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Ocean Acidification (OA) in Deep Time: Annotated Bibliography
Garrett Boudinot, 2015

Beauchamp, B. and Grasby, S. E., 2012, Permian lysocline shoaling and ocean acidification along NW Pangea led to carbonate eradication and chert expansion: Paleogeography, Paleoclimatology, and Paleoecology, v. 350**,** p. 73–90.

End Permian mass extinction is identified and explained as the result of OA. Framework is strata in the Canadian Arctic Archipelago (Sverdrup Basin), and mineralogical and biological indicators of environmental conditions. The main evidence for OA is a decrease in calcification and increase in chert precipitation. The localized CCD and lysocline are mapped based on the observed stratigraphic changes, and are interpreted as a long term (tens of millions of years) process of OA. Geochemical calculations, which rely heavily on the relationship between OA and silicate weathering, are used to explain the long term acidification. Under these considerations, the increase in atmospheric CO_2, and ultimately OA, was caused in large part by a decrease in silicate weathering on Pangaea following the erosion of the Variscan-Hercynian-Alleghanian mountain belt and buildup of thick soil beds. Coupled with the outgassing of the Siberian Trap eruptions, this model provides a good explanation for the global decrease in calcifiers, as well as other anomalies noted at the end of the Permian.

Erba, E., Bottini, C., Weissert, H.J., and Keller, C. E., 2010, Calcareous nannoplankton response to surface-water acidification around ocean anoxic event 1a: Science, v. 329, p. 428-432.

The relationship between OA and anoxia is of great interest, yet the details of this interplay remain obscure. Role of OA in sediment record of OAE1 is explored using carbon and oxygen isotopic evidence and nannofossils from global marine cores. Global anoxia was preceded by volcanism-driven OA, which over time reached deep waters before receding and allowing recovery of calcification amidst anoxic conditions. Multiple "pulses" of CO2 are found in the isotopic excursions, and the effects that these had highlight the differences between short-term and long-term OA. Focus is not on the causes of the event's end, but rather on OA at the onset of the event, and its migration to deep waters before allowing recovery of calcifiers.

Gazeau, F., van Rijswijk, P., Pozzato, L., and Middleburg, J.J., 2014, Impacts of ocean acidification on sediment processes in shallow waters of the Arctic Ocean: Plos1, v.9, p. 1-11.

The effect of OA on sedimentation and the geologic record is relatively unknown. This is odd, considering the reservoir size of carbonates, their geologic ubiquity, and their ecologic importance. A number of sediment cores from an Arctic fjord were incubated with varying concentrations of carbon dioxide for two weeks to quantify the effect that increased pCO_2 has on sedimentology and geochemical constraints. Their results revealed little effect of increased CO_2 on sediments, due to several experimental flaws including short duration of incubation time and restricted sediment kinetics. A main result was an increase in anammox (anaerobic ammonium oxidation), produced by bacteria and archaea, at the most low pH conditions. It was only at this lowest pH condition (pCO2~3000μatm) that carbonate dissolution was observed. Otherwise, this is one experiment that, despite its many downfalls, attempts to understand the relationship between ocean sediments and acidic conditions.

Greene, S. E., Martindale, R.C., Ritterbush, K.A., Bottjer, D.J., Corsetti, F.A., Berelson, W.M., 2012, Recognizing ocean acidification in deep time; an evaluation of the evidence for acidification across the Triassic-Jurassic boundary: Earth-Science Reviews, v. 113**,** p. 72–93.

Identifying periods of OA in deep time is difficult, but this paper illustrates how it can be done using globally distributed proxies to create global reconstructions of the carbon cycle at any one time. Mineralogical, fossil, and chemical evidence in stratigraphic sections of the Triassic-Jurassic boundary are used to investigate the role of OA in the T-J extinction event. Global carbon isotope excursions with reduced precipitation of carbonates and changes in faunal assemblages place the cause of OA on the Central Atlantic Magmatic Province emplacement. This illustratess that short term carbon cycle perturbations can have long lasting impacts.

Hoenisch**,** B., Ridgewell, A., Schmidt, D.N., Thomas, E., Gibbs, S.J., Slujis, A., Zeebe, R., Krump, L., Martindale, R.C., Greene, S.E., Kiessling, W., Ries, J., Zachos, J.C., Royer, D.L., Barker, S., Marchitto, T.M., Moywer, R., Pelejero, C., Ziveri, P., Foster, G.L., and Williams, B., 2012, The geological record of ocean acidification: Science, v. 335**,** p. 1058–1063.

The parameters at play during global OA events are complex, especially when interpreted from the geologic record. This review of the knowledge of OA in deep time helps to clarify those parameters. first described are the proxies used to identify three main parameters involved in OA: seawater pH, carbonate concentration, and surface ocean aqueous carbon dioxide concentrations.. Global processes at play in carbon cycle perturbations are described, followed by a review of past acidification events. The events are compared in terms of their duration and possible causes. Overall, OA in deep time is presented as useful in understanding future projections of OA from anthropogenic CO_2. models are formulated to apply processes of past events to future projected atmospheric CO_2. multiple points of view are combined, from carbon chemistry to ocean physics, to formulate a coherent picture of OA in deep time.

Kiessling, W., and Simpson, C., 2011, On the potential for ocean acidification to be a general cause of ancient reef crisis: Global Change Biology, v. 12, p. 56-67.

Reef extinction events, though sometimes concomitant with other mass extinctions, seem to behave independently of other extinctions. This article describes five mass extinctions and five reef extinctions, and investigates the role of OA in them reef species and marine organisms were used to run a number of statistical analyses to track the changes in diversity and extinction rates throughout each event. Their results suggest that four of the five reef crises were caused by OA. Two mass extinctions that do not coincide with coral extinctions are shown to not be OA-originated, the late Ordovician and end Cretaceous, and these are discussed. some events that did not bring extinction, such as the OAEs, are discussed in terms of their relationship with OA. The conclusions suggest that global warming and OA can be deleterious to reefs independently, with increased severity when coupled.

Ohno, S., Kadono, T., Kurosawa, K., Hamura, T., Sakaiya, T., Shigemori, K., Hironaka, Y., Sano, T., Watari, T., Otani, K., Matsui, T., and Sugita, S., 2014, Production of sulphate-rich vapour during the Chicxulub impact and implications for ocean acidification: Nature Geoscience, v. 7, p. 279-281.

the possibility of OA as a cause of the marine extinctions seen during the K-Pg extinction event is detailed. Working off of the hypothesis that the leading cause of the K-Pg was the Chicxulub impact, these authors analyzed sulfur chemistry in the lab to identify the likely products of the impact, identifying sulfur trioxide as dominant. this compound would readily fall to the sea surface as sulfuric acid, creating a massive OA event. Interestingly, Deccan outgassing is not discussed. This is useful in that it provides experiments to test hypotheses of past processes, but is best when compared with Tyrrell et al. for their contrasting interpretations.

Penman, D. E., Hönisch, B., Zeebe, R. E., Thomas, E. and Zachos, J. C., 2014, Rapid and sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum: Paleoceanography, v. 29**,** p. 357-369.

Although much of the evidence from the PETM indicates the occurrence of OA, little has been done to quantify its extent. Here, Boron was used to determine to what extent OA was at play, and for how long. Carbon isotopes, boron isotopes, B/Ca, and Mg/Ca ratios were all used to reconstruct the temperature rise and acidification extent before, during, and after the PETM at a high temporal resolution. the resulting paleoreconstructions were compared with models to make sense of the processes at play during their deposition. a sustained, rather than transient, input of carbon dioxide was required to attain the pH and temperature levels gathered from the proxies.

Tyrrell, T., Merico, A., and McKay, D.I.A., 2014, Severity of ocean acidification following the end-Cretaceous asteroid impact: Proceedings of the National Academy of Science, p. 1-6.

Multiple kill mechanisms have been attributed to the K-Pg mass extinction, and this article examines some of those hypothesized causes (e.g., volitization of gypsum-rich rocks, ocean stratification), and their likelihood in producing the evidence seen in the rock record. A numerical model is used to assess the extent and time scale on which each cause might function, and special attention is given to the role of OA in each scenario. Because of the complexity in the evidence of the K-Pg, this article is exemplary in its attention to detail of processes that may have been at play. Outcomes suggest that OA may have been, but was not necessarily, a contributor to the K-Pg extinction.

Veron, J. E.N, 2008, Mass extinctions and ocean acidification: biological constraints on geological dilemmas: Coral Reefs, v. 27, p. 459–472.

Five mass extinction events are described in terms of their evidence of OA, followed by an assessment of how various kill mechanisms might create acidic conditions in the ocean. Ultimately the author divides mass extinction mechanisms into two camps: physical perturbations, such as disease or bolide impact, and perturbations in the carbon cycle, including OA. The method makes clear the powerful effects of carbon cycle changes on the biosphere. The conclusions point to how past OA events inform future projections.

Zeebe**,** R. E., 2012, History of seawater carbonate chemistry, atmospheric CO_2 and ocean acidification: Annual Review of Earth and Planetary Sciences, v. 40**,** p. 141–165.

The complexity of OA cannot be overstated, and extends from various carbon cycle parameters affected and temporal scales involved. the intricacies of OA as a global geologic process are described. Carbon chemistryand various ascpects of the carbon cycle are detailed . Special attention is payed to the time scales on which OA can operate, from short term to long term causes and effects. Past periods that are certain to have been affected by OA are analyzed in terms of their causes and extent. A number of graphs are used to show relationships between numerous carbon proxies, time, and acidification, helping to make sense of the multiple variables at play.