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

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6 [1] Ocean sediment dissolved CH₄ concentrations are of interest for possible climate-driven venting from sea floor hydrate decomposition, for supporting the large-scale microbial anaerobic oxidation of CH₄ that holds the ocean CH₄ budget in balance, and for environmental issues of the oil and gas industry. Analyses of CH₄ from recovered cores near vent locations typically show a maximum of ~1 mM, close to the 1 atmosphere equilibrium value. We show from novel in situ measurement with a Raman-based probe that geochemically coherent profiles of dissolved CH₄ occur rising to 30 mM (pCH₄ = 3 MPa) or an excess pressure ~3× greater than CO₂ in a bottle of champagne. Normalization of the CH₄ Raman ν₁ peak to the ubiquitous water ν₁ bending peak provides a fundamental internal calibration. Very large losses of CH₄ and fractions of other gases (CO₂, H₂S) must typically occur from recovered cores at gas rich sites. The new data are consistent with observations of microbial biomass and observed CH₄ oxidation rates at hydrate rich sites and support estimates of a greatly expanded near surface oceanic pore water CH₄ reservoir. Citation: Zhang, X., K. C. Hester, W. Ussler, P. M. Walz, E. T. Peltzer, and P. G. Brewer (2011), In situ Raman-based measurements of high dissolved methane concentrations in hydrate-rich ocean sediments, Geophys. Res. Lett., 38, LXXXX, doi:10.1029/2011GL047141.

30. Introduction

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

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

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

[5] Seawater contains 28 mM sulfate ion, and SO₄²⁻ concentrations within anoxic sediments are often quickly reduced to zero by the diagenetic reaction [Reeburgh, 2007] schematically, that is neglecting the small contributions from any organoclastic sulfate reduction, given as

\[ CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \]

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

2. Experiments and Methods

[6] We have investigated these processes and in situ pore water concentrations by means of a newly developed ROV-
operated pore water probe [Zhang et al., 2010] based upon
Raman sensing of the extracted fluid. [7] The probe consists of a 35 cm long titanium rod through
which a 2 mm diameter hole has been drilled. Water samples are drawn in through an annular sintered metal frit of
10 µm pore size by actuating a hydraulic pump, calibrated
by observing the piston distance travelled versus known
bore area. The induced pressure differential pulls in fluid
through the probe body to an optical cell with sapphire window
dow through which the laser beam is focused. The volume
required for analysis including flushing is about 3 ml.

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

[9] The components of the diagenetic reaction are well-
suited to Raman sensing, which favors the symmetrical
molecules H₂S, CH₄, and SO₄. Raman detection of HCO₃⁻ ion at these concentrations presents a challenge due to its
low cross section. However solution pH in such sediments is
potentially observable in situ via Raman detection of the
natural pH sensitive “dye” provided by the ratio of the H₂S
and HS⁻ species (pK ~ 7) [Zhang et al., 2010]. Thus all
critical components of the diagenetic AOM equation are
potentially observable spectroscopically in situ.

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

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.

Spectra obtained were quantified by normalization
of the solute peak areas to the ubiquitous water signal
present [Dunk et al., 2005]. For quantitative measurement
the pore water SO₄, CH₄ and HS⁻/H₂S Raman peak intens-

ties were normalized to the 1640 Δcm⁻¹ ν₂ water bending
mode peak; the normalized peak areas are linear with
concentration. The concentration of water in sea water is
55 molar and is thus constant. Only small corrections for T,
S and P effects on the water ν₂ peak are required [Carey and
Korenowski, 1998] and were applied here. The relationships
between the Raman normalized peak intensity/area (R*)
and the SO₄²⁻, CH₄ and H₂S concentration used in this paper
are: R*SO₄ = 0.0028C.SO₄ (r² = 0.9994), R*H₂S = 0.0039C.H₂S
(r² = 0.9989)¹¹ and R*CH₄ = 0.0041C.CH₄ (r² = 0.9984),
measured by the SO₄²⁻ ion (960–1000 Δcm⁻¹) peak, the CH₄
(2860–2960 Δcm⁻¹) peak, the HS⁻/H₂S (2540–2640 Δcm⁻¹).

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 SO₄
peak at 981Δcm⁻¹ rapidly declines from its sea water value
of 28.9 mM to vanishingly small levels. In a mirror image of
this trend dissolved CH₄ with a Raman shift of 2910 Δcm⁻¹
rises strongly from nanomolar concentrations in deep sea
water to about 28 mM at 30 cm depth.
peaks, and the water (1500–1800 \( \text{D cm}^{-1} \)) peak under lab simulation conditions.

3. Results

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

chemically coherent depth profiles can be obtained at a single insertion point within a few minutes. The profile obtained shows geochemical signals quantitatively relating declining \( \text{SO}_4^{2-} \) and rising \( \text{CH}_4 \) and \( \text{H}_2\text{S} \) in ratios that identify the microbially-mediated diagenesis taking place.

[13] We compared Raman probe measurements of pore waters extracted from push cores with conventional shipboard chemical analyses of the same water sample. Extracted pore waters were preserved and sealed in glass ampoules for later analysis. Comparisons were made on samples from two sites at Hydrate Ridge, characterized by the presence of SI hydrate, from one site at Barkley Canyon, BC in oil-rich sediments where complex SII hydrates occur [Pohlman et al., 2005; Hester et al., 2009], and from two sites on the Santa Monica Basin mounds [Paull et al., 2008]. In each case strong agreement between Raman and conventional chemical measurements of pore water \( \text{SO}_4^{2-} \) profiles was obtained (Figure 3).

[14] In marked contrast, large differences in dissolved \( \text{CH}_4 \) were observed between in situ and shipboard measurements (Figure 4); \( \text{CH}_4 \) concentrations from Hydrate Ridge obtained by in situ measurement, show progressive increase with depth to values as high as 30 mM. \( \text{CH}_4 \) concentrations from recovered cores show reversal of this trend with depth from gas loss, visible as gas voids within the core, resulting in values 10–20 times less than observed in situ. The close agreement in \( \text{SO}_4^{2-} \) data shows that the gas bubbles did not significantly alter the non-volatile ion profiles.

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

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 \( \text{CH}_4 \) data shown in Figure 4.

Figure 4. Comparison of dissolved \( \text{CH}_4 \) 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 \( \text{CH}_4 \) environment are 10–20 times greater than in recovered cores.
face was recorded. The probe was then removed, and the sediment surface scraped away revealing a yellow hydrate slab and releasing abundant oil droplets. While the oil itself is strongly fluorescent, the work required to distort the oil droplets to pass through the 10 μm pore size filter far exceeds the pressure differential created. Thus oil was excluded from the sample measured and clean spectra were recorded as a bonus of this new tool.

From phase equilibrium calculations we estimate the saturated molecular boundary layer value for dissolved CH4 in contact with this hydrate [Sloan and Koh, 2007] as 54 mM; the saturated layer is typically only a few tens of microns thick and is limited by diffusive processes. The CH4 concentration found with the probe tip at about 13 mm from the slab was 28 mM indicating strong local gradients due to diffusive losses. The probe draws pore water in from a halo around the filter and thus the effective distance from the solid hydrate surface cannot be known with certainty.

4. Discussion

The in situ data from hydrate bearing sites reveal pCH4 of about 3 MPa, over 3x the pressure of CO2 in a typical bottle of champagne [Liger-Belair et al., 2002]. The explosive venting of a champagne bottle does not occur here since pressure is relieved slowly during core recovery, typically at 30–50 meters depth per minute. While homogeneous nucleation of gases from liquids requires overcoming a significant interfacial free energy, the vast number of heterogeneous nucleation sites provided by the sediment favors easy ex-solution of gas so that sediment texture is often relatively undisturbed. Henry’s Law calculations indicate that other gases (CO2, H2S) critical for geochemical modeling will partition into the escaping CH4 gas phase [Chanton et al., 1989] and will also be underestimated by conventional techniques.

The oceanic sedimentary methane budget is a delicate balance between enormous production and consumption fluxes where the vast majority of CH4 produced is oxidized anaerobically before it can be released to the ocean water column. The recent review by Reeburgh [2007] estimates sedimentary production as 85.3 Tg yr−1 and consumption as 75.5 Tg yr−1. However one estimate [Hinrichs and Boetius, 2002] based upon microbial consumption rate data suggests that sedimentary methane production is a factor of 4 higher at 304 Tg yr−1. Our data would tend to support that claim and more, and since production must equal or exceed consumption true CH4 production rates on continental shelves may well be significantly higher. The direct CH4 observations here are also consistent with the higher estimates of CH4 consumption inferred from SO42− ion gradients [Ussler and Paull, 2008].

The data here cluster around the critical 28 mM CH4 value. This is a natural poise for ocean sediments since the primary oxidant of CH4 is SO42− also at 28 mM, although small contributions from organoclastic sulfate reduction may also occur. In a typical diffusive dominated system dissolved CH4 concentrations exceeding this value will migrate to the sea floor and there be exposed to aerobic oxidation. Values of CH4 less than 28 mM will be anaerobically consumed by the diffusive invasion of SO42− driving the sulfate-methane interface deeper within the sediment column as clearly implied by widely used SO42− gradient predictor of depth to CH4 occurrence [Borowski et al., 1996].

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 CH4 we estimate that 0.5 Gt of carbon could have been released if all pore water was mixed into the water column.

Haflidason et al. [2004] report that only 250 km3 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 δ13C 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


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