A Plea for Temperature in Descriptions of the Oceanic Oxygen Status

BY PETER G. BREWER AND ANDREAS F. HOFMANN

ABSTRACT. For over 50 years, the ocean science community has traditionally reported hypoxic limits for marine animals simply as a concentration value independent of temperature and pressure, implying the same limit for the warmest shallow gulf or the coldest deep fjord. Similarly, deep-sea oxygen consumption rates are typically reported as exponential functions of depth. In implicitly combining temperature, pressure, and multiple other properties into a single variable, it becomes difficult to describe the future of an ocean under changing climate conditions. We report here on a series of recent papers that seek to provide improved descriptions, by mapping the ocean pO_2 field and then matching it to the various concentration limits proposed. We describe the availability of O_2 to marine animals as being governed by a diffusive boundary rate process similar to well-known descriptions of air-sea gas exchange. We also describe the challenge for a deep-sea animal exporting CO_2 through the same boundary layer with known chemical reactivity imposed. The end result is a clear sense that ocean warming in most regions will add stress to the aerobic functioning of marine life, that the oxygen minimum zones appear to be more challenging than ever, and that the deepest abyssal ocean will retain quite favorable aerobic conditions.

BACKGROUND

The concept of changing ocean chemistry with climate has emerged recently and rapidly. We now have unassailable measurements to confirm it—but it is surprising to observe how ill-prepared we are for dealing with some of the findings. In the GEOSECS (Geochemical Ocean Sections Study) decade of the 1970s, it was common to refer to geochemical profiles as "stationary in the Eulerian sense" when describing vertical profiles—but that would be unthinkable today. The most obvious case is the recent rise in awareness of ocean acidification, although in retrospect, red flags were apparent for many decades (Brewer, 2013). In this paper we review the background of increasing awareness of changes in the ocean's chemical state over the last several decades and examine possible ways in which new metrics can be applied that attempt to incorporate fundamental physico-chemical principles. The challenge is very real: for over 50 years, ocean scientists have, for what were good reasons at the time, taken shortcuts that so comingled

multiple properties that basic needs such as an explicit temperature dependence of rates has been avoided. Put very simply, we cannot predict climate change impacts on ocean chemistry if we do not have temperature-dependent terms in our equations. Nowhere has this been more apparent than in the treatment of oceanic consumption rates of oxygen and descriptions of hypoxia.

One of the earliest estimates of oceanic oxygen consumption rates appears in a classic paper by Riley (1951), where he noted the appearance of an exponential decline in rates with depth. This paper was followed by the analysis of Wyrtki (1962) in which the formulation of biogeochemical rates as an exponential function of depth was repeated. But Wyrtki clearly understood the conundrum this presented, for he noted that "[t]he consumption of oxygen is certainly dependent on the amount of oxidizable substances present," and "[t]emperature might have an appreciable effect, which would result in a higher consumption in the warm upper layers and in a smaller consumption in the deep colder layers,

but as the temperature decreases almost exponentially, like e^{-z}, such an effect would have already been included in the assumption of an exponential decrease of consumption." Thus, temperature dependence, the dominant control on chemical reaction rates, was blurred. There are good reasons for this—it is difficult to untangle the simultaneous effects of temperature, time, mixing, ventilation history, the quantity and state of organic matter present, and the effectiveness of microbial attack.

It is interesting to speculate, perhaps mischievously, how these early papers would appear had ocean chemists written them. The choice of an exponential form is near identical to the classical representations of the temperature dependence of chemical reaction rates given by van't Hoff (1884) and Arrhenius (1889), where the form for the rate constant $K = Ae^{-Q/T}$ is used, and a "pseudo" or "apparent" Arrhenius rate might then have been given. It is not surprising that this relationship has proved to be an enduring approximation to the ensemble of oxygen consumption processes. But, while this comingling of temperature with other functions can be convenient in the short term, it inevitably leads to difficulties in predicting the impacts of a warming ocean on chemical distributions and properties.

The attractiveness of a simple exponent with depth is obvious because most oceanic observations are made as vertical profiles, and, hence, the practice has endured. Munk (1966) repeated this formulation, as did Craig (1969) and Jenkins (1982). Because so many other oceanic chemical variables are so strongly correlated with oxygen consumption and the decomposition of organic matter, we find a representation of chemical variables as an exponential

function of depth to be very widely used throughout ocean chemistry. For example, the decline in particle flux with depth as organic matter is consumed was early given as an exponent of depth in the classic treatment of sediment trap data by Knauer and Martin (1981) and Martin et al. (1987).

At this time, we really do not have a strong sense of the *relative* importance of the interlocked properties of increasing stratification and reduced ventilation, the changing downward flux of organic matter, and the influence of temperature dependence of reaction rates—but we can be certain that temperature-dependent rates are present. The recent Intergovernmental Panel on Climate Change Working Group 1 (IPCC WG 1) Fifth Assessment Report (Chapter 6, Ciais et al., 2013) predicts that "[it] is *likely* that large decreases in oceanic dissolved oxygen will occur during the 21st century" but also notes that there are "large uncertainties in potential biogeochemical effects." However, the effects of temperature on metabolic rates are fundamental (Brown et al., 2004). In addition, while the focus has tended to be on immediate particle fluxes, the large stores of organic matter in continental shelf sediments must surely come into play as temperature rises and the diffusive flux of reduced species into the ocean increases (Gilbert et al., 2010).

More recently, quite careful analyses intended to clarify more specifically the role of temperature on water column

Peter G. Brewer *(brpe123@gmail.com) is Senior Scientist, Monterey Bay Aquarium Research Institute, Moss Landing, CA, USA.* **Andreas F. Hofmann** *is on the staff at the German Aerospace Center (DLR), Institute of Technical Thermodynamics, Stuttgart, Germany.*

rates have appeared. For example, analyses of the extensive Joint Global Ocean Flux Study (JGOFS) data sets (Laws et al., 2000) show very clearly that temperature alone accounts for some 86% of the variance in organic matter export from the euphotic zone. Iversen and Ploug (2013) address temperature effects on respiration rates and carbon fluxes below the euphotic zone, reporting a rate change of a factor of 3.5 when the temperature is reduced by 11°C, suggestive of a Q_{10} (temperature coefficient that is a measure of the rate of change of a biological or chemical system as a consequence of increasing the temperature of the system by 10°C) of about 3. Thamdrup and Fleischer (1998) observed temperature-dependent ocean microbial rate processes with a Q_{10} of about 3 in the upper water column where the highest rates of O_2 consumption are found. We may assume that oceanic microbes function pretty much as microbes do everywhere and, as the ocean warms, microbial oxidation rates in sediments and in the water column will increase. It would seem to make the most sense to begin by making an affirmative statement that, for a predicted ocean temperature change of 2°C, microbial O_2 reduction rates will increase by about 25%; however, the net outcome may be modified by uncertainties in changes in the flux of organic matter from the surface, and the loss of O_2 will be further enhanced by reduced ventilation. There are several recent careful reviews of the status of oceanic O_2 (e.g., Keeling et al., 2010), but all, while providing warnings, have stopped short of invoking specific temperature dependencies.

Locally, there are exceptions to this, particularly at a depth where the flux of reduced species that is separate from the downward vertical transport can occur.

One recent example is the rapid microbial oxidation of methane and other hydrocarbons released into the deep Gulf of Mexico from the Deepwater Horizon oil spill disaster (Kessler et al., 2011), which created a persistent local oxygen anomaly. But, there, too, the rates would have been faster in warmer waters irrespective of depth. Other Earth science disciplines do not share this legacy of reliance on nontemperature-dependent functions; for example, the decay of organic matter in soils is quite specifically described as a van't Hoff/Arrhenius function of temperature (e.g., Lloyd and Taylor, 1994).

EMERGING PROBLEMS IN THE OXYGEN STATUS OF THE OCEAN

Very clearly, oceanic dissolved oxygen levels are declining in many, but not all, regions. Nakanowatari et al. (2007) and Stramma et al. (2008) provide well-documented reports of temperature-related increasing O_2 consumption rates at depth, and Helm et al. (2011) extend the analysis of these observations. The conclusion of Helm et al. (2011) reads: "Approximately 15% of global oxygen decrease can be explained by a warmer mixed-layer reducing the capacity of water to store oxygen, while the remainder is consistent with an overall decrease in the exchange between surface waters and the ocean interior. Here we suggest that this reduction in water mass renewal rates on a global scale is a consequence of increased stratification caused by warmer surface waters."

The initial focus on reduced ventilation makes sense because it will be the first physical process to be disrupted. But the relative neglect of temperature-dependent biogeochemical rate changes at depth is of concern. By far the largest

changes in O_2 consumption occur not at great depth but rather immediately below the euphotic zone where climatic warming is already apparent. The chemical function of reduced solubility with rising temperature accounts for only ~ 15% of the observed change. The solubility dependence of O_2 is close to 14.7 μmol kg^{-1} for warming from 4°C to 6°C (a typical O_2 minimum example), and many areas of the ocean today have far lower concentrations of O_2 than this (Thamdrup et al., 2012; Ulloa et al., 2012). If the changes at depth of the consumption terms were to mirror the temperature dependence of the biogeochemical export flux from the euphotic zone noted by Laws et al. (2000), and in the future account for 85% of the signal, then we could face very large-scale reductions of oceanic oxygen.

DEFINITIONS OF HYPOXIA

The traditional lack of specific temperature terms in describing deep-ocean oxygen consumption appears to have been carried through to descriptions of impacts of lowered oxygen levels on marine life.

Hofmann et al. (2011) report on the confusing definitions of oceanic hypoxia. It is possible to find a huge range of temperature-independent claims. For example, Table 1 of Hofmann et al. (2011) includes some 28 references to the various definitions of hypoxia, in varying units, and none contain temperature- or depth-dependent terms. Although all of these definitions and observed limits have some well-intentioned basis, the end result is great confusion. For example, Diaz and Rosenberg (2008) report that mass mortality occurs at 0.7 ml L^{-1} O_2. This figure is equivalent to 31.3 μmol L^{-1}. Huge oceanic areas with abundant marine

life occur within this boundary, and the same limit is implied for warm surface waters or cold, deep fjords.

The term "dead zone" has been widely used and is recognized in the popular press. It has been used to describe the low-oxygen episodes in the Gulf of Mexico (Rabalais et al., 2010) and has been set at 61 μmol L^{-1}, about twice the level reported by Diaz and Rosenberg (2008), again without temperature

dependence. This stress level was found to be too stringent by Vaquer-Sunyer and Duarte (2008), who doubled it yet again to 4.6 mg O_2 L^{-1}, or 144 μmol L^{-1}—but vast oceanic fisheries exist within this oxygenated space. A possibly higher cautionary level was set by Gray et al. (2002), who reported that "growth is affected" at oxygen levels between 181 and 140 μmol L^{-1}. The range of values from 31–181 μmol L^{-1} with no specified temperature or pressure dependence appears unusual. We have also not been able to find any reference to the accompanying CO_2 levels in setting these limits. This appears odd, given the attention now paid to impacts of rising oceanic CO_2 levels and the expressed concerns over elevated CO_2 levels on deep-sea animal aerobic functioning (Seibel and Walsh, 2003).

The focus of the above articles is to report on the observed impacts of changing O_2 concentrations on various forms of marine life. It is very difficult

for physical scientists to use this information for oceanic assessments of climate change impacts, where temperature is a prime variable, or to deal in any useful way with this literature in its present form. Marine animals display wide variation in how they adapt to the particular external temperature and oxygen regimes of their niches. All animals are subject to the same physico-chemical laws that characterize the now-changing

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external boundary conditions. They cannot control their environments, but must react to them. We need better descriptors of these physical and chemical conditions.

THE EXTERNAL OCEANIC BOUNDARY CONDITION FOR A MARINE ORGANISM
Partial Pressure of O_2

In a first effort to address some of these concerns, Hofmann et al. (2011) mapped the oceanic oxygen field with pO_2 rather than concentration as a variable. This method has the advantage that temperature and pressure terms are now formally incorporated into the observed fields. Geochemists have long produced fields of oceanic pCO_2 (Takahashi et al., 1981), and it makes perfect sense to compare them to maps of pO_2. In one very early example of response to the need for better definition of physical and chemical conditions and its relationship to biological impacts, Redfield and

Goodkind (1929) tested the lethal limits for a squid in the laboratory in terms of the pO_2 to pCO_2 ratio. There are already regions in the ocean where $pCO_2 > pO_2$ (Brewer and Peltzer, 2009), likely posing stress beyond that characterized by O_2 concentration alone. These regions will surely grow in size.

The first challenge Hofmann et al. (2011) faced was to guess at the temperature implied in the various definitions of hypoxia that are based on concentration alone. Figure 1 shows a specific example of this by comparing the various thresholds proposed against a hydrographic station off the coast of Southern California with assumed temperature values. As the ocean is now changing in both temperature and O_2, such details will become critical if meaningful changes are to be described.

Estimating Rate Limits Imposed by the Physical Oceanic Environment

The challenge facing a deep-sea animal is the need to acquire O_2 at a rate sufficient to support its metabolic needs; a measure of concentration, or pO_2, alone is not sufficient to describe this process. In order to translate an observed concentration into a rate, we use the well-known diffusive boundary layer (DBL) model that successfully describes processes such as air-sea exchange rates and mineral dissolution rates. Hofmann et al. (2013a) applied this model to describe the external boundary condition that characterizes the exposed respiratory surface of a deep-sea animal by using the form

$$E_{DBL} = \frac{D\rho_{sw}}{L} \, KO'\Delta pO_2|_{DBL},$$

where E_{DBL} is the diffusive flux of O_2 across the DBL in $\mu mol s^{-1}/cm^{-2}$, D is the molecular diffusion coefficient for O_2 in $cm^2 s^{-1}$, L is the thickness of the diffusive boundary layer in centimeters, ρ_{sw} is the in situ density of seawater, and $\Delta pO_2|_{DBL}$ is the pO_2 gradient across the DBL, calculated using the standard form of Henry's Law and corrected for pressure as in Enns et al. (1965). The thickness L of the DBL is a critical property and, as with the well-known air-sea exchange rate functions, can be approximated by a simple planar model using laminar flow.

From these terms, we can describe a purely physical (organism-independent) property that characterizes as an upper limit the maximum oceanic "oxygen supply potential" per unit area of exposed respiratory surface. Note that the quantity represents a theoretical maximum as we approximate $\Delta pO_2|_{DBL}$ by the oxygen partial pressure in the free stream around the animal $[pO_2]f$. The supply potential SP_{O_2} is given by

$$SP_{O_2} := D\rho_{sw}KO'pO_2|_f = D\rho_{sw}[O_2]_f.$$

Figure 2 shows examples of the oceanic distribution of this property.

It is very clear that flow over an animal's surface, whether actively driven by species-induced flow or resulting from motions in the external ocean, is a critical property. As with increased wind speed at the air-sea interface, this flow increases the gas exchange rate. It is a highly nonlinear function of flow typically characterized by the Schmidt number.

This analysis shows that there will be a cascade of effects resulting from ocean warming. Gases are less soluble in warmer water, and although water in contact with the atmosphere has a $pO_2 \approx 0.21$ atm, once a water parcel has left the surface with its lesser O_2 mass, respiratory O_2 consumption will occur and interior O_2 levels will decline. Considering again only the external
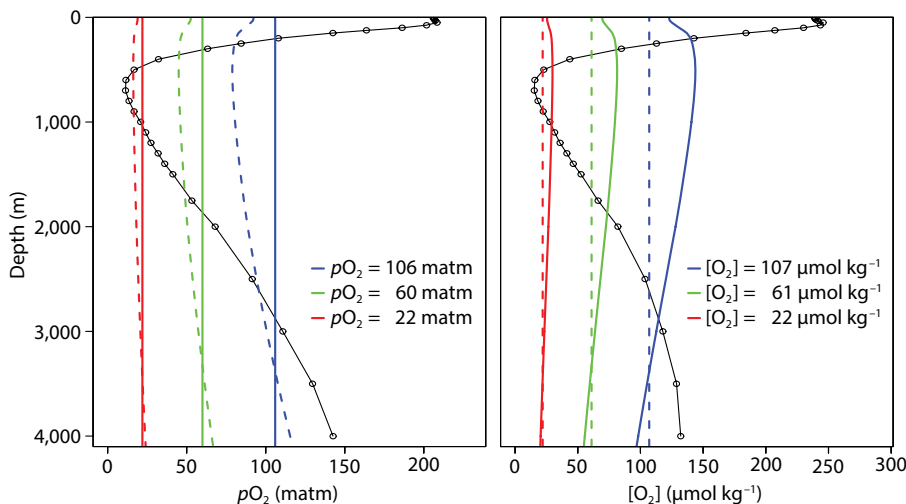

Figure 1. Dissolved oxygen profiles expressed as pO_2 (left panel) and $[O_2]$ (right panel) for an example station off the coast of Southern California (29.5°N, 120.5°W) obtained from the World Ocean Atlas 2009 oxygen climatology (Garcia et al., 2010), overlaid with thresholds for hypoxia categories (blue, green, and red lines). Solid lines = constant pO_2 thresholds. Dashed lines = constant $[O_2]$ thresholds. To be consistent with the literature (e.g., Levin et al., 2009; Rabalais et al., 2010), ≈ 2 mg O_2 $L^{-1} \approx 61$ μmol kg^{-1} is equivalent to 30% saturation, which implies T = 25°C. T = 25°C has been used to convert thresholds between pO_2 and $[O_2]$; however, the ambient surface temperatures at the example station are $\approx 17.6°C$, and thus, the constant pO_2 and constant $[O_2]$ threshold lines do not meet at the surface. The results show very clearly the wide range of hypoxia estimates; the red line is the severe hypoxia category of about 22 μmol kg^{-1}. This is twice the standard geochemical value of 10 μmol kg^{-1} that is typically taken to characterize the onset of suboxic conditions where onset of NO_3 reduction occurs. It is clear that a very wide range of depths may be described as hypoxic, depending on the definition given. *From Hofmann et al. (2011)*

functions, an animal at depth will experience some benefits from the warmer water: molecular diffusion terms will increase, thus increasing O_2 transport through the diffusive boundary layer, but it will also be exposed to lower external O_2 levels. Which effect has the greater impact? The answer is that the lowered O_2 levels dominate by far, and, in most, but not all cases, there will be increased difficulty in maintaining the desired O_2 supply rate.

Figure 3 shows one example of these effects. It graphs the relationship between the oxygen concentration required at the surface to support a given uptake rate against the equivalent concentration at depth, assuming a flow rate over the surface of 2 cm sec^{-1}. The calculation requires inclusion of the Henry's Law constants for in situ conditions and can be used to compare warm and shallow to cold and deep conditions (Hofmann et al., 2013a). The result shows that for typical ocean depth-temperature profiles, the equivalent O_2 profiles require about three times greater O_2 concentration at 1,000 m depth as at the surface in order to have O_2 supplied at the same rate. Because O_2 concentrations in nature decline rapidly with depth, there is double jeopardy—the absolute decline in concentration of dissolved O_2 and greater physical difficulty in gaining access to what is there.

The Added Impact of Rising CO_2 Levels

Ocean acidification is now widely recognized as an emerging ocean environmental stress (IPCC, 2011). Concerns have been expressed that rising CO_2 levels will adversely affect deep-sea animal aerobic functioning and will thus negatively interact with oxidative stress. For example, Seibel and Walsh (2003),

in comments addressing the possible direct disposal of fossil fuel CO_2 in the ocean (Brewer et al., 1999), noted that "[o]xygen transport proteins of deep sea animals are also highly sensitive to changes in pH." In the context of carbon capture and storage in the ocean, as first advanced by Marchetti (1977), Caldeira et al. (2005) reported that "[a]cute CO_2 exposure causes acidification of the blood, will hamper oxygen uptake and binding at the gills and reduce the amount of oxygen carried in the blood, limiting performance and at high concentrations could cause death." Thus, it seems wise to investigate the problem of animal export of CO_2 within the same physical framework of a boundary layer gas exchange process as we do for import of O_2.

Hofmann et al. (2013b) tackled this problem, with the physical description of the external boundary layer and its relationship to flow over the surface remaining the same. The key difference

lies in the chemical reaction rates. Dissolved O_2 is inert during its diffusive transport through the boundary layer and into the animal tissue, but the CO_2 molecule exported from the animal tissue surface is highly reactive with water. The reacto-diffusive equations describing this process can be complex. In completing a thorough analysis of this problem, Hofmann et al. (2013b) found that very useful simplifications can be made in a manner analogous to those described by Emerson (1975) and Zeebe and Wolf-Gladrow (2001).

The essential argument is that upon transfer of the free CO_2 molecule from the tissue to the surrounding seawater, a chemical reaction initiates, forming bicarbonate ion. Although the reaction rates of CO_2 with water are notoriously slow at low temperature and typical seawater pH, the rates are not zero. Some CO_2 is consumed, slightly lowering pCO_2 at the tissue's outer surface. The pCO_2 difference across the boundary
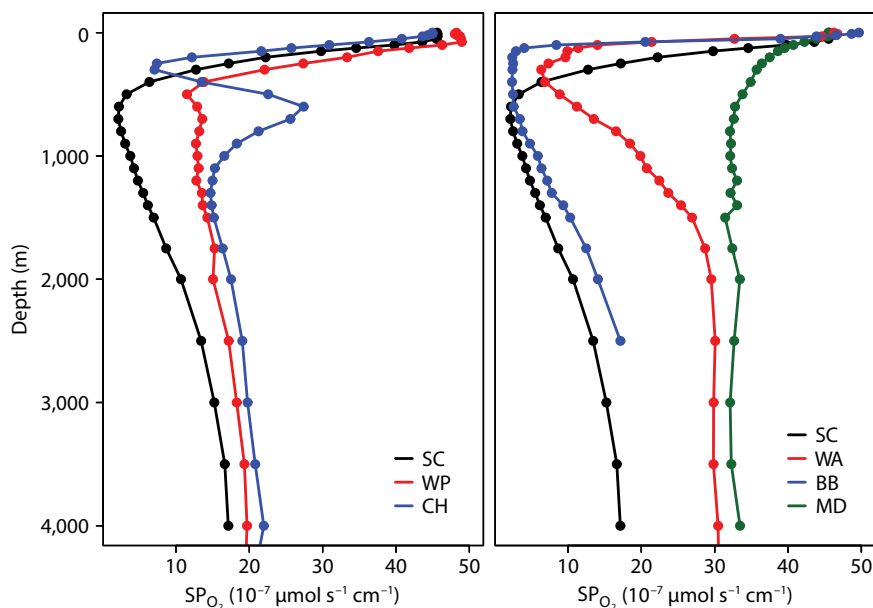

Figure 2. Oxygen supply potential SP$_{O_2}$ depth profiles of the water column at different hydrographic stations around the world. SC = Southern California (29.5°N, 120.5°W). CH = Chile (33.5°S, 75.5°W). WP = Western Pacific (11.5°N, 126.5°E). WA = Western Africa (15.5°S, 6.5°E). MD = Mediterranean (35.5°N, 18.5°E). BB = Bay of Bengal (18.5°N, 87.5°E). *From Hofmann et al. (2013a)*

layer provides the chemical driving force, and this reaction steepens the diffusional gradient, enhancing the outgoing flux. The simplest way to describe this process is by encapsulating the complex of chemical variables into a dimensionless Enhancement Factor (EF),

$$\text{EF} = \frac{E^{CO_2}}{E_{diff}^{CO_2}} = f(L^{CO_2}, T, S, P, \text{pH}_{free\ scale})$$

where E^{CO_2} represents the true CO_2 flux, including the effects of chemical reactions, and $E_{diff}^{CO_2}$ is the hypothetical diffusive flux that would occur if CO_2 were not chemically reactive in seawater.

The net result is that the diffusive efflux of respiratory CO_2 is always physically faster than the equivalent O_2 influx. Even with very high external oceanic p CO_2 conditions, this relationship will remain true. Put simply, while it is clearly physically possible for a marine animal to increase access to dissolved O_2 by increasing the flow over its surface,

it would be very difficult to rid itself of excess CO_2 by this tactic, as the efflux is not diffusion limited. Internal pH compensation would be a better strategy. In practice, deep-sea animals have evolved significant internal pH/CO_2 compensating mechanisms. It is logical to think that this may be due to the limitations posed by the external ocean boundary reacto-diffusive chemistry.

DISCUSSION

Physico-chemical processes based on temperature, hydrostatic pressure, and boundary layer effects play a significant role in defining the accessibility of O_2 for marine organisms.

The combination of varying temperature and depth with oceanic O_2 concentrations via fundamental rules such as Henry's Law and diffusion rates provides us with a fresh look and allows a more formal estimate of possible climate

change effects. For example, the very deep sea appears to be sufficiently well oxygenated that only quite small impacts may occur.

The intermediate-depth O_2 minimum zones appear more threatening than ever. Here, we find that the quasi-exponential decrease of temperature with depth (cf., Wyrtki, 1962) creates a zone where diffusion coefficients are low, making O_2 uptake more difficult; however, with the increase in pressure occurring only quasi-linearly, very little of the p O_2 pressure boost has occurred at these depths. This combination of significantly lower temperature, and only modestly increased pressure, when combined with the very low O_2 levels, creates a zone of O_2 stress significantly greater than that implied by concentration alone. ✍

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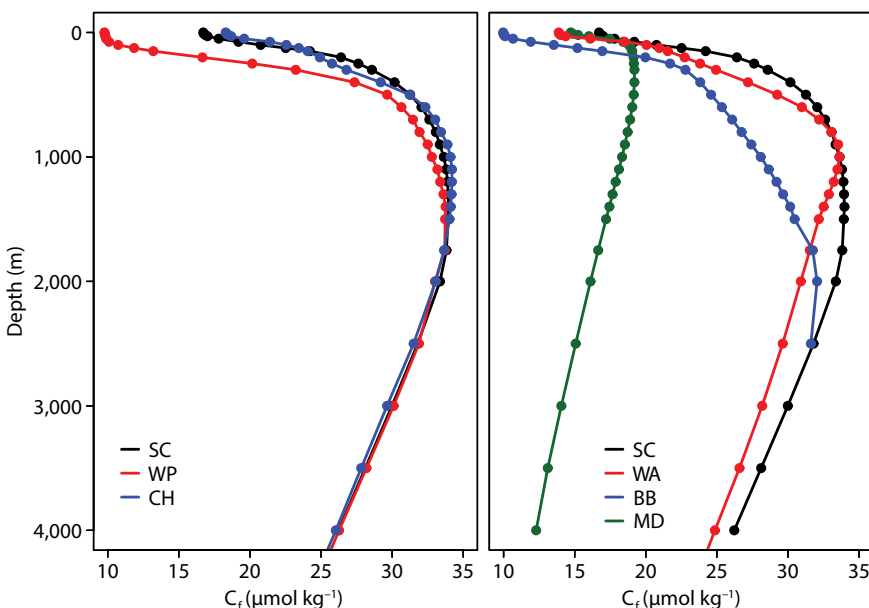
Figure 3. An example of the effects of temperature and pressure with depth—the minimal oxygen concentration (C_f) a given animal needs to survive (for an exact definition of C_f, see Hofmann et. al., 2013a). Depth profiles of the water column are from different hydrographic stations around the world. SC = Southern California (29.5°N, 120.5°W). CH = Chile (33.5°S, 75.5°W). WP = Western Pacific (11.5°N, 126.5°E). WA = Western Africa (15.5°S, 6.5°E). MD = Mediterranean (35.5°N, 18.5°E). BB = Bay of Bengal (18.5°N, 87.5°E). A generic flow velocity of u100 = 2 cm s^{-1} is assumed for all depths.

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