Biogeosciences Discuss.,
doi:10.5194/bg-2017-4-AC1, 2017

Biogeosciences
Discussions
Open Access

Interactive comment on "Changes in the Si / P weathering ratio and their effect on the selection of coccolithophores and diatoms" *by* Virginia García-Bernal et al.

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Received and published: 8 May 2017

We thank the reviewer for his/her helpful comments

R.C.: Reviewer comment

A.R.: Authors response

R.C: Hypotheses: The study offers two initial hypotheses for processes that may explain the relative rise of diatoms over coccolithophores (see Fig.1): increase in weathering Si:P supply to the ocean favouring silicifying organisms, or alternatively global deepening of the mixed layer favouring organisms with high specific and/or population growth rates. After presenting evidence that may or may not support increases in Si:P

of nutrient supply the authors conclude (p.8, lines 32-33): "the distinct fortunes of coccolithophores and diatoms during the Cenozoic era cannot be attributed exclusively to changing weathering fluxes and nutrient ratios." Why not? So, what should I be taking away from this study?

A.R: The ecological theories of nutrient supply ratio and nutrient supply dynamics are strongly supported by a large body of theoretical and experimental work. These theories are not mutually exclusive, e.g. an increase in the Si/P supply ratio is a necessary but insufficient condition for the rise of diatoms, which also require intermittent pulses of nutrient supply to outcompete other phytoplankton such as coccolithophores. On geological time scales, nutrient supply ratios are controlled by weathering ratios, whereas nutrient supply dynamics are dependent on wind-driven upper ocean turbulence (and the frequency of nutrient pulses to the upper mixed layer). Both features are essential requirements for the ecological success of diatoms. Previous work has focused on ocean turbulence (Tozzi et al., 2004; Falkowski and Oliver, 2007). However, the effect of weathering ratios remains underexplored. We explicitly clarify these apparently confusing aspects in the new version of the manuscript.

R.C: Observational evidence for environmental forcing: Four pieces of observational evidence are used without appropriate discussion: (1) the Follmi (1995) dataset for P burial is used without discussion of the mechanisms of P diagenesis and burial and without mention that shelf/slope sediments account for 75% of P burial (see e.g. Baturin 2007) without being well represented in the Follmi dataset.

A.R: We agree with the reviewer that the Follmi dataset for P burial is biased towards abyssal sediments whereas much of the marine P cycle takes place along continental margins. We comment on this issue in a new version of the manuscript and cite relevant literature on the topic. Regardless of this limitation, our modelling approach, aimed at supporting estimates derived from sedimentary proxies, did a reasonably good job.

R.C: (2) the lithium isotope record is used as a direct (and linear) proxy of silicate weathering although most colleagues would probably argue that it records secondary mineral formation and the congruency of weathering instead of the primary weathering reaction progress (see e.g. the original paper by Misra and Froelich, 2012);

A.R: We agree with the reviewer that the lithium isotope record does not provide a direct estimate of weathering rates but an indication of whether the dominant regime was weathering-limited or supply-limited (i.e. the weathering style). Weathering-limited regimes dominate in tectonically-active regions where intense physical erosion maintains fresh rock surfaces continuously exposed to chemical degradation. Conversely, supply-limited regimes dominate in flat terrains where thick soils prevent mineral surfaces from contact with the atmosphere and hence weathering rates are low. We did not use the lithium isotope record in strict proportionality to estimate weathering rates, but as a proxy for the dominant weathering regime. Our strategy was to assume a two-fold increase in silicate weathering over the last 40 million years following (Li and Elderfield, 2013)(computed from inverse models) and then, based on the Li isotope record of weathering styles, the curve of dissolved Si flux to the ocean basins was computed accordingly. Our calculation assumes that the particulate to dissolved flux ratio in the past was 1:4 whereas currently this ratio takes a value of 4:1. A thorough explanation is given in (Cermeño et al., 2015) (including a *.xls file with pertinent calculations in Supplementary information).

In the new version of the manuscript we include a more thorough explanation in methods on assumptions considered to obtain estimates of dissolved Si fluxes through time.

R.C: (3) SCOR is (p.4, lines 4-5) “a proxy of plankton functional group dominance” and no discussion is offered why this concept of “dominance” can be equated to relative biogeochemical importance (what is the SCOR for the most productive phytoplankton group, unicellular cyanobacteria?);

A.R: The SCOR index has been used to quantify the dominance of plankton functional groups such as coccolithophores, diatoms, foraminifera and radiolarians (Liow et al.,

2010; Hannisdal et al., 2012; Cermeño et al., 2015). Given that the microfossil record is largely limited to data of species presence/absence, estimates of dominance are commonly based on taxonomic richness (rather than abundance). However, taxonomic richness is not necessarily indicative of biogeochemical significance. The PaleoBiology database has global coverage, which allows us to compute the extent of geographic distribution (SCOR). The SCOR is thus a more realistic measure of biogeochemical significance than diversity. Unicellular cyanobacteria are ubiquitous and responsible for a large fraction of marine primary production in open ocean systems. Yet the lack of fossil record (not considering biochemical markers) and our inability to taxonomically resolve the group without the aid of molecular techniques prevent us from computing their SCOR.

R.C: (4) evidence for long-term increase in the pole-to-equator temperature gradient have important implications for deep water formation, the oceans overall density structure and meridional overturning but it cannot be simply related to seasonal mixed layer depth and mixed layer light conditions as is done here.

A.R: The pole-to-equator temperature gradient influences the vertical density structure of the oceans but also atmospheric circulation and wind patterns. The long-term increase in the pole-to-equator temperature gradient is expected to intensify atmospheric circulation patterns and wind stress, which enhanced upper ocean turbulence and upwelling along continental margins and equatorial divergences.

R.C: Modeling: The model setup is insufficiently described. In particular the parameterization of the “weathering flux-uplift relationship (p5 line 19 to p6 line 3) is not transparent. What uplift record is used to force silica weathering? Likewise, it would be important to see what forcing gives rise to the simulated P weathering flux. I suspect simulated CO2 could be a good criterion to discard unrealistic model scenarios, why is it not shown? How does the model Si weathering vary when using the default CO2 dependent weathering scaling? As it is currently the model is a black box, the forcing is unknown, the output is incomplete and discussion is lacking.

A.R: We used the uplift forcing provided as “default input” in COPSE version 5, which is based on the strontium isotope data from the Lowess fit (McArthur et al., 2001). In our modified version of COPSE, weathering is independent of atmospheric CO2 concentration. As it stands, weathering depends exclusively on the new uplift-weathering parameterization derived from (Maher and Chamberlain, 2014). We are undergoing new simulations to test both the combined effect of uplift and volcanic degassing on weathering fluxes.

Si weathering from COPSE’s default configuration decreases significantly towards the present primarily associated with a reduction in volcanic degassing. In the original model configuration, Si weathering is strongly dependent on volcanic degassing despite the latter being poorly constrained by data. Strontium isotopes, in contrast, suggest an increase in continental weathering and erosion coincident with the uplift of the Himalayas. This apparent controversy is further discussed in the new version of the manuscript as it seems to be a critical aspect of the model, at least for the last 40 million years.

R.C: Model-data and data-data comparison: Based on visual comparison the agreement between simulated and proxy-derived P and Si weathering fluxes is judged “remarkably coincident” and “satisfactory” (p 6 line 11,13). For P flux I find that the remarkable agreement cannot be coincidence, and for Si flux the poor match is unsatisfactory (model looks to follow strontium isotopes rather than lithium isotopes, the latter being used as the observational proxy). No objective analysis or relevant discussion is offered. Similarly, the authors find patterns in diatom and coccolithophores SCOR to be “consistent with changes in the Si/P weathering ratio (Fig. 4)” (p6 line 28-29). How so? I would have thought the various records are uncorrelated by any significance standard.

A.R: Our study attempts to put together estimates of P and Si flux to the ocean basins in order to explore the effect of the weathering flux ratio on the ecological success of marine diatoms. We previously realized that this specific issue has received little attention. Our strategy was to implement an Earth system biogeochemical model by adding a new parameterization for uplift-weathering following (Maher and Chamberlain, 2014) and then compare the simulation outputs with sedimentary proxy data. The reviewer notes that our Si weathering flux curve seems to follow strontium isotopes rather than lithium. We find no evidence supporting this claim – whereas the strontium isotope curve begins to increase remarkably roughly 40 million years ago, our Si weathering flux curve highlights a major change 20 million years ago, presumably associated with the thrusting of the Himalayas. The lack of a step-like curve as depicted by the lithium isotope record has to do with the fact that the pattern becomes smoothed as a result of the assumptions considered in our calculations [i.e., the particulate to dissolved flux ratio in the past was 1:4 whereas currently this ratio takes a value of 4:1]. Though there are differences between our estimates and those produced by the model (after some implementation and tuning of parameters), overall, the patterns were very much similar.

We also agree with the reviewer that the presumed relationship between the Si/P weathering flux ratios and the SCOR ratio is not straightforward. In future work we will need to carry out further studies at a higher temporal resolution to investigate such a linkage and its interrelationship with other factors; notwithstanding the Earth is a complex system with many independent forcing mechanisms acting simultaneously, often, in non-linear fashion. Experimental ecologists use to isolate factors and look at their potential effects on organisms, populations and communities. The geological record provides an averaged signature of multiple causes and effects, which clouds specific cause-and-effect relationships and precludes from a comprehensive understanding of specific mechanisms at play. Rather we report on a previously unexplored Si/P weathering ratio and discuss some potential interpretations of the linkage between continental weathering, ocean hydrodynamics and phytoplankton ecology. We think that the analysis add new and interesting information to compose a more detailed picture of the mechanisms that rose diatoms to ecological prominence.

R.C: Discussion: The authors should seek to clarify the motivation for their discussion so as to avoid the sense that it aims to make ad hoc attribution of proposed changes in nutrient weathering fluxes to various tectonic, climate and environmental changes over the course of the Cenozoic. As one example, using denudation related to Himalayan orogeny as the core explanation for increases in silicate weathering after 20 Myrs even though that timing lags 15 Myrs behind seawater strontium isotope changes related to the same tectonic event is not helpful without detailed discussion of the discussion. Other aspects of the final section âĂŤ such as the effect of the rise of diatoms on the biological pump and atmospheric CO2 or the suggestion of geoengineering silica fertilization of the ocean to sequester anthropogenic carbon âĂŤ are not sufficiently developed.

A.R: In a new version of the manuscript we include a more detailed discussion on the mechanisms underlying the patterns of Si and P weathering fluxes to the ocean basins and their influence on the ecological success of diatoms. Additionally, we elaborate on additional aspects concerning potential geoengineering implications of our results.

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