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Discussions

Interactive comment on "Review: the effects of secular variation in seawater Mg/Ca on marine biocalcification" *by* J. B. Ries

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First, I wish to thank the reviewers for their thorough and constructive analysis of my review article entitled "Review: the effects of secular variation in seawater Mg/Ca on marine biocalcification." Undoubtedly their recommendations will lead to a much improved manuscript. The purpose of this response letter is to outline the changes to the manuscript that will be made in the next stage of the review process. For the sake of clarity, I will respond to each of the reviewers' comments individually.

Responses to comments of Referee #1 (T. Steuber)

(1) p. 7329, last paragraph and page 7330, first paragraph; also p. 7333, first paragraph; page 7351, line 16; p. 7356, line 6; p. 7389, line 15: The Early Cretaceous is, in

fact, considered to be the time of a calcite sea (Hardie, 1996, Fig. 1 of this manuscript), and the late Early Cretaceous recorded the lowest Mg/Ca ratio after the Cambrian. The statement on p. 7329 is therefore not correct. Also, the first rudists that evolved during the Early Cretaceous were aragonite-dominated and developed calcite-dominated shells in the Late Cretaceous, when the seawater Mg/Ca was rising sharply (Steuber, 2002). Consequently, there seems to be a delay in the response of major carbonate producers to a changing seawater compositions (that seems to be well constrained for that time period). Also, rudists should not be considered as reef builders (see Gili, E., Masse, J.-P. & Skelton, P.W. 1995. Rudists as gregarious sediment-dwellers, not reef-builders, on Cretaceous carbonate platforms. Palaeogeography, Palaeoclimatology, Palaeoecology, 118: 245-267, 15 figs.; Amsterdam) but rather important or even dominant carbonate producers.

The statement that the Early Cretaceous interval was supportive of scleractinian calcification because it is considered an aragonite sea interval will be corrected. The mineralogical shift in the rudists (aragonite dominated to calcite dominated) will be discussed per the referee's suggestion, with specific reference to the Steuber (2002) manuscript. The apparent delay in response of skeletal mineralogy to changing seawater Mg/Ca that was noted by Steuber, particularly as evidenced by the rudists and scleractinian corals in Early Cretaceous time, will be discussed in the revised manuscript. Upon recommendation of the referee, all references to the rudists as "reef-builders" will be deleted; instead, they will be referred to as important or (as appropriate) dominant carbonate producers.

(2) p. 7333, line 15: How does modern pelagic carbonate sedimentation fit into the picture?

The aragonite-calcite sea hypothesis (Stanley and Hardie, 1998, 1999) does not attempt to explain mineralogical trends in all marine calcifiers (a common misconception), it applies only to the major reef builders and sediment producers that sacrifice biomineralogical control in order to rapidly calcify. Indeed, in the modern aragonite sea there are many organisms that secrete low-Mg calcite (oysters, barnacles, some coccolithophores), but these organisms are generally not major producers of limestone (i.e., carbonate sediments or reef deposits). Although pelagic calcifiers have, at intervals in the geologic past, been major producers of limestones and carbonate sediments (e.g., forams and coccolithophores in Cretaceous time), their current role in carbonate sediment production is relatively minor. Therefore, discussion of their modern role in sedimentation in the context of the calcite-aragonite sea hypothesis is probably not necessary and would unnecessarily lengthen the review.

(3) p. 7335, chapter 2.2.1: This is a well written review of the evolution of ideas about potential controlling factors of marine carbonate mineralogy that provides convincing lines of evidence that Mg/Ca is the major driver. The author may consider to refer to Steuber, T., and Veizer, J. 2002. Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. Geology, 30: 1123-1126, for independent, geochemical evidence for secular changes in marine carbonate mineralogy.

Unfortunately, the Steuber and Veizer (2002) reference was overlooked by the author during preparation of this section. Indeed it provides a valuable, independent proxy of seawater Mg/Ca throughout Phanerozoic time. This reference will be discussed in the revised manuscript.

(4) p. 7335, line 25: When discussing the saturation state of (surface) sea water, it would be important to briefly discuss regional variations (temperature, upwelling).

A discussion of regional variations in carbonate ion concentration resulting from differences in temperature, upwelling, and biological drawdown (via biocalcification) will be discussed in the revised manuscript.

(5) p. 7339, chapter 3: Are there records of fossil Bryopsidales that had a different mineralogy than the modern ones?

Although the experiments indicated that bryopsidalean algae will secrete a portion of

their CaCO3 as calcite in seawater formulated with a Mg/Ca ratio less than 2, there is no evidence of which I am aware that suggests that fossil Bryopsidales had an originally calcitic mineralogy during calcite intervals of the geologic past. However, I doubt that a systematic investigation of their original mineralogy has been conducted, particularly for algae that inhabited the calcite seas of Cretaceous time.

(6) p. 7348, chapter 4: Again, there is a problem with timing of events. While coccolithophores evolved during the Jurassic-mid-Cretaceous, the chalk was deposited later, i.e. when the seawater Mg/Ca began to rise. Chalk deposition was not coeval with minimum in the Mg/Ca ratio of seawater.

The discrepancy between the Mg/Ca minimum and the chalk production maximum in Cretaceous time will be discussed in the revised manuscript. However, the timing of the Mg/Ca minimum is not perfectly constrained over this interval; thus, the discrepancy in timing may result from error in the proximal and modeled Mg/Ca data over this interval. Also, even though the Mg/Ca minimum in Cretaceous time was reached in Early Cretaceous time, seawater Mg/Ca is not thought to have risen above 1.5 until Paleogene time (Demicco et al, 2005, Geology). Thus, even though seawater Mg/Ca was rising during the interval of most intense chalk production, it was still well within the calcite-sea range. It is also possible that other factors acted in conjunction with the low seawater Mg/Ca ratios of latter Cretaceous time, such as temperature or pCO2, to cause the coccolithophores to produce more chalk in latter Cretaceous time, after the seawater Mg/Ca minimum had been reached.

(7) p. 7351, line 4: This conclusion implies that modern coccoliths should consist of high Mg calcite (see also page 7350, line 6). Some clarification about the mineralogy of modern coccoliths is necessary here.

This is correct. Stanley, Ries, and Hardie (2004, Geology) report that two of the three species of coccolithophores that they investigated secreted high-Mg calcite in modern seawater of Mg/Ca = 5.2. The authors contend, in their original manuscript, that the ability for some coccolithophores to secrete high-Mg calcite has, for some reason, been long overlooked. A few sentences elaborating on this finding will be added to this section.

(8) p. 7363, chapter 6.2: According to my knowledge, coralline red algae precipitate carbonate with their cell walls. This is different to calcification e.g. in green algae. In this context, the results are surprising. The author may consider to discuss different modes of calcification in the algae studied.

These different modes of calcification between the coralline red algae and calcareous green algae will be noted in the revised manuscript, specifically with respect to the different responses to seawater Mg/Ca exhibited by these organisms.

(9) p. 7371, line 3: Here, it is stated with reference to Fig. 1 that the values reported by Dickson have been re-calculated. If this is correct, this should also be mentioned in the caption of Fig. 1.

This correction will be made in the revised manuscript.

(10) Chapter 8.5 seems to be a rather long summary of research about Precambrian seawater chemistry and the relevance of this chapter for the paper is not clear.

The summary of research about Precambrian seawater chemistry pertains to the suitability of using the primary mineralogy of Precambrian microbial carbonates as a proxy for seawater Mg/Ca. Specifically, given the reported differences between Phanerozoic and Precambrian seawater chemistry, would carbonate mineralogy of Precambrian carbonates be expected to reflect seawater Mg/Ca (i.e., given these chemical differences, would seawater Mg/Ca still have been the primary driver of carbonate mineralogy in Precambrian time?). However, I agree that this section is a bit lengthy and it should be trimmed down in the revised manuscript.

(11) Chapter 8.6: Potential excursions of up to two per mil will be largely obliterated by diagenesis and, more importantly, by secular variations in the oxygen and carbon

isotopic composition of seawater.

Yes, for d18O this is true. But excursions of 2 permil for d13C are reported in Precambrian rocks as responses to forcing events. It is possible that these excursions may simply reflect a change in primary carbonate mineralogy.

(12) Chapter 9.2 and caption of Fig. 29: This discussion misses an important aspect of modern (and possibly ancient) acidification events, i.e. carbonate compensation by fluctuations of the CCD. During ancient times of high CO2, presumably there was sufficient time for ocean circulation to buffer seawater by dissolution of deep-water carbonates. The impact of the modern rise of CO2 is related to the rapid (compared to ocean circulation) increase of atmospheric CO2 that reduces pH of sea surface water that cannot be buffered by carbonate compensation, i.e, rising of the CCD. Similar acidification events may have occurred during the Phanerozoic but require a rapid injection of large volumes of CO2 in the ocean atmosphere systems (events). The long episodes of calcite seas, coinciding with high pCO2 should not be considered as acidification events.

The effect of shoaling of the CCD on the seawater carbonate system during protracted intervals of elevated atmospheric CO2 will be discussed in the revised manuscript. However, it should be noted that even if the shoaling CCD is buffering the seawater carbonate system, I would still expect even gradual, tectonically driven elevations in atmospheric pCO2 to still cause net reductions in seawater [CO3=], and thus partially offset (in terms of ΩCaCO3) concomitant tectonically driven elevations in [Ca2+]. Regardless, true ocean acidification events will be distinguished from protracted intervals of high atmospheric CO2 in the revised manuscript. Reference to protracted intervals of elevated atmospheric CO2 as “events” will be removed.

(13) Caption Fig. 15: The molar Mg/Ca of Cretaceous is given as 0.5. here, although there is no evidence that it dropped significantly below 1.0.

The Mg content of fossil echinoids from Mid-Cretaceous time suggests that

Mg/Ca ratios may have approached 0.5 at this time (Dickson 2002, 2004). The MOR/hydrothermal flux models also suggest that seawater Mg/Ca remained near 0.5 throughout much of Cretaceous time. However, some of the other fossil evidence and the fluid inclusion data suggest that Mg/Ca ratios remained closer to 1.0.

(14) Fig. 29: In view of the discussion in chapter 9.2, it would be more straightforward to compare Ca concentration instead of Mg/Ca with pCO2.

The Mg/Ca curve is required for an earlier section on the manuscript. However, plotting the Ca2+ curve would also be useful for a latter section. A Ca2+ curve will be added to this figure; if the figure becomes too crowded, a new figure with pCO2 and Ca2+ will be produced.

(15) Technical comments: p. 7337, line 3: . . .and Folk (1974) has shown. . . p. 7343, line 3: . . .inverse changes. . . This is not clear in this context. Please rephrase. p. 7355, line 23: Reference to Hardie (1996) seems to be a mistake here. p. 7365, line 17: Petrographic conditions. . .. Replace by Diagenetic conditions. . . p. 7374, line 14: Delete 'And' at beginning of sentence. p. 7376, line 19: Should be 'mm-to-cm thick'?

These corrections will be made in the revised manuscript.

Responses to comments of Referee #2 (anonymous)

(1) I think this paper is better classified as a summary of the previous work by Ries and his colleagues (i.e., Ries et al., Stanley et al.). Most of the data have already been published elsewhere and as far as I can tell the present article does not add any revolutionary new ideas or interpretation of these data. Nevertheless, the experimental work and results of Ries and colleagues is very impressive and a summary of their results will serve as a very useful reference. However, in my opinion there are two problems with the current version of this manuscript that I suggest being addressed. First, I think the current version omits a number of important and highly relevant references pertaining to the factors controlling the mineralogy of carbonate minerals during

nucleation (especially kinetic controls), previous work on the controls of Mg composition of Mg-calcite minerals, and early and recent work on changes in Phanerozoic seawater composition including the seawater carbonic acid system on this time scale. Thus, I think the literature review and reporting in the current version of this manuscript is somewhat inadequate and could be improved.

Because the bulk of the experimental work reviewed was performed by the author of this review article, it is understandable that his review may be perceived partly as a summary of past work. However, it should be noted that the experimental work only represents a portion of the review article. A great deal of the review is focused on the vast body or previous work investigating the effect of the physicochemical properties of seawater on carbonate polymorph mineralogy (abiotic calcification), Mg incorporation in abiotic calcite, the history of seawater chemistry throughout Phanerozoic and Precambrian time (independent proxies and models), and the response of marine calcifiers to these changes as recorded in the fossil recordâĂŤnone of this work was conducted by the author of the review article. This should refute the suggestion that this review is simply a summary of the author's past work. Nonetheless, the author will conduct a secondary literature review to ensure that he has discussed all other experimental work investigating the effect of seawater Mg/Ca on modern marine calcifiers.

Section 2 (Background) will be expanded to include additional early and recent experimental work on (1) factors controlling the mineralogy of carbonate minerals, (2) factors controlling Mg incorporation in calcite minerals, and (3) the history of seawater chemistry throughout Phanerozoic time. The reviewer also suggests that the manuscript does not present any new ideas or perspectives. However, the manuscript contains the first discussion (at least of which I am aware) of (1) the implications of the experimental work for calcifying organisms' responses to future CO2-induced ocean acidification (by making new inferences about organisms' calcifying fluids and their biomineralogical control) and (2) the calcite-aragonite seas hypothesis in the context of past CO2-induced ocean acidification events (e.g., inverse relationship between [CO3=]

and [Ca2+] driven by tectonically induced reactions between hydrothermal brines and basalt along zones of ocean crust production; Section 9).

(2) Although I think the immense work conducted by Ries and colleagues is highly commendable, the big missing link of their work and in their interpretation of their results is the failure to not consider the kinetic controls of mineral nucleation as well as the importance of the availability/activity of reactants including Mg2+, Ca2+, AND CO32- (and consequently seawater saturation state) in controlling the composition and mineralogy of both abiotic and biotic carbonate precipitates. The Mg/Ca ratio only represents one part of the story and does not by itself fundamentally explain the observed mineral compositions.

As discussed above, the calcite-aragonite sea hypothesis does not apply to all marine calcifiers, but rather only to the very rapidly calcifying organisms (the reef builders and major sediment producers), as these organisms are more likely to sacrifice biomineralogical control to achieve rapid carbonate accretion. So it is not expected that seawater Mg/Ca would control the mineralogy of ALL marine calcifiers. Indeed, in the modern aragonite sea there are many organisms that secrete low-Mg calciteâĂŤbut in most cases they are not primary reef-builders and carbonate sediment producers. The failure to investigate the effects of CO3= on polymorph mineralogy is indeed a shortcoming of Ries' experimental work. However, these experiments have now been conducted and should be published shortly, yet not in time to be included in this review. However, the limitations of not investigating the effects of [CO3=] on the polymorph mineralogy of biogenic carbonates will be noted in the revised manuscript.

(3) In several places throughout the manuscript (e.g. pages 7331, 7365, 7367, 7368) Ries refers to Chave's (1954) observation that Mg content of M-calcite secreting organisms varies as a function of ambient seawater temperature. It is important to recognize that these observations also varied as a function of seawater carbonate ion concentration and carbonate saturation with changing latitude. Later work by for example Moberly (1968) and Mackenzie et al. (1983) interpreted this variability in Mg content as

a function of growth rate which is a function of both temperature and seawater carbonate saturation state. Furthermore, more recent experimental work by Agegian (Agegian 1985; Mackenzie and Agegian, 1989) has shown that the Mg content of coralline algae varies as a function of growth rate, carbonate saturation state and temperature.

These additional physicochemical factors influencing the Mg-content of calcitic marine organisms (along with the relevant publications) will be discussed in the revised manuscript.

(4) P7335, line 19-26: Reference to e.g., Morse et al., 1997.

This change will be made in the revised manuscript.

(5) P7341, line 7-10: Is this statement based on a completely qualitative assessment?

This statement is based on a quantitative assessment of the number of offspring algae that were produced under the various seawater Mg/Ca treatments.

(6) P7342, line 8: I suggest removing "Reducing [CO32-] via. . ." and just say "Calcification has the net effect of shifting the aqueous carbonate system towards elevated [CO2] and [H+]." It is not only the removal of [CO32-] per se that is causing the increase in [CO2] and [H+], but also the relative decrease in TA (owing to removal of Ca2+) to DIC caused by this process.

This change will be made in the revised manuscript.

(7) P7364, line 11-16: See for example Mackenzie et al., 1983, Tribble et al. 1995.

These references will be included and discussed in the revised manuscript.

(8) P7367, line 7-11. Why would Stanley and Hardie hypothesize that the Mg content of Mg calcite secreting organisms has varied with seawater Mg/Ca based on Chave's observation that the Mg content of such organisms varied as a function of temperature? Please clarify.

The tendency for the Mg content of Mg calcite secreting organisms to vary with temperature led Stanley and Hardie to hypothesize that the Mg content of Mg calcite secreting organisms varies with seawater Mg/Ca because the former observation demonstrated that Mg-calcite secreting organisms are not able to completely control their Mg content. Thus, these organisms would probably be equally unable to control changes in the Mg content of their shell in response to changes in seawater Mg/Ca. However, it was also the observation that seawater Mg/Ca influenced the Mg content of abiotic calcite that led them to make the above hypothesis. This will be noted in the revised manuscript.

(9) P7370, line 26-29: Yes, exactly! This needs to be emphasized stronger and considered in other parts of the manuscripts (especially growth rates and kinetic controls).

This will be reiterated in the conclusions section that addresses paleoceanographic reconstructions.

(10) P7384, line 15: The statement that regions of the world ocean will become undersaturated with respect to Mg-calcite minerals by year 2150 does not make sense. Many regions are already undersaturated with respect to high Mg-calcite phases. See for example Andersson et al., 2008.

“Mg-calcite” will be removed from this sentence in the revised manuscript.

Again, I thank the referees for their helpful comments and thorough reading of this review article.

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