

1 In situ Raman-based measurements of high dissolved methane 2 concentrations in hydrate-rich ocean sediments

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6 [1] Ocean sediment dissolved CH₄ concentrations are of
7 interest for possible climate-driven venting from sea floor
8 hydrate decomposition, for supporting the large-scale
9 microbial anaerobic oxidation of CH₄ that holds the oceanic
10 CH₄ budget in balance, and for environmental issues of the
11 oil and gas industry. Analyses of CH₄ from recovered cores
12 near vent locations typically show a maximum of ~1 mM,
13 close to the 1 atmosphere equilibrium value. We show from
14 novel in situ measurement with a Raman-based probe that
15 geochemically coherent profiles of dissolved CH₄ occur ris-
16 ing to 30 mM (*p*CH₄ = 3 MPa) or an excess pressure ~3×
17 greater than CO₂ in a bottle of champagne. Normalization
18 of the CH₄ Raman ν_1 peak to the ubiquitous water ν_2 bend-
19 ing peak provides a fundamental internal calibration. Very
20 large losses of CH₄ and fractions of other gases (CO₂,
21 H₂S) must typically occur from recovered cores at gas rich
22 sites. The new data are consistent with observations of micro-
23 bial biomass and observed CH₄ oxidation rates at hydrate
24 rich sites and support estimates of a greatly expanded near
25 surface oceanic pore water CH₄ reservoir. **Citation:** Zhang, X.,
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30 1. Introduction

31 [2] Each year hundreds of ocean sediment cores are taken
32 world-wide; many of them obtained specifically for pore
33 water analysis of methane [Reeburgh, 2007]. The intense
34 interest in sea floor methane arises from its role in hydrate
35 formation [Paull and Dillon, 2001; Hester and Brewer, 2009],
36 in venting from the sea floor with controversial climate con-
37 nections [Shakhova et al., 2010; Westbrook et al., 2009; Kerr,
38 2010], as a fossil fuel, and as a greenhouse gas. And also for
39 insights into the ingenious way in which a recently identi-
40 fied microbial consortium [Boetius et al., 2000; Orphan
41 et al., 2001] carries out the anaerobic oxidation of meth-
42 ane (AOM), first diagnosed decades earlier [Alperin and
43 Reeburgh, 1985], with the modest oxidation potential avail-
44 able from sulfate ion. This process occurs on a massive scale
45 consuming Tg quantities of methane each year and importantly
46 holding the planetary budget in balance [Reeburgh, 2007].

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[3] The standard procedure for sampling and analysis 54
relies upon recovering cores, sectioning samples, and either 55
squeezing to extract pore water [Reeburgh, 1967] or by head 56
space equilibration in sample vials. It has been known for 57
some time that this procedure could lead to significant under- 58
estimates [Paull and Ussler, 2001; Hinrichs and Boetius, 59
2002] but there have been no adequate tools to address this 60
problem. In situ pore water membrane equilibration devices 61
have been used [Lapham et al., 2010] and while these reveal 62
significantly higher concentrations than recovered cores, 63
the results pose difficulty in reconciling the observations 64
with observed hydrate dissolution rates [Hester et al., 2009]. 65

[4] At sites of high CH₄ concentration where conventional 66
pore water analyses from recovered cores typically converge 67
on a maximum of ~1 mM [Paull and Ussler, 2001]. This is 68
close to the 1-atm equilibrium value of 1.8 mM at 4°C 69
[Yamamoto et al., 1976] strongly suggesting that degassing has 70
occurred and that pore waters have equilibrated with the gas 71
head space of the core. Other lines of evidence also suggest 72
significant gas losses. When pressurized cores at hydrate- 73
rich sites have been recovered values up to 1,000 × higher are 74
found [Paull and Ussler, 2001], indicating hydrate decom- 75
position during pressure release and sample removal. Novel 76
pressure-core-sampling systems have recently been devel- 77
oped [Abegg et al., 2008] but these systems rely on sample 78
recovery and cannot provide real time data nor well resolved 79
chemical profiles. Equilibrium calculations show that the 80
aqueous phase in contact with solid hydrates must contain 81
~50 mM methane or more depending upon the specifics of 82
temperature, pressure and gas composition [Sloan and Koh, 83
2007]. Such values have not been measured in field studies. 84

[5] Seawater contains 28 mM sulfate ion, and SO₄²⁻ con- 85
centrations within anoxic sediments are often quickly reduced 86
to zero by the diagenetic reaction [Reeburgh, 2007] sche- 87
matically, that is neglecting the small contributions from any 88
organoclastic sulfate reduction, given as 89



indicating that 28 mM or more of methane must be supplied 90
to support completion of this reaction. Direct measurements 91
of microbial biomass and CH₄ oxidation rates at vent sites 92
give values far higher than can be explained by the observed 93
methane gradients, and loss of gas by ebullition from recov- 94
ered samples has been strongly suspected [Hinrichs and 95
Boetius, 2002]. 96

2. Experiments and Methods 97

[6] We have investigated these processes and in situ pore 98
water concentrations by means of a newly developed ROV- 99



Figure 1. (left) Map showing locations of vent sites observed where methane signals are brought close enough to the sea floor to permit observation with our probe. (right) The sea floor at Hydrate Ridge, OR, 850 m depth covered with bacterial mat as is typical, showing the push core quiver and the Raman probe about to be inserted. A simple insertion depth scale is attached to the probe surface. The Raman data are obtained in minutes; the collected push cores are typically stored in the quiver for several hours before recovery to the surface for shipboard chemical analyses.

100 operated pore water probe [Zhang *et al.*, 2010] based upon
101 Raman sensing of the extracted fluid.

102 [7] The probe consists of a 35 cm long titanium rod through
103 which a 2 mm diameter hole has been drilled. Water sam-
104 ples are drawn in through an annular sintered metal frit of
105 10 μm pore size by actuating a hydraulic pump, calibrated
106 by observing the piston distance travelled versus known
107 bore area. The induced pressure differential pulls in fluid
108 through the probe body to an optical cell with sapphire win-
109 dow through which the laser beam is focused. The volume
110 required for analysis including flushing is about 3 ml.

111 [8] The use of Raman spectroscopy in the oceans has long
112 been thought impossible because of both the technological
113 challenge of operating in the deep-sea environment [Brewer
114 *et al.*, 2004], and the very high fluorescence associated with
115 organic matter in marine sediments. Pilot experiments showed
116 that although recovered sediments themselves are fluores-
117 cent, pore waters observed in situ are not; fluorescence does
118 grow in quickly upon core recovery and oxygen invasion
119 [Zhang *et al.*, 2010].

120 [9] The components of the diagenetic reaction are well-
121 suited to Raman sensing, which favors the symmetrical
122 molecules H_2S , CH_4 , and SO_4^{2-} . Raman detection of HCO_3^-
123 ion at these concentrations presents a challenge due to its
124 low cross section. However solution pH in such sediments is
125 potentially observable in situ via Raman detection of the
126 natural pH sensitive “dye” provided by the ratio of the H_2S
127 and HS^- species ($\text{pK} \sim 7$) [Zhang *et al.*, 2010]. Thus all
128 critical components of the diagenetic AOM equation are
129 potentially observable spectroscopically in situ.

130 [10] We have performed a series of ROV-controlled
131 experiments at well-known sites of methane hydrate occur-
132 rence [Suess *et al.*, 1999; Hester *et al.*, 2007; Pohlman *et al.*,
133 2005] where high dissolved methane concentrations in sur-
134 ficial sediments are known to occur (Figure 1, left). For
135 comparison with standard techniques we took push cores
136 and then immediately inserted the Raman probe step-wise
137 into the sediment as close to the push core location as was
138 practical (Figure 1, right). In its present form the probe has a
139 practical insertion depth of 35–45 cm, close to the typical
140 length of push core recovery (~ 25 cm).

[11] Spectra obtained were quantified by normalization 141
of the solute peak areas to the ubiquitous water signal 142
present [Dunk *et al.*, 2005]. For quantitative measurement 143
the pore water SO_4^{2-} , CH_4 and $\text{HS}^-/\text{H}_2\text{S}$ Raman peak inten- 144
sities were normalized to the $1640 \Delta\text{cm}^{-1}$ ν_2 water bend- 145
ing mode peak; the normalized peak areas are linear with 146
concentration. The concentration of water in sea water is 147
55 molar and is thus constant. Only small corrections for T, 148
S and P effects on the water ν_2 peak are required [Carey and 149
Korenowski, 1998] and were applied here. The relationships 150
between the Raman normalized peak intensity/area (R^*) 151
and the SO_4^{2-} , CH_4 and H_2S concentration used in this paper 152
are: $R_{\text{SO}_4}^* = 0.0028C_{\text{SO}_4}$ ($r^2 = 0.9994$), $R_{\text{H}_2\text{S}}^* = 0.0039C_{\text{H}_2\text{S}}$ 153
($r^2 = 0.9989$)¹¹ and $R_{\text{CH}_4}^* = 0.0041C_{\text{CH}_4}$ ($r^2 = 0.9984$), 154
measured by the SO_4^{2-} ion ($960\text{--}1000 \Delta\text{cm}^{-1}$) peak, the CH_4 155
($2860\text{--}2960 \Delta\text{cm}^{-1}$) peak, the $\text{HS}^-/\text{H}_2\text{S}$ ($2540\text{--}2640 \Delta\text{cm}^{-1}$) 156

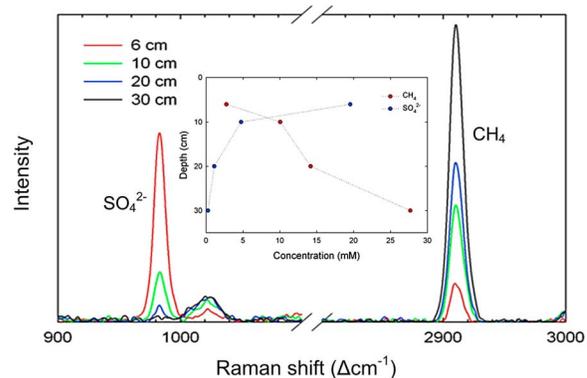


Figure 2. Compilation of Raman spectra obtained from step-wise probe insertion at a single station at Hydrate Ridge, OR; other sites sampled showed identical trends. The SO_4^{2-} peak at $981 \Delta\text{cm}^{-1}$ rapidly declines from its sea water value of 28.9 mM to vanishingly small levels. In a mirror image of this trend dissolved CH_4 with a Raman shift of $2910 \Delta\text{cm}^{-1}$ rises strongly from nanomolar concentrations in deep sea water to about 28 mM at 30 cm depth.

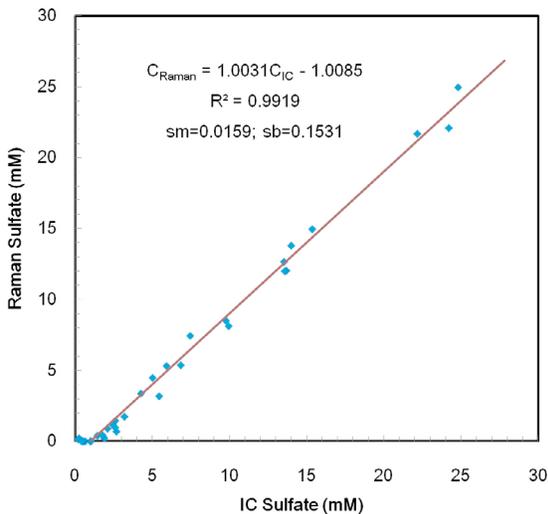


Figure 3. Plot of Raman in situ versus shipboard ion chromatography analyses for sulfate ion. Seven push cores were recovered from the summit of southern Hydrate Ridge, OR. The cores were sampled at 3-cm increments and 34 pore water samples were collected within about 2 h after recovery; the slope (1.0031 ± 0.0159) and intercept (-1.0085 ± 0.1531) show strong agreement, in marked contrast to the CH_4 data shown in Figure 4.

157 peaks, and the water ($1500\text{--}1800 \text{ cm}^{-1}$) peak under lab
158 simulation conditions.

159 3. Results

160 [12] We show from stacked spectra obtained at the south-
161 ern summit of Hydrate Ridge, OR (Figure 2) that geo-

chemically coherent depth profiles can be obtained at a single
162 insertion point within a few minutes. The profile obtained
163 shows geochemical signals quantitatively relating declining
164 SO_4 and rising CH_4 and H_2S in ratios that identify the
165 microbially-mediated diagenesis taking place.

[13] We compared Raman probe measurements of pore
167 waters extracted from push cores with conventional ship-
168 board chemical analyses of the same water sample. Extracted
169 pore waters were preserved and sealed in glass ampoules for
170 later analysis. Comparisons were made on samples from two
171 sites at Hydrate Ridge, characterized by the presence of SI
172 hydrate, from one site at Barkley Canyon, BC in oil-rich
173 sediments where complex SII hydrates occur [Pohlman
174 *et al.*, 2005; Hester *et al.*, 2009], and from two sites on
175 the Santa Monica Basin mounds [Paull *et al.*, 2008]. In each
176 case strong agreement between Raman and conventional
177 chemical measurements of pore water SO_4^{2-} profiles was
178 obtained (Figure 3).

[14] In marked contrast, large differences in dissolved CH_4
180 were observed between in situ and shipboard measure-
181 ment (Figure 4); CH_4 concentrations from Hydrate Ridge
182 obtained by in situ measurement, show progressive increase
183 with depth to values as high as 30 mM. CH_4 concentrations
184 from recovered cores show reversal of this trend with depth
185 from gas loss, visible as gas voids within the core, result-
186 ing in values 10–20 times less than observed in situ. The close
187 agreement in SO_4 data shows that the gas bubbles did not
188 significantly alter the non-volatile ion profiles.

[15] The configuration of the Raman probe permits data
190 acquisition in close proximity to solid hydrates. At the Barkley
191 Canyon site characterized by large, thinly-sedimented hydrate
192 mounds [Chapman *et al.*, 2004; Lapham *et al.*, 2010] we
193 inserted the probe until a hard, resistant surface was encoun-
194 tered at about 10 cm depth. A sample was drawn into the cell,
195 and a spectrum of pore water in contact with the hard sur-
196

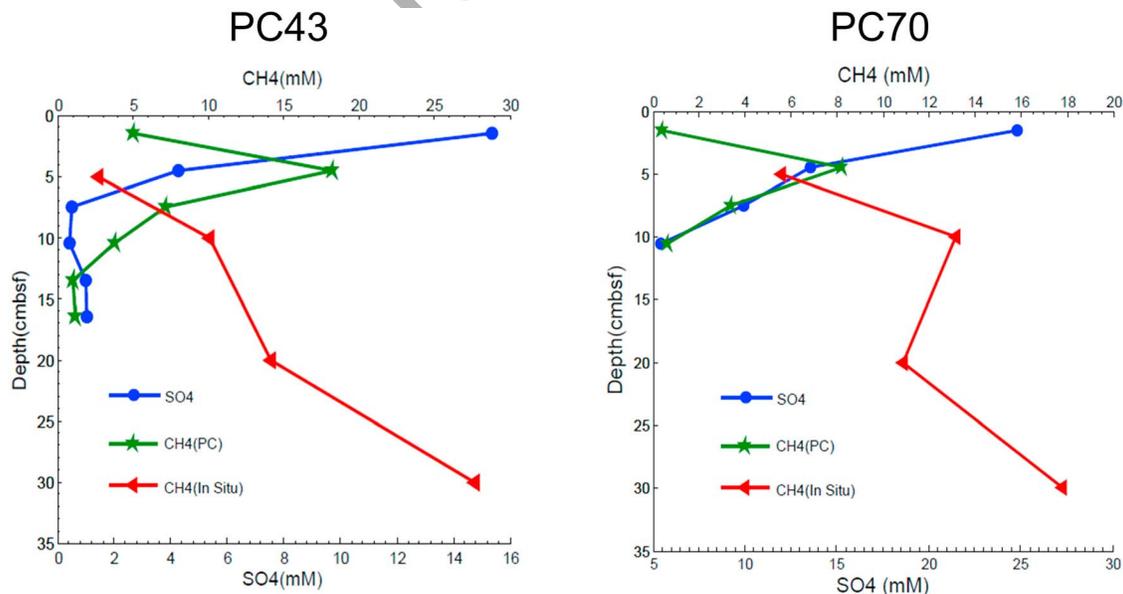


Figure 4. Comparison of dissolved CH_4 pore water data from in situ measurement (red lines) and from recovered samples (green lines) from two Hydrate Ridge cores. Every effort was made at sea to remove the cores from the ROV quiver and proceed with extrusion, squeezing, and sampling as quickly as possible; but in both cases it is clear that large-scale de-gassing has occurred rapidly. Because of the erratic nature of gas loss it is not possible to give a fixed offset; but clearly values obtained in situ in this high dissolved CH_4 environment are 10–20 times greater than in recovered cores.

197 face was recorded. The probe was then removed, and the
198 sediment surface scraped away revealing a yellow hydrate
199 slab and releasing abundant oil droplets. While the oil itself
200 is strongly fluorescent, the work required to distort the oil
201 droplets to pass through the 10 μm pore size frit far exceeds
202 the pressure differential created. Thus oil was excluded from
203 the sample measured and clean spectra were recorded as a
204 bonus of this new tool.

205 [16] From phase equilibrium calculations we estimate the
206 saturated molecular boundary layer value for dissolved CH_4
207 in contact with this hydrate [Sloan and Koh, 2007] as
208 54 mM; the saturated layer is typically only a few tens of
209 microns thick and is limited by diffusive processes. The
210 CH_4 concentration found with the probe tip at about 13 mm
211 from the slab was 28 mM indicating strong local gradients
212 due to diffusive losses. The probe draws pore water in from
213 a halo around the filter and thus the effective distance from
214 the solid hydrate surface cannot be known with certainty.

215 4. Discussion

216 [17] The in situ data from hydrate bearing sites reveal
217 $p\text{CH}_4$ of about 3 MPa, over 3x the pressure of CO_2 in a
218 typical bottle of champagne [Liger-Belair et al., 2002]. The
219 explosive venting of a champagne bottle does not occur here
220 since pressure is relieved slowly during core recovery, typi-
221 cally at 30–50 meters depth per minute. While homogeneous
222 nucleation of gases from liquids requires overcoming a sig-
223 nificant interfacial free energy, the vast number of heteroge-
224 neous nucleation sites provided by the sediment favors easy
225 ex-solution of gas so that sediment texture is often relatively
226 undisturbed. Henry's Law calculations indicate that other
227 gases (CO_2 , H_2S) critical for geochemical modeling will par-
228 tition into the escaping CH_4 gas phase [Chanton et al., 1989]
229 and will also be underestimated by conventional techniques.

230 [18] The oceanic sedimentary methane budget is a delicate
231 balance between enormous production and consumption
232 fluxes where the vast majority of CH_4 produced is oxidized
233 anaerobically before it can be released to the ocean water
234 column. The recent review by Reeburgh [2007] estimates
235 sedimentary production as 85.3 Tg yr^{-1} and consumption as
236 75.3 Tg yr^{-1} . However one estimate [Hinrichs and Boetius,
237 2002] based upon microbial consumption rate data suggests
238 that sedimentary methane production is a factor of 4 higher
239 at 304 Tg yr^{-1} . Our data would tend to support that claim
240 and more, and since production must equal or exceed con-
241 sumption true CH_4 production rates on continental shelves
242 may well be significantly higher. The direct CH_4 observa-
243 tions here are also consistent with the higher estimates of
244 CH_4 consumption inferred from SO_4^- ion gradients [Ussler
245 and Paull, 2008].

246 [19] The data here cluster around the critical 28 mM CH_4
247 value. This is a natural poise for ocean sediments since the
248 primary oxidant of CH_4 is SO_4^- ion also at 28 mM, although
249 small contributions from organoclastic sulfate reduction may
250 also occur. In a typical diffusive dominated system dissolved
251 CH_4 concentrations exceeding this value will migrate to the
252 sea floor and there be exposed to aerobic oxidation. Values
253 of CH_4 less than 28 mM will be anaerobically consumed by
254 the diffusive invasion of SO_4^- driving the sulfate-methane
255 interface deeper within the sediment column as clearly implied
256 by widely used SO_4^- gradient predictor of depth to CH_4
257 occurrence [Borowski et al., 1996].

[20] The existence of such a large and mobile pool of
dissolved methane in marine sediments raises questions
over the quantities that may be released during large-scale
sea floor slide events. Paull et al. [2007] have estimated that
1.4 Gt of carbon as methane hydrate could have been released
by the Storegga slide. Using the same slide volume, porosity
and a 30 mM pore water concentration of CH_4 we estimate
that 0.5 Gt of carbon could have been released if all pore
water were mixed into the water column.

[21] Hafliðason et al. [2004] report that only 250 km^3 of
sediments appear as turbidites in the Storegga slide reducing
this estimate of methane release to only 0.05 GtC. This
methane which has a strongly negative $\delta^{13}\text{C}$ signature would
be rapidly microbially oxidized in the water column [Scranton
and Brewer, 1978; Kessler et al., 2011] and would have left a
local isotopic signature.

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References

- Abegg, F., H.-J. Hohnberg, T. Pape, G. Bohrmann, and J. Freitag (2008),
Development and application of pressure-core-sampling systems for the
investigation of gas- and gas-hydrate-bearing sediments, *Deep Sea Res.,*
Part I, 55, 1590–1599, doi:10.1016/j.dsr.2008.06.006.
- Alperin, M. J., and W. S. Reeburgh (1985), Inhibition experiments on
anaerobic methane oxidation, *Appl. Environ. Microbiol.*, 50, 940–945.
- Boetius, A., et al. (2000), A marine microbial consortium apparently medi-
ating anaerobic oxidation of methane, *Nature*, 407, 623–626,
doi:10.1038/35036572.
- Borowski, W. S., C. K. Paull, and W. Ussler (1996), Marine pore water
sulfate profiles indicate methane flux from underlying gas hydrates,
Geology, 24, 655–658, doi:10.1130/0091-7613(1996)024<0655:MPWSP>
2.3.CO;2.
- Brewer, P. G., et al. (2004), Development of a laser Raman spectrometer
for deep-ocean science, *Deep Sea Res., Part I*, 51, 739–753, doi:10.1016/
j.dsr.2003.11.005.
- Carey, D. M., and G. M. Korenowski (1998), Measurement of the Raman
spectrum of liquid water, *J. Chem. Phys.*, 108, 2669–2675, doi:10.1063/
1.475659.
- Chanton, J. P., C. S. Martens, and C. A. Kelley (1989), Gas transport from
methane-saturated, tidal freshwater and wetland sediments, *Limnol.*
Oceanogr., 34, 807–819, doi:10.4319/lo.1989.34.5.0807.
- Chapman, R., J. Pohlman, R. Coffin, J. Chanton, and L. Lapham (2004),
Thermogenic gas hydrates in the northern Cascadia margin, *Eos Trans.*
AGU, 85, 361, doi:10.1029/2004EO380001.
- Dunk, R. M., E. T. Peltzer, P. Walz, and P. G. Brewer (2005), Seeing a
deep ocean CO_2 enrichment experiment in a new light: Laser Raman
detection of dissolved CO_2 in seawater, *Environ. Sci. Technol.*, 39,
9630–9636, doi:10.1021/es0511725.
- Hafliðason, H., H. P. Sejrup, A. Nygard, J. Miernet, P. Byrn, R. Lien, C. F.
Forsberg, K. Berg, and D. Masson (2004), The Storegga slide: Architec-
ture, geometry, and slide development, *Mar. Geol.*, 213, 201–234,
doi:10.1016/j.margeo.2004.10.007.
- Hester, K. C., and P. G. Brewer (2009), Clathrate hydrates in nature, *Annu.*
Rev. Mar. Sci., 1, 303–327, doi:10.1146/annurev.marine.
010908.163824.
- Hester, K. C., et al. (2007), Gas hydrate measurements at Hydrate Ridge using
Raman spectroscopy, *Geochim. Cosmochim. Acta*, 71, 2947–2959,
doi:10.1016/j.gca.2007.03.032.
- Hester, K. C., E. T. Peltzer, P. M. Walz, R. M. Dunk, E. D. Sloan, and P. G.
Brewer (2009), A natural hydrate dissolution experiment on complex
multi-component hydrates on the sea floor, *Geochim. Cosmochim. Acta*,
73, 6747–6756, doi:10.1016/j.gca.2009.08.007.
- Hinrichs, K.-U., and A. Boetius (2002), The anaerobic oxidation of meth-
ane: New insights in microbial ecology and biogeochemistry, in *Ocean*
Margin Systems, edited by G. Wefer et al., pp. 457–477, Springer,
Berlin.
- Kerr, R. A. (2010), “Arctic Armageddon” needs more science, less hype,
Science, 329, 620–621, doi:10.1126/science.329.5992.620.

- 329 Kessler, J. D., et al. (2011), A persistent oxygen anomaly reveals the fate of
 330 spilled methane in the deep Gulf of Mexico, *Science*, *331*, 312–315.
- 331 Lapham, L. L., J. P. Chanton, R. Chapman, and C. S. Martens (2010),
 332 Methane under-saturated fluids in deep-sea sediments: Implications for
 333 gas hydrate stability and rates of dissolution, *Earth Planet. Sci. Lett.*,
 334 *298*, 275–285, doi:10.1016/j.epsl.2010.07.016.
- 335 Liger-Belair, G., M. Vignes-Adler, C. Voisin, B. Robillard, and P. Jeandet
 336 (2002), Kinetics of gas discharging in a glass of champagne: The role of
 337 nucleation sites, *Langmuir*, *18*, 1294–1301, doi:10.1021/la0115987.
- 338 Orphan, V. J., C. House, K.-U. Hinrichs, K. McKeegan, and E. F. DeLong
 339 (2001), Methane-consuming archaea revealed by directly coupled iso-
 340 topic and phylogenetic analysis, *Science*, *293*, 484–487, doi:10.1126/
 341 science.1061338.
- 342 Paull, C. K., and W. P. Dillon (Eds.) (2001), *Natural Gas Hydrates: Occur-
 343 rence Distribution, and Detection*, *Geophys. Monogr. Ser.*, vol. 124,
 344 315 pp., AGU, Washington, D. C.
- 345 Paull, C. K., and W. Ussler (2001), History and significance of gas sam-
 346 pling during DSDP and ODP Drilling associated with gas hydrates, in
 347 *Natural Gas Hydrates: Occurrence Distribution, and Detection*, *Geophys.
 348 Monogr. Ser.*, vol. 124, edited by C. K. Paull and W. P. Dillon, pp. 53–65,
 349 AGU, Washington, D. C.
- 350 Paull, C. K., W. Ussler, and W. S. Holbrook (2007), Assessing methane
 351 release from the colossal Storegga submarine landslide, *Geophys. Res.
 352 Lett.*, *34*, L04601, doi:10.1029/2006GL028331.
- 353 Paull, C. K., W. R. Normark, W. Ussler, D. W. Caress, and R. Keaten
 354 (2008), Association among active seafloor deformation, mound forma-
 355 tion, and gas hydrate growth and accumulation within the seafloor of
 356 the Santa Monica Basin, offshore California, *Mar. Geol.*, *250*, 258–
 357 275, doi:10.1016/j.margeo.2008.01.011.
- 358 Pohlman, J. W., et al. (2005), The origin of thermodynamic gas hydrates on
 359 the northern Cascadia Margin as inferred from isotopic ($^{13}\text{C}/^{12}\text{C}$ and
 360 D/H) and molecular composition of hydrate and vent gas, *Org. Geochem.*,
 361 *36*, 703–716, doi:10.1016/j.orggeochem.2005.01.011.
- Reeburgh, W. S. (1967), An improved interstitial water sampler, *Limnol. Oceanogr.*, *12*, 163–165, doi:10.4319/lo.1967.12.1.0163.
- Reeburgh, W. S. (2007), Oceanic methane biogeochemistry, *Chem. Rev.*, *107*, 486–513, doi:10.1021/cr050362v.
- Scranton, M. I., and P. G. Brewer (1978), Consumption of dissolved methane in the deep ocean, *Limnol. Oceanogr.*, *23*, 1207–1213, doi:10.4319/lo.1978.23.6.1207.
- Shakhova, N., et al. (2010), Extensive methane venting to the atmosphere from sediments of the east Siberian Arctic shelf, *Science*, *327*, 1246–1250, doi:10.1126/science.1182221.
- Sloan, E. D., and C. A. Koh (2007), *Clathrate Hydrates of Natural Gases*, 721 pp., CRC Press, Boca Raton, Fla.
- Suess, E., et al. (1999), Gas hydrate destabilization: enhanced dewatering, benthic material turnover, and large methane plumes at the Cascadia convergent margin, *Earth Planet. Sci. Lett.*, *170*, 1–15, doi:10.1016/S0012-821X(99)00092-8.
- Ussler, W., and C. K. Paull (2008), Rates and consequences of anaerobic oxidation of methane and authigenic carbonate mineralization in deep-sea sediments inferred from pore water chemical profiles, *Earth Planet. Sci. Lett.*, *266*, 271–287, doi:10.1016/j.epsl.2007.10.056.
- Westbrook, G. K., et al. (2009), Escape of methane gas from the seabed along the west Spitzbergen continental margin, *Geophys. Res. Lett.*, *36*, L15608, doi:10.1029/2009GL039191.
- Yamamoto, S., J. B. Alkauskas, and T. E. Crozier (1976), Solubility of methane in distilled water and sea water, *J. Chem. Eng. Data*, *21*, 78–80.
- Zhang, X., et al. (2010), Development and deployment of a deep-sea Ramman probe for measurement of pore water geochemistry, *Deep Sea Res., Part 1*, *57*, 297–306, doi:10.1016/j.dsr.2009.11.004.
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