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GRAND CHALLENGES CENTENNIAL COLLECTION

The Molecular Basis for Understanding the Impacts of Ocean Warming

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Abstract A grand challenge for ocean chemists in the years ahead lies in the need to tackle the chemical consequences of ocean warming with the same rigor and intensity that has been brought to bear on the physical chemistry of ocean acidification. For over 50 years ocean chemistry has been dominated by the study of pH-dependent processes, but to address the biogeochemical impacts of ocean warming, we will need to rapidly advance the discipline of ocean chemical physics where temperature is the master variable and the basic unit is the Joule. Just as it would be impossible to understand the ocean CO_2 system without awareness of the essential pH-dependent CO_2-HCO_3-CO_3 equilibria, so too is it impossible to describe ocean chemical physics without knowledge of the bimolecular structure of water. Water, and water in sea water, is composed of a complex of dominant hydrogen bonded forms, and the singlet molecular H_2O species, in temperature-controlled equilibrium and the ratio of these forms, can now be precisely determined. The physical properties of sea water are traditionally described by fitting an ad hoc collection of coefficients to experimental data. They are more accurately described as temperature and pressure perturbations of the underlying molecular equilibrium state. Ocean oxygen consumption rates are accurately described as an Arrhenius function, and not as an exponential function of depth as has been the tradition for over 50 years. We do not now have good correlation between ocean models and observed warming and oxygen declines, and full anoxia with the emergence of hydrogen sulfide over large regions of the ocean is possible. The parallel ocean invasions of heat and fossil fuel CO_2 must be combined to estimate their full impact.

Plain Language Summary The ocean absorbs some 93% of all greenhouse gas-generated heat, and ocean warming is already creating observable impacts on marine life. To make reliable projections for the future, we cannot rely on Ptolemy-like rules, built as something to match field observations, to apply in the years to come. Instead, we will need to apply the laws of chemical physics to calculate and predict the changes that ocean warming will have on the physical properties of sea water and the associated impacts on marine life. This includes treating water as a fluid with defined temperature- and pressure-dependent chemical structures. Sea water is 96.5% water, and some 78–85% of water in the oceans has a form with a much higher molecular weight than the water molecule that typically comes to mind, with a single oxygen and two hydrogens. These varied structures are now directly relatable to the high heat capacity of water, why the speed of sound is faster in warmer water, and the viscosity of sea water that provides constraints on microbial motion. Microbial activity is a key driver to the amount of oxygen in different parts of the ocean, and if their activity is affected by increased warmth, it seems quite possible that large regions may exist with no oxygen at all. Marine life responds strongly to changing oxygen status. This is because both warmer waters can hold less oxygen, and because warming drives higher rates of microbial growth. Marine fisheries, and the great majority of all marine species, are already responding to these forces and are migrating toward cooler waters near the poles. Using known laws of science to connect chemistry, physics, and ocean warming would allow the ocean sciences to proceed on firmer footing and to improve future projections of the impact of ocean warming. The ocean is now experiencing the twinned invasions of heat and fossil fuel carbon dioxide that drive up its acid level. It is the combined impact of these two great waves, both resulting from our use of fossil fuels, that will be critical, and right now the correlations are not well known or examined.

Key Points:
- Ocean warming will increase rates of ocean oxygen consumption with impacts on marine life
- Ocean heat capacity is directly related to water molecular structure
- The basic discipline of chemical physics can be applied to these problems with considerable certainty

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1. Introduction

For well over 50 years the study of ocean chemistry has been dominated by the principles of pH-driven chemical equilibria—a branch of solution physical chemistry. This has proven to be a powerful tool, and it has been hugely successful. It is the most teachable form of ocean chemistry, and this approach dominates text

books in the field (Canfield et al., 2005; Stumm & Morgan, 1996)—but it provides an inadequate basis for what we will need to know in the decades ahead as ocean warming comes to the fore. In brief, we will need to add another string to our bow with rapid development of the parallel discipline of ocean chemical physics.

To the casual observer, the simple reversal of two words—chemical physics as opposed to physical chemistry—may seem to be a trivial matter, but it is not. The present-day pattern was established by critical papers in the early 1960s, born of the stimulus provided by the International Geophysical Year, which was created to repair international Earth science after the devastation of World War II.

In 1959 Sillén presented his paper on "The Physical Chemistry of Sea Water" at the First International Oceanographic Congress (Sillen, 1961) noting the "precarious" poise of sea water pH. There too Broecker et al. (1961) presented an early account of the use of box models calibrated by the first measurements of radiocarbon and tritium so as to estimate residence times of water masses. Some 50 years of oceanic CO_2 and tracer science were to follow, and the results have been invaluable.

Bolin (1960) presented the first authoritative account of the details of air-sea CO_2 exchange calculating the effect of the buffer capacity of sea water in responding to atmospheric CO_2 input. These concepts were then quickly tested with small adventures at sea (Dyrssen, 1965; Takahashi, 1961) leading directly toward a full half-century of related expeditionary work. Garrels and Thompson (1962) presented the first detailed account of the speciation of the major ions in sea water. Interestingly, it was Garrels the geologist who tackled the chemical details of major ion speciation, and it was Sillén the academic chemist who tackled the broad picture of the Earth balance of the acids released by volcanoes and the bases liberated by the weathering of silicate rocks.

It would be hard to overestimate the enduring impact of these papers, which, when coupled with the 1957 climate/CO_2 warning publication (Revelle & Suess, 1957), addressed the critical role of the oceanic CO_2 system and established pH as the master variable for ocean chemistry. These very early efforts underlie essentially all the modern work on ocean acidification today, and this has been carefully tracked in a recent historical review (Brewer, 2013). Few ocean chemists today are aware of how strongly, and narrowly, their careers have been guided by these early papers.

But the parallel problem of ocean warming is not well addressed within this framework, and the lack of tools for this is now striking. Ocean chemists have become so strongly focused on the invasion of fossil fuel CO_2 that the impacts of changing temperature have been relatively ignored. This stands in marked contrast to terrestrial science where large effects on ecosystems are quickly emerging, and early views of a possible benefit from plant CO_2 "fertilization" have largely disappeared. For comparison, while the ocean today annually absorbs some 25% of mankind's CO_2 emissions to the atmosphere (Ciais et al., 2013), it absorbs an astonishing 93% of all the heat trapped by the accumulated greenhouse gases (Rhein et al., 2013).

The accumulation of heat within the ocean is directly observable (Abraham et al., 2013; Cheng et al., 2017), just as is the accumulation of anthropogenic CO_2 (DeVries, 2014; Gruber et al., 2019; Khatiwala et al., 2013), and this is now driving significant changes in ocean biogeochemical properties. It is the combination of these factors that will drive changes in the ocean of the near future.

Changes in ocean pH are having impacts on aragonite shell forming animals and coral reef systems (Gattuso & Hanson, 2011), and the physical chemistry basis for this is now well understood. But the impacts of ocean warming are far larger and are driving ocean oxygen losses (Shepherd et al., 2017). Ocean warming increases chemical rates of all kinds—diffusive, metabolic, and so forth—and the laws governing this are well known. It is not that ocean chemists have neglected temperature terms but that far too often these are ad hoc fits of temperature in degrees Celsius rather than the application of even the simplest laws of chemical physics. Economically critical fisheries are well observed to be moving poleward at a remarkable rate (Murawski, 1993; Perry et al., 2005) driven by temperature with consequences for food security; the impact on overall fisheries production is still uncertain (Free et al., 2019) but tends to be negative. The scientific challenge here is that these are retrospective observations—the fish, and the food they eat, migrate poleward, and the change is then documented. The case for North American fisheries is best observed and reported, but very similar migrations must be occurring in other regions, and the challenge of observing and prediction is a worldwide problem. Ocean warming also results in the poleward migration of prokaryotes, often carried by host species, such as the vibrios, and with it observable human health impacts (Vezzulli et al., 2016).

Poleward migration of the great majority of marine species, driven by temperature, is highly likely, and early documentation of this is reported by Poloczanska et al. (2013).

Projections for fisheries shifts on the North American continental shelf have been made (Morley et al., 2018) with mixed results. But the end game is not known, and there is in general no useful forward prediction. Scientists tend to see complexity, but the fisheries industry needs clear answers, and these concerns have been well voiced. Hotz (2018) succinctly described the problem in an article in the Wall Street Journal: "Higher temperatures mean less dissolved oxygen in the water while increasing a fish's demand for oxygen by speeding up its metabolism." We thus have the unusual situation where journalists invoke the principles of chemical physics, whereas scientists rely on statistical correlations. We will need to provide answers, and make valid predictions, in scientific terms.

For ocean physical chemistry the master variable is pH, the characteristic diagram is the Bjerrum plot, and calculations are based on the activity of an ion; pH electrodes are an essential experimental tool. For ocean chemical physics the master variable is temperature, the characteristic diagrams are the van 't Hoff and Arrhenius plots, and the basic unit is the Joule; lasers are the essential tool for identifying the molecular structures.

The discipline of chemical physics is a far better match to ocean physics and biology, although great care will be needed and we are now only at the very early stages. At this time it is possible only to briefly sketch out what directions this might take as new minds go to work, and new tools become available. This paper is not a comprehensive review but a look forward, and I provide only a very brief set of the challenges and possibilities here.

2. Ocean Warming and the Structure of Water in Sea Water

An outsider entering our field would surely at first be puzzled by the near universal adoption of a Ptolemy-like approach to ocean warming where coefficients (typically in degrees Celsius) are fit to data to achieve a superficially satisfactory fit, but without understanding the underlying molecular basis. The challenge for ocean chemists is to move beyond this.

Climate change and the transfer of some 25×10^{22} J of heat to the ocean since 1960 (Cheng et al., 2017) have resulted in sea level rise due in large part to the thermometric expansion of sea water. The molecular description of this is not well represented in our field, nor is the molecular basis for the high heat capacity of water. The expansion of water arises not just from the normal increase in the translational energy of the molecules but also from the breaking of hydrogen bonds and a change in water speciation. Understanding of this is essential for accurate representation of the changes taking place.

Just as it would be very difficult to understand ocean CO_2 chemistry if one was not aware that sea water contained HCO_3^-, CO_3^{2-}, and CO_2 species in pH-dependent equilibrium, so too is it very difficult to represent the physical properties of water if one is not aware that it is composed of the single H_2O molecule and a complex of hydrogen-bonded (HB) forms in temperature-dependent equilibrium. For sea water a third form of water in singlet form in the solvation shell around a cation is present, unaffected by temperature. The challenge is to correctly represent the changing physical properties of the ocean on a firm molecular basis.

The chemical speciation of ions in sea water has long been studied by ocean chemists (Millero, 1974), but sea water is 96.5% water, and the details of the speciation of the water molecules themselves have essentially been neglected by ocean scientists. The aqueous fluid is typically treated simply as a collection of bulk property coefficients with the primary function being as a medium for the dissolution of salts and gases.

It has long been known (Walrafen, 1964) that water exists in a temperature-controlled dynamic equilibrium between the HB and non-hydrogen-bonded (nHB) forms. Some 78–85% of water in sea water exists in the HB form (Brewer et al., 2018), primarily as the tetrahedral pentameter $(H_2O)_5$ (Walrafen, 1964; Figure 1). The ratio of these forms is accurately represented as a van 't Hoff function (Brewer et al., 2018; Carey & Korenowski, 1998; Smith et al., 2005).

The details of what we refer to here as the HB forms are notoriously complex since a complicated field of many species is always present. This should not be disturbing: In ocean CO_2 chemistry, the conventional phrase "carbonate ion" is commonly used when in fact CO_3^{2-} exists in a large assemblage of ion pair forms.

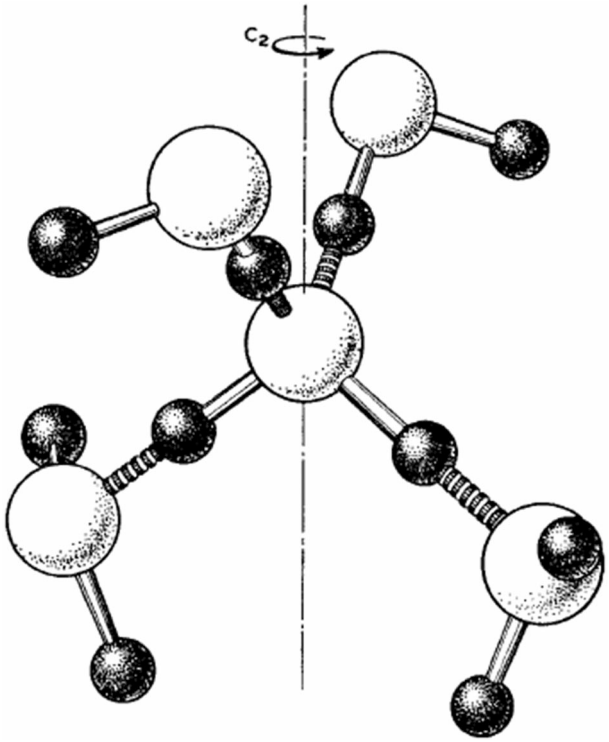

Figure 1. The original depiction of the compact tetrahedral water pentamer showing the dominant hydrogen-bonded structure (Walrafen, 1964). Some 78–85% of water molecules in the ocean exist dominantly in this form but also in a complex of related HB clusters (Keutsch & Saykally, 2001). These are in a rapidly exchanging thermal equilibrium with the single H_2O (non-hydrogen-bonded) species.

One description is that by Kumar et al. (2007), who report their results as "consistent with the traditional idea that water is highly disordered, but with more or less tetrahedral local symmetry, with at least 3 H bonds per molecule, some of which are stronger than others, and a majority of water molecules are double donors."

The relationship to sea level rise is that the pentamer form, favored as the local energy minimum state with decreasing temperature, is the most compact form of the water molecular structure possible; it hugely reduces the polarity compared to the strongly polar single nHB form. In warmer waters the fraction of the compact $(H_2O)_5$ molecule is reduced, adding to the expansion of the fluid.

The parallels with the well-known pH-dependent equilibria between carbonate and bicarbonate ions are clear, and the equilibrium constant between the HB and nHB forms can be written out (Brewer et al., 2017; Carey & Korenowski, 1998) as

$$(H_2O)_{HB} \leftrightarrow (H_2O)_{nHB},$$

where $K = [H_2O]_{nHB}/[H_2O]_{HB}$,and $d\ln(K)/d(1/T) = -\Delta H/R$, where R is the ideal gas constant.

The enthalpy of the hydrogen bond is close to 2 kcal/mol (Silverstein et al., 2000; Smith et al., 2005).

This speciation is clearly seen in Raman spectra of sea water (Brewer et al., 2018) where the spectral band between 2,800 and 3,800 cm^{-1} contains information on the stretching modes of principal water species. This spectral band can be deconvolved into five components, each with a specific vibrational assignment (Figure 2).

These spectra can now be observed on an expeditionary basis (Brewer et al., 2017, 2018; Zhang et al., 2012). For pure and for sea water, the temperature-driven equilibrium between the HB and nHB forms is the primary driver of physical changes, and these HB and nHB forms play very different roles. It is the single molecule nHB form that exchanges with the atmosphere and drives mineral dissolution. The HB forms are responsible for the surface tension, compressibility, viscosity, and speed of sound in sea water. The vastly greater fraction of water in the ocean, some 78–85%, is in the HB form. Under the extreme high-temperature and high-pressure conditions of hydrothermal vents, remarkable in situ Raman data show extraordinary enrichment of the nHB form (Li et al., 2018) that must drive enhanced water-rock interactions.

For ocean science we have to consider salinity and pressure effects. The effect of the salts, dominantly the cations, is to sequester water molecules in the solvation shell around an ion. Typically six water molecules are arranged around each cation held by dative covalent bonds. These water molecules are not HB nor are they free; they are loosely bound and appear in Raman spectra as not well resolved from the nHB singlet molecule peaks. The quantity in the solvation shell is not affected by temperature or pressure—it is simply a linear function of the quantity of salts present. One of the challenges for ocean chemists is to provide a better description of the cumulative effect of the ionic solvation shells.

The effect of pressure is to force some of the dominant water pentamers into an interleaved state, with no making or breaking of hydrogen bonds, to create a local potential energy minimum (Canpolat et al., 1998). This molecular equilibrium exerts the fundamental control on the physical properties of water/sea water under pressure.

2.1. The Physical Properties of Sea Water

The compendium of bulk fluid physical properties of sea water that we have today is typically presented as a lengthy string of coefficients, represented in the Equation of Seawater (TEOS-10) as a Gibbs function (IOC et al., 2010), but with no clear molecular basis. For example, the speed of sound in sea water may be

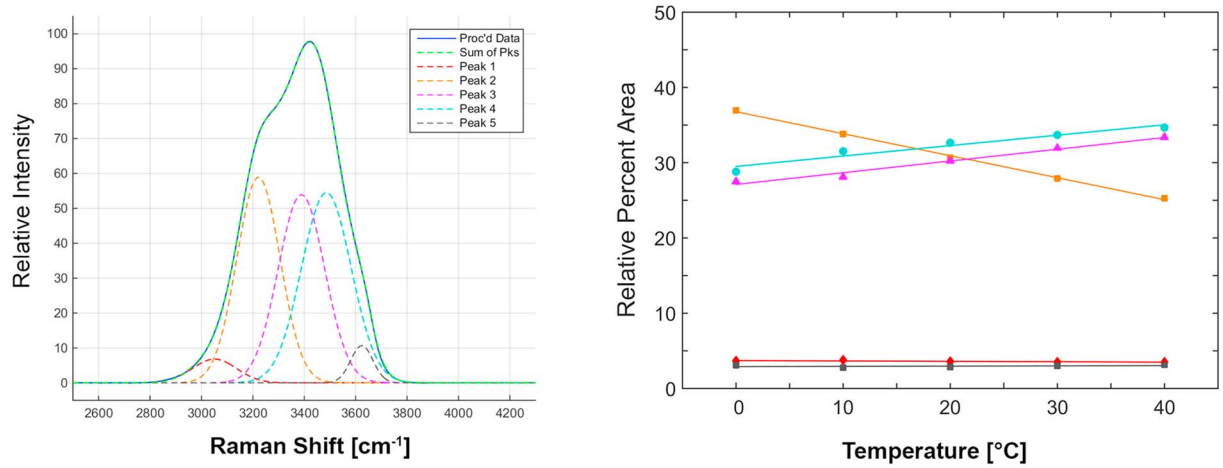

Figure 2. Left panel: the Raman spectrum of seawater deconvolved into its five component peaks. Right panel: the effect of increasing temperature showing the rise of the single H_2O form, and the decline of the H-bonded forms. These changes follow the rule where $\ln x = 1/T$, where T is the absolute temperature in Kelvins (K), and it is likely that this provides the basic scaling law for many climate change impacts on the ocean (Brewer et al., 2018).

calculated in TEOS-10 with high accuracy from a string of 104 coefficients; but in contrast simply presenting the experimental data in the form of a van 't Hoff plot reduces this to only 28 coefficients with equal or better accuracy (Brewer et al., 2015). This is consistent with the underlying T- and P-dependent equilibrium in the structure of water in sea water, and this has now been directly observed (Brewer et al., 2017; Brewer et al., 2018).

Another example is the temperature-dependent viscosity of sea water, essential for understanding the energetics of the mobility of marine life, and particularly of microbial motility, at low Reynolds number (Purcell, 1976). Purcell's classic account dealt with the way dimensional mechanics scaled: But he did not address the chemical physics of water noting only that the viscosity of water has got “one of these activation energy things” thereby carefully avoiding any discussion of temperature.

The viscosity of sea water is not represented in the TEOS10 compilation, but experimental data do exist (Stanley & Batten, 1969) from a series of rolling ball viscometer experiments. There it was found that “(1) The relative viscosity of sea water is always greater than that of pure water at comparable temperature and pressures; (2) the pressure of minimum relative viscosity of pure water decreases with the addition of an electrolyte; and (3) the activation energies of viscous flow of sea water decrease in a uniform manner with increasing pressure and temperature.”

It is difficult to reconcile all these observations from the limited information presented since relative values are reported. But their Figure 6 shows that the estimated activation energy of viscous flow centers around 4 kcal/mol. This is consistent with the observation of Walrafen (1964) that the breaking of two hydrogen bonds is required to disrupt the water pentamer, and the 2 kcal/mol strength of the individual hydrogen bond (Silverstein et al., 2000; Smith et al., 2005). It seems very likely that the observed midwater minimum in sea water viscosity can be described in terms of water molecular structure. But that is a challenge for the future.

3. The Changing Oxygen Status of the Ocean

The most familiar example of the temperature dependence of microbial oxidation rates is in the everyday use of refrigerators to slow food spoilage. The fundamental rules have been known for well over a century (Arrhenius, 1889; van't Hoff, 1884) so that when the ocean warms, we should expect oxygen consumption rates to increase. There is considerable evidence for this, and significant ocean oxygen declines have been observed (Helm et al., 2011; Stramma et al., 2008), but the explanation for this is by no means clear cut. We should note that even the simple reduction in gas solubility of 14 μmol/kg for 2 °C warming could lead to complete anoxia in some regions where dissolved oxygen levels are already <10 μmol/kg (Brewer &

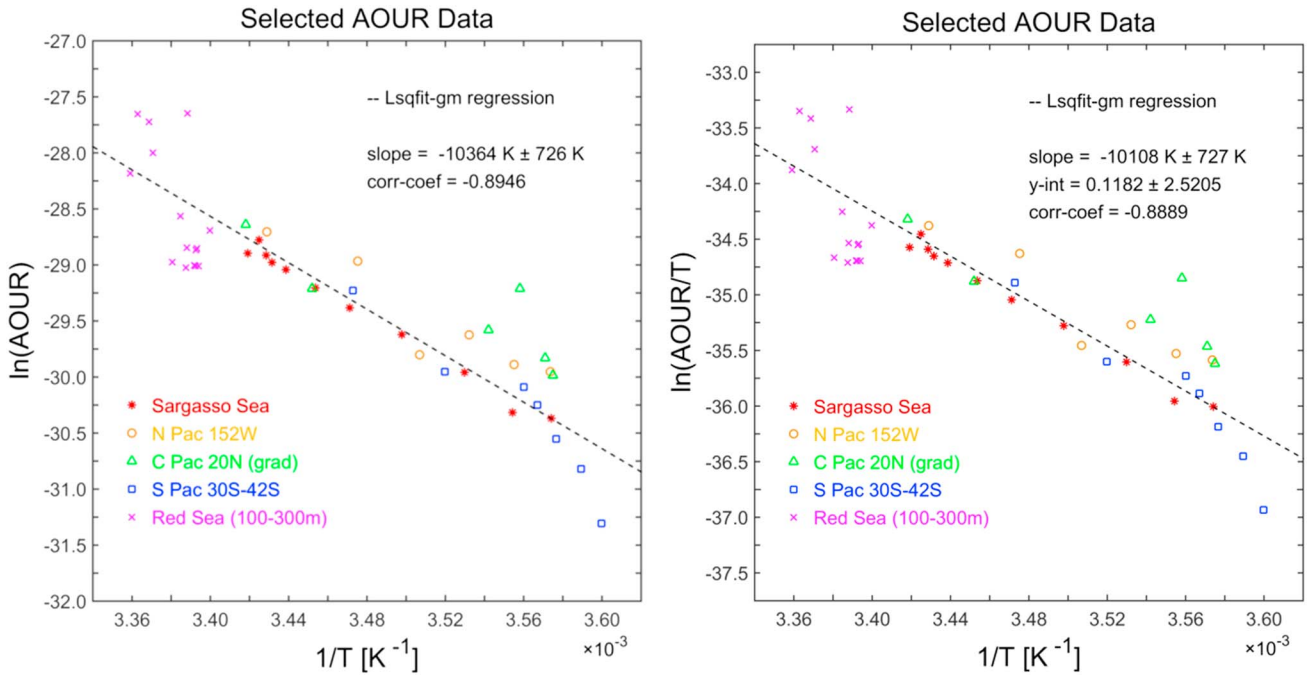

Figure 3. Compilation of all tracer-derived ocean oxygen consumption rates presented as an Arrhenius plot (left panel) and as an Eyring plot (right panel). The result yields an Arrhenius activation energy of 86.3 kJ/mol, giving a Q_{10} of 3.63. The Eyring (Eyring, 1935) plot yields a Gibbs energy of activation of 140 kJ/mol. The energy gain for organisms consuming marine organic matter is 56.5 kJ/mol (From Brewer & Peltzer, 2017).

Peltzer, 2016; Shaffer et al., 2009) and the oxidative buffer capacity of the NO_3 ion is small (Brewer et al., 2014)

It has been the tradition in the ocean sciences for well over 50 years to report observations and models of ocean biogeochemical properties and rates as a function of depth, simply as a matter of convenience (Riley, 1951; Wyrtki, 1962). Ocean oxygen consumption rates are slow, and the most reliable estimates are derived from transient tracer observations. Recent work (Brewer & Peltzer, 2016; Brewer & Peltzer, 2017) has shown that the entire database of tracer-derived oxygen consumption rates is consistent with an Arrhenius activation energy for marine organic matter of 86.3 kJ/mol (Figure 3), leading to a Q_{10} of 3.63.

There have been efforts to examine the consequences of temperature dependence of the decay of sinking organic matter within the context of existing depth based models, and weak feedback to the oceanic CO_2 system has been identified. But typically, a Q_{10} of 2 is assumed for model purposes, and the actual values are not derived. Segschneider and Bendtsen (2013) noted (astonishingly) that the temperature dependence of the decay of organic matter in the ocean "is, in general, not included in marine biogeochemistry models currently used for Coupled Model Intercomparison project Phase 5 (CMIP5) climate projections." This topic was reviewed by Shepherd et al. (2017) who noted that some hybrid models combining both temperature and depth dependent functions have now been used.

The lack of attention to a formal use of the Arrhenius equation is regrettable; in Figure 3 we show the full ensemble of published tracer-derived deep ocean oxygen consumption rates, all initially described as a function of depth, plotted as an Arrhenius function.

The reason for showing both the Arrhenius and the Eyring functions in Figure 3 is simply that the Arrhenius equation was originally developed from collision theory and concerns early arose that this might not be applicable to enzyme-based systems. Eyring (1935) in his classic paper imaginatively conceived of the link between the two fields as follows: "The activated complex has very nearly the properties of an ordinary molecule except that instead of having only the three regular translational degrees of freedom it has a fourth, along which it first approaches the barrier, crosses it, and then flies into pieces." In Brewer and Peltzer (2017) we showed that the Eyring function does provide a more tightly constrained fit to the observed ocean rates consistent with its biological nature.

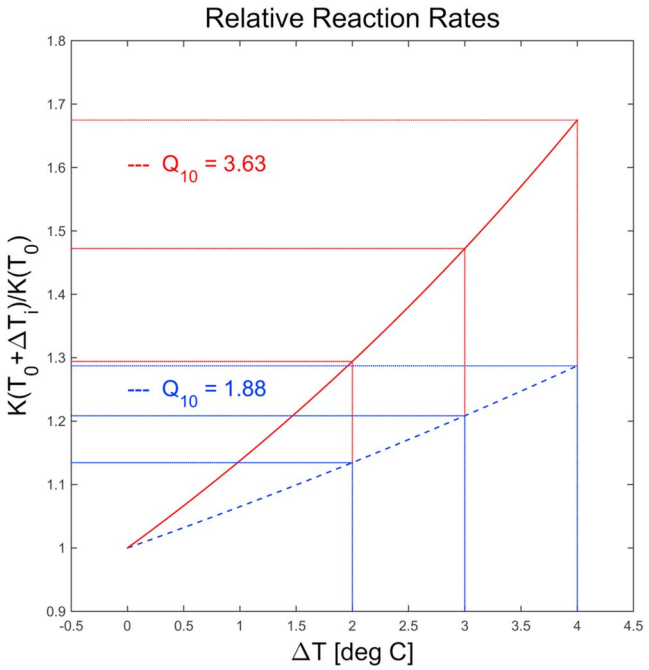

Figure 4. The impact on O_2 consumption rates for a Q_{10} of 3.63 (Brewer et al., 2017) leads to an increase 29% for 2 °C and 47% for 3 °C warming with the likelihood of widespread anoxia in large areas of the ocean at middepths. The estimate of a Q_{10} of only 1.88 (Taucher & Oschlies, 2011) leads to much lower oxygen losses

Figure 3 serves to collate essentially the entire database of tracer-derived ocean oxygen consumption rates over a vast area of the ocean and does so on a theoretically consistent basis. The Arrhenius activation energy derived is similar to that observed for the temperature-dependent decay of organic matter on land. Based on this result, ocean oxygen consumption rates could increase by 29% for 2 °C warming and by a remarkable 47% for 3 °C warming (Figure 4).

This analysis raises as many questions as it answers. The first problem we encounter is that the data are seemingly independent of the quantity of organic matter; observed ocean oxygen consumption rates are traditionally agnostic on this point. This cannot be so, and the appearance is very much as if the quantity of organic matter oxidized in the upper ocean (both dissolved and particulate) is a constant. The model of Laws et al. (2000) based on the analysis of a very large data set finds that temperature is the dominant control on organic matter export from the euphotic zone, and their result may be consistent with this finding. That is that the large variations in primary productivity are matched by equal and opposite export quantities, with a constant remaining to be oxidized in the waters of the upper ocean.

This seems far too simple to be acceptable, and the direct application of the model of Laws et al. (2000) by Siegel et al. (2014) yields upper ocean fields not compatible with current satellite observations. Marsay et al. (2015) do discuss a hybrid temperature and depth-dependent model of sediment trap data finding that "future increases in ocean temperature will likely lead to shallower remineralization of POC." Taken together the correlations with temperature strongly suggests that the rich benthic ecosystems at high latitude may increasingly be facing a reduced flux of organic matter as the ocean warms. The challenge is to place this on a firm foundation.

The second problem is that this result is in marked disagreement with a large body of microbial geochemistry studies in marine sediments (Robador et al., 2016; Sawicka et al., 2012). Here the bulk of the experimental evidence shows that microbial ecosystem rates become optimal for the temperature at which they are now established and that warming will simply be compensated for by adjustment of the population with no net change in overall rate. It may be that the time scales for the two systems—the open system of the water column and the semiclosed system in marine sediments—allow for different rules to prevail.

This same debate is played out on land in studying the temperature-dependent decay of organic carbon in soils (SOC). Many studies report a strong correlation of observed rates with a van 't Hoff-Arrhenius function (Craine et al., 2010; Lloyd & Taylor, 1994), but other models are also tested. Wang et al. (2017) report on an ecosystem model based on the Michaelis-Menten equation was used with a finding that "Continued warming accelerates the decomposition of SOC (soil organic carbon) by relieving the temperature limitation on microbial activities and the catalytic activities of intracellular and extracellular microbial enzymes."

There is now nascent evidence from long-term observations of the changing status of dissolved CO_2 in coastal ocean waters, where the rate of increase in concentration of CO_2 is well above the simple atmospheric signal (Reimer et al., 2017), suggesting that the warming of coastal regions has resulted in increased microbial respiration of sedimentary organic carbon.

The end result is that there is today a considerable disagreement between model predictions and observations of the trends in ocean oxygen concentrations (Shepherd et al., 2017; Stramma et al., 2012), and observations of microbial rates in marine sediments. The changes in ocean oxygen, beyond simple temperature-dependent solubility, reflect changes in the flux of organic matter that provide the food supply for deep sea life, and possible widespread hypoxia, and that is a matter of concern. It must also be clear that the challenges associated with the physical supply of fresh oxygen from the wind-driven circulation remain.

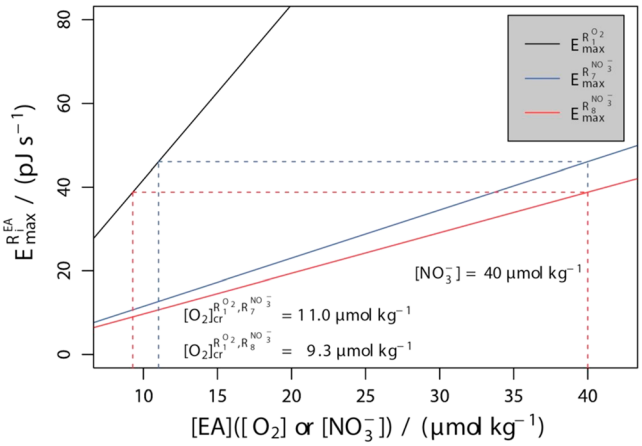

Figure 5. Graphical determination of the energy yield ratio for the microbial oxidation of marine organic matter per mole of electron acceptor (either O_2 or NO_3). The energy yield is equal at a ratio of about 3.8 NO_3 to O_2. In this case the temperature dependence of the rates cancels out due to the different diffusivities of the chemical species, and the ratio appears constant over a wide range of temperature. From Brewer et al. (2014).

What seems likely is that models based on the known temperature-dependent rules of chemical physics have a better chance of success than models based on ad hoc fits to depth profiles. But right now the gap seems large, and we have many unknowns; significant discrepancies have been noted, suggesting that the biological carbon flux, often fit simply with empirical and mechanistic models (Dunne et al., 2005), may well be more constant than current satellite-derived fields predict (Emerson, 2014).

4. The Rules of Microbial Chemical Choices

The discipline of chemical physics is well suited to addressing the challenge posed by the remarkable rise in ocean molecular biology, and the newer field deployable instruments that supply increasingly large quantities of genomic data (Scholin et al., 2017). The chemical basis for the sequence of microbial reactions that commonly occur in the ocean was clearly laid out over 50 years ago (Redfield et al., 1963) by drawing analogies with the waste water management literature. There it was stated as "The order and extent to which these steps proceed depends on the free energy available from the respective reactions and on the concentration of the reactants." One could hardly argue with such classic simplicity, but the specifics of this have rarely been tested in the ocean, and microbes can make use of extraordinarily low oceanic concentrations—it has long been known that even subnanomolar concentrations of dissolved methane are observably consumed in the deep sea (Scranton & Brewer, 1978).

A recent review of the physical basis for bacterial decision making (Kondev, 2014) directly estimated the low energy cost required for microbes to conserve options for oxidizing different or very dilute substrates where collisions may only infrequently arise. The classic example of a lag period required for the microbes to adapt to the new opportunity was examined in these terms.

In the ocean sciences we find both gradual and rapid changes present. A gradual change is revealed in the manner in which under increasing hypoxia microbes choose to use either O_2 or NO_3 to gain oxygen atoms—at some point the energy gain is equal and the reactions proceed in parallel: See Figure 5 (Brewer et al., 2014). The equivalence point is simply defined by the product of the free energy times the concentration, precisely as predicted some 50 years earlier. The rates can be examined by making use of diffusive boundary layer theory very much as in the familiar example of gas exchange rates across the sea surface; the same rules apply for gas transfer across a respiratory membrane (Hofmann et al., 2013) where under ocean warming the enhanced diffusivity of the oxygen molecule must be balanced against the loss of solubility. Here the solubility loss is the dominant effect, and organisms with high aerobic demand will migrate, or suffer, under ocean warming conditions (Poertner & Knust, 2007).

This rule is very general; it can appear odd in microenvironments where the very small scale gradients differ from concentrations in the bulk fluid (Wright et al., 2012), but microbes are excellent chemical engineers and are essentially always able to "compute" the most energy efficient chemical pathway for their immediate environment based on the mix of available resources, allowing winners to flourish.

For an example of rapid change producing an energy-driven sequence of microbial reactions, we can examine the fate of the large quantity of oil and gas released in the deep waters of the Gulf of Mexico on the occasion of the tragic April 2010 Deepwater Horizon oil spill (Ryerson et al., 2012). This event has been investigated in more detail than any other comparable spill. Here the very rapid release of some 4.1 million barrels of oil and 10^{10} moles of natural gas at 1,500-m depth overwhelmed the local microbial population, which then had to adjust to the new circumstance leading to boom and bust. The time course of microbial respiration from this event was followed both by direct observation (Du & Kessler, 2012), and by stable isotope analyses. The rise and fall of methanotrophy was carefully documented by Crespo-Medina et al. (2014). But again we do not have the temperature-dependent rates of the event determined.

For an example of lag times in an ocean microbial population sensing changing chemical energy opportunity, we can examine the elegant laboratory simulation of the Deepwater Horizon oil spill event by Hu

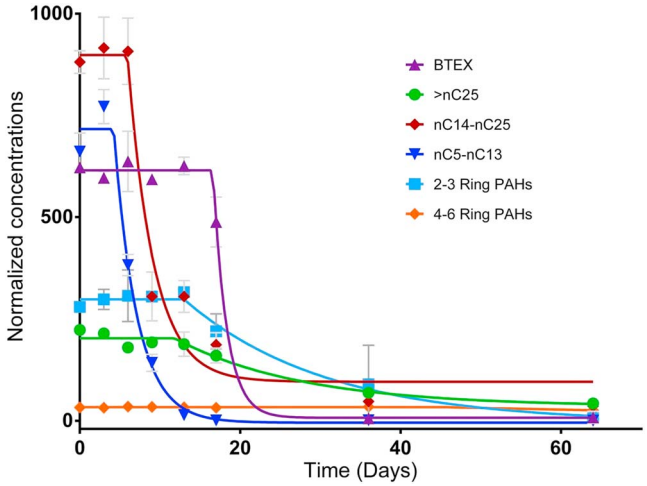

Figure 6. From Hu et al. (2017). Degradation of Deepwater Horizon oil components in a laboratory experiment, with concentrations normalized to the recaltricant biomarker 30αβ-hopane. The acronym BTEX refers to benzene-toluene-ethylbenzene-xylene. The data are fitted to a model of one-phase decay from a plateau after a lag period. The results show degradation of linear alkanes first, with four to six ring polycyclic aromatics last. The sequence is clearly dictated by ease of oxidation as defined by the activation energies, although these were not defined here, nor is the temperature dependence found.

et al. (2017). Here the changes occurring over a 64-day period in a series of stainless steel vessels containing sea water collected from the site and maintained at in situ temperature were followed both for the genomic patterns and the changing quantity of hydrocarbons present. Their results are shown in Figure 6.

Ocean scientists have typically been shy of carrying out incubation experiments due to concerns over wall effects, but the clear success here suggests that new approaches may yield useful results.

Of particular interest is the question of how genomic information may be transferred to ocean numerical models. The sequence of degradation events appears to be consistent with assumptions as to the likely activation energies as the chemical species most difficult to oxidize are the last to be consumed. But the primary focus in the publication by Hu et al. (2017) is on the genomic identification of the microbial species present. The available energy and temperature dependence, essential for prediction of events in other oceanic regions, is not given, and genomic information alone does not translate into numerical ocean model predictions—the essential translation can only be provided by knowing the chemical energetics. Plainly, there is room for much greater interaction of ocean chemical physics with the burgeoning field of molecular biology.

It should be plain that microbes do not crudely "burn" methane and associated hydrocarbons in a heat engine as we do; there we are lucky if a thermal efficiency of 40% is approached.

5. Convergence: Combining the Twin Invasions of Heat and Fossil Fuel CO_2 Into the Ocean

Considerations of the consequences of the twinned invasions of heat and fossil fuel CO_2 into the ocean are by no means exclusive or separate—although today we have the appearance of two allied armies marching in parallel, yet convergence is hugely desirable. It is now commonplace in IPCC reports to express concern over "multiple stressors," yet the two major stressors are rarely combined in any direct way.

The papers assessing the regional signal of the oceanic invasion of heat typically do not cite the literature on the related invasion of fossil fuel CO_2, yet both derive from the same atmospheric phenomenon. Of the two it is the fossil fuel CO_2/pH anomaly that is now the easier to detect, and from tentative beginnings (Brewer, 1978) very detailed mapped fields are now available (Byrne et al., 2010) where even regional decadal changes are documented, and global maps are now available (DeVries, 2014; Khatiwala et al., 2013).

The maps arising from the assessment of the ocean heat anomaly are typically presented in different formats than those of the ocean CO_2 fields (Abraham et al., 2013; Cheng et al., 2017), and direct comparison is not easy. Changing temperature gives rise to changing density with dynamical consequences, whereas the changes in density created by fossil fuel CO_2 invasion are small (Brewer, 1997); fossil fuel CO_2 is a passive tracer, and the related heat anomaly is not. Nonetheless, the rise in atmospheric temperature and the rise in atmospheric CO_2 are broadly coupled—that is, the essential basis for all anthropogenic-driven climate change arguments; but the relative oceanic input functions are not well known. In general, the entire surface ocean responds to these forcings, but the regional differences in heat flux and CO_2 flux are considerable. It is odd that it has not been well examined how closely these two fields are correlated, or the degree to which the passive tracer of the fossil fuel signal can serve as a proxy for the far more dynamic invasion of heat. This would seem to be a high priority, for it is the combined impacts of changing temperature and pH that will be of the greatest concern.

6. Conclusions

It is possible here only to provide a brief sketch of the challenges ahead, but all have a similar theme in that there is a basis in quite simple chemical physics for relating ongoing ocean warming to fundamental

processes of interest to ocean chemists. It is disturbing to report that the habit of reporting chemical rates as a function of depth has now endured for over 50 years. This should not continue; temperature and time are the critical physical variables, and they should not be conflated as an ad hoc function of depth if we wish to have reliable predictions of the future.

There are many examples of the combined impacts of ocean warming and ocean acidification—coral reef bleaching is driven by ocean warming, and carbonate dissolution is driven by diminished carbonate ion concentration. But while we have a fairly accurate picture of the manner in which pH changes drive mineral dissolution, the mechanism underlying the critical temperature at which corals expel their zooxanthellae and become bleached is poorly known. With the increasing urbanization of our coasts prediction of the fate of introduced chemical species is needed, and very often the rates are critically temperature dependent and microbially mediated. None of this will be easy, and in particular, the gap between microbial studies and ocean physics seems unusually large. If ocean chemistry is to provide a linkage, then some very careful experiments will have to be done and reported on a sound physical basis.

Most puzzling has been the lack of convergence of the twin studies of the penetration of fossil fuel CO_2, and the penetration of greenhouse gas-driven heat, into the ocean. Both are driven by atmospheric forcing and are occurring contemporaneously with a slight Northern Hemisphere bias. It is very likely that these two fields are reasonably well correlated and both the correlations and the deviations will be important. One should also mention the imminent loss of information from chemical transient tracers—^{14}C, ^{3}H-^{3}He, and the CFCs—that have done so much to inform us of ocean residence times and rates over the last 50 years. These declines are not temperature dependent but simply result from the passage of time and the dilution and flattening of the signals. A further challenge for ocean chemists will be to derive new tactics to gain essential rate information as the 21st century evolves.

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