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Key Points:

- Stable oxygen isotopes sensitively track the photochemical oxidation of *Deepwater Horizon* surface oil
- Molecular oxygen appears to be the major source of oxygen photochemically added to hydrocarbons
- The kinetic isotope effect of photochemical oxidation is consistently -9% for oil and for a variety of organic carbon sources

Supporting Information:

- Supporting Information S1

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Oxygen Isotopes ($\delta^{18}\text{O}$) Trace Photochemical Hydrocarbon Oxidation at the Sea Surface

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Abstract Although photochemical oxidation is an environmental process that drives organic carbon (OC) cycling, its quantitative detection remains analytically challenging. Here, we use samples from the *Deepwater Horizon* oil spill to test the hypothesis that the stable oxygen isotope composition of oil ($\delta^{18}\text{O}_{\text{Oil}}$) is a sensitive marker for photochemical oxidation. In less than one-week, $\delta^{18}\text{O}_{\text{Oil}}$ increased from -0.6 to 7.2% , a shift representing $\sim 25\%$ of the $\delta^{18}\text{O}_{\text{OC}}$ dynamic range observed in nature. By accounting for different oxygen sources (H_2O or O_2) and kinetic isotopic fractionation of photochemically incorporated O_2 , which was -9% for a wide range of OC sources, a mass balance was established for the surface oil's elemental oxygen content and $\delta^{18}\text{O}$. This $\delta^{18}\text{O}$ -based approach provides novel insights into the sources and pathways of hydrocarbon photo-oxidation, thereby improving our understanding of the fate and transport of petroleum hydrocarbons in sunlit waters, and our capacity to respond effectively to future spills.

Plain Language Summary Sunlight alters the physical and chemical properties of petroleum hydrocarbons released into aquatic ecosystems. These alterations impact the performance of chemical tools used in response to oil spills, and thus there is substantial interest in improving approaches to track these alterations and our understanding of the driving mechanisms. In this study, we developed a stable oxygen isotope-based approach to track photochemical oxidation of oil and validated it using samples from the 2010 *Deepwater Horizon* oil spill. Our isotope-based approach revealed two key insights into the photochemical oxidation mechanism. First, the major source of oxygen added to the oil by sunlight appears to be molecular oxygen rather than water. Second, molecular oxygen kinetic isotope fractionation during photochemical oxidation was remarkably similar for a wide range of organic carbon types, such as crude oil and dissolved organic carbon, raising the possibility of a common step in the oxidation mechanism. This new stable oxygen isotope-based approach will improve our capacity to respond effectively to future oil spills, and can be applied to track the cycling of a broad range of organic carbon sources.

1. Background

Photochemical oxidation is an environmental process that drives organic carbon (OC) cycling through air, land, and water (Andrews et al., 2000; Austin & Vivanco, 2006; Cory et al., 2014; Jimenez et al., 2009; Latch & McNeill, 2006; Miller & Zepp, 1995; Ward, Sharpless, et al., 2018). Sunlight acts to either completely oxidize OC to carbon dioxide (CO_2 ; Cory et al., 2014; Miller & Zepp, 1995) or partially oxidize OC to compounds that accumulate in different ecosystems. A wide range of OC sources in the air, land, and water are susceptible to partial photo-oxidation, including aerosols (Jimenez et al., 2009), plant litter (Austin & Vivanco, 2006), crude oil (Payne & Phillips, 1985; Ward, Sharpless, et al., 2018), pollutants (Boreen et al., 2003), biomolecules (Boreen et al., 2008; Lundeen & McNeill, 2013), black carbon (Fu et al., 2016; Ward et al., 2014), lipids (Collins et al., 2018), and dissolved (DOC; Latch & McNeill, 2006; Cory et al., 2010; Cory et al., 2014) and particulate OC (Estapa & Mayer, 2010). In light of the growing awareness that partial photo-oxidation can be a critical control on the fate and transport of OC, there is a need for robust methods to quantify its occurrence in the environment.

Two approaches have commonly been used to trace partial oxidation of OC, bulk oxygen content and mass spectrometry, each with its strengths and weaknesses. For example, increases in bulk oxygen content of OC using elemental analysis can imply partial photo-oxidation of OC (Jimenez et al., 2009; Ward, Sharpless, et al., 2018). The major strengths of this approach are that it is quantitative, relatively inexpensive, and routine. The major weakness is its low sensitivity, requiring considerable addition of oxygen to the carbon backbone. Accordingly, in cases where extensive partial photo-oxidation of OC occurs, such as the oxidation of aerosols (Jimenez et al., 2009) and crude oil (Ward, Armstrong, et al., 2018), the bulk oxygen content approach has proved successful. A second weakness is that changes in bulk oxygen content do not provide information about the underlying chemical or physical causes (e.g., reactive addition versus enrichment by evaporation).

Second, partially oxidized OC can be traced at a molecular-level using mass spectrometry (e.g., Aeppli et al., 2018; Cao & Tarr, 2017; Cory et al., 2010; Ruddy et al., 2014). The strength of mass spectrometry is two-fold: it is sensitive and provides insights into the diverse array of compounds produced by sunlight. For example, Fourier transform ion-cyclotron resonance mass spectrometry identified thousands of partially photo-oxidized products in oil residues deposited on Gulf of Mexico beaches after the *Deepwater Horizon* (DWH) spill (Ruddy et al., 2014). The major weaknesses of this approach are difficulties in quantifying molecular abundance and the costs of specialized equipment and personnel. Coupled gas- or liquid-chromatography with quadrupole or time-of-flight mass spectrometry techniques have been applied to quantify partial photo-oxidation products; however, only a small fraction of total products was quantifiable (<1%) even with multiple derivatization steps, and the analysis remains costly and highly specialized (Aeppli et al., 2018; Cao & Tarr, 2017).

Despite over fifty years of research characterizing the stable oxygen isotope composition of OC ($\delta^{18}\text{O}_{\text{OC}}$; Gray & Thompson, 1976), few studies have explored the possibility that $\delta^{18}\text{O}$ may provide an alternative approach to trace photochemical transformations of OC. There are two major potential strengths of this natural abundance stable isotope-based approach. First, in principle, it has high sensitivity because the isotopic signature of the two sources of oxygen expected to be added to OC by sunlight differ by 25‰ ($\delta^{18}\text{O}_{\text{O}_2} = 24.6\text{‰}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}} = 0\text{‰}$; Benson & Krause, 1984; Barkan & Luz, 2005), much larger than the analytical precision of $\delta^{18}\text{O}_{\text{OC}}$ measurements (typically $\leq 0.3\text{‰}$). Second, not all oxygen-containing functionalities in OC exchange with water (e.g., hydroxyl are non-exchangeable while carbonyl are exchangeable), and for the exchangeable functionalities, the rate of exchange is expected to be extremely slow at near-neutral pH (Stalker et al., 1994; Wedeking & Hayes, 1983). Given the rapid nature of partial photo-oxidation (hours to days), transformation products should therefore retain the isotopic signature of added oxygen. Together, small changes in the oxygen content of OC could translate into easily resolvable differences in $\delta^{18}\text{O}_{\text{OC}}$.

There are also potential challenges of this isotope-based approach. First, the relative importance of the two likely sources of oxygen photochemically added to OC (i.e., H_2O or O_2) is unknown for OC in aquatic ecosystems. Second, the magnitude of oxygen isotopic fractionation during photochemical oxidation is unknown for most OC sources. One study reported that consumption of dissolved O_2 via photochemical oxidation of DOC proceeds via a kinetic isotope fractionation pathway where ^{16}O is preferentially incorporated into DOC relative to ^{18}O , with an isotope effect of -8 to -10‰ (Chomicki & Schiff, 2008). The magnitude of this isotope effect for other OC sources is unknown. However, given the differences in physical and chemical properties across OC sources, including photochemical sensitizers, the magnitude of kinetic fractionation could vary. Third, while oxygen isotope exchange between algal-derived OC and seawater is expected to be slow (half-life of hundreds of years; Wedeking & Hayes, 1983), the kinetics of this process are unknown for a wide range of OC sources and water types, presenting a potential challenge for distinguishing the primary source of oxygen from subsequent exchange reactions. Nonetheless, existing reports seem to indicate that $\delta^{18}\text{O}_{\text{OC}}$ may be a potentially useful tracer of photo-oxidation in surface waters.

Here, we use the 2010 DWH oil spill as a case study on the use of $\delta^{18}\text{O}$ as a tracer of hydrocarbon partial photo-oxidation. By combining field and laboratory-based evidence, we constrain the elemental and isotopic mass balance of oxygen in DWH surface oil. This isotope-based approach also provided novel insights into the sources and pathways of oxygen photochemically added to petroleum hydrocarbons at the sea surface.

2. Methods

2.1. $\delta^{18}\text{O}$ measurements of native oil and field residues.

Three types of oil were analyzed for their stable oxygen isotope composition ($\delta^{18}\text{O}_{\text{Oil}}$), as defined by equation (1):

$$\delta^{18}\text{O}_{\text{Oil}} = \left(\frac{{}^{18}\text{R}_{\text{sample}}}{{}^{18}\text{R}_{\text{standard}}} - 1 \right) \quad (1)$$

where ${}^{18}\text{R}$ is the isotope ratio of a sample or standard (VSMOW), as defined by equation (2):

$${}^{18}\text{R} = \left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}} \right) \quad (2)$$

“Native source oil” represents the oil released into the Gulf of Mexico during the 2010 DWH spill (i.e., National Institute of Standard and Technology Standard Reference Material, “Gulf of Mexico Crude Oil”; SRM 2779). “Surface oil” represents oil residues skimmed off the Gulf of Mexico sea surface in May–July of 2010 (Ward, Sharpless, et al., 2018). “Deposited oil” represents weathered oil residues collected from Gulf of Mexico beaches in July and August of 2010. All oil types were characterized for $\delta^{18}\text{O}_{\text{Oil}}$ using an Elementar PyroCube interfaced to an Isoprime VisION at the University of California Davis Stable Isotope Facility. Elemental composition and residence times of the oil residues were previously reported (Ward, Sharpless, et al., 2018). Sample extraction protocols, experimental reproducibility tests, and additional methodological details and discussion are described in the Supporting Information 1.1 and 1.4 (Aeppli et al., 2012; Burwood & Speers, 1974; Land & Macpherson, 1992; Lichtenthaler et al., 1989).

2.2. Determining the Source of Oxygen Added to Sea-Surface Hydrocarbons by Sunlight

Ultimately, there are two sources of oxygen that could have been photochemically added to DWH oil: seawater (H_2O) or molecular oxygen (O_2). To determine the relative contribution of these sources, we exposed oil-on-water films to simulated sunlight in the presence and absence of dissolved oxygen and monitored oxygen-containing functional groups using Fourier transform infrared spectroscopy. The oil films were prepared as previously described (Ward, Sharpless, et al., 2018), with a few modifications. Custom-made 12-mL quartz vials were filled with no headspace and sealed with GL-14 caps with custom-made 3-mm thick Viton septa. Synthetic seawater (35 g/L sodium chloride; pH 8.1 ± 0.1) was used in all experiments. Water for O_2 -free treatments was purged with ultra-high purity N_2 for one hour then transported to an N_2 -purged glove-box (Coy Laboratory Products), where the vials were filled before irradiation. The exposure time in the Atlas XLS+ solar simulator was 24 hours. To minimize variability in irradiance within the simulator chamber, the vials were placed in the center of the simulator along the horizontal profile of the long-arc Xe lamp. All dark-controls and light-exposed treatments were conducted in duplicate. All extracts were prepared for infrared spectroscopy analysis as described in the Supporting Information 1.2.

2.3. Mass Balance Calculations

The oxygen isotopic composition of an oil residue collected in the Gulf of Mexico can be described by equation (3):

$${}^{18}\text{F}_{\text{Oil}} = \sum (f_{\text{Sources}} \times {}^{18}\text{F}_{\text{Source}}) \quad (3)$$

Where ${}^{18}\text{F}$ is described by equation (4):

$${}^{18}\text{F} = \frac{{}^{18}\text{O}}{{}^{16}\text{O} + {}^{17}\text{O} + {}^{18}\text{O}} \quad (4)$$

Assuming oxygen isotopes are present in natural abundance in all reservoirs, the following approximation described by equation (5) is appropriate:

$${}^{18}\text{R}_{\text{Oil}} = \sum (f_{\text{Sources}} \times \alpha_{\text{Source-oil}} \times {}^{18}\text{R}_{\text{Source}}) \quad (5)$$

Where ${}^{18}\text{R}_{\text{Oil}}$ is described by equation (2), f is the fractional contribution of each source to the total oxygen in the oil residue, ${}^{18}\text{R}_{\text{Source}}$ is the oxygen isotope composition of each source, and $\alpha_{\text{source-oil}}$ is the source-specific

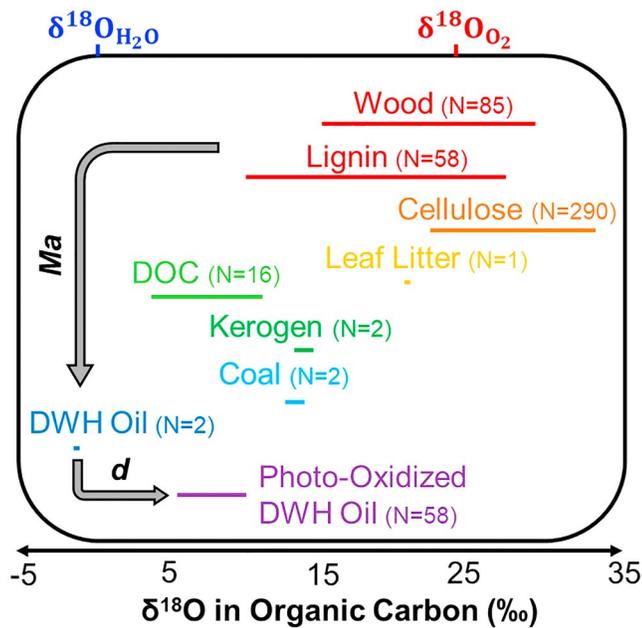


Figure 1. Synthesis of the oxygen isotopic composition of organic carbon ($\delta^{18}\text{O}_{\text{OC}}$) reported in this study and in the literature. Oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) and molecular oxygen ($\delta^{18}\text{O}_{\text{O}_2}$) are depicted at zero and 24.6‰, respectively. Million years is abbreviated as Ma, while day is abbreviated as d.

isotopic effect associated with photochemical incorporation of O atoms into the oil (methods described in Supporting Information 1.3). The sources of oxygen in the three types of oil collected from the Gulf of Mexico include the organically bound oxygen initially in the oil, and oxygen photochemically added to the surface oil from O_2 from H_2O . The fractional contribution of each source to the total oxygen in the oil residue was calculated using results from the previously described photochemical incubations (Section 2.3). Mass balance error bars are reported as ± 1 standard deviation from the mean. A more detailed discussion of the methodology can be found in the supporting information (Barkan & Luz, 2005; Kana et al., 1994; Sutherland et al., 2018).

3. Results and Discussion

3.1. Field Samples Reveal Rapid and Extensive Shifts in $\delta^{18}\text{O}_{\text{Oil}}$

The stable oxygen isotopic composition of DWH oil ($\delta^{18}\text{O}_{\text{Oil}}$) changed substantially after floating on the Gulf of Mexico for ~five days (Figures 1 & 2(a), Supporting Information 1.1 and 1.4). Source oil (green square) represents the native oil spilled into the Gulf. Surface oil (black triangles) are oil residues skimmed off the Gulf in May–July of 2010. Deposited oil (red circles) are oil residues collected from Gulf beaches in July and August of 2010. In less than one-week, $\delta^{18}\text{O}_{\text{Oil}}$ increased from $-0.6 \pm 0.3\text{‰}$ (native oil; $\pm 1\text{SD}$) to $+7.2 \pm 1.1\text{‰}$ ($\pm 1\text{SD}$; Figure 2(a)). This 8‰ enrichment during transit to the coastal zone is at least 25-fold larger than the experimental error determined from triplicate extractions of the same deposited oil residue (0.3‰; Supporting Information 1.1). The magnitude of this rapid (< one-week) isotopic shift in $\delta^{18}\text{O}_{\text{Oil}}$ is striking, encompassing approximately 25% of the $\delta^{18}\text{O}_{\text{OC}}$ dynamic range comprised of naturally observed organic materials that span geologic time (Figure 1, Table S1, Gray & Thompson, 1976; Gray & Thompson, 1977; Ramesh et al., 1985; Buhay & Edwards, 1995; Werner et al., 1996; Farquhar et al., 1997; Anderson et al., 1998; Saurer et al., 1998; Barbour et al., 2001; Saurer et al., 2002; McCarroll & Loader, 2004; Matthews, 2010; Tartèse et al., 2016).

3.2. Explaining the Rapid and Extensive Shifts in $\delta^{18}\text{O}_{\text{Oil}}$

Using a combined field- and laboratory-approach, our objective was to establish an oxygen isotope mass balance that explains the rapid and extensive shifts in DWH surface oil elemental content and $\delta^{18}\text{O}_{\text{Oil}}$ (Figures 2(a) and 3(a)). The first step to constructing a mass balance is identifying the elemental and isotopic starting- and end-points. The initial oxygen elemental and isotopic compositions of the native oil were $0.4 \pm 0.1\%$ and $-0.6 \pm 0.3\text{‰}$ (black square; Figure 3(a)), respectively. Assuming that 50% of the total surface oil mass evaporated (Gros et al., 2014) and that non-oxygenated hydrocarbons (mainly saturated hydrocarbons) preferentially evaporated (Reddy et al., 2012), the elemental and isotopic oxygen composition of the non-soluble, non-volatile surface oil would have doubled to 0.8% and left the $\delta^{18}\text{O}_{\text{Oil}}$ unchanged at -0.6‰ , respectively (gray square; Figure 3(a)).

Our previous work established that photo-oxidation accounted for the rapid and extensive increase in oxygen content of DWH surface oil, from 0.8 to $6.2 \pm 1.0\%$ in less than seven days (Figure 3(a); Ward, Sharpless, et al., 2018). Therefore, in this study, our mass balance calculations assume that sunlight also drove the shifts in isotopic composition from -0.6 to $+7.2 \pm 1.1\text{‰}$ (orange square; Figure 3(a)). Consistent with this assumption, a widely applied and vetted indicator for the onset of biological degradation of refined, crude, and naturally seeped oil (i.e., octadecane to phytane ratio) remained constant while the $\delta^{18}\text{O}_{\text{Oil}}$ increased by 8‰ (Figure 2(b)). This result confirms that shifts in both the elemental and isotopic composition of DWH surface oil were not the result of biological degradation but were driven by partial photo-oxidation.

The next requirement for mass balance is determining the sources of the oxygen added to the surface oil by reaction with sunlight. There are two possible sources, seawater (assumed $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of 0.0‰) or

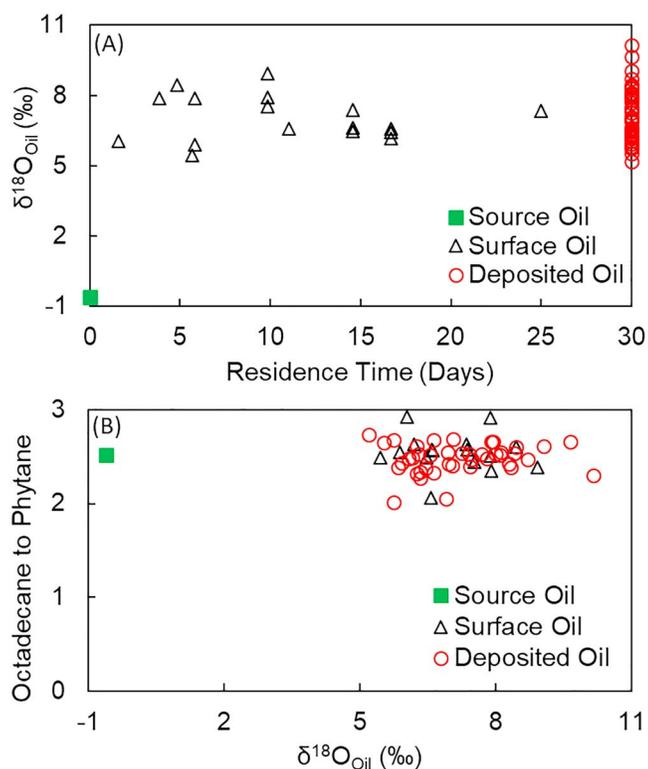


Figure 2. (a) Oxygen isotopic composition of oil ($\delta^{18}\text{O}_{\text{Oil}}$) released during the *Deepwater Horizon* spill versus residence time (days) in the environment. Source oil is the native oil spilled into the environment, surface oil was skimmed off the Gulf of Mexico in may–June of 2010, and deposited oil was collected from Gulf of Mexico beaches in July and August of 2010. (b) $\delta^{18}\text{O}_{\text{Oil}}$ of different oil types versus the octadecane to phytane ratio of the oil, a diagnostic indicator of biological degradation.

molecular oxygen (assumed $\delta^{18}\text{O}_{\text{O}_2}$ value of 24.6‰; Figure 3(a)). Qualitatively, the 8‰ enrichment of DWH surface oil suggests that O_2 was a source of the added oxygen. To test for the contribution of each source to the total oxygen incorporation, we exposed oil and water mixtures to simulated sunlight in the presence and absence of O_2 (i.e., air-saturated vs. N_2 -saturated). In the absence of O_2 , the photochemical generation of carboxyl C, a functionality that correlates linearly to the oxygen content of DWH surface oil ($R^2 = 0.98$; Ward, Sharpless, et al., 2018), was reduced by $86 \pm 7\%$ ($\pm 1\text{SD}$; Figure 3(b)). The generation of hydroxyl functionalities was similarly reduced by $88 \pm 3\%$ ($\pm 1\text{SD}$; Figure 3(b)). These results both highlight the importance of O_2 in the observed reactions. Assuming 86% of the added oxygen was from O_2 (Figure 3(b)) and that no kinetic isotopic fractionation occurred during photo-oxidation, a value for $\delta^{18}\text{O}_{\text{Oil}}$ of approximately +18‰ is predicted (purple square; Figure 3(a)), substantially higher than the observed +7‰ (orange square; Figure 3a). Consequently, we measured the kinetic isotope fractionation associated with photo-oxidation of DWH oil to determine if preferential incorporation of ^{16}O from O_2 could explain this observed discrepancy.

In the laboratory, photochemical O_2 consumption (i.e., incorporation of dissolved O_2 into oil hydrocarbons; Figure 3(c); x-axis) exhibited a normal kinetic isotope effect of $-9.0 \pm 0.3\%$ ($^{18}\epsilon_{\text{oxidation}}$, in which ^{16}O was preferentially consumed compared to ^{18}O ; Figure 3(c)). Incorporating this fractionation factor into the mass balance reveals, on average, a 4‰ offset between calculated ($+11.4 \pm 1.7\%$, green square; Figure 3(a)) and measured $\delta^{18}\text{O}_{\text{Oil}}$ ($+7.2 \pm 1.1\%$, orange square; Figure 3(a)). This discrepancy suggests that an additional process is contributing to the isotopic composition of photo-oxidized oil.

Here we consider four possible processes that may contribute to the $\delta^{18}\text{O}_{\text{Oil}}$ mass balance discrepancy. First, it is possible that $\delta^{18}\text{O}_{\text{O}_2}$ was lower than the equilibrium value of +24.6‰ used in the mass balance calculations because of active photosynthetic O_2 production and limited air-sea exchange. Satisfying isotopic mass balance would require $\delta^{18}\text{O}_{\text{O}_2}$ to have been $\sim 20\%$, 4 to 5‰ lower than the equilibrium value of +24.6‰ used in the calculations. Consistent with this requirement, in four out of five Gulf of Mexico surface waters sampled in May of 2010, i.e., during the period of surface oiling, reported $\delta^{18}\text{O}_{\text{O}_2}$ values were 2 to 4‰ lower than the equilibrium value (Ostrom et al., 2014). Thus, although constrained by only a few samples, our mass balance discrepancy could merely be explained by the natural variability of $\delta^{18}\text{O}_{\text{O}_2}$ in Gulf of Mexico waters during the DWH spill.

Second, it is possible that our experimental system underestimates the contribution of H_2O to oxygen photochemically added to the oil. Anthracene, for example, can undergo a multi-step photo-oxidation pathway where molecular oxygen is initially added to form anthraquinone, which can undergo secondary oxidation reactions involving either O_2 or H_2O (Vione et al., 2006). The relative importance of such multi-step pathways to total oil oxidation is unknown. Nonetheless, our experimental system was not capable of discerning this two-step process and thus could have underestimated the contribution of oxygen from H_2O . If this process were significant, achieving mass balance would require, on average, 46% of the photochemically added oxygen to have come from H_2O (assuming no kinetic fractionation of the oxygen added from H_2O).

Third, it is possible that oxygen-containing functionalities added by sunlight could have subsequently exchanged or equilibrated with seawater ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$, 0.0‰). It is well-established that certain oxygen-functionalities are exchangeable with water (e.g., carbonyl; Wedeking & Hayes, 1983; Stalker et al., 1994). However, at near neutral pH the half-life of oxygen isotope exchange between algal OC and seawater is estimated to be on the order of hundreds of years (Wedeking & Hayes, 1983). Assuming the half-life of oxygen exchange for oil photo-transformation products is similar to algal OC, an assumption that should be

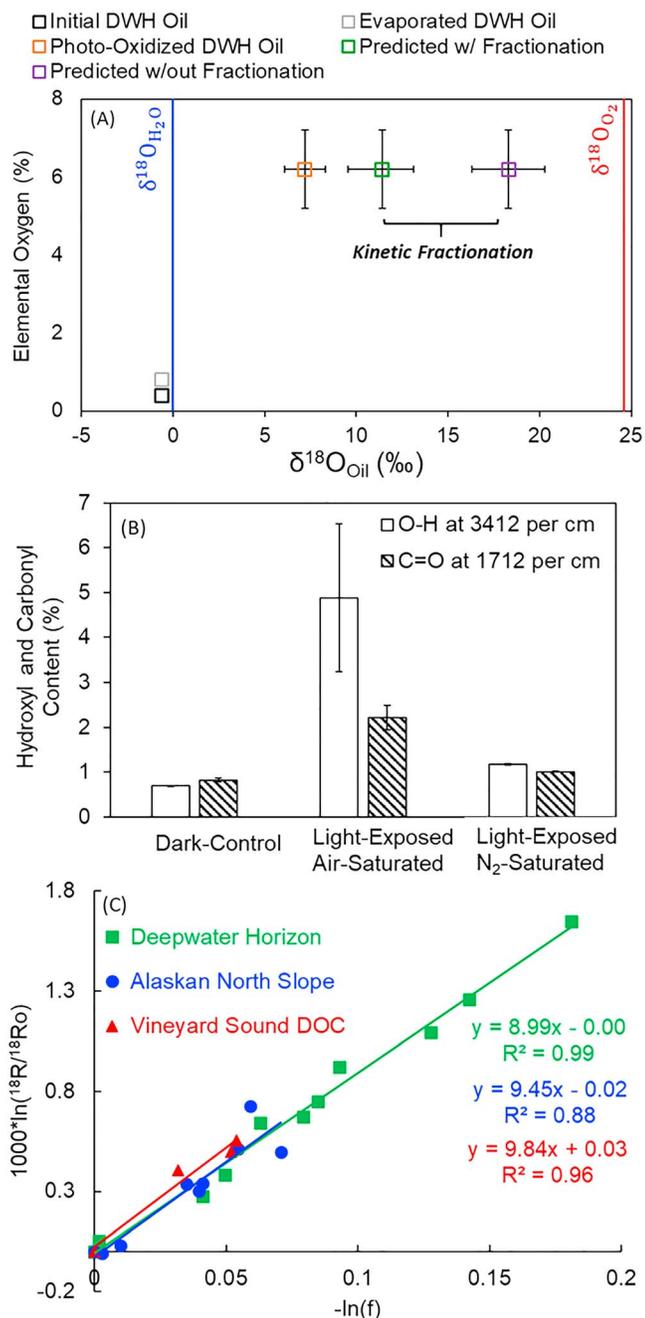


Figure 3. (a) Oxygen mass balance of *Deepwater Horizon* (DWH) oil released into the Gulf of Mexico in the summer of 2010. For reference, oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) and molecular O_2 ($\delta^{18}\text{O}_{\text{O}_2}$) are depicted at zero and 24.6‰, respectively. (b) Experimental determination of the source of oxygen (i.e., H_2O or O_2) incorporated into oil by sunlight. (c) Closed-system Rayleigh distillation plots showing the experimental determination of the kinetic oxygen isotope fractionation of dissolved O_2 during photochemical oxidation of crude oil and dissolved organic carbon. The fraction of dissolved O_2 remaining in the vial, f , was quantified as the ratio of O_2/Ar relative to dark-controls. Where applicable, all error bars are reported as one standard deviation from the mean.

explicitly tested in future work, the day- to week-long timescales of photo-oxidation reported in this study are significantly faster than subsequent exchange reactions. Accordingly, $\delta^{18}\text{O}_{\text{Oil}}$ remained constant across residence times ranging from three to 30 days in Gulf of Mexico surface waters (Figure 2(a)), suggesting that the magnitude and rate of isotopic exchange subsequent to photo-oxidation were either minor and instantaneous or substantially slower than the day- to week-long timescales of photo-oxidation.

Fourth, it is possible that isotopic fractionation of DWH oil experimentally determined in the laboratory may not accurately reflect isotopic fractionation in nature. This is because our experimental system measures the kinetic isotope fractionation imparted to the remaining pool of dissolved O_2 after reaction with sunlight, rather than the direct measurement of oxygen photochemically incorporated into oil. For example, a kinetic isotope effect associated with diffusion of O_2 across the oil–water interface may mask the intrinsic isotope effect associated with oil photo-oxidation, although this potential for masking has never been quantified. To test how diffusion could impact the measured $\delta^{18}\text{O}_{\text{O}_2}$ fractionation of DWH oil (a light, sweet crude with low viscosity and density; Holder et al., 2015), we also measured $\delta^{18}\text{O}_{\text{O}_2}$ fractionation of Alaskan North Slope crude oil (a medium crude with higher viscosity and density; Holder et al., 2015). We expected that these differences in oil properties could impact diffusion of O_2 across the oil–water interface and, in turn, isotope fractionation of $\delta^{18}\text{O}_{\text{O}_2}$ during photochemical oxidation. However, isotopic fractionation was similar for both oils ($^{18}\epsilon_{\text{oxidation}}$ of DWH oil = $-9.0 \pm 0.3\text{‰}$; $^{18}\epsilon_{\text{oxidation}}$ of Alaskan North Slope = $-9.4 \pm 1.3\text{‰}$, Figure 3(c)), suggesting that any fractionation due to diffusion was minimal. Furthermore, photochemical fractionation of $\delta^{18}\text{O}_{\text{O}_2}$ of the two crude oils reported in this study was similar to marine DOC ($^{18}\epsilon_{\text{oxidation}} = -9.8 \pm 1.3\text{‰}$, Figure 3(c)) and previously reported values for terrigenous DOC ($^{18}\epsilon_{\text{oxidation}} = -8$ to -10‰ ; Chomicki & Schiff, 2008), systems where interfacial diffusion of O_2 presumably does not impact isotopic fractionation. These collective observations suggest that physical boundary layer or diffusion limitation effects did not substantially influence the accuracy of photochemical $\delta^{18}\text{O}_{\text{O}_2}$ fractionation or the mass balance.

3.3. Potential Applications of $\delta^{18}\text{O}$ to Track Hydrocarbon Oxidation

Here, we identify three potential applications of $\delta^{18}\text{O}$ to track petroleum hydrocarbon oxidation in aquatic ecosystems. First, in addition to tracking hydrocarbon photo-oxidation in high-light, low-latitude waters (e.g., Gulf of Mexico; Figure 1), the $\delta^{18}\text{O}$ -based approach may prove useful for tracking petroleum hydrocarbon oxidation in low-light, high-latitude waters (e.g., Arctic Ocean) where the extent of photo-oxidation may be expected to be lower.

Second, $\delta^{18}\text{O}$ may also provide a means to distinguish between different crude oil weathering processes. Saturated compounds are preferentially evaporated at the sea surface; thus, we would expect the preferential enrichment of native, non-volatile, oxygenated compounds to have minimal impact on $\delta^{18}\text{O}_{\text{Oil}}$. In theory, this decoupling should

enable differentiation of evaporation from processes that impact the isotopic composition of hydrocarbons, such as photochemical and microbial oxidation. Conveniently, $^{18}\epsilon_{\text{oxidation}}$ by photo-

oxidation (i.e., $^{18}\epsilon = -9\text{‰}$) is potentially distinct from biological oxidation (e.g., $^{18}\epsilon = \sim -15$ to -30‰ ; Guy et al., 1993; Helman, 2005). Taken together, $\delta^{18}\text{O}$ may be a promising approach to disentangle the relative importance of evaporation, photochemical oxidation, and biological oxidation – environmental processes that can simultaneously alter the apparent level of oxidation of petroleum hydrocarbons released into aquatic ecosystems.

Third, the utility of $\delta^{18}\text{O}$ likely extends beyond tracking the partial photo-oxidation of crude oil. While a wide range of OC sources are susceptible to partial photo-oxidation, we expect $\delta^{18}\text{O}$ to most effectively track the partial photo-oxidation of compounds with low initial oxygen content such as hydrocarbons, lipids, aerosols, black carbon, and organic pollutants. Therefore, relatively small additions of oxygen may induce relatively large shifts in $\delta^{18}\text{O}$ (e.g., Figures 1 and 2(a)). To realize the full potential of $\delta^{18}\text{O}$ as a tracer of OC oxidation, future research should focus on characterizing three variables: (i) the relative contribution of oxygen sources, i.e., O_2 or H_2O added to OC by photo-oxidation; (ii) the variation in $^{18}\epsilon_{\text{oxidation}}$ during partial photo-oxidation (see Section 3.4 below); and (iii) the environmental controls and kinetics of isotopic exchange processes between oxygen-functionalities and surface waters.

3.4. New Insights Into the Sources and Pathways of Hydrocarbon Photo-Oxidation

The strong dependence on O_2 for hydrocarbon partial photo-oxidation reported in this study is consistent with the expected pathways and controls of photo-oxidation. For example, O_2 is a critical reactant in the direct photochemical oxidation of polycyclic aromatic hydrocarbons (Fasnacht & Blough, 2003) and in indirect crude oil photo-oxidation pathways. The reactive oxygen species (ROS) singlet oxygen ($^1\text{O}_2$) can indirectly oxidize oil components and initiate secondary reactions that generate C-centered radicals and react with ground-state O_2 yielding partially oxidized transformation products (Larson & Hunt, 1978; Lichtenthaler et al., 1989; Thingstad & Pengerud, 1982). The importance of the secondary reactions can be gauged from the fact that the majority fraction of photo-products in DWH oil residues appears to have originated from saturated hydrocarbons that would not be able to react with $^1\text{O}_2$ (Hall et al., 2013; Ruddy et al., 2014). A similar observation was made with regard to photo-production of fatty acids during the IXTOC-I oil spill (Overton et al., 1980).

The close agreement of $^{18}\epsilon_{\text{oxidation}}$ across a wide range of OC sources with varying physical and chemical properties (i.e., light and medium crude oil, marine and terrestrial DOC) raises the possibility that the isotope fractionating step may be independent of OC source (Figure 3(c)). This result is surprising because the initial sensitizers for crude oil (polycyclic aromatic hydrocarbons, resins, and asphaltenes; Payne & Phillips, 1985) are different than for DOC (tannins, lignin, pigments, and thermally altered organic matter; Ward & Cory, 2016; Ward et al., 2017), and thus the major photo-oxidation pathways are expected to differ considerably. One possibility could be that a key step in all cases is formation of $^1\text{O}_2$, a strong but selective oxidant produced by photosensitization from a wide range of OC sources and implicated in their photooxidation (Cory et al., 2010; Larson & Hunt, 1978; Latch & McNeill, 2006; Thingstad & Pengerud, 1982). In this case, isotope effects on the efficiency of energy transfer to form $^1\text{O}_2$ may be responsible (Turro, 1985). An alternative possibility could be a free-radical mechanism common to the various OC sources, where the isotope effect arises from reaction of C-centered radicals with ground state O_2 to generate peroxy radicals. Interestingly, the rate constants for this reaction are similar for a variety of OC types in various solvents (Maillard et al., 1983; Marchaj et al., 1991), which suggests that any associated kinetic isotope effect would not depend strongly on the physical nature of the system (i.e., crude oil or DOC). Although peroxy radicals have been implicated in the photo-oxidation of crude oil (Larson & Hunt, 1978; Lichtenthaler et al., 1989; Thingstad & Pengerud, 1982) and DOC (Sharpless & Blough, 2014), their general significance to OC photochemical processing is poorly constrained (Sharpless & Blough, 2014). Future work should explore the validity of these hypothesized explanations for the constant kinetic isotope effect of OC photochemical oxidation.

4. Concluding Remarks

We demonstrated that $\delta^{18}\text{O}$ is a sensitive, routine, and quantitative tracer of hydrocarbon photo-oxidation at the sea surface. In addition to improved sensitivity, $\delta^{18}\text{O}$ may provide a means to disentangle the relative importance of pathways that can simultaneously weather hydrocarbons in surface waters, such as

evaporation, photochemical oxidation, and biological oxidation. By establishing an elemental and isotopic mass balance of oxygen in DWH surface oil, we gained two key insights into the sources and pathways of hydrocarbon photo-oxidation. First, O₂ rather than seawater appears to be the primary source of photochemically added oxygen. Second, the kinetic isotopic fractionation of dissolved O₂ photochemically incorporated into hydrocarbons ($^{18}\epsilon_{\text{oxidation}} = -9\text{‰}$) appears to be independent of OC physical and chemical properties, raising the possibility that a variety of OC types (e.g., crude oil and DOC) share a common step in the photochemical oxidation mechanism. Collectively, $\delta^{18}\text{O}$ is a novel approach to track the oxidative fate of hydrocarbons released to aquatic systems, which may improve our capacity to respond effectively to future accidents (Ward, Armstrong, et al., 2018).

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