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Instruments and Methods

Development of a laser Raman spectrometer for deep-ocean science

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Abstract

We have extensively modified and successfully used a laser Raman spectrometer (DORISS, deep-ocean Raman in situ spectrometer) for geochemical studies in the deep ocean. The initial instrument, from Kaiser Optical, was separated into three components: an optical head, a laser-power supply telemetry unit, and the spectrometer. These components were modified to fit into custom designed pressure housings, and connected by deep-sea cables and optical penetrators designed to minimize signal loss. The instrument ensemble has been field deployed on remotely operated vehicles (ROVs) for a variety of experiments and observations, with successful operation at 1.6°C, 3600 m depth. Power supply, instrument control, and signal telemetry are provided through the ROV tether, which contains copper conductors and single mode optical fibers. The optical head is deployable by the ROV robotic arm for sample analysis; the remaining components are fixed within the vehicle tool-sled. Challenges of system calibration at depth, temperature and pressure artifacts, and system control through over 4 km of cable were successfully overcome. We present exemplary spectra obtained in situ of gas, liquid, and solid specimens, and of the ubiquitous signal of sea water itself. Future challenges include weight and size reduction, and advances in precise beam positioning on mineral targets on the sea floor.
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1. Introduction

Geochemical studies in the deep ocean have traditionally relied upon sample recovery by bottles, cores, and dredges deployed from surface ships, or collected by manned submersibles and remotely operated vehicles (ROVs), to provide specimens for ship or shore based analysis. And while this remains the principal technique, there is a compelling case to be made for advances in in situ detection and analysis. Advances in measurement techniques have been greatly aided by the development and increasing use of deep-ocean submersibles and ROVs. These vehicles now provide sophisticated carrying platforms with the power, telemetry and data handling, and precise manipulation capabilities (Brewer et al., 1999) to support advanced geochemical measurement

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systems (Kleinberg et al., 2003). In this paper we describe the adaptation of a laser Raman spectrometer (LRS) for in situ measurements in the deep ocean, and its successful deployment from ROVs operated by the Monterey Bay Aquarium Research Institute (MBARI). In principle the system we describe here could be adapted for use on a variety of ROVs and research submersibles available worldwide. We present exemplary spectra of sea water itself, and of selected geochemical targets examined in a carefully constructed set of controlled field experiments during the development phase, and we briefly describe some important calibration protocols. The verification of these spectra through companion laboratory studies, and detailed discussion of the spectra obtained, is reported by Pasteris et al. (submitted).

A unique advantage of Raman spectroscopy for the field geochemist (Pasteris, 1998) lies in its ability to measure solid, liquid, and gas phases, thereby greatly extending the range of possible targets. The Raman technique can measure very small samples and can provide geochemical traverses across a heterogeneous sample. However, the instrument we describe here has not yet achieved scanning capability.

Sensors typically used (Varney, 2000) for oceanic geochemical research are either electrodes and optrodes, or small-scale pumped fluid devices, for dissolved species detection. These have become sophisticated and are used for mapping geochemical fields and probing seafloor sediment fluids. However, they are typically single species detection systems, not broadly applicable, and the in situ measurement of solid and gaseous phases, has so far not been possible. It is ironic that a prototype Raman spectrometer has been developed for possible exploration of planetary surfaces (Wang et al., 1998, 1999) such as Mars, yet the $>70\%$ of Earth's surface that is ocean has until now not been made accessible to this important tool.

There are many examples of important targets in the deep ocean potentially accessible by Raman spectroscopy. These include the in situ identification of rocks and minerals on the sea floor and the determination of chemical composition of pore water, gas seeps, and sea floor hydrothermal vents. Other interests include biologically (including microbially) precipitated solids such as the polymorphs of elemental sulfur produced by bacteria such as *Thioploca* and *Beggiatoa* (Pasteris et al., 2001). It has been reported that Raman spectroscopy can "characterize in situ the molecular components of pigments and other significant organic and inorganic constituents of a microbial community within its lithic habitat" (Wynn-Williams et al., 2002), although achieving this goal on the ocean floor would seem to be a significant challenge.

It is possible to distinguish between the biologically produced $CaCO_3$ polymorphs aragonite and calcite, and to investigate phosphate minerals and barite deposits on the seafloor. Other Raman active solids of interest on the seafloor include the silicates quartz and feldspar, the iron oxides magnetite and hematite, and the various manganese oxide precipitates. Clathrate hydrate phases (Sloan, 1998; Buffett, 2000; Max, 2000), which incorporate methane and many other gas species into their structure offer a compelling case for measurement in place. These hydrates are not stable at atmospheric pressure and room temperature, but exist in vast quantities in ocean margin sediments where the stability conditions are met. While hydrate specimens may be liberated from the sea floor (Brewer et al., 2002a), they are exceptionally difficult to recover in an unaltered state, and in situ analysis would provide unique information. The Raman spectrum of both CH_4 and CO_2 hydrates has been elegantly investigated in the laboratory (Sum et al., 1997; Subramanian and Sloan, 1999), and in situ analysis would permit the determination of the unaltered state, cage structures, and compositions.

Materials experimentally introduced into the ocean for research purposes may also be Raman active, such as in experiments to investigate the feasibility of fossil fuel CO_2 disposal (Brewer et al., 1999). Finally, possibly toxic material associated with deep ocean waste sites or accidents, where sample recovery may be hazardous, will require non-invasive analysis methods, such as may be provided by laser interrogation.

Nonetheless the challenges of carrying out Raman spectroscopy in the deep ocean are formidable. The Raman signal is notoriously

weak, although possibilities for signal enhancement do exist (e.g. Altkorn et al., 2001). The vast majority of dissolved chemical species in sea water are not Raman active, or are present at micromolar concentrations or less, and thus do not present useful Raman analytes. Water itself has a subdued Raman signature, unlike the overwhelming IR signature of water. Thus the ubiquitous signal of sea water is not likely to produce spectrally complex interferences in the Raman optical path. Fluorescence, on the other hand, is the bane of Raman spectroscopy, and there are many fluorescent oceanic species, including chlorophyll and related pigments. These are abundant in ocean surface waters, but are also rapidly transported to depth by sinking particles. It was unknown at the outset of our work how significant a problem for obtaining oceanic Raman spectra this might be.

Raman instrumentation has been typically fragile, requiring thermal stability, and a vibration free environment. Modern developments in optoelectronics have only now reached the point where these limitations may be overcome. Nonetheless, ships expose the instrumentation to significant physical motions, days of vibration during transit, and physical shock during loading and unloading. Deep ocean water is cold, and during a single lowering to the sea floor the instrumentation may be exposed to temperature changes from 20°C to 2°C in 1 h. The pressure casings that house the instrument must provide protection for a 40 MPa increase in pressure without distorting the encased optical configuration. During expedition work it is very common for instrument reconfiguration to be required, often on a daily basis, and so the system must be capable of open access under often trying field conditions.

Finally, weight and size limitations, power requirements, remote instrument control and positioning, and data telemetry through over 4 km of ROV tether, also provide significant challenges. Signal loss associated with the optical connectors required for pressure housings, and electrical and optical noise that may be introduced by the vehicle, are also issues to be faced. In Fig. 1 we show MBARI's ROV "Tiburon" used for several of our experiments, with the DORISS spectrometer system installed in the vehicle tool sled.

Fig. 1. MBARI's remotely operated vehicle "Tiburon", in side view. The base vehicle weight is 3084 kg. Front, with manipulators and cameras not shown, is to the right of the image. The syntactic foam pack that provides buoyancy is on top, the core vehicle power, thrust, telemetry, and computing, systems are housed in the middle. Below is the tool sled with the drawer used to house the DORISS system seen at bottom left.

2. Experimental

2.1. Selection of an instrument

The research team comprises groups from both MBARI and Washington University, St. Louis. The primary laboratory work was based at Washington University; the primary ocean program was based at MBARI. Each team acquired an initially identical instrument for research compatibility. The MBARI instrument has been very significantly modified in conversion to the

DORISS unit; the Washington University instrument remains in its original configuration. The field experiments for system development were carried out jointly by both teams in the deep waters of Monterey Bay, California.

The DORISS system we have developed is based on a laboratory model laser Raman spectroscopic system from Kaiser Optical Systems, Inc. (KOSI). A schematic diagram of the various components is given in Fig. 2. The requirement for robust handling demanded that the core instrument have as few moving parts as possible, and that the laser give a stable output over a wide temperature range. A frequency-doubled Nd:YAG laser operating at 532 nm was chosen (model DPSS532 by Coherent) because of its stability and its ability to be cooled simply by thermal conduction through the walls of the high-pressure housing. The 532-nm excitation wavelength was selected for its relatively efficient propagation through sea water. The Raman shift is not a function of the exciting wavelength, but the efficiency of Raman scattering from a substance decreases as a function of λ^4, and thus a shorter wavelength laser offers significant advantages. Wavelengths shorter than 532-nm also excite greater fluorescence, and thus the laser selected represents an optimal choice.

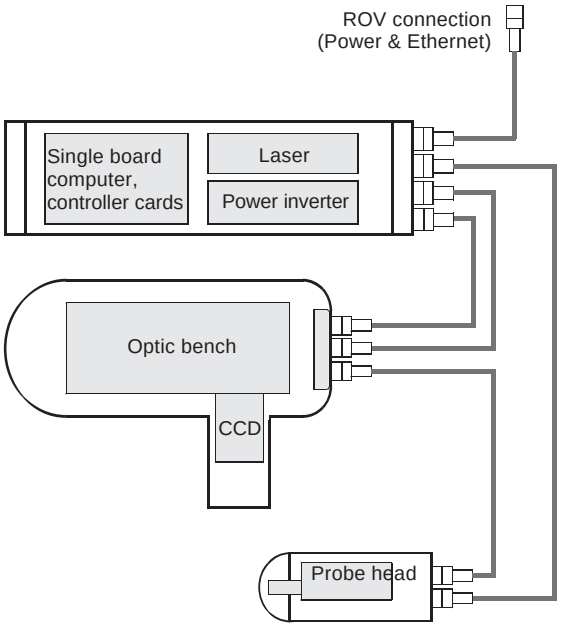

Fig. 2. Schematic of the DORISS system, showing the two pressure housings for the power/laser/computer, and the optical bench. These are carried in the vehicle tool-sled, and are connected to the probe head by pressure tolerant optical fiber cables. The probe head used for sample interrogation is carried on the front of the vehicle so as to be accessible by the vehicle robotic arm.

The requirement for analysis of such a wide range of materials and processes of scientific interest requires a core Raman spectrometer that measures the full spectral range of 100–4000 Δcm^{-1}. The wide spectral coverage is required so that data can be collected in the low-wavenumber range (on sulfur and sulfur containing minerals), mid-range (on most minerals and on volatiles such as CO_2, O_2, N_2), and high range (for organic compounds and for the OH-groups of clathrate hydrates and hydroxylated minerals such as zeolites and clays). Appropriate resolution is required to distinguish mixtures of phases with similar band positions, such as carbonates and experimentally introduced materials with contrasting isotopic shifts (e.g., ^{12}C and ^{13}C).

The selected instrument was a Kaiser HoloSpec f/1.8i spectrometer (Owen et al., 1998) with a holographic transmissive grating and a front-illuminated cooled CCD camera with 2048×512 pixels by Andor Technology. The spectrum is split into two stripes on the face of the camera, thus providing a mapping of 1 cm^{-1} per pixel. This is coupled by fiber optics to Kaiser's Mark II holographic filtered probe head with two interchangeable sampling optics: a "stand-off" optic, and an immersion probe (Fig. 3). We adapted the stand-off optic for housing behind a hemi-spherical deep-sea camera glass dome. It provided a $\sim$10X objective lens with a focal length in air of $\sim$6.4 cm. When immersed in sea water the dome-shielded optic provided a 10 cm working distance for target placement from the outer face of the glass dome. The immersion probe consists of a 2 mm focal length lens integrated into a 25.4 cm long metal tube with a plane sapphire end window and a working distance that is variable over a range of 1–7 mm from the probe tip. The two sampling optics require different pressure housing end caps. The stand-off optic is used by behind the glass dome window (shown assembled in Fig. 3). When the immersion optic is used, the

Fig. 3. The probe head, showing the pressure housing (above), and both the stand-off optic, in which the laser beam projects through the glass dome, and the immersion probe with a planar sapphire window at the tip. When the immersion optic is used the dome window is replaced with the flat end cap (seen on the right side of the picture) and a gland seal is used to seal around the probe. We determine ahead of the dive which optic will be appropriate for the target we anticipate. Since the range of focus is far greater for the stand-off optic this offers more flexibility, albeit with somewhat lower sensitivity. The time taken for optic exchange is a few (3–4) h, mostly for fine scale adjustment to achieve maximum laser output.

dome window is replaced by a flat titanium end cap with a gland seal that seals around the protruding optic with the plane sapphire window. The probe extends directly into the water ~20 cm.

2.2. Doriss development

2.2.1. Modification of the original instrument

Communication and control capability for the instrument via Ethernet was added by KOSI at our request at the time of purchase. This is now a standard feature for KOSI instruments. Our need for frequent field adjustment made it necessary to modify two of the original instrument alignment mechanisms. First, the laser-fiber alignment mechanism was replaced with a lockable precision three-axis micrometer stage to facilitate the alignment of the 62.5 μm diameter excitation fiber optic cable to the laser output port. This alignment is critical for delivering and maintaining the maximum laser power to the sample of interest, and correspondingly to obtaining the maximum instrument sensitivity.

Second, the alignment of the lens that focuses the collected Raman signal on the spectrometer slit, which in part determines the spectrometer resolution, is also critical. We found that slight mechanical shock, temperature changes, or orientation deviations could cause the lens-to-slit alignment to shift, degrading the signal. The original KOSI slit alignment mechanism, designed for use in fixed installations on land, used a manual knob to translate the spot across the slit. We have replaced this mechanism with a remotely controllable motor driven stage. The stage translates the scattered-light spot across the slit in 0.5 μm increments. This translation allows a field scientist to optimize the optical throughput of the instrument in real time while at full ocean depth on an individual measurement basis to compensate for changes in the lens/slit alignment that may have occurred during deployment.

2.2.2. Encapsulation

The spectrometer components (schematically shown in Fig. 2) are packaged in three separate pressure vessels capable of withstanding 41 MPa with a 25 percent safety margin. The probe head is contained within a 35.5 cm long by 14 cm diameter titanium pressure vessel (Fig. 3) that has a removable end cap to facilitate the change between different optical configurations. Each probe head configuration weighs 18 kg including supporting frame and manipulator handle. High-pressure tolerant fiber optic cables carry the laser excitation beam to the probe head, and return the Raman scattered signals from the probe head to the spectrometer pressure vessel. The excitation fiber is 62.5 μm diameter; the collection fiber is 100 μm diameter. Signal loss was found to be unacceptably high in standard optical fiber connectors needed to penetrate the pressure housings. The cables we are now using are direct feed-through penetrating cables. These fiber optic cables are standard, pressure-tolerant polyurethane jacketed underwater cables purchased from Falmat, Inc. of San Marcos, CA. Pressure testing performed at MBARI found very small pressure effects on the throughput of the cables.

The electronics (power, telemetry, and laser) pressure vessel (Fig. 4) is 100 cm long, 25.4 cm in

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Appendix

A vigorous debate over sulfate ion association in sea water was stimulated by the claim by Kester and Pytkowicz (1970) that the anomalous sound absorption due to relaxation of the $Mg–H_2O–SO_4$ pair should increase with depth. This was followed by a Raman spectroscopic study (Daly et al., 1972) that purported to support this model. The basis for this experimental attack is that aqueous $MgSO_4$ solutions of $\sim 0.5\,M$ at room temperature show the strong ν_1 stretching band at $981\,\Delta cm^{-1}$, and a weak shoulder on the peak at around $995\,\Delta cm^{-1}$ resulting from $Mg–SO_4$ ionic interaction, which thus yields a slight asymmetry to the profile. Davis and Oliver (1973) challenged the work of Daly et al. (1972), and reported that "it is not possible to distinguish the two types of solvent separated ion pairs from each other, or the sulfate in solvent separated ion pairs from the solvated sulfate ion." Further high-pressure work by Chatterjee et al. (1974) supported the conclusions of Davis and Oliver (1973). This rebuttal of the claims of Kester and Pytkowicz (1970) was strongly supported by Fisher (1978). Recent work (Rull and Sobron, 1994; Frantz et al., 1994) confirms by both experiment and models that such weak pairing is reflected only as a shoulder on the principal peak, and that this is only detectable at high solution strengths, and at temperatures higher than the deep ocean. We therefore conclude that the small fraction ($\sim 4\%$) of $Mg–SO_4$ contact ion pairs in sea water, does not affect our observed signal.

References

Abbott, T., Buchanan, G.W., Kruus, P., Lee, K.C., 1982. ^{13}C Nuclear magnetic resonance and Raman investigations of aqueous carbon dioxide systems. Canadian Journal of Chemistry 60, 1000–1006.

Altkorn, R., Malinsky, M.D., Van Duyne, R.P., Koev, I., 2001. Intensity considerations in liquid core optical fiber Raman spectroscopy. Applied Spectroscopy 55, 373–381.

Berger, A.J., Wang, Y., Sammeth, D.M., Itzkan, I., Kneipp, K., Feld, M.S., 1995. Aqueous dissolved-gas measurements using near-infrared Raman spectroscopy. Applied Spectroscopy 49, 1164–1169.

Borowski, W.S., Paull, C.K., Ussler, W., 1999. Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: sensitivity to underlying methane and gas hydrates. Marine Geology 159, 131–154.

Brewer, P.G., Friederich, G., Peltzer, E.T., Orr Jr., F.M., 1999. Direct experiments on the ocean disposal of fossil fuel CO_2. Science 284, 943–945.

Brewer, P.G., Paull, C., Peltzer, E.T., Ussler, W., Rehder, G., Friederich, G., 2002a. Measurements of the fate of gas hydrates during transit through the ocean water column. Geophysical Research Letters 29, doi: 10.1029/2002GL014727.

Brewer, P.G., Peltzer, E.T., Friederich, G., Rehder, G., 2002b. Experimental determination of the fate of rising CO_2 droplets in seawater. Environmental Science and Technology 36, 5441–5446.

Brewer, P.G., Pasteris, J., Malby, G., Peltzer, E.T., White, S., Freeman, J., Wopenka, B., Brown, M., Cline, D., 2002c. Laser Raman spectroscopy used to study the ocean at 3600-m depth. EOS, Transactions, American Geophysical Union 83, 469–470.

Buffett, B.A., 2000. Clathrate hydrates. Annual Review of Earth and Planetary Sciences 28, 477–507.

Chatterjee, R.M., Adams, W.A., Davis, A.R., 1974. A high-pressure laser Raman spectroscopic investigation of aqueous magnesium sulfate solutions. The Journal of Physical Chemistry 78, 246–250.

Chen, R.F., 2000. A laser-based fiber-optic fluorometer for in situ seawater measurements. In: Varney, M.S. (Ed.), Chemical sensors in oceanography. Gordon and Breach, London, pp. 189–209.

Coble, P.G., 1996. Characterization of marine and terrestrial DOM in sea water by rising excitation-emission spectroscopy. Marine Chemistry 51, 325–346.

Daly, F.P., Brown, C.W., Kester, D.R., 1972. Sodium and magnesium sulfate ion pairing: evidence from Raman spectroscopy. The Journal of Physical Chemistry 76, 3664–3668.

Davis, A.R., Oliver, B.G., 1973. Raman spectroscopic evidence for contact ion pairing in aqueous magnesium sulfate solutions. The Journal of Physical Chemistry 77, 1315–1316.

Dickensheets, D.L., Wynn-Williams, D.D., Edwards, H.G.M., Schoen, C., Crowder, C., Newton, E.M., 2000. A novel miniature confocal microscope/Raman spectrometer system for biomolecular analysis on future Mars missions after Antarctic trials. Journal of Raman Spectroscopy 31, 633–635.

Dickson, A., 2001. Reference materials for oceanic measurements. Oceanography 14 (4), 21–22.

Diller, D.E., Chang, R.F., 1980. Composition of mixtures of natural gas conponents determined by Raman spectrometry. Applied Spectroscopy 34, 411–414.

Fisher, F., 1978. Comment on "a high-pressure laser Raman spectroscopic investigation of aqueous magnesium sulfate solutions". The Journal of Physical Chemistry 82, 495–496.

Frantz, J.D., Dubessy, J., Mysen, B.O., 1994. Ion-pairing in aqueous $MgSO_4$ solutions along an isochore to 500°C and 11 kbar using Raman spectroscopy in conjunction with the diamond-anvil cell. Chemical Geology 116, 181–188.

Haugan, P.M., Drange, H., 1992. Sequestration of CO_2 in the deep ocean by shallow injection. Nature 357, 318–320.

Kester, D.R., Pytkowicz, R.M., 1970. Effect of temperature and pressure on sulfate ion association in sea water. Geochimica et Cosmochimica Acta 34, 1039–1051.

Kleinberg, R.L., Flaum, C., Straley, C., Brewer, P.G., Malby, G.E., Peltzer, E.T., Friederich, G., Yesinowski, J.P., 2003. Seafloor nuclear magnetic resonance assay of methane hydrate in sediment and rock. Journal of Geophysical Research 108, doi:10.1029/2001JB000919.

Masutani, S.M., Kinoshita, C.M., Nihous, G.C., Teng, H., Vega, L.A., Sharma, S.K., 1995. Laboratory experiments of CO_2 injection into the ocean. In: Handa, N., Ohsumi, T. (Eds.), Direct Ocean Disposal of Carbon dioxide. Terra Scientific Publishing, Tokyo, pp. 239–252.

Max, M.D., 2000. Natural Gas Hydrate in Oceanic and Permafrost Environments. Kluwer, Academic Publishers, Dordrecht, 414 pp.

Murata, K., Kawakami, K., Matsunaga, Y., Yamashita, S., 1997. Determination of sulfate in brackish waters by laser Raman spectroscopy. Analytica Chimica Acta 344, 153–157.

Nakamoto, K., 1997. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry. Wiley, New York, 387 pp.

Owen, H., Battery, D.E., Pelletier, M.J., Slater, J., 1998. New spectroscopic instrument based on volume holographic optical elements. Proceedings SPIE 2406, 260.

Pasteris, J., 1998. The laser Raman microprobe as a tool for the economic geologist. In: McKibben, M.A., Shanks, W.C., Ridley, W.I. (Eds.), Applications of microanalytical techniques to understanding mineralizing processes. Society of Economic Geologists, Littleton, CO, pp. 233–250.

Pasteris, J.D., Freeman, J.J., Goffredi, S.K., Buck, K.R., 2001. Raman spectroscopic and laser scanning confocal microscopic analysis of sulfur-precipitating marine bacteria. Chemical Geology 180, 3–18.

Pasteris, J.D., Wopenka, B., Freeman, J.J., Brewer, P.G., White, S.N., Peltzer, E.T., George, E., Malby, G.E., Spectroscopic successes and challenges: Raman spectroscopy at 3.6 Km depth in the ocean. Applied Spectroscopy, in review.

Raman, C.V., 1930. The molecular scattering of light. Nobel Prize Lecture.

Rull, F., Sobron, F., 1994. Band profile analysis of the Raman spectra of sulfate ions in aqueous solutions. Journal of Raman Spectroscopy 25, 693–698.

Saito, T., Kajishima, T., Naguosa, R., 2000. CO_2 sequestration at sea by gas-lift system of shallow injection and deep releasing. Environmental Science and Technology 34, 4140–4145.

Schiferl, D., Nicol, M., Zaug, J.M., Sharma, S.K., Cooney, T.F., Wang, S.Y., Anthony, T.R., Fleischer, J.F, 1997. The diamond $^{13}C/^{12}C$ isotope Raman pressure sensor system for high-temperature/pressure diamond-anvil cells with reactive samples. Journal of Applied Physics 82, 3256–3265.

Seitz, J.C., Pasteris, J.D., Chou, I.-M., 1993. Raman spectroscopic characterization of gas mixtures. I. Quantitative composition and pressure determinations of CH_4, N_2, and their mixtures. American Journal of Science 293, 297–321.

Seitz, J.C., Pasteris, J.D., Chou, I.-M., 1996. Raman spectroscopic characterization of gas mixtures. II. Quantitative composition and pressure determination of the CO_2–CH_4 system. American Journal of Science 296, 577–600.

Sloan, E.D., 1998. Clathrate Hydrates of Natural Gases. Marcel Dekker, New York, 705 pp.

Subramanian, S., Sloan Jr., E.D., 1999. Molecular measurements of methane hydrate formation. Fluid Phase Equilibria, 158–160, 813–820.

Sum, A.K., Burruss, R.C., Sloan Jr., E.D., 1997. Measurement of clathrate hydrates via Raman spectroscopy. Journal of Physical Chemistry 101, 7371–7377.

Tedesco, J.M., Davis, K.L., 1999. Calibration of dispersive Raman process analyzers. Proceedings of SPIE, 3537 200–212.

Varney, M.S. (Ed.), 2000. Chemical Sensors in Oceanography, Gordon and Breach, The Netherlands, p. 333.

Venkataraman, G., 1988. Journey into Light: Life and Science of C.V. Raman. Indian Academy of Sciences.

Walrafen, G.E., 1964. Raman spectral studies of water structure. The Journal of Chemical Physics 40, 3249–3256.

Wang, A., Haskin, L.A., Cortez, E., 1998. Prototype Raman Spectroscopic sensor for in situ mineral characterization on planetary surfaces. Applied Spectroscopy 52, 477–487.

Wang, A., Jolliff, B.J., Haskin, L.A., 1999. Raman spectroscopic characterization of a highly weathered basalt: igneous mineralogy, alteration products, and a microorganism. Journal of Geophysical Research 104, 27067–27077.

Wang, A., Haskin, L.A., Lane, A.L., Wdowiak, T.J., Squyres, S.W., Wilson, R.J., Hovland, L.E., Manatt, K.S., Raouf, N., Smith, C.D., 2003. Development of the Mars microbeam Raman spectrometer (MMRS). Journal of Geophysical Research 108, doi: 10.1029/2002JE001902.

Wynn-Williams, D.D., Edwards, H.G.M., Newton, E.M., Holder, J.M., 2002. Pigmentation as a survival strategy for ancient and modern photosynthetic microbes under high ultraviolet stress on planetary surfaces. International Journal of Astrobiology 1, 39–49.

Zheng, X., Fu, W., Albin, S., Wise, K.L., A. Javey, K.L., Cooper, J.B., 2001. Self-referencing Raman probes for quantitative analysis. Applied Spectroscopy 55, 382–388.