ACCURATE IN SITU OBSERVATION OF DEEP-SEA SEDIMENT DISSOLVED METHANE PROFILES IN HYDRATE BEARING PROVINCES

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ABSTRACT
The application of Raman spectroscopic techniques in the laboratory and in the field has made extraordinary advances in hydrate science possible, enabling us to link complex chemical data and models with real time field observations. The application of Raman techniques to field-going systems operational at ocean depths >1,000m required considerable breakthroughs. And the application to hydrates and dissolved methane within marine sediments was long thought to be impossible. Here we report such advances and their application. We have made, by means of a Raman probe ROV operated in situ, accurate measurements of the dissolved methane concentrations in the pore waters that bathe hydrate deposits. We show that concentrations in situ are ~ 30x greater than those obtained from recovered cores. The traditional method of recovering cores for ship board sectioning and squeezing for pore water analysis has long been suspected of yielding results that are far too low. In situ Raman measurements at hydrate sites such as Hydrate Ridge (OR), Barkley Canyon (BC), and Santa Monica (CA) reveal pore water profiles in which the CH4-H2S-SO4 signals are tightly correlated and geochemically coherent. In marked contrast analyses of recovered cores show coherence only in the SO4 signal; the gaseous CH4 and H2S signals diverge strongly from the in situ data. The spectroscopic data are quantifiable by reference to the ubiquitous water peaks. The spectra reveal HS− and H2S peaks (pKa =7), thereby opening a route towards in situ determination of pH, and pH2S as the key indicator to inclusion of H2S in the hydrate matrix. The observed pH of pore waters of hydrate bearing sediments in situ is 28-30x atmospheric or ~5x the pressure in a bottle of champagne. The reservoir of pore water methane has been greatly underestimated; the impact of climate change on this system remains to be examined.

Keywords: Raman, sediments, methane, pore waters

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INTRODUCTION
The application of Raman techniques to study of the structure and composition of hydrates in the laboratory was pioneered by Sloan and colleagues [1] in 1997 as a laboratory technique that yielded exceptional insights into hydrate structure and formation rates. The first deep-sea field experiments on controlled hydrate formation in sediments were carried out in the same year [2].

Remarkably it is now possible to combine these two fields and apply techniques derived from the laboratory to create experiments on the sea floor that were undreamed of a dozen years ago. The progress made and the now extension of this work to accurate measurements within hydrate bearing marine sediments is the focus of this paper.

The first execution of a controlled hydrate formation experiment in the deep sea [2] was enabled by access to a scientific ROV. Previously the use of such vehicles had been limited to sample collection, imaging, pipeline operations etc. The concept of using an ROV for execution of a relatively complex chemical experiment in the deep ocean was largely unknown. This theme has continued and the progress in pairing scientific ROVs with advanced instrumentation has been rapid.

Early experiments on natural hydrates in the deep sea involved collection into funnels and breakdown to gas, either by heating or simply bringing the system to a depth above the phase boundary, for analysis. ROVs were also used for dynamic experiments in which freely rising material was imaged during transit it’s rise rate and breakdown dynamics recorded [3] and insights into hydrate release during slumping was gained [4].

But these techniques were not able to address a critical issue forhydrate science, the direct identification of the molecular characteristics of the solid phase in situ. The success of laboratory Raman systems offered promise but no deep ocean Raman system had ever been attempted. The barriers were substantial; no manufacturer had conceived of a Raman system suitable for adaptation to the deep-sea. There is basically zero history of Raman techniques (laboratory or field) in the ocean sciences. Fluorescence, the bane of Raman, is common in ocean geochemistry, and the weak Raman effect makes it ill suited for application to dissolved species of common interest to ocean scientists.

EARLY DEVELOPMENT
A careful survey of possible instruments by team members from MBARI and Washington University resulted in a Kaiser Optical Systems instrument being the choice for a development platform [5, 6]. The prototype instrument developed [5] was far from ideal. It was of awkward shape for adaptation to a pressure housing and although the optical components were of high quality it had flimsy mechanical mountings for lens, slit, and shutter. The optical bench design of a cooled CCD mounted at right angles to the main body resulting in a wart-like side housing that proved difficult to manage. The schematic layout is shown in Figure 1.

Figure 1. Schematic layout of the prototype deep-ocean Raman system. The basic concept of a central optical system controlled via an Ethernet connection and carried by an ROV with copper/optical cables to a probe head for robotic arm positioning has endured.
The first use of this system for deep-sea experimental work involved the use of highly controlled “artificial” experiments designed to gain experimental familiarity and to test capabilities. The oceanic CO₂ system was the experimental choice and key lessons were learned in devising novel procedures for hydrate controlled rate processes [7] and importantly for identifying means of precisely quantifying the signal by self referencing to the ubiquitous and near constant water peaks [8]. This latter point is critical and normalization of the sensed Raman signal to the ν₂ water bending peak at 1640Δcm⁻¹ has become the standard procedure for a great many deep-sea experimental studies enabling quantification of the concentration of many reacting species in solution to ±5% or better.

The first images of a laser Raman system operating in the deep sea with fish in full view proved so attractive that the manufacturer (KOSI) committed to a full new system build incorporating many of the features we had requested. A more compact layout, redesign of the optical bench to avoid the awkward 90º angle of the CCD camera, far more robust mountings of the lens and shutter etc. The system was housed on a shock resistant mounts, could pass a drop test, and was now far more suitable for expedition work (Figure 2).

Figure 2. The compact DORISS II laser Raman system. The unit is housed in a Ti pressure housing for deployment. An on-board PC104 stack is used for communication/control.

The first use of this system for measurement of naturally occurring hydrates in situ was accomplished at Hydrate Ridge, OR [9]. In that work it was shown by direct measurement that the hydrates formed on the sea floor did indeed contain gaseous inclusions indicative of their rapid and recent formation, thus confirming the work of others [10] on recovered samples which had been the object of suspicion since such gas inclusions could have been formed by depressurization during unprotected recovery.

The work very clearly led towards support of the concept of formation of massive hydrate deposits near the sea floor via bubble transport [11] rather than by stripping of fluids of their dissolved load. The observations at Hydrate Ridge and later of the complex mixed structure hydrates on the Cascadia margin at Barkley Canyon lead to testing of the gas bubble stream source hypothesis of massive complex hydrate formation via an extended sea floor hydrate synthesis and growth/annealing study [12]. This confirmed the viability of the individual bubble reactor model as a pathway to growth of complex mixed hydrate structures from a single gas stream containing both sI and sII hydrate structure formers.

An image of the Raman system recording the structure and composition of a natural hydrate outcrop exposed at the Barkley Canyon site is shown in Figure 3.

Figure 3. Laser focusing on a massive hydrate outcrop for Raman detection of composition and structure.
RAMAN SENSING OF SEDIMENT PORE WATERS - INSTRUMENT DESIGN
The success of Raman detection of hydrate structure and composition in nature led to questions of how these systems are supported by the pore water fluids within which they grow and with which they must maintain chemical equilibrium if they are long to survive. The pore fluids are mobile and the hydrate masses will soon dissolve unless equality of chemical potential with the fluid that bathes them is maintained [13]. The tactic of simply focusing the laser beam (as seen e.g. in Figure 3) on or within marine sediments to detect pore fluid geochemistry will simply not work. Marine sediments are opaque and highly fluorescent so that any possible Raman signal is lost.
The history of sampling and observing the status of dissolved methane and associated gases in marine pore waters is fraught with problems of long standing [14] and inability to reconcile observed microbial systems with the fluxes supported by analyses of dissolved methane from recovered cores [15]. We have now developed a system for the Raman detection of pore water composition thus enabling for the first time the in situ detection of the dissolved gas status of the pore fluids in high methane concentration areas [16].
The Raman pore water probe basically consists of a metal rod through which a small diameter hole has been bored. A cylindrical metal frit is fitted at one end for insertion into the sediments. A small negative pressure gradient is created via activation of a hydraulic ram and pore fluid is pulled through the frit towards a small optical cell with a sapphire window at the other end of the probe. The Raman laser beam is focused through the sapphire window into a small sample cavity for signal detection. Once the spectrum is obtained the probe can be inserted to greater depth, or repositioned to another site. The small sediment cake that is accreted on the surface of the metal frit is easily removed by reversing fluid flow and pumping the sample out of the cell, thereby flushing the system. This apparently simple system took considerable development and required overcoming several technical and scientific obstacles of long standing. The first scientific barrier was to overcome the long-held belief that marine pore waters are highly fluorescent and are thus unsuitable for Raman sensing - the “it won’t work” syndrome.
Our first step was to examine pore waters obtained by conventional means and archived in sealed glass ampoules. These showed quite variable but small fluorescence so that with background correction the residual SO$_4^{2-}$ signal could be easily resolved [16]. The recognition that some samples had low fluorescence suggested to us that fresh natural (i.e. measured in situ) may have very low to near-zero fluorescence and so a pilot experiment was performed. In Figure 4 we show a diagram of the prototype sensor quickly fabricated for proof-of-concept for the first field test of Raman detection of pore waters.

Figure 4. Diagram of the construction of a prototype Raman sediment probe. The initial unit was only a few cm long. From [16].
This first unit was deployed on a test basis at the Clam Field South location in Monterey Bay where anoxic sediments are exposed at the surface and sulfur-oxidizing *Calypogena* clams are abundant. Such sites are typical of hydrate containing regions. Surprisingly to us the first spectra obtained were astonishingly optically clean with very little fluorescence. We did observe that fluorescence grew in very quickly upon oxygen invasion during recovery. A spectrum obtained is shown in Figure 5.

![Figure 5](image1.png)

**Figure 5.** Raman spectrum of pore water compared to overlying sea water showing the marked reduction in sulfate ion. From [16].

The final probe design encompassed a number of lessons learned and was able to penetrate to about 40 cm depth. A longer probe would pose handling problems for ROV pilots and would have increased dead volume in the present design form. This depth of insertion is equal to or greater than conventional ROV push cores. Experience showed that insertion of the 12.7 mm diameter probe into typical sediments was easy.

![Figure 6](image2.png)

**Figure 6.** Finished version of the sediment probe with the pressure housings built of titanium. The optical components housed just above the sapphire window are visible.

**RAMAN SENSING OF PORE WATERS AT HYDRATE BEARING SITES**

The first field test of this system at sites of known hydrate occurrence took place at Hydrate Ridge, OR at a depth of 850m. Disturbance of local sediments produced copious quantities of free floating hydrates. Insertions of the sediment probe quickly lead to detection of the classic signals of reduced sulfate ion, with traces of sulfide and a clear dissolved methane signal. It was soon realized that sequential depth steps of the probe were possible since insertion to the next depth scraped the sediment plug attached to the filter frit surface revealing a fresh surface for sample intake. The resulting stacked spectra depth profile is shown in Figure 7.

![Figure 7](image3.png)

**Figure 7.** Compilation of stacked Raman spectra obtained at Hydrate Ridge, OR [17]. The decline in the $\text{SO}_4^{2-}$ peak at 981 $\Delta \text{cm}^{-1}$ is exactly paralleled by the rise in the $\text{CH}_4$ peak at 2910 $\Delta \text{cm}^{-1}$ over an insertion depth of 30 cm.

The results shown in Figure 7 [17] are exactly as predicted by organic matter diagenesis theory and are entirely consistent with the anaerobic oxidation of methane first identified decades ago by Alperin and Reeburgh [18] but never before seen with such clarity. The results show very clearly the manner in which methane concentrations in such sediments must persist at 28 mM or greater or else they will be microbially consumed by the invading wave of sulfate ion.
Recovered cores show a much different story reflecting long-standing difficulties in this field. Push cores taken adjacent to the Raman probe site and returned to the ship for conventional squeezing and analysis show evidence of massive gas losses. In Figure 8 we show the comparison of in situ Raman data on dissolved methane versus data on pore water squeezed from core samples in the laboratory. It is clear that massive gas losses by a factor of 25-30 have occurred.

Figure 8. From [17]. Comparison of methane and sulfate data from in situ and recovered core data. The in situ Raman data show methane concentrations rising to ~30 mM; the recovered cores show ~ 1mM at the same depth. Large scale mass loss of gas from ebullition during recovery has occurred.

The finding of very large differences between recovered cores and in situ measurement was long predicted [14, 15] but the ramifications are still being explored. The existence of such a large pool of mobile methane in near surface sediments provokes further inquiry into the fate of this matter and its sensitivity to rapid release. The global size of this pool is not yet known but the estimate of a methane production rate in sediments of 304 Tg yr\(^{-1}\) [15] now seems reasonable. This dissolved methane is easily releasable to the water column during a submarine landslide and it is possible to make rough estimates. The colossal Storegga slide events have been carefully examined and Paull et al. [19] have estimated that a maximum quantity of 1.4 Gt of carbon could have been released as hydrate during these events. If we take a mean dissolved CH4 concentration of 30 mM for this pore water then we estimate [17] that 0.5 Gt C could have been released from the pore water reservoir; a more probable figure is 0.05 Gt C.

CONTACT WITH A HYDRATE SURFACE

At the Barkley Canyon site we inserted the probe until a hard surface was encountered at about 12 cm depth and sample the pore water. The observed value was 28 mM. Scraping away the sediment cover revealed a large slab of dense yellow sII hydrate. The observed value is well below the saturated boundary layer condition of about 50 mM. The probe draws in water from a halo around the probe tip and thus cannot observe the very thin saturated layer. Nonetheless the finding indicates that the hydrate masses are bathed in under-saturated pore water and are thus actively dissolving. Similarly lower than saturation values for this site are also reported by Lapham et al. [20].

DETECTING THE SULFIDE SIGNAL

The existence of methane, and therefore methane hydrates in sediment pore waters is fundamentally tied to the presence of sulfide. The microbial oxidation of methane by sulfate is ubiquitous and no methane could long persist unless sulfate is completely removed and build up of sulfide occurs. But there is remarkably little information on the sulfide signature of hydrates in nature and the signal is generally weak [9].

We now are able to observe the dissolved sulfide signal in sediment pore waters [17] and the quantities align very well with the anticipated amounts from complete reduction of 28 mM sulfate ion with a small
additional contribution from organoclastic material.

Raman observation offers the advantage of seeing both the H2S and HS⁻ forms which present themselves as a natural pH sensitive dye. The dissociation constant for H2S is very close to 7, and since the pH of most anoxic pore waters is very close to 7 this suggests that the sulfide system may provide an elegant and sensitive pH indicator. In Figure 9 we show the Raman spectrum of sulfide species in methane rich pore waters.

![Figure 9. Raman spectrum of the pore water dissolved sulfide signal obtained at a methane rich mound. The sulfide peaks have been deconvoluted into the HS⁻ form at 2573 \( \Delta \text{cm}^{-1} \) and H₂S form at 2592 \( \Delta \text{cm}^{-1} \). The Raman response factor for the HS⁻ form is approximately 3x that for the H₂S form; in practice the concentration of both forms are almost equal.]

The critical condition for incorporation of sulfide into the hydrate structure is \( \text{pH}_{2S} \) - the ionic HS⁻ form will be excluded - and the solution pH will determine the H₂S fraction of the total sulfide present. So far as we are aware pH dependent terms are not normally incorporated into hydrate formation models, although in this case it is clearly relevant. We are actively pursuing the details of this signal. The typical pH of pore waters in methane rich-sulfidic environments is 7.0 - 7.2, so that only 45-50% of the total sulfide concentration is available for incorporation into the hydrate lattice. The selective inclusion of the H₂S form upon hydrate formation will have only small influence on the pore water pH which is dominated by the CO₂ system species.

**SUMMARY**

Rapid in situ detection of the chemical characteristics of the pore fluids that bathe methane hydrates is now possible via highly developed Raman techniques. The data available to date shed new light on the abundance of the pore water methane reservoir, and show very strong contrast with data from recovered cores so that typical dissolved methane values are 28-30 mM and higher, rather than the 1 mM signal typically seen. The saturated boundary layer condition for hydrate stability has not been observed in the bulk fluid suggesting that active dissolution driven by diffusive losses is quite rapidly occurring for the near surface hydrates we have examined.

The classical pore water diagenetic equation schematically given as:

\[
\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}
\]

contains terms (\( \text{CH}_4, \text{SO}_4, \text{HS}^- \)) that are fully determinable within a single spectral acquisition. The HCO₃⁻ term has a very weak Raman signal, but the solution pH is potentially determinable via the well resolved H₂S - HS⁻ ratio and thus the system is very close to being fully constrained. The pH₂S term that provides the thermodynamic condition for incorporation of the ubiquitous sulfide component into the hydrate matrix is typically set at about 50% of the total H₂S signal, thus helping to explain the quite small sulfide signal seen in most hydrates, and also suggesting that the incorporation of pH dependent terms into models of hydrate formation in nature would be useful.

**REFERENCES**


[18] Alperin MJ, Reeburgh WS Inhibition experiments on anaerobic methane
