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

Anonymous Referee #2

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Dear editor,

I have carefully read the manuscript by DeCarlo and others that describes the use of Raman spectroscopy to determine conditions at which (biogenic) calcium carbonate is precipitated. Overall, this manuscript contains an impressive amount of data, including results from inorganic experiments, culture experiment and field data. I have one serious concern about the (in)directness of the relation between $\upsilon 1$ FWHM and the saturation state, that needs revising before this manuscript can be accepted for publication in Biogeosciences.

The correlation between the Raman shift and the Ω may well be specific to the (inorganic) experiment and may not be general. As the authors explain in the introduction and methods, the actual shift in the spectrum is caused by other elements (impurities)

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or lattice distortions. In the well-constrained inorganic precipitation experiment (DeCarlo et al., 2015; Holcomb et al., 2016), the incorporation of impurities is apparently directly affected by the saturation state (since precipitation rate depends directly on omega and partitioning of elements depends directly on precipitation rate). Now, partitioning of elements (e.g. Mg, Sr) does not only rely on precipitation rate, but on a suite of other parameters, including temperature, seawater composition, photosynthetic activity and salinity. Not to mention species-specific differences in chemical composition of the aragonite (or calcite). This implies that changes in the $\upsilon 1$ FWHM may change with Mg/Ca or Sr/Ca, but those are not always and only related to changes in seawater Ω in biogenic material. This does not defy the outcome of this study, but in my opinion does warrant a more careful discussion.

For example, the 'apparent' control of [CO32-] on $\upsilon 1$ FWHM as shown in figure 3 may be just as real as that of ΩAr. Despite the outcome of the statistical modelling, both these two parameters seem equal explanations for the observed change in Raman shift, because both these parameters are (in a very similar way) responsible for the concentration of impurities in the aragonite. Therefore, the last sentence of the caption of figure 3 is misleading and needs to be changed.

Using a similar reasoning, the coral's results do not necessarily reflect only (or even primarily) the saturation state of the fluid from which they calcify. The results are highly interesting, but the results from the inorganic precipitation experiments do not justify the interpretation spelled out by the authors. As an example: on page 10, lines 1-2 for example, the change in $\upsilon 1$ FWHM is claimed to solely reflect omega, which should be nuanced.

page 11, lines 6-8 When looking at the 6 experiments with varying temperature, only two experiments with different temperatures were conducted at the same Ωar, according to figure 2. Is this enough to conclude that $\upsilon 1$ FWHM is not sensitive to precipitation rate? Figure 2b still shows a certain decreasing trend with increasing precipitation rate, especially when taking the average of the different experiments. Again, future work should be focused on a more decoupled experimental set-up, to also investigate the observed correlation with solid Mg/Ca and fluid [CO_3^{2-}].

Page 12, lines 6-22: this may be a crucial paragraph since the authors describe here why the Mg/Ca of the calcifying fluid is not related to the $\upsilon 1$ FWHM, but rather Ω controls the incorporation of impurities and hence the average C-O bond length. However, this does not mean that Mg/Ca of the calcifying fluid could not have an equal effect on the Raman spectrum and hence, the measured $\upsilon 1$ FWHM (e.g. in corals) may reflect either (or a combination) of fluid Mg/Ca and Ω.

Sections 4.3 and 4.4 may need to reflect another interpretation and rephrasing to avoid the suggestion that $\upsilon 1$ FWHM directly and only reflects Ω.

In addition, there are some minor issues that I listed below that may help to further improve the manuscript.

page 2, line 17: saturation state is not the only thing that determines growth rates. Presence of inhibitors (Reddy et al., 2012. J Cryst Growth 352: 151-154) and the Ca:CO32- stoichiometry (Nehrke et al., 2007. Geochim Cosmochim Acta 71: 2240-2249) also affect growth rates.

page 2, lines 17-22: this is a bit of a stretch. First, the authors acknowledge that it is not certain (“if one exists”) to what extent the internal and external saturation states are related. Therefore, knowing the internal saturation state does not necessarily result in an accurate forecast of the fate of coral calcification (even when ignoring the response of coral biomineralization to other environmental changes). Please rephrase.

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