interface curvatures as determined by individual pore geometry. As this behaviour has been observed for both synthetic and (more) natural (i.e. cement pastes composed of a variety of natural minerals), for both hydrates and ice, it is very likely that similar phenomena will occur during hydrate growth and dissociation in fine-grained natural sediments.

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