We thank A. D. Wanamaker Jr. and reviewer 2 for their comments to improve the manuscript and we appreciate their positive feedback regarding the importance of this study and its implications. In general, both reviewers mention that the implications and findings of this study should be discussed in a broader context of oceanographic and paleoceanographic settings. Intentionally, we were cautious and did not scale up our laboratory findings to the complex ecological settings in nature. However, we are happy to expand the discussion towards the broader paleoceanographic implications and other marine calcifiers; especially foraminifera (see answers below).

Several comments of Wanamaker Jr. and reviewer 2 are similar in content and message. Consequently, our replies to the reviewers are combined in one answer (when possible) rather than answering each reviewer separately.

Response to reviewers:

Wanamaker:
The implications of these results are huge (and not likely limited to the species studied here) and need to be discussed more strongly in the discussion and conclusion sections. In other words, are the interpretations from previous studies during high pCO2 conditions (e.g., Paleocene-Eocene thermal maximum) using Sr/Ca ratios from these calcitic coccolithophores as an environmental proxy remotely valid? Please consider this question in a broad sense. This study also reveals that caution might be in order for researchers who use Sr/Ca or Mg/Ca ratios in other biominerals as a proxy for seawater temperature or productivity. This is especially important/true under the increasing pCO2 conditions that are being experienced in the atmosphere and oceans.
Reviewer 2:
A synthesis of the results within a broader context of oceanographic and paleoceanographic settings where these trace element proxies are applied would significantly strengthen this manuscript and highlight its scientific contribution.
The dependence of Sr/Ca as a proxy for temperature and growth rate is well- established. This study shows that the partitioning of Sr into coccolithophore calcite is also dependent on seawater carbonate chemistry. Importantly, these results challenge interpretations made in previous studies using Sr/Ca as a paleoenvironmental proxy, and complicate the

interpretation of coccolithophore Sr/Ca from high-pCO2 environments. This is a key contribution of this paper, and I think it should be stated more strongly in the abstract.
The results suggest that Sr/Ca is not a reliable proxy for productivity and temperature at elevated pCO2 or with modified seawater carbonate chemistry. The implications of these results are substantial. The discussion and conclusion hint at one potential scenario where previous interpretations could be compromised (the Paleocene-Eocene Thermal Maximum). I think the authors should address this in further detail, and explore additional oceanographic or paleoceanographic settings where interpretations from Sr/Ca could be affected by their results.

Answer:

We will add additional paragraphs discussing the broader implications of this study in regard to paleoceanography and biomineralization. The following points will be addressed in the revised manuscript:

- Species variations in coccolith Sr/Ca and Mg/Ca ratios and a comparison of the findings with a recent established biomineralization model for foraminifera (Nehrke et al. 2013).
- Implications for the interpretation of coccolith elemental ratios regarding the Paleocene-Eocene Thermal Maximum and changes in sea level (Stoll and Schrag 2001, Stoll et al. 2007a, Bolton et al. 2012). Our results indicate that several environmental factors have to be considered when interpreting coccolith Sr/Ca and Mg/Ca ratios. This complicates a paleoproxy application from geological times which experienced major environmental shifts.
- Discussion on the variations in Sr/Ca ratios induced by nutrient limitation compared to changes in temperature and/or carbonate chemistry (Stoll et al. 2007b). We did not intentionally conduct experiments to investigate the effect of nutrient limitation on coccolith Sr/Ca ratios but we feel that a discussion on this topic will improve the quality of our manuscript.

Furthermore, we include these points in the conclusions section and we state the complications associated with the interpretation of Sr/Ca ratios as productivity proxy in the abstract (as mentioned by reviewer 2).

Reviewer 2:

The introduction is fairly long, and only in the third paragraph does it start to succinctly frame the scientific importance of this particular study. This section should be shortened and focused to better highlight the contributions of this study to paleoproxy and biomineralization research. For example, the authors suggest in the conclusions that there is a need for updating coccolith partition coefficients, and how the application of these equations can fit into a broader scientific context (such as paleoproxy use or ocean acidification). This could also be addressed briefly in the introduction, to better frame the hypotheses this study tests.

Answer:

We amend the introduction according to the suggestions of reviewer 2 and give it a clearer focus by shortening/cutting non-essential sentences.

Reviewer 2:

Data presented here suggest that the effect of pCO2 on DSr is minor compared to that of nutrient limitation. Are there existing field studies or culture studies that have addressed the effect of spatial variability of nutrient limitation on coccolith Sr/Ca? If not, could the authors suggest how to test this hypothesis further?

Answer:

This is a very good and important point raised by reviewer 2 and as mentioned earlier we add a discussion on the effect of nutrient limitation on coccolith Sr/Ca ratios. Unfortunately, literature regarding the effect of different degrees of nutrient limitation is scarce but we discuss two publications presenting culture studies dealing with this topic (Rickaby et al. 2002, Stoll et al. 2007).

Reviewer 2:

Mg/Ca:

Page 15: The results demonstrate inter-specific differences in measured Mg/Ca ratios. What implications does this have for choices of species in paleo-reconstructions?

Answer:

The apparent inter-specific difference in Mg/Ca ratios of coccolithophores is striking. This implies that Mg/Ca measurements of coccolithophore calcite sediment samples might inherit a species composition bias. This problem can be solved by picking single coccoliths of the same species from sediment samples. However, the current method and procedure to measure Mg/Ca ratios in coccolithophores requires a substantial amount of sample material. In the new manuscript version, we elucidate alternative methods to measure inorganic Mg in coccolithophore calcite to resolve this issue.

Wanamaker:

The differing uptake of Sr and Mg during biomineralization is fascinating- and very likely (as the authors state) represent unique pathways of incorporation. The authors caution that Mg/Ca ratios in coccolithophore tests likely do not represent oceanic Mg/Ca ratios of seawater due to the different calcification pathways between Mg, Sr, and Ca. I think this statement should also be included in the conclusion section.

Reviewer 2:

On pages 16-17, the authors explore the idea that the mechanisms controlling biological cycling of Mg and Ca are so different that these two cations are effectively decoupled, and act independently. This is a fascinating idea. If the incorporation of Mg into biogenic calcite is tightly controlled by Mg-binding proteins, what are the implications for biomineralization mechanisms in other calcifying organisms? Are there implications for the existing Mg/Ca paleothermometers which have been calibrated for other calcifying organisms such as planktic foraminifera, especially from geologic times with different Mg/Ca seawater?

I think that exploring these concepts in the discussion would add valuable insight to this manuscript. At the very least, the idea of decoupling Mg and Ca incorporation mechanisms should be mentioned in the conclusions.

Answer:

Mg and Ca are two essential cations, both intensively involved in specific cellular mechanisms and physiological reactions. Whereas Ca is crucial for cellular signalling, membrane structure and cell division, Mg is heavily involved in all energy demanding processes and acts as the central ion of the chlorin ring in chlorophyll. Thus, the idea of different mechanisms controlling the uptake and cellular cycling of these two cations seems reasonable from a physiological point of view. We explore this idea further in the revised manuscript and discuss its implication regarding foraminifera (Nehrke et al. 2013) and coccolithophore calcification at geological times of different Mg/Ca seawater ratios. Furthermore, as suggested by both reviewers, the decoupling of Mg and Ca/Sr incorporation will be stated in the conclusion section and the revised abstract.

Wanamaker:

Are Mg/Ca ratios under the pCO2 conditions noted in this study a valid proxy for productivity? If so, what potential problems might exist with this interpretation?

Answer:

The interpretation that coccolith Mg/Ca ratios (DMg, respectively) might be used as a proxy for productivity should be handled with great care. Even though a correlation between chlorophyll-a production and DMg was present for all coccolithophore species, it remains very speculative to relate chlorophyll-a production to cellular or population productivity. The production of chlorophyll-a by phytoplankton is primarily a function of light intensity and species specific photo-acclimation.

Our data indicate only a poor correlation between cellular productivity in terms of particulate organic carbon production and coccolith DMg (r^2=0.53 for *E. huxleyi*, *C. braarudii* and *C. quadriperforatus* and r^2=0.31 for *G. oceanica*, using the same log transformation as in Fig. 4). However, assuming that cellular Ca and Mg concentrations are under tight physiological control (as mentioned above), we could speculate that changes in the coccolith Mg/Ca ratio reflect a disturbance of this cellular homeostasis. In a broader sense, an increase in DMg might translate to physiological stress, indicated by increasing DMg with elevated pCO2/decreased pH and increased stress due to nutrient limitation (*G. oceanica* at 25°C).

In the revised manuscript version, we discuss the difficulties relating coccolith DMg to productivity and briefly raise the idea to use coccolith DMg as an indicator for cellular stress.

Wanamaker:

Multiple impacts on element/Ca ratios:

Although I do not think it is absolutely necessary in this study, might the authors consider multiple linear regression techniques to model the concurrent effects of pCO2, growth rates, and temperature on DSr? This may provide some additional insight on the relative importance of each of these parameters on Sr/Ca ratios for each of the coccolithophore species.

Answer:

We appreciate the suggestion of a multiple regression analysis. We think that the species individual data sets are not sufficient for species specific multiple regression analysis.

Combining all coccolithophore species in one data set results in the following predictive equation:

$DSr = 0.0063*T\ (°C) + 2.68*10^{-5}*pCO_2\ (\mu atm) + 0.024*\mu\ (d^{-1}) + 0.228$

with $p(T)<0.0001$, $p(pCO_2)<0.0001$ and $p(\mu)=0.043$.

However, we feel that a predictive equation for coccolith DSr is not in the scope of the manuscript because the equation would not consider other environmental parameters such as nutrient limitation. In order to produce such an equation more calibration data from laboratory experiments would be necessary. The accumulation of data regarding the parameters which influence biomineralization in coccolithophores substantially increases our understanding. However, important pieces are still missing and a predictive equation (as above) might imply that this would not be the case. Therefore, we choose to remain cautious until further research reveals the missing gaps.

Reviewer 2:

Additional comments:

This manuscript provides a detailed description of the experimental setup used in calibration experiments, which is for the most part exemplary in its completeness. The authors describe two different methods for altering carbonate chemistry: modifying total alkalinity while keeping DIC constant, and modifying DIC while keeping total alkalinity constant. Why were these various methods selected? What are the implications for the dependence of DSr on different carbonate chemistry parameters? The rationale behind this part of the experimental setup, and the implications for interpreting records from high-pCO2 environments, should be addressed in more detail.

Answer:

Selecting two different methods to change the carbonate chemistry might sound confusing. Yet, from a cellular perspective, it are the changes in the individual carbonate species (CO_2, HCO_3, CO_3) and pH, rather than DIC and TA, that drive changes in cellular physiology and biomineralization. In this sense, both methods are comparable and, indeed, result in similar responses (e.g. DSr). We make this point clearer in the discussion.

We appreciate the question regarding the driving carbonate chemistry parameter but our experiments were not designed to disentangle the effects of each carbonate parameter from each other. This would require a different experimental setup and is certainly the next step to understand elemental partitioning in coccoliths under changing carbonate chemistry. A similar approach has been recently conducted to elucidate the physiological response of coccolithophores to variations in single carbonate chemistry parameters (Bach et al. 2013). We include this outlook and discuss the difficulties regarding the interpretation of changing carbonate chemistry in the new manuscript version.

Wanamaker:

Potential formatting issue:

On page 12, there are five equations listed for DSr but none noted for DMg. Was this intentional? My suggestion is that you be consistent- either include/exclude both Sr and Mg partition equations.

Reviewer 2:

On page 12, the text shows equations DSr. Were there also supposed to be Mg equations? I suggest either including all regression equations, for both Sr and Mg, or not list any within the text.

Answer:

We follow the suggestions of the reviewers and add the equations for DMg in the text body.

Reviewer 2:

Figure 1b: It would be clearer to list the partition coefficients for individual experiments on the figure (e.g., “DSr = “), although adding regression lines might make the figure illegible

Answer:

We tried the suggestion, but as reviewer 2 already stated the figure becomes quite confusing and hard to read when adding all equations for DSr.

References:

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Nehrke et al. 2013. A new model for biomineralization and trace-element signatures of Foraminifera tests. Biogeosciences, 10, 6759-6767.

Rickaby et al. 2002. Growth rate dependence of Sr incorporation during calcification of Emiliania huxleyi. Global Biogeochemical Cycles, 16, 1006, doi:10.1029/2001GB001408.

Stoll and Schrag 2001. Sr/Ca variations in Cretaceous carbonates: relation to productivity and sea level changes. Palaeogeography, Palaeoclimatology, Palaeoecology, 168, 311-336.

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