Secular decline of seawater calcium increases seawater buffering and pH

HAIN, M. P.[1], SIGMAN, D. M.[2], HIGGINS, J. A.[3] AND HAUG, G. H.[4]

[1]University of Southampton; m.p.hain@soton.ac.uk
[2]Princeton University; sigman@princeton.edu
[3]Princeton University; jahiggin@princeton.edu
[4]ETH Zürich; gerald.haug@erdw.ethz.ch

Reconstructed changes in seawater calcium and magnesium concentration ([Ca^{2+}], [Mg^{2+}]) predictably affect the ocean's acid/base and carbon chemistry. Yet inaccurate formulations of chemical equilibrium "constants" are currently in use to account for these changes. Here we develop an efficient implementation of the MIAMI Ionic Interaction Model [1] to predict all chemical equilibrium constants required for carbon chemistry calculations under variable [Ca^{2+}] and [Mg^{2+}] [2]. We investigate the impact of [Ca^{2+}] and [Mg^{2+}] on the relationships among the ocean's pH, CO_2, dissolved inorganic carbon (DIC), saturation state of $CaCO_3$ (Ω), and buffer capacity. Increasing [Ca^{2+}] and/or [Mg^{2+}] enhances "ion pairing," which increases seawater buffering by increasing the concentration ratio of total to "free" (uncomplexed) carbonate ion. An increase in [Ca^{2+}], however, also causes a decline in carbonate ion to maintain a given Ω, thereby overwhelming the ion pairing effect and decreasing seawater buffering. Given the reconstructions of Eocene [Ca^{2+}] and [Mg^{2+}] ([Ca^{2+}]~20mM; [Mg^{2+}]~30 mM), Eocene seawater would have required essentially the same DIC as today to simultaneously explain a similar-to-modern Ω and the estimated Eocene atmospheric CO_2 of ~1000 ppm. During the Cretaceous, at ~4 times modern [Ca^{2+}], ocean buffering would have been at a minimum. Overall, during times of high seawater [Ca^{2+}], $CaCO_3$ saturation, pH, and atmospheric CO_2 were more susceptible to perturbations of the global carbon cycle. For example, given both

Eocene and Cretaceous seawater [Ca^{2+}] and [Mg^{2+}], a doubling of atmospheric CO_2 would require less carbon addition to the ocean/atmosphere system than under modern seawater composition. Moreover, increase in seawater buffering since the Cretaceous may have been a driver of evolution by raising energetic demands of biologically controlled calcification and CO_2 concentration mechanisms that aid photosynthesis.

[1] Millero F.J., and Pierrot, D. (1998) *Aquatic Geochemistry*, **4**, 153-199 [2] Hain, M., Sigman, D., Higgins, J., Haug, G. (2015) *Global Biogeochemical Cycles*, doi:10.1002/2014GB004986