

tants and react faster than expected on the basis of bulk solution concentrations of the reactants. Thus, CDOM is a microreactor that enhances the reactivity of a molecule by bringing it into close association with a very reactive intermediate.

Latch and McNeill now demonstrate that hydrophobic molecules bound to CDOM encounter much higher concentrations of singlet oxygen produced photochemically from CDOM by light in the solar spectrum. A probe that is essentially completely bound to CDOM reports a $^1\text{O}_2$ activity that is more than 100 times the average concentration encountered by hydrophilic furfuryl alcohol. The environmental significance of this finding is that a hydrophobic molecule that is only 10% bound to CDOM will still encounter a $^1\text{O}_2$ activity that is 10 times the average concentration in the whole solution. Therefore, the potential for degradation of compounds susceptible to reaction with $^1\text{O}_2$ is much greater than expected on the basis of experiments with furfuryl alcohol. Latch and McNeill introduce a model for distribution of $^1\text{O}_2$ and find that it is limited to the CDOM matrix and to a "corona" that extends out a few nanometers from each CDOM molecule. Thus, it appears that most of the solution contains essentially no $^1\text{O}_2$. The concept of a corona predicts enhanced reactivity not only of hydrophobic compounds but also of cations such as protonated amines attracted to the net negative charge of DOM. Blough (3) in fact

observed this to be the case for cationic nitroxides reacting with photochemically produced radicals.

The localized nature of these reactions leads to quantitative differences from results expected for a homogeneous solution. Hydrophilic scavengers of $^1\text{O}_2$ or other reactive intermediates have little affinity for the DOM matrix and therefore have a low probability of being present where $^1\text{O}_2$ is formed. Thus, they are much less effective at interfering with the reaction of a hydrophobic molecule than would be expected in a homogeneous water solution. Latch and McNeill demonstrate this for azide ion, which has little quenching effect on the intra-DOM reaction, and also for D_2O , which promotes reaction in homogeneous solution by stabilizing $^1\text{O}_2$ but has no promotional effect on the intra-DOM reaction. Conversely, a hydrophobic scavenger (β -carotene in this case) is much more effective than expected. However, molar concentrations of hydrophobic compounds in natural waters tend to be much lower than the concentrations of DOM, leaving most of the DOM molecules unoccupied. Consequently, substantial quenching of intra-DOM reactions by hydrophilic or hydrophobic scavengers is unlikely under normal environmental conditions.

Latch and McNeill use custom-made probe molecules that are ideal for these types of studies. Hydrophobic molecules are difficult to work with in water solution because of their low solu-

bility and tendency to attach to surfaces. By measuring the chemiluminescence of the reaction product, the authors are able to achieve very low detection limits on small subsamples. This helps to minimize spurious results from molecules attached to the container wall that might be included if the entire solution was extracted. They are also able to observe production of a product rather than disappearance of a reactant, which greatly aids monitoring slow reactions that can still be important in the environment.

Intra-DOM reactions have received little attention, but as the present work demonstrates, they may be important photochemical mechanisms for transformation of organic chemicals in the environment. This has recently been shown to be true for intra-DOM reaction of the insecticide mirex in Lake Ontario (5), and is likely to be so for other compounds and other systems as well.

References

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EVOLUTION

Tracing Oxygen's Imprint on Earth's Metabolic Evolution

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Life on Earth created, and is dependent on, nonequilibrium cycles of electron transfers involving primarily five elements: hydrogen, carbon, nitrogen, oxygen, and sulfur (1). Although biophysical and biochemical reactions catalyze specific electron transfers at a local, molecular level, the metabolic consequences are global. Through opportunity and selection, metabolic pathways evolved to form an interdependent, planetary "electron market" where reductants and oxidants are traded across the globe. The exchanges are made on a planetary scale because gases, produced by all organisms, can be transported around Earth's surface by the ocean and atmosphere. Exactly how these five elements came to form an electron market

place remains largely unresolved, however. On page 1764 of this issue, Raymond and Segrè (2) use an ingenious bioinformatics approach to reveal the evolution of metabolic pathways. Their analysis elegantly reveals not only the profound role that molecular oxygen (O_2) has played in shaping the electron market place, but also the evolutionary constraints on, and trajectories of, the ensemble of electron traders.

Before the evolution of free O_2 ~2.3 billion years ago (3, 4), there was a glut of reducing equivalents on Earth's surface. The first traders consumed electrons from the large populations of potential donors, including H_2 , H_2S , and CH_4 (5). These electrons, extracted either with the release of energy or with the aid of low-energy (infrared) solar photons, were sold at relatively low energy prices to acceptors such as CO_2 and, to a lesser extent, SO_4 . Although there was a very large pool of an alternative electron acceptor, N_2 , considerable metabolic energy is required to reduce the gas to NH_3 at physiological tempera-

As oxygen built up in Earth's atmosphere during the Precambrian, organisms evolved more complex biochemical networks. This expansion made feasible oxygen-dependent metabolisms that coopted parts of preexisting anaerobic ones.

tures. Over the first 2 billion years of Earth's history, the electron market evolved to produce a well-structured set of metabolic pathways distributed among groups of interconnected anaerobic microbes, each selected to conduct one, or at most a small subset, of redox reactions. Because of the relatively large investment in energy to oxidize water, the biggest electron-donor pool, H_2O , remained biologically inaccessible.

When and how the first photosynthetic organisms evolved that were capable of oxidizing water to oxygen remains one of the great mysteries in the evolution of life on Earth (6). However, between ~3.2 and 2.4 billion years ago, either through progressive gene duplication events and selection, or by massive lateral transfer of genes, or both (7, 8), an organism emerged that was capable of extracting four electrons from two molecules of water to form free O_2 as a metabolic waste product. This waste product proved not only highly useful as an electron acceptor, but also potentially damaging to the intricate metabolic

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