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Interactive comment on “Relative roles of endolithic algae and carbonate chemistry variability in the skeletal dissolution of crustose coralline algae” by C. Reyes-Nivia et al.

C. Reyes-Nivia et al.

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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. Please also find attached our response as a PDF document to be able to see complex formats highlighting how we have changed particular sections of the manuscript.

Comment: 1. The first paragraph on p. 7 requires some attention. First a minor

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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 (AT) 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,

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pCO₂, AT, and salinity (35.3 ppt) were used to calculate pH, bicarbonate (HCO₃), and carbonate (CO₃) with CO₂SYS (Pierrot et al., 2006) using K₁, K₂ 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 % MgCO₃. Mol % MgCO₃ 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: Ω HMC = {Mg²⁺}x {Ca²⁺}(1-x) {CO₃²⁻} / KMg-cal(x), where brackets are the ion activities, x is the mol fraction magnesium ions, and KMg-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 (KMg-cal(x) = -log 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 ef-

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fects 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.

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C2701/2014/bgd-11-C2701-2014-supplement.pdf>

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