

Dear Anonymous Referee #2

Thank you so much for the precise summary and valuable observations on the Discussion paper by Reyes-Nivia et al. We are very please you found this study interesting and our conclusions coherent with our findings. We also appreciate you recognize our rigorous data analysis. In the next lines we provide detailed answers to your comments:

Comment: 1. *The first paragraph on p. 7 requires some attention. First a minor comment: mol% MgCO₃ is repeated in the first sentence on the page.*

Answer: This typo has been corrected by deleting the extra mol% MgCO₃

Comment: 2. *Second and more important and substantive comment: the authors base some of their conclusions on the solubility curve chosen for the biogenic Mg-calcite partial solid solution. They state that estimations of the saturation state of the experimental seawater chambers “are based on the stoichiometric solubility products using the biogenic “minimally prepared” solubility curve of Plummer and Mackenzie (1974)” for the Mg-calcite phases as a function of MgCO₃. Despite the reference to Diaz-Pulido et al. (2012), I think in this paper, the authors need to justify using this curve by a fuller explanation of the problems involved with the solubilities of the Mg-calcites by considering the works of Mackenzie et al. (1983); Bischoff et al. (1987 and references therein); Morse et al. (2006); Andersson et al. (2008); and see summary in Mackenzie and Andersson (2013). Furthermore, although I know it can be done, it will not be clear to the average reader how the authors have taken the experimental data of Plummer and Mackenzie (1974) reported as ion activity products (IAP) Mg-calcite and recalculated them into stoichiometric solubility products.*

Answer: We have taken the reviewer’s comment on board and have now provided a detailed (but succinct) explanation of 1- how the stoichiometric saturation state for Mg-calcite was calculated based on experimental data taken from literature (IAP), 2- the issues associated with the solubility of Mg-calcites and 3- justification on why we used the “minimally prepared” solubility curve of Plummer and Mackenzie (1974). New text added to the ms in bold style:

Methods P4: Seawater samples for total alkalinity (A_T) analysis were collected from the light and dark experimental tanks at noon and midnight at the end of the study to include the largest variation in seawater alkalinity and pH. Seawater samples were analyzed by potentiometric titration (T50, Mettler Toledo) with replicates within a sample ($n = 2-3$) having a maximum error of 3 $\mu\text{mol kg}^{-1}$ (Dickson et al., 2003). Temperature, $p\text{CO}_2$, A_T , and salinity (35.3 ppt) were used to calculate pH, bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) with CO2SYS (Pierrot et al., 2006) using K_1 , K_2 constants (Mehrbach et al., 1973; Dickson and Millero, 1987) and the seawater scale. The saturation state of seawater with respect to high-Mg calcite (Ω_{HMC}) was calculated for a 17 mol % MgCO_3 . Mol % MgCO_3 was calculated for 10 *P. onkodes* fragments collected at the study site (17.3 ± 0.25 SEM; $n = 10$), using Powder X-ray diffraction (XRD) techniques described in Nash et al. (Nash et al., In press; Nash et al., 2011). XRD analyses were conducted by M. Nash at the Australian National University.

Methods P5 (new): Estimations of Ω_{HMC} were conducted according Diaz-Pulido et al. (Diaz-Pulido et al., 2012), which are based on the stoichiometric solubility products using the biogenic ‘minimally prepared’ solubility curve of Plummer and Mackenzie (Plummer and Mackenzie, 1974) and equation #8 in Morse et al. (Morse et al., 2006). **Equation reads as**

follow: $\Omega_{\text{HMC}} = \{\text{Mg}^{2+}\}^x \{\text{Ca}^{2+}\}^{(1-x)} \{\text{CO}_3^{2-}\} / K_{\text{Mg-cal}(x)}$, where brackets are the ion activities, x is the mol fraction magnesium ions, and $K_{\text{Mg-cal}}$ is the equilibrium constant with respect to Mg-calcite. Since stoichiometric solubility products with respect to this mineral phase have not been determined, experimental ion activity products (IAP) from Plummer and Mackenzie (1974) were used to recalculate the stoichiometric saturation ($K_{\text{Mg-cal}(x)} = -\log \text{IAP} = -7.7071$ at 25 °C). Several studies (see detailed revisions by) (Mackenzie and Andersson, 2013; Morse et al., 2006) have identified difficulties in the determination of the solubility of biogenic Mg-calcites, which are associated to the structural disorder and impurities in biogenic skeletons (Bischoff et al., 1983; Bischoff et al., 1985; Mackenzie et al., 1983). Such physical and chemical heterogeneities produce a broad variety of solubilities for Mg-calcites of similar Mg content and a large offset in solubility compared to the synthetically produced Mg-calcite mineral (Bischoff et al 1987, Morse et al 2006). The biogenic ‘minimally prepared’ curve was chosen over the biogenic ‘cleaned’ solubility curve (Bischoff et al., 1993; Bischoff et al., 1987) (e.g Bischoff et al 1987, 1993), as recent modeling and empirical studies show the ‘minimally prepared’ curve not only more accurately represents the behavior of Mg-calcites in biogenic skeletons, but also reveals the implications and effects of ocean acidification on Mg-calcites phases in natural environments (Andersson et al., 2007; Andersson et al., 2008; Mackenzie and Andersson, 2013; Morse et al., 2006).

Comment 3. *In addition, since the authors are interested in the rates of dissolution of the CCAs as a function of seawater acidity and T, it should be pointed out that the rates do not simply depend on solubility of the carbonate phase but also on factors like skeletal microarchitecture (Walter and Morse 1985).*

Answer: According to reviewer’s suggestion, we will include this information at the end of paragraph 3 in the Discussion section (in bold):

Increased CO₂ and temperature enhanced the dissolution of CCA skeletons, both in the presence or absence of endolithic algae, although the magnitude of dissolution was much larger when endolithic algae were absent. Previous studies found that projected changes in ocean acidity and temperature cause mortality and subsequent dissolution of CCA (Anthony et al., 2008; Diaz-Pulido et al., 2012; Martin and Gattuso, 2009), and here we demonstrated the rate of skeletal dissolution is enhanced under elevated OA and warming following CCA mortality. Using comparable experimental treatments, we previously found (Reyes-Nivia et al., 2013) that dissolution of coral skeletons by endolithic algae was also higher at elevated CO₂-T conditions, but skeletons in the dark (without endolithic algae) did not dissolve. The variable response of coral and CCA skeletons to future CO₂-T scenarios may be due to differences in skeletal mineralogy as corals are aragonitic and less prone to dissolution (Morse et al., 2006). **In addition, skeletal microstructure and grain size may also play a role in controlling the dissolution rates of marine biogenic carbonates (Walter and Morse 1984, 1985) and future studies need to take these factors into account. Yet, based on the solubility of carbonate phases,** our results confirm a potentially higher susceptibility to dissolution of those reefs where the carbonate framework is mainly composed of CCA skeletons.

References

- Andersson, A., Bates, N., and Mackenzie, F.: Dissolution of carbonate sediments under rising $p\text{CO}_2$ and ocean acidification: observations from Devil’s Hole, Bermuda, *Aquat. Geochem.*, 13, 237-264, doi:10.1007/s10498-007-9018-8, 2007.
- Andersson, A. J., Mackenzie, F. T., and Bates, N. R.: Life on the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers, *Mar. Ecol. Prog. Ser.*, 373, 265-273, doi:10.3354/meps07639, 2008.

Anthony, K. R. N., Kline, D. I., Diaz-Pulido, G., Dove, S., and Hoegh-Guldberg, O.: Ocean acidification causes bleaching and productivity loss in coral reef builders, *Proc. Natl. Acad. Sci. U. S. A.*, 105, 17442-17446, doi:10.1073/pnas.0804478105 2008.

Bischoff, W., Bertram, M., Mackenzie, F., and Bishop, F.: Diagenetic stabilization pathways of magnesian calcites, *Carbonate. Evaporite.*, 8, 82-89, doi:10.1007/bf03175165, 1993.

Bischoff, W. D., Bishop, F. C., and Mackenzie, F. T.: Biogenically produced Mg-calcite; inhomogeneities in chemical and physical properties; comparison with synthetic phases, *Am. Mineral.*, 68, 1183-1188, 1983.

Bischoff, W. D., Sharma, S. K., and MacKenzie, F. T.: Carbonate ion disorder in synthetic and biogenic magnesian calcites; a Raman spectral study, *Am. Mineral.*, 70, 581-589, 1985.

Bischoff, W. D., Mackenzie, F. T., and Bishop, F. C.: Stabilities of synthetic magnesian calcites in aqueous solution: Comparison with biogenic materials, *Geochim. Cosmochim. Acta*, 51, 1413-1423, doi:10.1016/0016-7037(87)90325-5, 1987.

Diaz-Pulido, G., Anthony, K. R. N., Kline, D. I., Dove, S., and Hoegh-Guldberg, O.: Interactions between ocean acidification and warming on the mortality and dissolution of coralline algae, *J. Phycol.*, 48, 32-39, doi:10.1111/j.1529-8817.2011.01084.x, 2012.

Dickson, A. G., and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep-Sea Res.*, 34, 1733-1743, doi:10.1016/0198-0149(87)90021-5, 1987.

Dickson, A. G., Afghan, J. D., and Anderson, G. C.: Reference materials for oceanic CO₂ analysis: a method for the certification of total alkalinity, *Mar. Chem.*, 80, 185-197, doi:10.1016/S0304-4203(02)00133-0, 2003.

Mackenzie, F. T., Bischoff, W. D., Bishop, F. C., Loijens, M., Schoonmaker, J., and Wollast, R.: Magnesian calcites; low-temperature occurrence, solubility and solid-solution behavior, *Rev. Mineral. Geochem.*, 11, 97-144, 1983.

Mackenzie, F. T., and Andersson, A. J.: The Marine Carbon System and Ocean Acidification during Phanerozoic Time, *Geochemical Perspectives*, 2(1), European Union of Geochemistry, 227 pp., 2013.

Martin, S., and Gattuso, J. P.: Response of Mediterranean coralline algae to ocean acidification and elevated temperature, *Glob. Change Bio.*, 15, 2089-2100, doi:10.1111/j.1365-2486.2009.01874.x, 2009.

Mehrbach, C., H., C. C., Hawley, J. E., and M., P. R.: Measurement of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, 18, 897-907, 1973.

Morse, J. W., Andersson, A. J., and Mackenzie, F. T.: Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO₂ and "ocean acidification": role of high Mg-calcites, *Geochim. Cosmochim. Acta*, 70, 5814-5830, doi:10.1016/j.gca.2006.08.017, 2006.

Nash, M. C., Troitzsch, U., Opdyke, B. N., Trafford, J. M., Russell, B. D., and Kline, D. I.: First discovery of dolomite and magnesite in living coralline algae and its geobiological implications, *Biogeosciences*, 8, 3331-3340, doi:10.5194/bg-8-3331-2011, 2011.

Nash, M. C., Opdyke, B. N., Wu, Z., Xu, H., and Trafford, J. M.: Simple X-ray diffraction techniques to identify Mg-calcite, dolomite and magnesite in tropical coralline algae and assess peak asymmetry, *J. Sediment. Res.*, In press.

Plummer, L. N., and Mackenzie, F. T.: Predicting mineral solubility from rate data; application to the dissolution of magnesian calcites, *Am. J. Sci.*, 274, 61-83, doi:10.2475/ajs.274.1.61, 1974.

Reyes-Nivia, C., Diaz-Pulido, G., Kline, D. I., Hoegh-Guldberg, O., and Dove, S.: Ocean acidification and warming scenarios increase microbioerosion of coral skeletons, *Glob. Change Bio.*, 19, 1919-1929, doi:10.1111/gcb.12158, 2013.