

Interactive comment on “Coral calcifying fluid aragonite saturation states derived from Raman spectroscopy” by Thomas M. DeCarlo et al.

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Received and published: 28 July 2017

Reviewer comment 1: The submitted manuscript of DeCarlo et al. reports interesting innovative research results regarding the use of Raman spectroscopy for the determination of aragonite saturation state in inorganic experiments and during coral calcification. As such it is timely, of broad scientific interest and fits into the scope of BG.

I would expect this material to be publishable after careful revision.

Before explaining some of my concerns I need to underline I am not at all a Raman spectroscopy expert. Thus, Raman-specific technical details need to be reviewed by a respective expert before any decision on publication can be made.

In general I like this manuscript for its interesting approach which warrents publication

in my opinion. Nevertheless, some conclusions, I think, should be presented more carefully, underlining the potential and open questions of this approach.

BGD

Response 1: We thank the reviewer for the supportive comments and careful consideration of our manuscript. We appreciate the issues raised, which highlight a couple areas of the manuscript that require clarification. Below, we respond to the reviewer's specific comments. While our results and conclusions remain the same, we agree with the reviewer that we need to add a few details to further explain how the calculations are performed.

Reviewer comment 2: It appears strange to me, the calibration (inorganic) yields results for the coral which are presented as correct reconstruction of internal cf saturation state. The calibration in my opinion is not entirely correct or it is not very clearly explained. I'd tried to recalculate the regression based on the data provided in the supplements. It appears, the uncertainties of the saturation state data from the experiment have not been included in the uncertainty estimate of the calibration. It rather looks like the means of FWHM plotted vs. Omega and a log-fit applied. This is critical as later the FWHM is used to reconstruct Omega. I hope, the point is clear, it would need quite the opposite plot and fit, Omega vs. FWHM for a calibartion useful for the desired calculation. Well, the fit obviously, changes in this case.

Response 2: We appreciate the reviewer's comment, which has alerted us to a point that we will clarify in the revised manuscript. The reviewer is correct that our calibration is based on fitting FWHM to the log of Ω_{Ar} (see Table 2). We use Ω_{Ar} as the independent variable (x-axis in Figure 2) and FWHM as the dependent variable (y-axis in Figure 2) because our proposed mechanism is that Ω_{Ar} causes changes in FWHM (see section 4.1). However, we agree with the reviewer that this type of regression does not take errors in Ω_{Ar} into account, and that an alternative approach would be to fit Ω_{Ar} as a function of FWHM. We tried this method using the measured data from the WITec instrument (Figure R1-1 below). The difference between the two approaches is very small, e.g. approximately 0.1

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Ω_{Ar} unit difference for JCp-1. Nevertheless, we will add a similar plot and the alternative calibration equation in the supplement for clarity.

BGD

Reviewer comment 3: In any way, I could not replicate the JCp-1 Omega of 12.3 with either of the calibrations. Could it be, each individual Raman result had been converted into a result for Omega and those results have been used to calculate an average of 12.3? If so, I did not get this from the manuscript... The Omega calculated from the mean FWHM would be >13, if I did the calculations right.

Response 3: The reviewer is correct that we converted FWHM to Ω_{Ar} for each of the 440 JCp-1 measurements, and then we took the average of these Ω_{Ar} values. This will be clarified in the revised manuscript. However, the effect on the derived mean Ω_{Ar} is very small. We repeated these calculations using the reported JCp-1 mean FWHM (3.51 cm^{-1}) and the equation in Table 2 where $\Omega_{Ar} = e^{\frac{(FWHM - 2.09)}{0.57}}$, which gives 12.08. Thus, the difference from that reported in the manuscript (where Ω_{Ar} is calculated separately from each Raman spectra) is only 0.22 units. This is shown in the attached .R script, which also reproduces Figure R1-1 and calculates the JCp-1 derived Ω_{Ar} using the alternative calibration technique described in response to comment 2. In any case, the derived Ω_{Ar} is always between 12.08 and 12.30, which is within error of that reported in the manuscript (12.3 ± 0.3). Thus, while we cannot reproduce the Ω_{Ar} of 13 stated by the reviewer, we agree that these calculations were not described clearly enough in the manuscript. At the revision stage, we will explain the calculations in more detail and clarify that the JCp-1 analyses were conducted on the WITec instrument, as this may be the source of the confusion.

We also wish to point out that we have posted the .R scripts to repeat all the analyses in the manuscript and reproduce the figures at the following link: <https://codeocean.com/2017/06/30/code-for-quot-coral-calcifying-fluid-aragonite-saturation-states-derived-from-raman-spectroscopy-quot/code>

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The calculations that produce JCp-1 Ω_{Ar} of 12.3 ± 0.3 from the raw data can be found there as well.

BGD

Reviewer comment 4: Considering the large uncertainties of the source data (Omega from inorganic experiments), and the fact, that corals do not perform such experiments to grow their skeleton, it appears not realistic to claim the precise reconstruction of coral of Omega +1-2, as stated in the abstract. Despite this critique I am confident and look forward to see this published as a paper in BG.

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Response 4: We agree with the reviewer that there are substantial uncertainties in Ω_{Ar} over the course of each abiogenic experiment, and this is discussed in detail on page 8. While the statistics of the calibration support our claim that Ω_{Ar} can be derived within 1-2 units, we will modify this statement as suggested by the reviewer to reflect that the calibration is developed on abiogenic aragonites. However, the comparison between coral geochemistry and our Raman-derived Ω_{Ar} supports the notion that our calibration does represent calcifying fluid Ω_{Ar} .

Figure Caption: Figure R1-1. Measured Raman FWHM plotted against fluid Ω_{Ar} for the abiogenic aragonites analysed with the WITec instrument. The red curve shows the calibration when FWHM is fit as a function of Ω_{Ar} , and the blue curve shows the calibration when Ω_{Ar} is fit as a function of FWHM. A similar plot with repeat measurements of this calibration over multiple days is shown in Figure S3.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-194/bg-2017-194-AC1-supplement.zip>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-194>, 2017.

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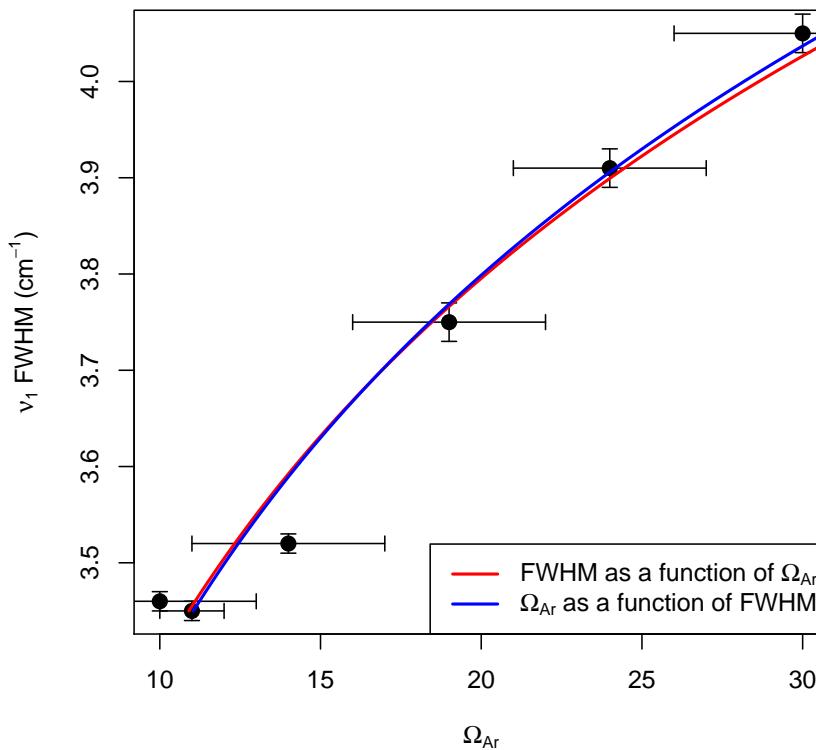


Fig. 1. Figure R1-1