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GAS HYDRATE GROWTH MORPHOLOGIES AND THEIR EFFECT ON THE STIFFNESS AND DAMPING OF A HYDRATE BEARING SAND

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ABSTRACT

Using a specially constructed Gas Hydrate Resonant Column (GHRC), the University of Southampton explored different methods of hydrate synthesis and measured the properties of the resulting sediments, such as shear wave velocity (V_s), compressional wave velocity (V_p) and their respective attenuation measurements (Q_s^{-1} and Q_p^{-1}). Two approaches were considered. The first utilises an excess gas technique, where known water volume in the pore space dictates the quantity of hydrate. The second approach uses a known quantity of methane gas within the water saturated pore space to constrain the volume of hydrate. Results from the two techniques show that hydrates formed in excess gas environments cause stiffening of the sediment structure at low concentrations (3%), whereas, even at high concentrations of hydrate (40%) in excess water environments, only moderate increase in stiffness was observed. Additionally, attenuation results show a peak in damping at approximately 5% hydrate in excess gas tests, whereas in excess water tests, damping continues to increase with increasing hydrate content in the pore space. By considering the results from the two approaches, it becomes apparent that formation method has an influence on the properties of the hydrate bearing sand, and must therefore influence the morphology of the hydrate in the pore space.

Keywords: hydrate morphology, wave velocity, seismic attenuation, resonant column

NOMENCLATURE

A	Dimensionless stiffness constant
a	Van Der Waals coefficient (atml^2/mol^2)
b	velocity stress exponent
b'	Van Der Waals coefficient (l/mol)
H_c	Hydrate content (%)
M_g	molar mass methane hydrate (g/mol)
n	number of moles
P	Pressure (atm)
Q_s^{-1}	shear wave attenuation
R	universal gas constant (latm/K/mol)
T	Temperature (K)
V_v	Volume (l)
V_s	Shear wave velocity (ms^{-1})
V_{lf}	Longitudinal wave velocity (ms^{-1})
σ'	isotropic effective stress
ρ_{hy}	density of hydrate (g/l)

INTRODUCTION

The interaction between hydrate and the host sediment at the grain level has been highlighted in recent years as laboratory and analytical investigations have shown that hydrate is not restricted to forming in a unique way in the pore space [1-4]. As gas hydrates become an ever more important area of interest, there is a need for greater knowledge of the effects that gas hydrate morphology can have on the host sediment properties to correctly interpret amounts in the sub-sea.

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The Gas Hydrate Resonant Column (GHRC) was developed at the University of Southampton, UK, to aid in these investigations, by testing sediments at frequencies and strain rates comparable to seismic surveys. The first tests conducted in the GHRC were made using a technique with partially saturated conditions [5], and restricted the results to showing one type of hydrate growth morphology. Since the development of the apparatus, a new formation methodology, making hydrate in fully water saturated conditions has allowed for the formation morphology of hydrate in the pore space to be investigated.

This paper reports on the results from a series of tests designed to investigate hydrate formation in saturated sands. The aim is to compare results from saturated hydrate tests with those from Priest's [5] partially saturated hydrate tests, and therefore determine if the morphology of hydrate in the pore space has an effect on the mechanical properties.

APPARATUS AND METHODOLOGY

The Gas Hydrate Resonant Column (GHRC) is a geotechnical testing apparatus that allows for sediments to be tested at frequencies relevant to those used in seismic surveying. The GHRC is based around a standard Stokoe resonant column, but a number of modifications were made to allow for the GHRC to be suitable for gas hydrate formation. A pressure cell and environment chamber were added to provide temperature and pressure conditions suitable for growth of hydrate inside a specimen. The pressure cell is rated to 25MPa with the environment chamber capable of temperatures between -20℃ and 50℃. For more details on the development of the GHRC, see Clayton et al [6].

Methodology for making hydrate in water saturated sands

Previous work in the GHRC by Priest utilized the method adopted by Stern [7] which made hydrate in partially saturated sediments. Hydrate was made in gas saturated, or "dry" environments. As the aim of this research is to make hydrate in water saturated, or "wet" conditions, a different methodology needed to be adopted.

There are three methods for hydrate formation in saturated conditions:

1) A saturated specimen has gas injected into it until a pre-determined quantity of water has been pushed out as a measure of hydrate content.
2) A dry specimen is filled with gas to a certain pressure, with water then injected to drive the pore pressure up into the hydrate stability zone and saturate the specimen.
3) Hydrate is formed out of the dissolved gas phase.

Although making hydrate by the first method has been successfully implemented by Winters [4], Stoll and Bryan [8] and Brewer *et al* [9], this method was deemed unsuitable for making hydrate in the GHRC as distribution of the hydrate within a sand specimen cannot be controlled sufficiently.

Making hydrate from the dissolved gas phase had some limitations with regards to the GHRC. The solubility of methane in water is low and pressure dependant. Therefore, hydrate formation from dissolved methane gas would create a maximum of 4% hydrate in the pore space, given the maximum cell pressure of 25MPa in the GHRC. Tohidi [2] and Buffett [10] have shown that CO_2 can be used to successfully form hydrate out of solution, however, the research shown here aimed to produce results that were directly comparable with the work of Priest from 2005, and so required testing of methane hydrate specifically.

The second method was therefore considered as the best option for forming hydrate in fully water saturated sands. In order to ensure that high hydrate content would be achievable whilst maintaining a homogenous distribution of water and gas, a number of tests were conducted. Dry, evacuated sands were taken and, under a constant effective stress of 250kPa, injected with water to various pressures – achieving different saturation levels. The sands were then frozen, sectioned and their water content analyzed. It was found that at high pressures, an acceptably uniform distribution of water was achieved when water was slowly injected from both ends of a sand specimen.

Calculating Hydrate Content

Once it had been established that a uniform distribution of gas and water would be achievable by the water injection method, the calculations for hydrate content in the pore space could be made. The water injection method allows for the back pressure to be applied and maintained by water from a GDS Digital Pressure Controller (DPC), and so the hydrate content will be limited by the quantity of gas in the specimen before water injection.

Methane quantity can be established through pressure in the pore space. If the temperature of the system is kept constant and the volume the gas can occupy is also a constant, then the number of moles of CH_4 needed for hydrate growth is controlled by the pressure of the gas. By assuming 100% cage occupancy, one mole of methane gas will produce one mole of hydrate when provided with an unlimited water supply. The number of moles of hydrate (n) needed for a given hydrate content (H_c) is:

$$\frac{V_v H_c \rho_{hy}}{100 M_g} = n \qquad (1)$$

where V_v is the total volume of voids in the specimen; ρ_{hy} is the density of methane hydrate (approximately 910g/l); M_g is the molar mass of methane hydrate (119.63g/mol); and H_c is given in percent. From this, the pressure that must be applied to the specimen to obtain the required moles in the pore space can be determined from:

$$PV = nRT \qquad (2)$$

Where T is temperature in degrees Kelvin; n is the number of moles; P is the pressure in atmospheres; and R is the universal gas constant (0.082058latm/K/mol). As methane is a non-ideal gas, the Van Der Waals equation must be employed to correct the values from the ideal gas equation:

$$\left[P + a\left(\frac{n}{V_v}\right)^2\right]\left(\frac{V_v}{n} - b'\right) = RT \qquad (3)$$

where a and b' are Van Der Waals coefficients relating to methane and are valued at $2.3\text{atml}^2/\text{mol}^2$ and 0.0430l/mol respectively.

Although as stated the solubility of hydrate is low, at 15MPa and 2°C which is the average target temperature and pressure values for the GHRC hydrate tests, there is a degree of dissolution. The number of moles lost into solution is calculated by using the solubility mole fraction from Chapoy *et al.* [11] as 4.024×10^{-3} for methane at 15MPa and 0°C. By knowing the quantity of water the system will be exposed to, a maximum value for methane dissolution can be calculated, and added to the original value gained from equation 1.

Specimen Preparation

Specimens in the fully saturated or "wet side" tests were prepared in a standard way. The material used in all these tests was Grade E Leighton Buzzard sand, which is a uniform silica sand with 85% of the material falling between 90-150μm in size. Dry sand was packed into a butyl membrane by use of a split mould to make a cylindrical specimen of 140mm by 70mm dimensions. Once the specimen was formed, a vacuum of ~50kPa was applied, and the split mould removed. Thermistors were attached to the side of the specimen for temperature measurement. The resonant column drive head was then attached to the specimen. An LDVT was then placed on the drive mechanism to monitor height changes. Then an initial confining pressure of 250kPa was applied using nitrogen gas.

Once a dry specimen was inside the GHRC, methane gas could be injected into the sand. As detailed above, the quantity of methane injected into the specimen would control the hydrate content in the pore space. Table 1 shows the values needed to achieve a range of hydrate contents. As methane was injected into the specimen, the cell pressure was also increased to maintain an effective stress of 205kPa at all times. Once the correct quantity of methane gas had been injected, the inlet was locked off, and water could be injected slowly through the ports in the top and bottom caps until a pore pressure of 15MPa was reached inside the specimen, with a corresponding cell pressure of 15.25MPa, for hydrate contents up to 20%. For specimens containing 30 and 40% hydrate content, the pressure target was increased to 20MPa to ensure saturated conditions would be achieved.

The specimen was then taken into the hydrate stability field by lowering the specimen temperature as shown in figure 1. After the top pressure of either 15MPa or 20MPa was reached (point B in figure 1) the temperature was dropped to 2℃ for hydrate formation (point C in figure 1). During the temperature drop and subsequent hydrate formation, the back pressure was controlled and monitored by the GDS DPC.

Hydrate Content %	Starting pressure required / kPa
2	1012
5	1535
10	2381
15	3194
20	3976
30	5455
40	6833

Table 1 Methane pressures needed to achieve the corresponding hydrate content in the pore space

The specimens were left within the stability zone conditions until water output from the GDS DPC had decreased to a negligible amount. At this point it was considered that conversion of methane gas into hydrate had been completed as there was no further decrease in back pressure, hence no gas being consumed. Hydrate content in the pore space was monitored by the volume of water injected using the GDS DPC during the temperature decrease and hydrate formation.

Resonant Column Testing

Using the GHRC, the seismic velocities V_s and V_p, and associated attenuation (Q_s^{-1} and Q_p^{-1} respectively) of a column of sediment can be obtained from it's resonant frequency. The resonant frequency is obtained when the output from an accelerometer, mounted on the top cap, reaches a maximum value during a frequency sweep. Details of the full data reduction for both torsional and flexural excitation can be found in Priest *et al.* [5]. Attenuation of the system is measured by the free vibration decay (FVD) method. The specimen is vibrated at it's resonant frequency before shutting off power to the drive system and allowing the vibration to decay. The response is monitored and plotted to produce a decay curve, from which the damping, and hence the attenuation of the system can be found. Further details of how attenuation measurements are derived from the resonant column can be found in Priest *et al* [12].

The testing program of the water saturated sand and hydrate specimens allowed for the dynamic response to be observed in loading and unloading. A load--unload cycle was applied to the specimens with resonant column tests made at 250, 500, 750, 1000, 1500 and 2000kPa isotropic effective stress. Each load step was held for 30 minutes to allow for initial consolidation of the specimen before a resonant column test was undertaken. Torsional and flexural resonant frequencies were measured at each step, along with attenuation measurements. In order to allow for repetitive testing, and to ensure that the seismic velocities obtained from these tests would be comparable to geophysical survey data, strain levels in both torsional and flexural testing were kept low, and did not exceed 9 x 10^{-6} strain.

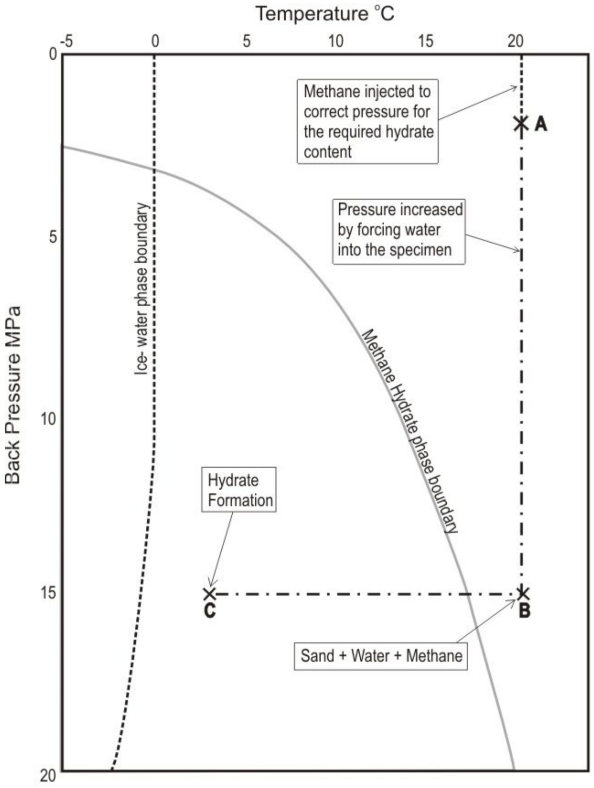

Figure 1 Plan of the route taken by wet side tests into the hydrate stability zone (also marked)

RESULTS AND DISCUSSION

Specimens with 5 different volumes of hydrate within the pore space, ranging from 0% hydrate content to 40%, were made and tested in the resonant column. This gave a range of hydrate contents in saturated (wet side) conditions that could be directly compared with those from partially saturated (dry side) tests.

Seismic Velocities

Figure 2 shows the shear wave velocity V_s for each specimen plotted against the effective confining pressure for the wet side tests. The first observation that can be made from this plot is that methane hydrate in the pore space does not have an impact on V_s until 30% of the pore space is filled with hydrate. If this behaviour is compared with the data from dry side tests (figure 3), it can be seen that the two formation techniques have different effects on the sediment for similar hydrate contents. In dry side tests, seismic velocity increases as hydrate content in the pore space increases, whereas in wet side tests no effect is seen until almost a third of the pore space is filled. This figure suggests that hydrate is acting as a cementing agent when formed in the dry side tests, bonding effectively at grain contacts when there is enough hydrate to do so. In the fully water saturated tests (wet side), the observed increase in V_s is low in comparison to the increases seen when hydrate bonds at grain contacts, and so these may be exhibiting a grain supporting behaviour [3, 13, 14].

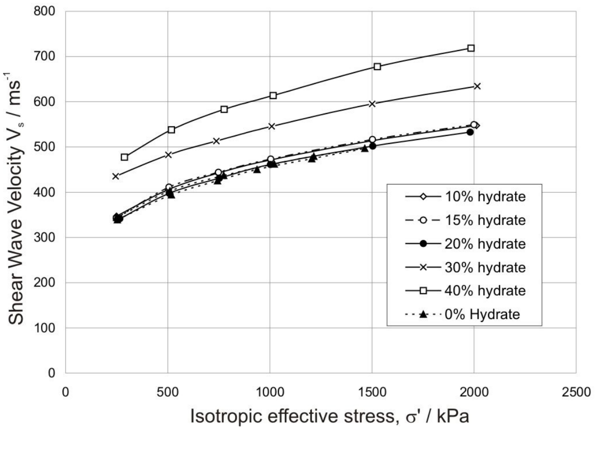

Figure 2 Shear wave velocity V_s against isotropic effective stress σ' for wet side tests

The second observation that is apparent from figure 2 is that each plot appears to have a similar curvature during the increased effective stress application. This suggests that the effective stress dependency from 0% to 40% hydrate content is the same, or similar for each test.

The relationship of effective stress and shear wave velocity has been investigated [15], and shown to be:

$$V_s = A\sigma'^b \qquad (4)$$

Where A and b are constants. This relationship, and the value of the b exponent, can give information on the degree of bonding in a sediment. Bonding reduces the compliance of sediments to effective stress, and the b value should move towards 0 as bonding increases. Figure 4 shows the b values obtained from the wet side and dry side tests for V_s and V_{lf} in the load cycle. It can be seen that for both wet and dry side tests, the b value at 0% hydrate content is between 0.2 and 0.25, a value expected for a clean un-bonded sand [16]. In the dry side tests, the b value then drops to a value of around 0.025 for hydrate contents above 3%, whereas the wet side tests continue to show a high b value around 0.2.

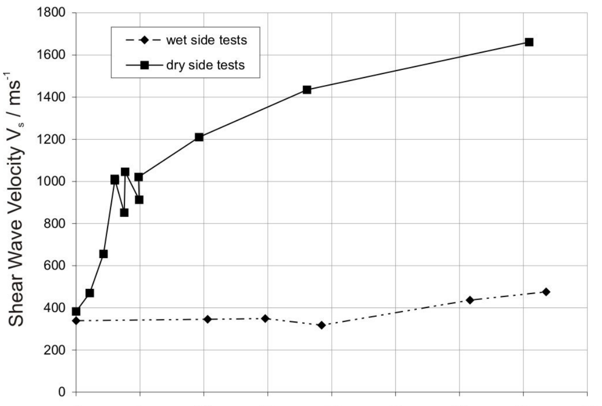

Figure 3 A comparison of shear wave velocity V_s against hydrate content H_c for all tests

The b values from the wet side tests would suggest that bonding does not occur, even with up to 40% hydrate in the pore space.

The formation method for wet and dry side tests can be used to explain the behaviour seen in the above figures. In dry side tests, or conditions where there the environment is gas saturated, the hydrate will grow where the water lies – as that is the restricting factor on hydrate content. In partially saturated sands, water tends to collect at grain contacts and coat individual sand grains. Hydrate will therefore preferentially grow at grain contacts (figure 5 (b)) with the effect of acting as a cement. As hydrate content is increased, it begins to fill the pores, but the increased stiffening is likely to be the increased quantity of 'cement' at grain contacts.

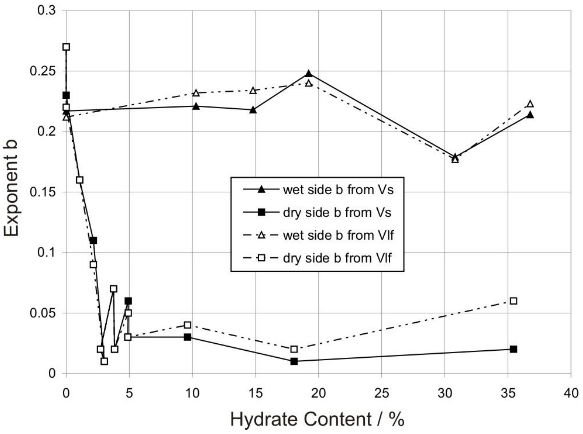

Figure 4 A comparison of hydrate content plotted against the b exponent for all tests

In wet side, or fully water saturated tests, the morphology of hydrate appears to be different. In this environment, before hydrate formation there are gas bubbles suspended in water filled pores. As the specimen is taken into the hydrate stability field quickly (over 2-3 hours), hydrate will form at the gas/water interface [2], ie around gas bubbles (figure 5 (a)). Hydrate has now become a pore filling component, and only large amounts of hydrate in the pore space will have a significant effect on seismic velocity. Figure 2 shows this increase in stiffness to be at around 30% hydrate content.

The b exponent behaviour in figure 4 showing the lack of bonding in wet side tests also suggests a non-bonding nature of hydrate in fully water saturated conditions.

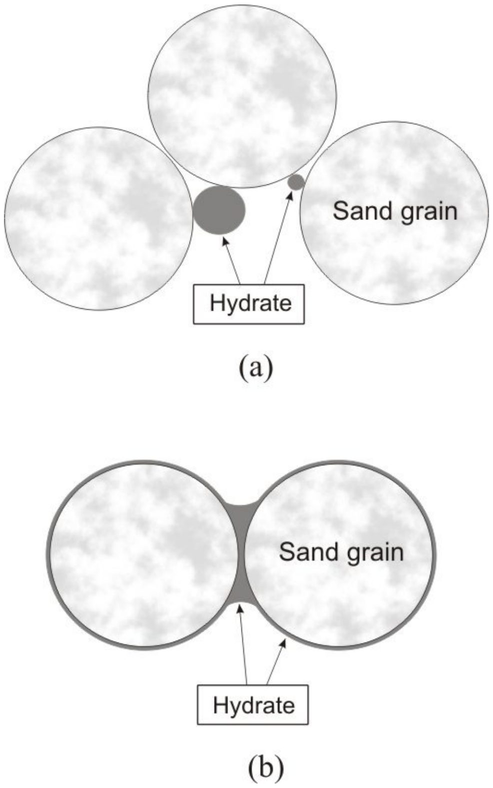

Figure 5 (a) Location of hydrate in the pore space in fully water saturated conditions: Hydrate forms around gas bubbles. (b) Location of hydrate in partially saturated conditions: hydrate forms where water collects at grain contacts

Attenuation

Figure 6 compares the shear wave attenuation Q_s^{-1} for a range of hydrate contents, from both the wet and dry tests. It can be seen that in the dry side tests, attenuation is at a high between 3 and 5% hydrate content. It then drops to a relatively constant value from 10 – 40% hydrate content. In the wet side tests however, attenuation increases with increasing hydrate content. The attenuation values from flexure also show the same behaviour, although the values are, on average, twice as high in the wet side tests.

The attenuation results for the dry side tests show the bonding effect of hydrate after 5% hydrate content. Attenuation in the dry side hydrate tests is attributed to the squirt flow phenomena [17]. A small amount of free water is retained on the surface of the sand grains and causes increased attenuation up to a critical value (3-5% H_c). Once this critical value has been reached, attenuation decreases as hydrate restricts grain movement by full bonding [12].

In water saturated conditions, squirt flow also dominates attenuation at low frequencies and strains. The results shown in figure 6 from the wet side tests suggest that this mechanism is prevalent in saturated sand/hydrate specimens.

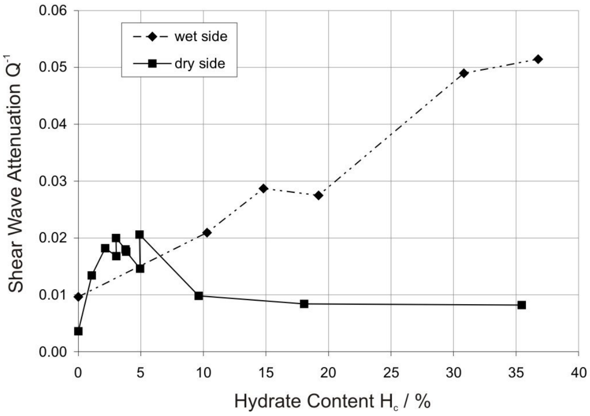

Figure 6 Comparison of shear wave attenuation against hydrate content for wet and dry side tests

As hydrate does not bond sands in saturated conditions, there is no restriction of grain movement even at high hydrate contents. It would be expected therefore that the attenuation would not rise and then decrease, as seen in the dry side tests. The continued increase in attenuation with increasing hydrate content suggests that there is another mechanism contributing to the existing squirt flow at sand grain contacts involved in the wet side test specimens.

Methane hydrate has a porous nature. Diffusion of gas and water through hydrate has been observed at the grain level [2]. When formed by rapidly cooling a sediment, hydrate preferentially grows at the gas water interface, and porous hydrate is formed. During the passing of a seismic wave, this porous hydrate is likely to deform and squirt flow through the hydrate grains themselves may occur. Squirt flow may also develop between hydrate grains and sand grains, where hydrate rests at grain boundaries. The increase in hydrate content will therefore provide more conduits for water movement, and so attenuation increases.

The nature of hydrates in saturated environments shown here suggests that detection of hydrate from seismic surveys by a change in seismic velocity could prove unreliable. Methane hydrate changes the stiffness of a sand by a small margin in these conditions, and disseminated hydrate bodies may have been missed in the past due to them not affecting the sediment velocity. The attenuation results however suggest that damping in sediments will be increased with hydrate content, even when relatively low percentages of the pore space are filled. This may therefore become a more reliable method of detecting hydrate in fully water saturated sediments.

CONCLUSIONS

A new method for making methane hydrate in saturated sediments was developed. Specimens with different quantities of hydrate in the pore space were made and tested. Seismic velocity results showed that methane hydrate did not affect the stiffness of the sediment until 30% hydrate in the pore space was reached. Attenuation results however, showed that damping in hydrated sands increased with increasing hydrate content.

The results from the saturated tests were compared with the partially saturated hydrate tests of Priest *et al.* [5]. Seismic velocities and attenuation measurements were compared for each of the testing methods, and it was found that specimens formed in partially saturated (dry) conditions bonded the sediment, whereas hydrates formed in saturated (wet) conditions did not. It was therefore concluded that hydrate with different morphologies were formed in the pore space, with the inherent behaviour dependant on the environment of formation.

It was finally suggested that attenuation measurements in marine hydrate bearing sediments may be a better device for detecting and quantifying hydrate in the sub-sea than seismic velocity alone.

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