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## **Balancing of Ocean Acidification by Superoxide Redox Chemistry?**

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Ocean acidification is typically caused by production of carbonic acid ( $\text{H}_2\text{CO}_3$ ) through the dissolution of increasing atmospheric  $\text{CO}_2$ , which adds to DIC (dissolved  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) produced in seawater by several processes including biological ones (primary production followed by respiration).<sup>1-3</sup> Acidification can decrease the saturation states of carbonate minerals, which may considerably endanger the dynamics, structure and biodiversity of coral reefs and other marine calcifying organisms.<sup>2-3</sup> The consequence is the decline in the early development stages of shellfish, coral reefs or other marine calcifiers, with impacts on fertilization, sexual reproduction, cleavage, larval settlement, survival and growth, finally causing a substantial population decline.<sup>2</sup> Decline in shellfish or coral reefs, which form the foundation of marine ecosystems, would markedly affect the whole food webs and marine population dynamics.<sup>2</sup>

Despite the apparent straightforwardness of such a scenario, the actual determination of the impact of atmospheric  $\text{CO}_2$  on seawater pH is a difficult task. This happens primarily because of the relatively small pH changes, unless very long time spans are taken into account. Moreover, pH modifications can also take place at a local scale because of several possible confounding factors,<sup>4</sup> of which we will show the potential role of superoxide chemistry. Among additional causes for seawater pH variation, one is the acidification connected with eutrophication phenomena that have increased worldwide since the last few decades. Indeed, changes in land-use practices can induce the release of high amounts of nutrients and terrestrial organic matter (OM) to coastal seawaters, including dissolved OM (DOM) and particulate OM (POM).<sup>1-2</sup> The transformation of organic P and N into phosphate and nitrate because of microbial or photochemical processes can cause a significant decrease of the alkalinity of coastal seawater and, therefore, a decrease in pH.<sup>2</sup> Another possibility (although limited in space and time) is the elevated production of  $\text{CO}_2$  and DIC during harmful algal blooms, which can significantly alter the pH of seawater as long as they are operational.<sup>1</sup> Eutrophication phenomena and algal blooms can both be enhanced by global warming, which causes an increase of surface seawater temperature and leads to a longer summer stratification period. In warm, sunlit surface seawater the photochemical and biological processes

that are involved in the degradation of DOM and POM can be strongly enhanced, leading to increased production of CO<sub>2</sub> and of anionic species that decrease the alkalinity of seawater.<sup>2</sup> The third possible issue is connected with atmospheric acid rain, most notably involving HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> that can directly lower the seawater pH.<sup>2</sup> All such processes are usually limited to the coastal areas that are most affected by eutrophication phenomena, while acid rains are not expected to have a comparatively important impact on the pH of the open ocean.

Within this context, an additional factor of potential importance is represented by the chemistry of superoxide. The radical ion O<sub>2</sub><sup>-•</sup> is produced by various sources including extracellular generation by heterotrophic bacteria that are commonly detected in lakes, soil, hydrothermal vents, marine sediments, estuaries and oceans.<sup>5</sup> Rates of superoxide production normalized to the proportion of metabolically active cells are found to vary between 0.02 ± 0.02 amol cell<sup>-1</sup> hour<sup>-1</sup> (mean ± standard error) and 19.4 ± 5.2 amol cell<sup>-1</sup> hour<sup>-1</sup>.<sup>5</sup> Such production rates could lead to an alteration of seawater pH because of H<sup>+</sup> consumption upon dismutation of superoxide (2 O<sub>2</sub><sup>-•</sup> + 2H<sup>+</sup> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>). The latter process is catalyzed by redox-active metals such as Cu(I/II) and Fe(II/III) and possibly (but still controversially) by organic compounds with redox-capable moieties.<sup>6</sup> With a biological generation rate of O<sub>2</sub><sup>-•</sup> prudentially assumed to be 0.2 pmol dm<sup>-3</sup> s<sup>-1</sup>, which is only 10% of that reported by Diaz et al.<sup>5</sup>, based on superoxide dismutation alone one can have a H<sup>+</sup> consumption rate of ~6 μmol dm<sup>-3</sup> year<sup>-1</sup>. A simplified seawater model shows that the process would be able to compensate for an acidification rate of 0.1-0.3 pH units year<sup>-1</sup> (Fig. 1), which is far higher than the observed acidification rate. The dismutation of superoxide has thus potential to significantly impact the pH of seawater, but it is clear that before drawing any firm conclusion over this issue it is mandatory to carry out a complete assessment of the charge balance of the whole process. The complete charge balance involves: (i) O<sub>2</sub><sup>-•</sup> generation *via* both (photo)chemical and biological processes, in particular because the initial production of HO<sub>2</sub><sup>•</sup> would compensate for the H<sup>+</sup> consumption in O<sub>2</sub><sup>-•</sup> dismutation; (ii) the relative role of O<sub>2</sub><sup>-•</sup> dismutation *vs.* scavenging upon oxidation (O<sub>2</sub><sup>-•</sup> → O<sub>2</sub> + e<sup>-</sup>) or reduction (O<sub>2</sub><sup>-•</sup> + e<sup>-</sup> + 2 H<sup>+</sup> → H<sub>2</sub>O<sub>2</sub>) reactions, which entail a different number of exchanged H<sup>+</sup> ions, and (iii) the possible involvement of H<sup>+</sup> in the semi-reactions of the redox couples (metal species and complexes, organic compounds and so on) reacting with O<sub>2</sub><sup>-•</sup> and related oxygen species. A full understanding of all the processes (both major and secondary ones) of O<sub>2</sub><sup>-•</sup> production and scavenging is vital to get insight into seawater acidification as well as redox state. Indeed, although the H<sup>+</sup> balance of HO<sub>2</sub><sup>•</sup> generation and O<sub>2</sub><sup>-•</sup> dismutation closes to zero, a small local prevalence of additional processes such as superoxide oxidation or reduction could modify seawater pH, because the chemistry of superoxide is potentially able to exchange much more H<sup>+</sup> ions than those involved in dissolution of atmospheric CO<sub>2</sub>.

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**Fig. 1.** Equilibrium pH of seawater as a function of the concentrations of bicarbonate and added  $H^+$ .

