Interactive comment on “The influence of seawater pH on U/Ca ratios in the scleractinian cold-water coral Lophelia pertusa” by J. Raddatz et al.

Anonymous Referee #2

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General comments:

This is the first study on L. pertusa U/Ca evaluation as a pH proxy. The authors have an interesting, although limited, selection of corals for their study, and they make an attempt to sample different skeletal features of their corals. However, they should discuss their data more thoroughly in light of their last paper on Mg/Ca ratios, and other literature especially concerning intra coral variability, biomineralization, U incorporation, co-variation with other ambient seawater conditions, and statistical evaluation of their dataset.

Specific comments:
The authors suggest that they sampled corals from fibrous to COCs material, by drilling from the theca to the centre of the polyp. However, such an approach does not guarantee that they indeed sampled fibers and COCs separately. The authors observe a decrease in the U/Ca measurements by a factor of $\sim 50\%$ towards the inner part of the coral, but their Mg/Ca transect does not show an increase of a factor of $\sim 2$, which would be indicative of presence of COCs (e.g. Gagnon et al. 2007), along the same transect but only $\sim 30\%$ (Raddatz et al. 2013: 2.9 to 3.9 mmol/mol). Could the authors please provide evidence of actually sampling COCs separately from fibrous parts of the coral skeleton?

It is an interesting idea to explain the difference in the U/Ca vs pH sensitivity between CWC and tropical corals through pH up-regulation. However, the authors also mention the additional effect of temperature on tropical coral U/Ca. Please clarify. Assuming a pH up-regulation, as derived from $d^{11}B$ measurements in literature, could the authors quantify the U/Ca proportion of their signature driven by such mechanism, and what would the residual be driven by? In 15718 the authors mention that the theca U/Ca suggest that the corals do not elevate their internal pH; however their proxy is empirical between U/Ca and pH, therefore they wouldn’t be able to see in absolute terms any elevation of internal pH as any such elevation would be included in the regression! Could the authors discuss these further?

The authors apply their calibration to what they assume to be COCs to discuss COCs-pH (and no uncertainty is provided) when their U/Ca vs pH relationship is proposed as valid only for theca material. That raises a valid concern on their reconstructed COCs pH which the authors should clarify. The authors should also address the discrepancy between their findings and those of Blamart et al. 2007. If they suggest similarities between the boron isotope proxy in cold water corals, and their suggested U/Ca-pH proxy, why do these proxies display opposing trends between fibers and COCs?

It is unclear why there is no relationship between coral U/Ca and ambient seawater carbonate ion but there is a relationship with ambient pH. If U/Ca is solely dependent on
pH, there should be a relationship with \( \text{CO}_3^- \) even if weaker. Could this be driven by the co-variation of pH with temperature and salinity for the Atlantic sites? The relationship between \( U/\text{Ca} \) and carbonate ion seems to mostly fail at those sites. The authors attempt to exclude a temperature dependence on their \( U/\text{Ca} \) data by comparing two sites with contrasting temperatures but similar pH and \( U/\text{Ca} \) values. However these sites are also characterized by different salinity conditions. Additionally, the uncertainty in the authors’ \( U/\text{Ca} \) vs pH regression could limit such a comparison when it is based only on two corals. The authors will need to demonstrate that the major dependence of \( U/\text{Ca} \) is pH, by for example examining the residual of this relationship to temperature and salinity or follow different and more thorough statistical approaches (e.g. Marshall et al. 2013).

Flogel et al. 2013: what is the method for pH measurement and what is the exact uncertainty? The authors do provide a “in general” uncertainty of 0.01, but since pH is their dependent parameter, that was potentially measured in their study, better accuracy would be desirable. Also please provide all carbonate system parameters and their associated uncertainty. Additionally, could the authors give some more information on their data as taken from Flogel et al. 2013? In this paper some data are actually taken from other references and from databases not necessarily from actual measurements from the coral locations.

The mechanism that could dictate coral \( U/\text{Ca} \) sensitivity to the carbonate system in seawater is oversimplified. Could the authors elaborate on additional mechanisms beyond \( U \) speciation in seawater, e.g. diffusion, adsorption/desorption processes, growth rate, and others? If the authors suggest that Lophelia \( U/\text{Ca} \) is related to seawater pH but not carbonate ion concentrations they should suggest a mechanism that could explain such observation. As is now, \( U \) speciation should be affected by both pH and carbonate ion. Please clarify.

The distribution of corals at different pH regions is very small (please clarify on line 22); most points are within 7.9 and 8 pH! Even in this region the \( U/\text{Ca} \) varies
from 1.6-1.9 umol/mol (~20%). The statistics of the U/Ca calibration are driven by the two high pH points, therefore not providing reliable reconstruction uncertainty by simple linear regression methods. The authors would need to expand on their statistical processing of their data to more reliably address the limitations of their dataset. Also the authors mention that the uncertainty in pH reconstruction is based on standard error. Could they please give more details? Would that be a 95% CI?

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