



SHERI N. WHITE

Monterey Bay Aquarium Research Institute
7700 Sandholdt Rd.
Moss Landing, CA 95039

Phone: (831) 775-1903
Fax: (831) 775-1620
Email: sheri@mbari.org

October 13, 2004

Dr. Frank J. Millero
Editor-in-Chief, Marine Chemistry
Rosenstiel School of Marine and Atmospheric Science
University of Miami
4600 Rickenbacker Causeway
Miami, FL 33149-1098

Dr. Millero:

Enclosed is a hard copy and electronic copies of our manuscript "Determination of gas bubble fractionation rates in the deep ocean by laser Raman spectroscopy" (MARCHE 1946), and camera ready figures. We have revised the text and figures to address the comments of the two reviewers. Our responses to the reviewers are below. We appreciate their positive comments on the paper.

Reviewer 1: Gordon Taylor

Abstract – The dates of the experiments were removed and the text was slightly condensed.

Introduction – The introduction has been reorganized to hopefully flow more smoothly from the concept of CO₂ sequestration to our experiments and the potential of laser Raman spectroscopy.

Methods – We have shortened the first explanatory paragraph slightly, and feel that it is a very cursory description of Raman spectroscopy. The second and third paragraphs explain the method of area ratio comparison that we use in this paper, and thus we feel that they are necessary as is.

Pg. 8 – "Raman efficiency" should indeed be "Raman scattering efficiency". It has been changed here as well as on page 4.

Pg. 11 – We have removed the redundant portions of the text referring to the difference in Raman scattering efficiencies.

Table 2 – " R^2 " has been changed to " r^2 " and the significant figures have been reduced to three.

The 10x10x10 cm gas cube – References to the size of the cube have been changed to "1000 cm³" throughout the paper.

Reviewer 2: Gregor Rehder

Abstract – We have removed the result of the exponential for the October data from the abstract.

Methods, section 2.2 – The sentence “It should be noted...” has been moved to the end of the paragraph as the reviewer suggested. The sentence “Additionally, the detection limit...” was moved to follow the sentence “During the development of” because those two sentences describe the key factors affecting the detection limit.

Methods, section 2.3 – The redundant text has been removed, and only a brief sentence remains noting that area ratios were examined.

Section 3.2 – The sentence “In this experiment, we attempted to mimic the bubble experiments of Brewer et al., 2002b” was removed.

Laser power – A sentence stating the laser power for both deployments was moved into the instrumentation section. (Laser power cannot be currently measured at depth. Measurements made on deck prior to dives are assumed to be representative of the laser power during the dive.)

Discussion, section 5.1 – We have edited the third paragraph to remove portions that the reviewer suggested were misleading.

Discussion, section 5.2 – For equation 4 (mistakenly referred to as “Equation 1” by the reviewer), we have added the units for z (cm) in the text and added the conversion factor 1/1000 to the equation such that it is dimensionally correct.

Tables 3a and 3b; Diffusion coefficients – The Jähne et al., 1987 reference was added. The calculated diffusion coefficient from Jähne et al., 1987 was the same as the interpolated value from Broecker & Peng, 1974.

Tables 3a and 3b; Solubility – The CO_2 solubilities are both listed as 10^{-2} . The solubilities listed in Table 3a are literature values for the surface ocean in equilibrium with the atmosphere. The values in Table 3b were calculated for the temperature, pressure, and salinity conditions of our experiment.

Tables 3a and 3b; Gas Concentration – The reviewer caught our neglect in listing the temperatures for the gas concentration values. Table 3a values (from Broecker & Peng, 1982) are average surface ocean concentrations at 0°C . The values in Table 3b are the background concentrations at 300 m depth and 8°C . We have added the temperatures to the table.

Discussion, section 5.2, last paragraph – The reviewer notes that the boundary layer thickness used to compare fluxes of CO_2 and N_2 ($40\text{ }\mu\text{m}$ – the average ocean boundary layer thickness) is arbitrary. The value is indeed arbitrary and was chosen simply to compare the flux of CO_2 and N_2 . In fact, it turns out to be quite similar to the boundary layer thickness of the gas cube.

Discussion, section 5.3, third paragraph – The reference to the previous use of a $40\text{ }\mu\text{m}$ boundary layer thickness was removed.

Table 5 – We believe the reviewer is referring to Tables 4 & 6 here. The reason that the peak area of the nitrogen band does not increase by as much as the mole fraction of nitrogen is because the density of the gas mixture decreases as the nitrogen concentration increases (shown in the last column of the table). For both experiments the focal volume of the laser is

completely inside the gas volume throughout the experiment, so there is no change in the “optical path” as questioned by the reviewer. We did not include a figure of the increasing nitrogen band because the increase cannot be easily seen in the spectra, particularly without a fixed reference band in close proximity (such as the fixed diamond band for the decreasing CO₂ bands).

Conclusions – We agree with the reviewer that we have made too large a jump in reasoning to compare directly the static exchanges of gas at fixed depth that we observe with the predictions of a rising stream of bubbles. We have removed the comment directly comparing the rates we observe with the rates obtained by Saito and colleagues, and have rearranged the paragraphs.

Minor things:

2.1 first paragraph – We do not see a colon in the last sentence.

4.1 7th line – The double space was removed before “differences” and in other places in the document.

5.2 last paragraph – The “in” was deleted

Fig. Caption 4 – “cub” was changed to “cube”

Fig. Caption 5 – “tub” was changed to “tube”

Fig. 1 quality – The figure was replaced with a higher quality figure that shows only the Stokes scatter (which is all that is discussed in this paper).

Fig. 8 – The increase in the nitrogen peak is not as obvious as the decrease in the carbon dioxide peak (since it completely disappears). That is why the nitrogen peak is not shown.

We hope you find this revision satisfactory.

Sincerely,

Sheri N. White

c.c. Peter Liss