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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.

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The authors appreciate the constructive comments of referee II which will significantly improve this manuscript.

1) The referee raises concern about the sampling method and doubts that the Mg/Ca ratios of the intra coral profile in Raddatz et al. (2013) reflects just COC values and compares our study with the results of Gagnon et al. (2007). The latter study analysed Sr/Ca and Mg/Ca ratios in the solitary very slow growing cold-water coral Desmophyllum dianthus, which occurs in a larger range of environmental conditions. We think that in terms of absolute elemental ratios this study is not comparable to the study of

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Raddatz et al. (2013). Furthermore, previous studies that analysed Mg/Ca ratios in *Lophelia pertusa* do show comparable absolute values in the theca wall as well as in the COC (compare Cohen et al. (2006) and Sinclair et al. (2006)). These studies could clearly identify the COC by SEM pictures. In particular, the study of Raddatz et al. (2013) shows intra coral Mg/Ca ratios from min. 2.5 (theca wall) to max. 3.9 mmol/mol (COC) similar to 2.6 to 4.2 mmol/mol (Cohen et al. 2006) and 2.0 to 3.4 mmol/mol (Sinclair et al. 2006), excluding the interior values as we did not measure this part. Therefore, based on the Mg/Ca ratios of Raddatz et al. (2013) in comparison with micro-analytical studies we think we have sampled relatively pure COC. We add this information into the discussion of the revised MS.

2) We agree with the referee that we need to explain the potential temperature effect on U/Ca in our discussion (see 4.1). It was shown by several studies that there is - at high tropical sea surface temperatures - an effect on the U/Ca ratios. As this dependency appears to be inversely any increase in temperature would decrease the U/Ca ratios. For example taking the equation Min et al. (1995), $T ({}^{\circ}\text{C}) = 48.0 - 21.5 * \text{U/Ca} (\mu\text{mol/mol})$ with a value of our data set 1.13 ($\mu\text{mol/mol}$, 6.0 ${}^{\circ}\text{C}$ Stjernsund) would result in too warm temperatures for a CWC site (23.7 ${}^{\circ}\text{C}$). Hence, as tropical corals have similar U/Ca ratios compared to some of our bulk samples we are not able to quantify any residual of this mechanism. Future studies should compare tropical and cold-water corals at the same pH to investigate of pH on coral pH up regulation and uranium incorporation Moreover, we agree with the referee, that our proxy calibration is only empirical and we are not able state about the up regulation of the theca wall as this would be covered by the regression!

3) Clearly applying an empirical relationship based on the theca sampling to the one coral sampled through to the COC is a over simplification. However, in the absence of an inorganic relationship to apply, we have conducted this exercise and it is interesting to note the results. We have added a statement highlighting the speculative nature of this calculation in the revised MS.

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4) We agree with the referee, that we need to improve our statistical approach. As we have analysed in situ hydrographic parameter we have to consider the potential of any covariance. Therefore, besides simple linear/multiple regressions correlations, we applied the method of examining the residuals of the U/Ca-pH calibration to compare them with the other hydrographic parameter. However, temperature, salinity and carbonate ion concentrations display a negligible correlation of $r^2 = <0.3$ for the entire dataset. We have added the details of this additional data analysis to results of the revised manuscript.

Previous studies have shown that U/Ca ratios measured in scleractinian cold-water corals are related to the carbonate ion concentration (Anagnostou et al., 2011), whereas our study does not show any correlation between these two parameters, but between U/Ca and pH, similar to Inoue et al. (2011).

I) This may be due to the fact that the pH in our study was measured at the coral site and the carbonate concentrations is only calculated from various parameters, which probably results in some of the scatter. Furthermore, except for the Mediterranean samples (probably due to the higher DIC values in the Mediterranean Sea) the range in the calculated CO_3^{2-} concentrations are quite small and hence may not result in any significant correlation. II) The measured DIC values of Flögel et al. (in press) do show a significant positive correlation ($r^2=0.9$) to the coral U/Ca ratios, when restricting the dataset to the North Atlantic. Taking the entire sample set the only parameter that correlates significantly ($r^2=0.8$) with U/Ca is pH. Therefore we assume that the pH is not solely driven by the carbonate ion concentration. III) The pH of seawater does not need to be necessarily correlated to the carbonate ion concentration. Low pH values represent lots of hydrogen ions (H^+) (acidic), whereas at high pH less H^+ , but more hydroxide ions (OH^-), are present. The total alkalinity is defined by the amount of all ions that are available in seawater (e.g., BOH^- , PO_4^{3-} , SiO_4^{4-} , CO_3^{2-} , HCO_3^-) and in turn are able to buffer a change in H^+ concentrations. Therefore H^+ concentrations are not solely buffered by the CO_3^{2-} concentration.

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5) We have provided additional information in the method section of the revised MS. Our coral U/Ca–pH calibration is based on the seawater pH determinations presented in Flögel et al. (2014). We have provided more information about the measurement methods and uncertainties in the revised MS. As clearly stated in the revised MS all seawater pH values from the coral locations were measured on the ship by Flögel et al. (2014). 6) According to the reviewers statement we reworked the uncertainties for paleo-pH reconstructions. Considering the scatter in our U/Ca–pH calibration around the trendline (residuals) of around $0.3 \mu\text{mol/mol}$, pH values cannot better reconstructed than ± 0.15 pH. This information is updated in the revised ms.

References: Anagnostou, E., Sherrell, R. M., Gagnon, A., LaVigne, M., Field, M. P., and McDonough, W.F.: Seawater nutrient and carbonate ion concentrations recorded as P/Ca, Ba/ Ca, and U/Ca in the deep-sea coral *Desmophyllum dianthus*, *Geochim. Cosmochim. Acta*, 75, 2529–2543, 2011.

Cohen, A. L., Gaetani, G. A., Lundälv, T., Corliss, B. H., and George, R. Y.: Compositional variability in a cold-water scleractinian, *Lophelia pertusa*: New insights into "vital effects", *Geochem. Geophys. Geosys.*, 7, 12, Q12004, 2006.

Flögel, S., Dullo, W.-Chr., Pfannkuche, O., Kiriakoulakis, K., and Rüggeberg, A.: Geochemical and physical constraints for the occurrence of living cold-water corals, *Deep-Sea Res. Part II*, Vol., pp., doi:10.1016/j.dsrr.2013.06.006, 2014.

Gagnon, A. C., Adkins, J. F., Fernandez, D. P., and Robinson, L. F.: Sr/Ca and Mg/Ca vital effects correlated with skeletal architecture in a scleractinian deep-sea coral and the role of Rayleigh fractionation, *Earth Planet. Sci. Lett.*, 261, 280–295, 2007.

Inoue, M., Suwa, R., Suzuki, A., Sakai, K., and Kawahata, H. : Effects of seawater pH on growth and skeletal U/Ca ratios of *Acropora digitifera* coral polyps, *Geophys. Res. Lett.*, 38, 12, L12809, doi:10.1029/2011GL047786, 2011.

Min, G. R., Edwards, L. R., Taylor, F. W., Recy, J., Gallup, C. D., and Beck W. J.: Annual

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10, C8292–C8296, 2014

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cycles of U/Ca in coral skeletons and U/Ca thermometry, *Geochim. Cosmochim. Acta*, 59, 2025– 2042, 1995.

Raddatz, J., Liebetrau, V., Rüggeberg, A., Hathorne, E., Krabbenhöft, A., Eisenhauer, A., Böhm, F., Vollstaedt, H., Fietzke, J., López Correa, M., Freiwald, A., and Dullo, W.-Chr.: Stable Sr-isotope, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios in the scleractinian cold-water coral *Lophelia pertusa*, *Chem. Geol.*, 352, pp. 143-152. doi: 10.1016/j.chemgeo.2013.06.013, 2013.

Sinclair, D. J., Williams B., and Risk, M.: A biological origin for climate signals in corals—Trace element “vital effects” are ubiquitous in Scleractinian coral skeletons, *Geophys. Res. Lett.*, 33, L17707, doi:10.1029/2006GL027183, 2006.

Interactive comment on *Biogeosciences Discuss.*, 10, 15711, 2013.

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10, C8292–C8296, 2014

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