# Organic matter photochemistry: Singlet oxygen precursor lifetimes

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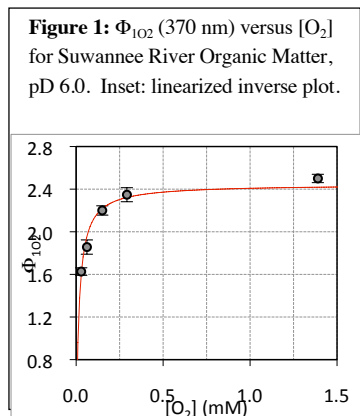
Background

Dissolved organic matter (DOM) photochemistry plays a key role in pollutant fate and carbon cycling [1, 2]. Central to this are various reactive intermediates whose production and reactions can alter the DOM. These include $^1O_2$, O_2^- and H_2O_2, e (aq)$^-$, •OH, and triplet DOM states ($^3DOM^*$) [3]. Various evidence suggests that $^3DOM^*$ is the $^1O_2$ precursor.

$$^1DOM + h\nu \rightarrow {}^1DOM^* \rightarrow {}^3DOM^* \qquad (1)$$

$$^3DOM^* + {}^3O_2 \rightarrow {}^1DOM + {}^1O_2 \qquad (2)$$
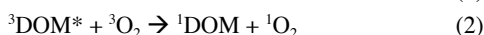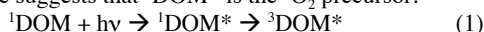
Intersystem crossing from the excited singlet forms $^3DOM^*$ which then transfers energy to O_2. Despite many studies on $^1O_2$ production, the photophysical properties of $^3DOM^*$ are not well known. This work uses the O_2 dependence of $^1O_2$ quantum yields (Φ_{1O2}) to estimate the yields and lifetimes of $^3DOM^*$ as a function of wavelength. Experiments employed a Xe lamp, bandpass filters, and fufuryl alcohol as a $^1O_2$ probe. Buffered D_2O was used as a solvent to increase the $^1O_2$ lifetime, allowing for extensive experimentation.

Results and Discussion

Figure 1 displays data for Suwannee River OM at 370 nm. The asymptote above 0.5 mM O_2 shows that all $^3DOM^*$ precursors to $^1O_2$ are being trapped and that their quantum yield is 0.025. The ratio of the intercept to slope of the inverse linear plot equals the lifetime of $^3DOM^*$ multiplied by the total rate constant for its quenching by and energy transfer to O_2. Assuming a total value of 10^{10} M^{-1} s^{-1} for these processes yields a $^3DOM^*$ lifetime of 6.5 μs, which is also found at 313 and 415 nm. Other samples have similar lifetimes that are also invariant with wavelength. However, the quantum yields vary by more than two-fold. This suggests that Φ_{1O2} is controlled by absolute yields of $^3DOM^*$ rather than its decay kinetics.

Figure 1: Φ_{1O2} (370 nm) versus [O_2] for Suwannee River Organic Matter, pD 6.0. Inset: linearized inverse plot.

[1] Guerard *et al.* (2009) *Environ. Sci. Technol.* **43**, 8587–8592. [2] Xie *et al.* (2004) *Environ. Sci. Technol.* **38**, 4113–4119. [3] Blough & Zepp (1995) in *Active Oxygen in Chemistry*, Blackie Academic, 280–333.

Dissolution-precipitation as a possible mechanism of C-O-H fluid/melt segregation in the deep mantle

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Trace amounts of fluid dispersed in the mantle cannot be easily removed from the crystalline framework if that insoluble in the fluid. However, at the mantle conditions water and carbonates are excellent silicate solvents. Hence, the migration of a fluid droplet through a solid may proceed by a combination of dissolution and deposition of the solid at the forward and rear faces of the fluid/melt droplet respectively, and solute flow across the droplet. The driving force for this process is a concentration gradient of solid silicate in the fluid. This can be caused by temperature gradient, differences in stable and metastable phase solubilities, and stress.

In this study we measured MgO-SiO$_2$ diffusion in the K$_2$Mg (CO$_3$)$_2$ (KMC), K$_2$Mg (CO$_3$)$_2$2H$_2$O (KMCH), and H$_2$O at 17 and 24 GPa. The summary of obtained data is shown in the figure below along with available literature data on diffusion in the silicate and carbonate melts and water fluid.
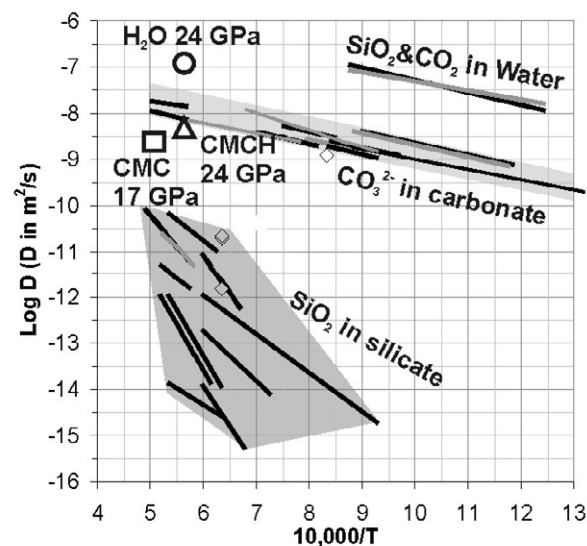
Based on obtained results we estimate stress driven fluid migration rate. For example, at low mantle conditions (2000 K and 25 GPa) migration rate of 10-μm inclusion of hydrous fluid estimated to be 1-2 km/y at 10 MPa stress level.