

Measurements of the fate of gas hydrates during transit through the ocean water column

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[1] We report on controlled experiments to document the fate of naturally occurring methane hydrate released from the sea floor (780 m, 4.3°C) by remotely operated vehicle (ROV) disturbance. Images of buoyant sediment-coated solids rising (~0.24 m/s) from the debris cloud, soon revealed clear crystals of methane hydrate as surficial material sloughed off. Decomposition and visible degassing began close to the predicted phase boundary, yet pieces initially of ~0.10 m size easily survived transit to the surface ocean. Smaller pieces dissolved or dissociated before reaching the surface ocean, yet effectively transferred gas to depths where atmospheric ventilation times are short relative to methane oxidation rates. **INDEX TERMS:** 4820 Oceanography: Biological and Chemical: Gases; 4806 Oceanography: Biological and Chemical: Carbon cycling; 1050 Geochemistry: Marine geochemistry (4835, 4850); 4219 Oceanography: General: Continental shelf processes; 1635 Global Change: Oceans (4203). **Citation:** Brewer, P. G., C. Paull, E. T. Peltzer, W. Ussler, G. Rehder, and G. Friederich, Measurements of the fate of gas hydrates during transit through the ocean water column, *Geophys. Res. Lett.*, 29(22), 2081, doi:10.1029/2002GL014727, 2002.

1. Introduction

[2] Methane gas hydrates have attracted recent attention both because of the enormous size of the present day reservoir in the shallow marine geosphere [Kvenvolden, 1993], and because of mounting evidence of massive methane releases associated with climate change in the geologic past [Dickens *et al.*, 1995; Henriot and Mienert, 1998; Norris and Röhl, 1999; Katz *et al.*, 1999].

[3] Methane releases from hydrates in the present day ocean are also of great interest, due to concerns over stability in the face of climate change [Kvenvolden, 1993], and for practical reasons associated with possible energy extraction [Kleinberg and Brewer, 2001]. Hydrate exposures at the sea floor [MacDonald *et al.*, 1994; Suess *et al.*, 1999] are particularly vulnerable to sudden releases, and this has been invoked in association with sea floor slumps [Dillon *et al.*, 1998] and the resulting tsunamis [Hovland, 1999]. Over 1000 kg of hydrate were recently inadvertently recovered in a trawl net [Spence *et al.*, 2001], and brought on board a fishing vessel. Questions remain about the rate at which hydrate-bearing material released from the sea floor can transit the ocean water column, the dissolution rates of solid hydrates

in the methane under-saturated ocean, and the minimum size of hydrate particles required for transfer of methane to the atmosphere. We have carried out small-scale controlled field experiments designed to image and quantify some of these processes.

2. Experimental

[4] Our experiments took place on July 13–14, 2000. We used the remotely operated vehicle (ROV) Tiburon [Brewer *et al.*, 1999] to locate an area of known hydrate occurrence on a local topographic high, the southern summit of Hydrate Ridge at 44° 34.22' N, 125° 11.22' W. Extensive fields of white bacterial mats provided a first visual cue of elevated near surface gas concentrations. Probing of the mats with the vehicle arm (Kraft Telerobotics) initially revealed a soft substrate, but a search soon located a site which produced gas bubbling immediately on contact, with a hard substrate, sensed by manipulator arm feedback, about 0.20 m below the surface.

[5] Methane hydrate is less dense than sea water and is retained in place by attaching to, and infilling, the sediment matrix. The hydrates were liberated by using the 360° wrist rotation capability of the vehicle arm to cut into the hard surface. Clumps of gray/brown solid hydrates were at once seen rising from the cloud of gas bubbles and sediment debris.

[6] Gases venting to the water column were sampled by an inverted funnel with a 6-port rotary valve assembly attached to evacuated stainless steel cylinders (75 ml). Condensation of the bubble stream to a mass of solid hydrate within the sampling apparatus was immediate. The vehicle was then flown above the hydrate decomposition boundary at 400 m, valves opened, and the dissociated gas sampled. Gas chromatography revealed a primary composition of 98.5% CH₄, 1% air, 0.01% CO₂. Gases contained within the sediment were sampled by short push cores that were placed in a pressure-retaining sampler, and returned to the surface at the *in situ* pressure and temperature conditions. Controlled venting of the sampler, and analysis of the trapped gas, gave near identical results to analyses of the venting bubble stream.

3. Results

[7] We investigated the properties of these buoyant solids both by tracking a piece of hydrate in free ascent, and by monitoring hydrate captured within an imaging box (Figure 1) so as to retain it, while still free floating, closely within the field of view. Significant variations in hydrate fabric and type have been reported [Suess *et al.*, 1999] for this site, and

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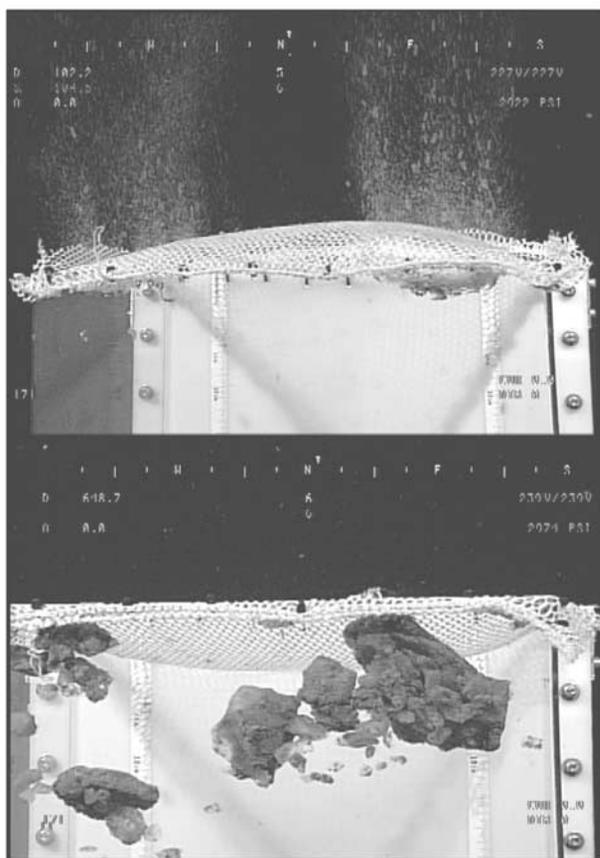


Figure 1. (Lower panel) View of floating mass of hydrate crystals at 600 m depth contained in the imaging box (0.25 m deep, 0.30 m wide) during ascent, and below the hydrate phase boundary. Surface debris has begun to wash off, revealing transparent ice like crystals. The containing mesh cover is visible at top, a numerical scale is fixed to the rear wall, and the solid back panel reduces visual clutter from marine snow. (Upper panel) Image of the same specimens vigorously degassing at 100 m depth having survived transit through the water column.

we present here observations of large variations in dissolution rate in the ocean water column.

[8] The free ascent rate was determined by following, for 180 m of ascent, a dirty white, disk-shaped piece with an initial diameter of about 0.10 m and a thickness of about 0.06 m (estimated by comparison with vehicle arm dimensions). The mean rise rate observed was 0.240 m/s; after an initial increase in the rise rate over the first 50 m to a maximum velocity of 0.269 m/s, presumably due to the loss of adhering sediment, the piece slowly decelerated (Figure 2a) as it dissolved.

[9] The true size of a piece of hydrate floating in the open ocean cannot be estimated without some frame of reference. However, by making the spherical approximation, we can provide a first order estimate. The terminal velocity of a rigid sphere is given by equation (1):

$$U = \left[8 \cdot g \cdot r \cdot (\rho_{sw} - \rho_{hyd}) / (3 \cdot \rho_{hyd}) \right]^{0.5}, \quad (1)$$

where g is the acceleration of gravity, r is the fragment radius, and ρ_{hyd} and ρ_{sw} are the densities of the hydrate and seawater. The average sea water density was $1.03 \cdot 10^3 \text{ kg/m}^3$ (range $1.0299 - 1.0304 \cdot 10^3 \text{ kg/m}^3$) in the depth range from 625 to 725 m, and a density of the hydrate of $0.93 \cdot 10^3 \text{ kg/m}^3$ [Sloan, 1997] was assumed. We thus estimate the changing radius of the particle (Figure 2b) from the

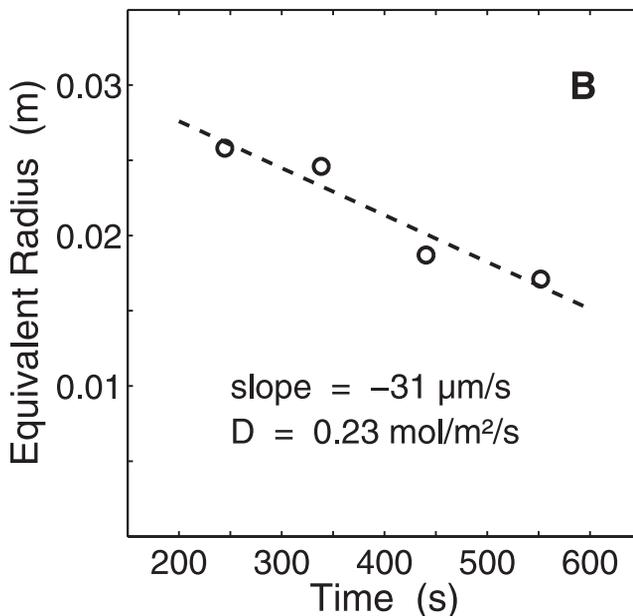
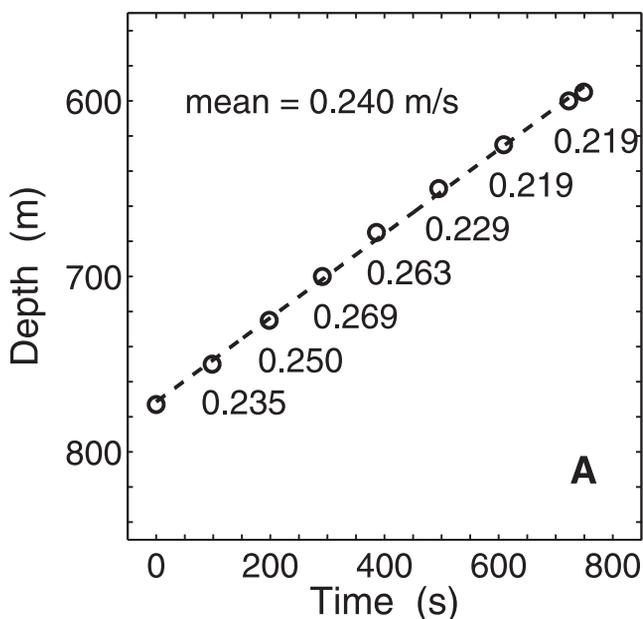


Figure 2. (a) Ascent rate of free-floating hydrate released from the seafloor. Dots indicate the times/depths extracted from the vehicle log. The line is a linear fit to the data; the numbers indicate the rise rate between two time/depth points. After an initial increase in rise velocity, the rise rate decreased slightly with time. (b) Estimate of the changing size of the free floating hydrate as a function of time, derived from the spherical approximation, and the change in the rise velocity after initial acceleration. The slope indicates a shrinking rate of the radius of $31 \cdot 10^{-6} \text{ m/s}$.

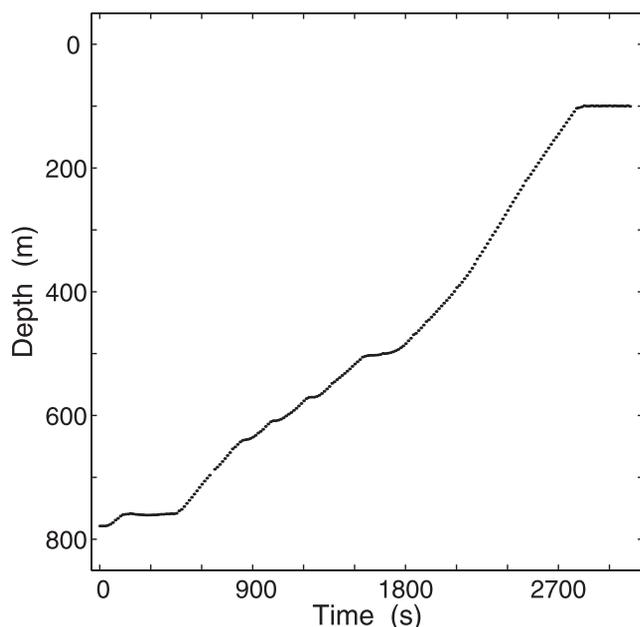


Figure 3. Rise rate of the vehicle for the 40 minute controlled imaging transit from 780 m depth to 100 m. The initial wait was to adjust vehicle buoyancy. The rate ≈ 0.21 m/s from 780–500 m closely approximates that for free ascent in Figure 2a. The slowed rise at 500 m was deliberate to observe behavior close to the pure methane hydrate phase boundary. The ascent rate ≈ 0.42 m/s above 500 m is a lower limit. The vehicle was held steady at 100 m to observe complete disappearance of hydrate.

observed rise velocities to be $31 \bullet 10^{-6}$ m/s. This mean shrinking rate can be transferred to a dissolution rate by using the equation:

$$(r_t - r_0) = -V_m \bullet D \bullet (t - t_0) \quad (2)$$

where V_m is the specific volume, r_0 and r_t are initial fragment radius and fragment radius at time t , t_0 is the initial time, and D is the dissolution rate. For a hydrate composition of $\text{CH}_4 \bullet 6\text{H}_2\text{O}$, a dissolution rate of 0.23 mol/ m^2/s is derived. This dissolution rate represents the combined effects of hydrate dissolution and detachment of smaller parts of the fabric.

[10] Although the tracked piece was not spherical, and the calculated density is for solid methane hydrate without impurities or pores, the result is in reasonable agreement with the observations. For the equivalent sphere of 0.064 m diameter the calculated shrinking rate would lead to complete dissolution after about 800 s. In comparison visual contact with the sample was lost about 600 s after achieving maximum velocity, and the piece was almost completely dissolved by that time.

[11] For the controlled imaging study we fractured a layer of hydrate that yielded numerous larger specimens that were initially of a dirty gray-brown color. These accumulated beneath the mesh top of the imaging box that had been placed over the robotic arm. Once sufficient material had been harvested the vehicle lifted off, buoyancy was adjusted, and the 3 ton vehicle was piloted upwards at approximately the rise rate of the captured hydrate. In

practice the vehicle ascent rate could not match the rise velocity of the larger pieces. Our data thus give a lower limit for the rise rate, and upper limit of time of exposure in the water column. In Figure 3 we show the rise rate of the vehicle for the sea floor to surface transit.

[12] The larger pieces of hydrate were soon revealed as hard, transparent, crystalline objects. Although the specimens were contained, they were nonetheless in complex free motion, and obtaining size information poses a challenge. Video frame grabs of the largest specimen (Figure 1 lower), were taken when it was oriented in a systematic way. The dimensions were measured along two lines with recognizable shape irregularities at the edges. The results (mean \pm one standard deviation: 0.1093 ± 0.0093 m long, 0.0827 ± 0.0037 m wide) showed no evidence of shrinking during the 18 minutes 23 seconds of transit from the sea floor to the hydrate phase boundary (Figure 3). If we set a two standard deviations difference as our criterion for detecting a change in size we can set an upper bound for the dissolution rate. We thus estimate the change in width to be less than 0.0074 m which yields an upper bound for the shrinking rate of $<6.7 \bullet 10^{-6}$ m/s. With an assumed density of $0.93 \bullet 10^3$ kg/ m^3 for pure methane hydrate [Sloan, 1997] and stoichiometry of $\text{CH}_4 \bullet 6\text{H}_2\text{O}$, we infer the dissolution rate of this specimen to be <0.025 mol $\text{CH}_4/\text{m}^2/\text{s}$.

4. Discussion

[13] We were particularly interested in behavior at the hydrate phase boundary (Figure 4). During the cruise we assumed that this would be close to the pure methane

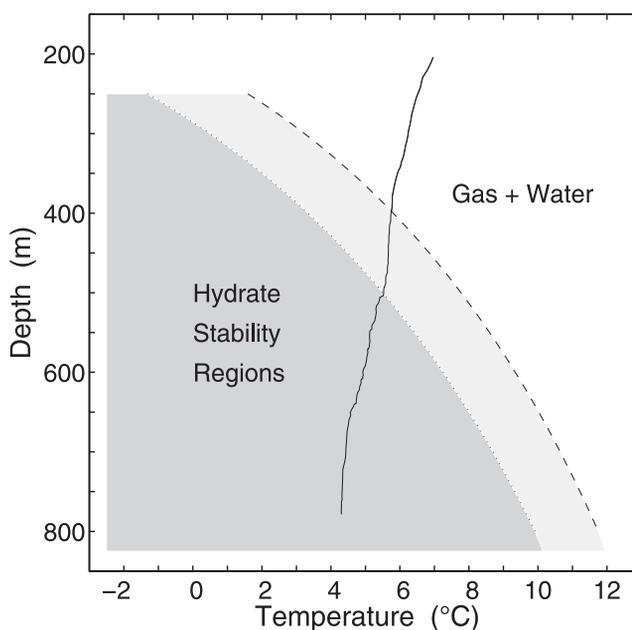


Figure 4. Hydrate phase diagram with the local temperature profile from the dive overlaid. Two phase boundaries are shown; that, as conventionally assumed, for pure methane, and that for the gas mixture obtained from in situ plume sampling and analysis. Evolution of gas bubbles was not observed until the vehicle approached within 10m of the upper boundary.

boundary, and the vehicle rise rate was slowed at 500 m for close observation. No bubbles were seen, and transit upwards continued. We did observe a bubble stream beginning at 410 m, well above the pure methane horizon. In post cruise analysis we determined the composition of gas venting from the sea floor [Peltzer *et al.*, 2000], and substituted this into a Gibbs free energy minimization procedure (Multi-flash 2.6, Infochem Computer Services) to calculate the appropriate boundary condition [Peltzer and Brewer, 2000]. Both the pure methane and the observed gas composition boundaries are shown in Figure 4. The appearance of first bubble evolution closely matches the computed phase boundary, some 100 m above the conventionally assumed pure methane boundary. Bubbles were seen first as a slow release, but rapidly became a vigorous stream, adding buoyancy to the hydrate, and increasing the rise rate. The reaction is endothermic, and thus cooling of the solid occurs, helping to slow dissociation. The net result was that remaining pieces of hydrate of 0.01–0.02 m size dissociated completely, while pieces of 0.08–0.10 m size easily survived the transit to transfer methane directly to the atmosphere (Figure 1 upper).

[14] Our data show that even small pieces of hydrate can survive transit through 800 m of water column and deliver methane to the atmosphere in less than one hour. These results significantly understate the impact of a larger scale methane release, since the quantities here are so small that background sea water methane concentrations are not affected by the release. In a large-scale plume with elevated methane concentrations, the dissolution rates would be slowed.

[15] In practice direct contact of the hydrate with the sea surface is not required; the key property is dissolution within the oceanic mixed layer to produce values in excess of atmospheric equilibrium. The mixed layer by definition is in daily contact with the atmosphere. In summer shallow mixed layers are formed, but winter cooling and wind forcing can drive mixed layers to 200–400 m deep over much of the ocean. Water column microbial methane oxidation rates [Scranton and Brewer, 1978; Rehder *et al.*, 1999] are sufficiently slow (half-life \approx 50 years for deep ocean concentrations) that a very large fraction of methane transported to these depths can be ventilated to the atmosphere within the 6 month average time scale for deep mixing events. Since the depth differential between the top of the hydrate stability zone (typically \approx 500 m) and the depth of winter-time mixing is small, we may expect very efficient transfer to the atmosphere of methane released as hydrate from the sea floor.

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References

- Brewer, P. G., G. Friederich, E. T. Peltzer, and F. M. Orr Jr., Direct experiments on the ocean disposal of fossil fuel CO₂, *Science*, 284, 943–945, 1999.
- Dickens, G. R., J. R. O'Neil, D. K. Rea, and R. M. Owen, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene, *Paleoceanogr.*, 10, 965–971, 1995.
- Dillon, W. P., W. W. Danforth, D. R. Hutchinson, R. M. Drury, M. H. Taylor, and J. S. Booth, Evidence for faulting related to dissociation of gas hydrate and release of methane off the southeastern United States, in *Gas Hydrates: Relevance to World Margin Stability and Climate Change*, edited by J. P. Henriet, J. Mienert, Geol. Soc., London, Spec. Publ. 137, 293–302, 1998.
- Henriet, J.-P., and J. Mienert (Eds.), *Gas Hydrates: Relevance to World Margin Stability and Climate Change*, Geol. Soc., London, Spec. Publ., 137, 1998.
- Hovland, M., Gas, fire, and water, *Eos Trans. AGU*, 80, 552, 1999.
- Katz, M. E., D. K. Pak, G. R. Dickens, and K. G. Miller, The source and fate of massive carbon input during the Latest Paleocene Thermal Maximum, *Science*, 286, 1531–1533, 1999.
- Kleinberg, R., and P. G. Brewer, Probing gas hydrate deposits, *Am. Sci.*, 89, 244–251, 2001.
- Kvenvolden, K. A., Gas hydrates: geological perspective and global change, *Rev. Geophys.*, 31, 173–187, 1993.
- MacDonald, I. R., N. L. Guinasso Jr., R. Sassen, J. M. Brooks, L. Lee, and K. T. Scott, Gas hydrate that breaches the sea floor on the continental slope of the Gulf of Mexico, *Geology*, 22, 699–702, 1994.
- Norris, R. D., and U. Röhl, Carbon cycling and chronology of climate warming during the Paleocene/Eocene transition, *Nature*, 401, 775–778, 1999.
- Peltzer, E. T., D. Donohoue, C. K. Paull, G. Rehder, G. Friederich, W. Ussler, and P. G. Brewer, Novel observations of vent gas chemistry, and evidence for the presence of Structure H hydrate, offshore Oregon, *Eos, Trans. AGU*, 81, Suppl. No. 48, OS 61 B-12, 2000.
- Peltzer, E. T., and P. G. Brewer, Practical physical chemistry and empirical predictions of methane hydrate stability, in *Natural Gas Hydrate in Oceanic and Permafrost Environments*, edited by M. Max, Kluwer, 17–28, 2000.
- Rehder, G., R. S. Keir, E. Suess, and M. Rhein, Methane in the ocean controlled by microbial oxidation and atmospheric history, *Geophys. Res. Lett.*, 26, 587–590, 1999.
- Scranton, M. I., and P. G. Brewer, Consumption of dissolved methane in the deep ocean, *Limnol. Oceanogr.*, 23, 1207–1213, 1978.
- Sloan, E. D., Jr., *Clathrate Hydrates of Natural Gases* Dekker, New York, 2nd edition, 1997.
- Spence, G. D., N. R. Chapman, R. D. Hyndman, and C. Cleary, Fishing trawler nets massive “catch” of methane hydrates, *Eos, Trans. AGU*, 82, 621–627, 2001.
- Suess, E., M. E. Torres, G. Bohrmann, R. W. Collier, J. Greinert, P. Linke, G. Rehder, A. Trehu, K. Wallman, G. Winckler, and E. Zuleger, Gas hydrate destabilization: enhanced dewatering, benthic material turnover, and large methane plumes at the Cascadia convergent margin, *Earth Planet. Sci. Lett.*, 170, 1–15, 1999.
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