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Molecular Characterization of Photochemically Produced Asphaltenes via Photooxidation of Deasphalted Crude Oils

Taylor J. Glattke, Martha L. Chacón-Patiño,* Alan G. Marshall,* and Ryan P. Rodgers*

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ABSTRACT: The ability of molecular characterization to expose the chemical and structural composition of petroleum photooxidation products can aid future optimization of oil spill remediation techniques. Previous studies have documented molecular changes induced by photochemical reactions, their compositional/structural dependence, and thus revealed that they are sample-dependent. The work herein describes the photochemical transformation of nonasphaltenic petroleum compounds (maltenes) into asphaltenes. *Pentane-soluble* species (maltenes) were isolated from three geologically diverse crude oils and photooxidized in a solar simulator microcosm to investigate their transformation into *pentane-insoluble* molecules (asphaltenes), referred to as photochemically produced asphaltenes (PPA). All oils, photoproducts, and solubility fractions were characterized by positive-ion (+) atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and tandem-MS to access their molecular composition and structural features. The oil-soluble photooxidation products from the three deasphalted oils exhibit asphaltene contents between ~7–19 wt % after photoirradiation, which reveals the photogeneration of asphaltenes from oils initially devoid of asphaltenes. The variation in asphaltene yield after photoirradiation suggests that the quantity of PPA is sample-dependent. PPA are shown to have lower molecular weights, much higher oxygen content, and lower aromaticity than native asphaltenes from nonoxidized oils. Compositional trends for oxygen-containing photoproducts suggest that production of new asphaltenes in the environment might occur via concurrent photooxidation, photofragmentation, and photoinduced polymerization of native petroleum compounds.

■ INTRODUCTION

Petroleum Weathering in the Environment. Weathered spilled oils are known for increased content of oxygenenriched molecules and recalcitrant petroleum compounds, called asphaltenes.^{1,2} Several works suggest that evaporation and photooxidation are important processes responsible for significant mass loss in oil spills within the first 30 days.^{3,4} After evaporation, the remaining oil contains a high concentration of asphaltenes, defined as the alkane-insoluble (pentane or heptane, nC_5/nC_7) but toluene/benzene-soluble portion of crude oil. Asphaltenes in field samples are likely a mixture of oxidized asphaltenic compounds, asphaltenes initially present in the spilled oil ("native"), and potentially new photochemically produced asphaltenes (PPA).¹ PPA are newly formed compounds from photoinduced transformation and have a solubility behavior consistent with that of petroleum asphaltenes (alkane-insoluble/toluene-soluble).

Light and medium oils can lose up to 75% of their initial volume to weathering processes within the first month of exposure.⁴ Conversely, heavy petroleum samples typically lose less than 10%.^{4,5} Previous studies demonstrate selective depletion of low carbon number (C_9-C_{13}) *n*-alkanes, which leave behind higher molecular weight compounds with high heteroatom content.⁶ Specifically, an increase in oxygenated compounds after photooxidation has been observed in weathered samples.^{7–9} For instance, Lemkau et al.¹⁰ found photooxidation products with up to eight oxygen atoms per molecule in field samples collected from the Cosco Busan

heavy fuel oil spill in San Francisco, CA. Other reports by Ruddy, Niles, and Tarr indicate that photoproducts from petroleum in the environment comprise acidic and ketone/ aldehyde functionalities, which are readily accessible by negative- and positive-ion electrospray ionization (ESI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).^{2,11–13} Furthermore, oil- and water-soluble photooxidation products have been shown to contain abundant oxygenated S- and N-containing compounds (S_xO_y and N_xO_y).^{7,9,10,14,15} Many of these weathering products may exhibit solubility behavior consistent with asphaltenes, i.e., remain oil-soluble but alkane-insoluble. In addition, a higher content of alkyl-side chains (higher carbon number) decreases water solubility.^{16–18} Thus, several works suggest that watersoluble photoproducts have carbon numbers between ~10– 30, whereas nonweathered petroleum and oil-soluble photoproducts typically have a carbon number above 30.¹⁶

Asphaltene Content in Field Samples May Hint at Mass Losses Due to Evaporation. Lewan et al.¹ propose that the quantity of asphaltenes in field samples, as well as their chemical features, can be used to measure oil losses due to

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evaporation and photooxidation. However, asphaltene weathering increases oxygen content, which complicates their use to estimate mass loss in active spills. Instead, the authors also suggest that asphaltene quantification and gas chromatography (GC) amenable parameters must be collectively used. Nevertheless, there are several facts that challenge this hypothesis: 1) weathering of native asphaltenes, as well as the production of new asphaltenic compounds, might be sample-dependent, and 2) GC does not reveal the totality of oxygen-containing molecules present in weathered oil.¹⁹ Therefore, to determine if asphaltene content and composition in field samples are useful parameters to understand oil losses, it is necessary to investigate the molecular changes of native asphaltenes and potential generation of PPA species upon photooxidation.

Asphaltene Transformation in Oil Spills. Recent works demonstrate that upon sunlight irradiation, asphaltenes can produce oil- and water-soluble compounds with up to 18 oxygen atoms per molecule.^{16–18} Chacón-Patiño et al.¹⁷ demonstrated that water solubility increases as a function of increasing oxygen content and decreasing molecular weight, which is sample- and structure-dependent.

Asphaltenes are comprised of two structural motifs: one aromatic core with alkyl-side chains, known as single-core or "island" motif, or several aromatic cores linked by covalent bonds, known as multicore or "archipelago" motif.^{20,21} The dominance of one structural motif over the other is sampledependent and correlates with asphaltene behavior under thermal stress (e.g., thermal cracking).²¹⁻²³ Samples with abundant single-core motifs produce gas (from the alkyl-side chains) and carbonaceous residue ("coke", from the aromatic core). Conversely, asphaltenes with high content of multicore motifs produce low-molecular weight (<300 g/mol), heptanesoluble, polycyclic aromatic hydrocarbons (PAHs).^{13,22,24} These differences in thermal behavior are noteworthy, as a recent study demonstrated that asphaltene degradation by sunlight follows similar trends.¹⁶ Upon photooxidation in a solar simulator microcosm, Wyoming deposit asphaltenes, which contain abundant single-core motifs, produce an insoluble dark solid (tar) and no water-soluble species. The remnant oil-soluble photoproducts preserve the carbon number and aromaticity of the precursor material, which suggests photodegradation resistance. Conversely, Athabasca bitumen asphaltenes, with dominant multicore structures, produce abundant oil- and water-soluble photoproducts. The molecular composition of the water-solubles features higher oxygen content (up to 18 oxygen atoms) and lower molecular weight (m/z < 450) than the asphaltene starting material, which suggests the occurrence of photoinduced oxidation and fragmentation of the parent asphaltenes.¹⁶⁻¹⁸

Other works conducted by Pesarini et al.²⁵ demonstrate that 5 h of solar irradiation increases asphaltene concentration in petroleum, from 4 to 7 wt % in a medium Brazilian oil, and from 6 to 8 wt % in an Arabian crude. The authors concluded that photooxidation incorporates polar functionalities, such as carboxylic acid and hydroxyl groups into the newly produced asphaltenes, and hypothesized that such transformation takes place in a period of time short enough to be of environmental concern.²⁵ However, the oxidized native asphaltenes and new photochemically produced asphaltenic species persist in the environment and can stabilize water-in-oil emulsions, producing surface "mousses" typically observed after oil spills.^{25–29} Although the discovery of these environmentally formed

asphaltenes has been reported, little is known about their molecular composition compared to native asphaltenes and maltenes.

Here, we focus on the transformation of maltenes (nC_{5} - and toluene-soluble) into PPA (nC_{5} -insoluble/toluene-soluble), and their comprehensive characterization by FT-ICR MS and infrared multiphoton dissociation (IRMPD). Petroleum samples of three different geological origins (i.e., Wyoming and two South American crudes) were deasphalted by dilution with $nC_{s}(1/40 \text{ v/v})$. The deasphalted oils (maltenes) were irradiated in a solar simulator microcosm. The oil-soluble photoproducts were fractionated by precipitation with nC_5 into oxidized maltenes and PPA. The three oils yielded different amounts of PPA species (\sim 7.6, \sim 9.8, \sim 19.7 wt %), indicating that the photochemical transformation of maltenes into asphaltenes is sample-dependent. Moreover, the molecular composition of PPA species suggests that Wyoming crude oil incorporates more oxygen atoms into oil-soluble/alkaneinsoluble species than the South American oils. Therefore, it is difficult to use asphaltene quantity and characterization by GC (which does not fully characterize weathered oils) to determine mass losses from oil spills. Furthermore, the amount of PPA produced has been demonstrated to be sampledependent and is thus not an accurate way to estimate mass losses. Structural analyses by FT-ICR MS with infrared multiphoton dissociation (IRMPD) suggest that single-core motifs are dominant in native maltenes (precursor material for PPA) and native asphaltenes, whereas PPA species contain abundant multicore compounds. Thus, addition reactions between oxidized/low-carbon-number PAHs appear to be central in the production of multicore motifs in PPA. Comprehensive molecular characterization of native asphaltenes and PPA, via extrography fractionation and ultrahigh resolution FT-ICR MS, suggests that these samples feature different molecular motifs, aromaticity, and oxygen content. PPA exhibit abundant multicore motifs, are much less aromatic, and reveal abundant polyfunctional compounds (i.e., up to eight oxygen atoms per molecule). Such molecular composition (e.g., low-molecular weight, abundant oxygen) accords with the chemistry of interfacially active petroleum fractions, known to stabilize water-in-oil emulsions (e.g., oil mousses) in oil spills.^{17,30}

EXPERIMENTAL METHODS

Materials. High-performance liquid chromatography (HPLC) grade *n*-pentane (nC_5) , *n*-heptane $(nC_7 \text{ or Hep})$, toluene (Tol), cyclohexane, dichloromethane (DCM), acetone, methanol (MeOH), and water (H₂O) were obtained from J.T. Baker (Philipsburg, NJ) and used as received. HPLC-grade tetrahydrofuran (THF) with no solvent stabilizer was obtained from Alfa Aesar. Filter paper Whatman 2 was used for asphaltene filtration. High-purity glass microfiber thimbles were utilized for asphaltene cleaning and extraction by Soxhlet extraction (Whatman, GE Healthcare, Little Chalfont, U.K.). Chromatographic grade silica gel (SiO₂) was obtained from Fluka Analytical (70–230 mesh, pore size 60 Å) and used for extrography fractionation. Wyoming petroleum, NIST Vanadium Standard crude oil (Venezuelan heavy), and a Venezuelan extra heavy oil were supplied by Nalco Champion and Chevron Corporation.³¹

Deasphalting of Petroleum Samples. nC_5 asphaltenes were precipitated from crude oils following the standard procedure ASTM D6560–12, with slight modifications, as reported elsewhere.³² The use of nC_5 for asphaltene precipitation, instead of nC_7 , removes a greater mass of "asphaltenic" material from the parent oil.^{33,34} Briefly, the stepwise addition of nC_5 to the crude oil (40/1 v/v) was assisted by sonication (Branson Ultrasonics, Danbury, CT, 22 kHz, and 130 W). The mixture was allowed to stand overnight, and solids were separated from the nC_5 maltenes by filtration (Whatman 2). Collected maltenes were dried under nitrogen and stored in the dark. Asphaltenes were cleaned by extended Soxhlet extraction with nC_5 to extract coprecipitated maltenes. Subsequent extraction with nC_7 yielded two asphaltene fractions: nC_{5-6} asphaltenes, also known as "in-between" asphaltenes (nC_5 -insoluble, nC_7 -soluble) and nC_7 asphaltenes (nC_5/nC_7 -insoluble).²¹

Photooxidation of Deasphalted Oils in a Solar Simulator Microcosm. 500 mg nC_5 maltenes were diluted with 250 μ L of cyclohexane under sonication and loaded onto 40 mL of HPLC-grade water in a jacketed beaker coupled with a water chiller at 27 °C (oil film thickness is ~122 μ m). The prepared jacketed beaker was placed in an ATLAS Suntest CPS solar simulator (300–800 nm, 250–765 W/m² irradiance range, 1500 W xenon lamp)³⁵ and irradiated for 48 h, with magnetic stirring (100 rpm). The period of irradiation is equivalent to 12 days of natural sunlight.³⁶

Separation of Oil-/Water-Soluble Photoproducts and Precipitation of PPA. After the 48-h irradiation period, the jacketed beaker was removed from the solar simulator microcosm, and oil/ water phases were separated through filtration with a wet filter paper (Whatman #2, HPLC-grade water). The dried oil-soluble photooxidation products were dissolved in 1 mL of toluene and further diluted with 40 mL of nC_5 , added dropwise, to precipitate alkaneinsoluble compounds. The dilution was assisted by sonication (Branson Ultrasonics, Danbury, CT, 22 kHz, and 130 W). The mixture was allowed to stand for 24 h. The oxidized maltenes (nC_5 soluble) were separated from the alkane-insoluble material (PPA) by centrifugation (Eppendorf 5810R, 3500 rpm for 10 min at 25 °C). Oxidized maltenes and PPA compounds were dried under nitrogen, weighed, and stored in the dark prior to analysis.

Extrography Fractionation of Native Asphaltenes and PPA. Native nC_7 asphaltenes and PPA compounds were separated into fractions with abundant single-core (island) or multicore (archipelago) motifs by a shortened version of the extrography method published elsewhere.³⁷ Extrography involves sample adsorption on a polar adsorbent (e.g., cellulose, alumina, silica gel) and subsequent extraction with specific solvents. In short, asphaltenes were adsorbed onto silica gel (1% mass loading); the mixture was dried under nitrogen, and then Soxhlet-extracted with acetone, Hep/Tol (1:1), and Tol/THF/MeOH (1:1:0.05). Asphaltene samples and fractions were dried under nitrogen, weighed, and stored in the dark.

Molecular-Level Characterization by 9.4 T Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Stock solutions of native asphaltenes, native/oxidized maltenes, PPA samples, and the extrography fractions were prepared in 100% toluene at a concentration of 10 mg/mL and further diluted in 100% toluene to a concentration of 100 μ g/mL for analysis by positive-ion (+) atmospheric pressure photoionization (APPI), coupled with a custom-built 9.4 T FT-ICR mass spectrometer.³⁸ Samples were directly infused at 50 µL/min into an Ion Max APPI source (Thermo Fisher Scientific) with a vaporizer temperature of 320 °C for maltenes and 350 °C for asphaltenes, because asphaltenes require a higher temperature to produce a comparable ion current based on optimized conditions. Gas-phase neutrals were photoionized with 10.2 eV photons from an ultraviolet krypton lamp (Syagen Technology, Inc., Tustin, CA, U.S.A.). Positive ions were transferred into the mass spectrometer via a heated metal capillary (~350 °C) and analyzed by a dynamically harmonized ICR cell.³⁹ For each spectrum, 200 timedomain transients were coadded.⁴⁰ Custom Predator and PetroOrg Software assisted data collection, Fourier transformation, mass spectral calibration, molecular formula assignment, and data visualization.40-

Structural Analysis of Native Species and Photoproducts by Multinotch Stored Waveform Inverse Fourier Transform (SWIFT) Isolation and Infrared Multiphoton Dissociation (IRMPD). For structural analysis, compounds with high double bond equivalents (DBE = number of rings plus double bonds to carbon), within a 4 Da range at m/z 452–455, were isolated by a multinotch SWIFT waveform and fragmented via IRMPD ($\lambda = 10.6$ μ m, 40W, 10–700 ms irradiation, Synrad CO₂ laser, Mukilteo, WA), as reported elsewhere. $^{43-45}$ The multinotch SWIFT waveform isolates precursor ions with a mass defect <0.25000 Da (DBE > 18) and allows them to remain in the ICR cell for fragmentation by IRMPD. 45 After dissociation, the composition of the fragment ions was accessed by conventional FT-ICR MS. 45

RESULTS AND DISCUSSION

PPA Yield is Sample-Dependent. This work focuses on the production of PPA by photooxidation of deasphalted oils in a solar simulator microcosm, and investigates how they differ from native asphaltenes and precursor maltenes. To determine whether or not PPA production (quantity and chemistry) is sample-dependent, we selected Wyoming, NIST Vanadium standard, and Venezuelan extra heavy crudes due to their different molecular composition and geological origin.^{13,46,47}

Photooxidation of deasphalted crude oils was performed with a solar simulator microcosm, which mimics petroleum weathering in the environment.^{36,48,49} Figure 1 displays the



Figure 1. Films of deasphalted oils before (top panel) and after 48 h of solar irradiation (middle panel), and precipitation of PPA by dilution with nC_5 (lower panel). Yields of PPA are included.

deasphalted crude oil films, i.e., maltenes diluted with cyclohexane on HPLC-grade water, before (top panel) and after 48 h of irradiation (middle panel).³⁶ Photographs in the middle panel highlight the effects of sunlight on oils from different geographical regions. After photooxidation, the water for Wyoming maltenes is a bright yellow color, which suggests the production of abundant water-soluble species. All three oils yield oil-soluble photoproducts, evident as a layer of brown material (with a mousse consistency and a strong adherence to the glassware) on water (middle panel), similar to those observed in oil spill field samples. These characteristics indicate a high contribution of polarizable/oxygen-containing compounds. Photographs in the bottom panel feature the precipitation of the asphaltene mass fraction (PPA compounds) by dilution of the irradiated oil-soluble products with nC_5 . The irradiated oil-soluble products are used to calculate PPA content in eq 1 due to mass losses of the initial oil which result from evaporation, water-solubles, and sample transfer. The content of PPA species in the oxidized oils, calculated by eq 1, is as follows: Wyoming crude = 7.6 ± 0.4 wt %, NIST Vanadium Standard crude = 9.8 ± 0.3 wt %, and Venezuelan extra heavy crude = 19.6 ± 0.1 wt %. Thus, the results demonstrate that the quantity of produced asphaltenes, via weathering of deasphalted oils (or maltenes), is sample-dependent.

Heteroatom Content of Native Species and Their Photoproducts. Molecular formulas, assigned to the mass spectral peaks obtained by (+) APPI FT-ICR MS, were sorted into heteroatom compound classes. For instance, compounds with carbon, hydrogen, and two oxygen atoms belong to the class O_2 . Readers should consider that APPI produces radical cations (M^{+•}) and protonated molecules ([M + H]⁺). Figure 2



Figure 2. Heteroatom class distribution derived from (+) APPI 9.4 T FT-ICR MS analysis of native and oxidized maltenes (blue shades), and native and photochemically produced asphaltenes (PPA) (red shades) for Wyoming (upper panel) and NIST Vanadium standard (lower panel) crude oils.

displays the combined relative abundances for $M^{+\bullet}$ and $[M + H]^+$ ions (plotted together) for various heteroatom classes from native maltenes (blue), oxidized maltenes (light blue), native asphaltenes (red), and PPA (pink) species for Wyoming and NIST Vanadium Standard crude oils. The same information, but plotted separately for the $M^{+\bullet}$ and $[M + H]^+$ ions can be found in Supporting Information Figures S1 and S2. Wyoming and NIST native maltenes exhibit the typical class distribution of alkane-soluble species, including abundant nonpolar compounds (class HC) and sulfur-containing molecules (class S₁), which account for >75% of ion relative abundance (RA).^{50,51} Observed differences in molecular composition of the fractions can be attributed to sampledependency during photooxidation. Furthermore, native maltenes contain compound classes with low oxygen content (O₁, O₂, O₁S₁, O₂S₁ classes, summed RA < 18%).

The oil-soluble photoproducts were separated into oxidized maltenes and PPA species. Figure 2 indicates that the content of nonpolar HC and S₁ remains high for the oxidized maltenes from both oils (RA ~ 52-70%). However, they contain a

higher relative abundance of molecules with more oxygen atoms, e.g., O_2 , O_3 , O_4 , O_2S_1 , and O_3S_1 classes, which are either less abundant or absent in the precursor maltenes. The results confirm that regardless of geological origin, solar irradiation incorporates oxygen atoms into maltenic compounds as previously reported.^{2,7–9,15,16,52–54} SI Figures S3 and S4 demonstrate that the Venezuelan extra heavy crude heteroatom trends are comparable to those for Wyoming and NIST oils. The results for the three crudes suggest that Wyoming native maltenes can incorporate more oxygen atoms into alkane-soluble species.

Wyoming native asphaltenes are naturally depleted in HC and S₁ species (RA < 10%); ~ 90% of the detected ions include at least one nitrogen or one oxygen atom. Those compounds contain more oxygen atoms than Wyoming native maltenes, as is evidenced by the higher abundance of N_1O_3 , O_4 , O_3S_1 classes (RA ~ 9%). Furthermore, Wyoming PPA feature a heteroatom class trend similar to that for native asphaltenes: decreased content of HC and S₁ compounds (RA ~ 6.03%), but much higher abundance of oxygen-rich, O_x , $O_x S_y$ and $N_x O_y$ classes, which produce a pseudo-Gaussian distribution with up to eight oxygen atoms. These results suggest that oxygen content, and therefore, heteroatom-based interactions (e.g., hydrogen bonding), drive the solubility behavior of the photooxidation products. At the molecular level, the high oxygen content of PPA species causes insolubility in alkanes; nanoaggregate insolubility results from strong inter/intramolecular interactions driven by polarizable molecular moieties. Along these lines, PPA fit into the solubility definition of asphaltenes (alkane-insoluble/toluenesoluble); their low DBE nature suggests that insolubility in alkanes is unlikely due to pi-stacking (aromatic interactions). At the molecular level, elevated oxygen content may result in a larger dipole moment and lead to alkane insolubility. Moreover, the presence of several oxygen atoms per molecule may allow for multiple intermolecular interactions (e.g., hydrogen bonding) with several neighboring compounds, causing stronger aggregation (a known characteristic of asphaltenes), and therefore, insolubility in alkanes.

NIST oxidized maltenes and PPA display compositional trends relatively similar to those for Wyoming crude oil. NIST PPA present $\sim 1.5-2.0$ -fold higher content of oxygen-rich classes (i.e., O_2 , O_3 , and O_3S_1) than oxidized maltenes; however, NIST PPA do not contain heavily oxidized $O_6 - O_8$, $N_1O_4 - N_1O_5$, and $O_4S_1 - O_7S_1$ classes. These oxidation trends extend to the PPA species for the Venezuelan extra heavy crude (Figure S3): PPA present a higher oxygen content than oxidized maltenes and native asphaltenes. It is important to note that PPA compounds for the Venezuelan oil contain more oxygen atoms (up to O_6 , SO_6 , and NO_4) than the NIST sample, but overall, exhibit a lower oxygen content than Wyoming PPA. Thus, the results demonstrate that quantity and molecular composition of PPA species are sampledependent. Therefore, understanding the amount of mass loss in active oil spills, due to evaporation and photooxidation, by gravimetric determination of asphaltenes in field samples and GC amenable parameters is unreliable. Moreover, it is well-known that GC access to oxygen-containing species becomes more difficult with increasing oxygen content.

The presence of O_4-O_8 compounds (polyfunctional species) in PPA is consistent with the idea that alkaneinsoluble aggregates in petroleum form supramolecular networks. This aggregation model describes crude oil as a mixture of monofunctional and polyfunctional compounds. Asphaltenes contain abundant polyfunctional species, and each one may be capable of interacting with various neighboring molecules, producing a complex supramolecular network insoluble in short alkanes (e.g., nC_5 and nC_7). Conversely, maltenes comprise abundant monofunctional compounds (e.g., O_1 , O_1S_1 , S_1 classes), which contain only one active site for intermolecular interaction; thus, their aggregation is weaker, which increases their solubility in alkanes.^{20,55}

The fraction of relative abundance (X_{RA}) for radical cations and protonated molecules gives further insight on the chemistry of native petroleum compounds and photoproducts. Samples that preferentially ionize as protonated species rather than radical cations feature strong proton affinities in the gas phase, correlating to an increased tendency to hydrogen-bond in solution.^{45,56} Figure 3 shows the fraction of relative



Figure 3. Fraction of ion relative abundance (X_{RA}) for protonated molecules (red) and radical cations (blue) for native and oxidized maltenes, native asphaltenes, and PPA, for Wyoming (upper panel) and NIST Vanadium standard crude oil (lower panel), derived from (+) APPI 9.4 T FT-ICR MS characterization.

abundance (X_{RA}) for protonated compounds (red) and radical cations (blue) for native maltenes and asphaltenes, oxidized maltenes, and PPA for Wyoming and NIST oils. X_{RA} is calculated from eq 2. The results indicate that Wyoming native maltenes and asphaltenes preferentially ionize as radical cations $(X_{RA} > 0.72)$; whereas, the photoproducts reveal higher proportions of protonated molecules. In particular, PPA yield more protonated species ($X_{RA} > 0.54$), suggesting that photooxidation incorporates abundant oxygen-containing functionalities, likely capable of hydrogen bonding in solution, into the newly formed asphaltene compounds. Similarly, for the NIST Vanadium Standard crude, native maltenes and asphaltenes disproportionally produce radical cations by APPI $(X_{RA} = 0.70, 0.56)$; whereas, their relative abundance decreases for the oxidation products; NIST PPA species produce more protonated cations ($X_{RA} > 0.56$). Figure S5 of the Supporting Information presents the results for Venezuelan extra heavy oil, indicating that protonated cations are dominant in PPA compounds. Thus, the higher oxygen content and presumably increased tendency to hydrogen-bond in solution suggest that

PPA may reveal a stronger tendency to stabilize water-in-oil emulsions.

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$$X_{RA} = \frac{\sum RA \ of \ [M+H]^+ \ (or \ M^+)}{100}$$
(2)

Compositional Trends for Native Species and their Photoproducts. Isoabundance-contoured plots of DBE versus carbon number represent the molecular composition of native species and photoproducts analyzed by (+) APPI FT-ICR MS (Figure 4). Higher DBE values indicate higher



Figure 4. Isoabundance color-contoured plots of DBE versus carbon number for abundant precursor compound classes $HC + O_1$, S_1 , and N_1 present in native maltenes (top row, upper panel), and O_{xy} S_1O_{xy} and N_1O_x photooxidation products revealed by oxidized maltenes and PPA (middle/lower row, upper panel). Native asphaltenes are included for comparison (lower panel).

aromaticity, higher carbon numbers suggest more alkylsubstitution, and the color scale represents ion relative abundance. Compounds with equal DBE belong to the same homologous series (i.e., species with the same aromaticity but varying carbon number). The red dashed line illustrates the PAH planar limit (DBE = ~0.899 * carbon number), which indicates the highest possible DBE value for petroleum-derived molecules at a given carbon number while remaining planar; above that limit, compounds exhibit a nonplanar aromatic structure.⁵⁷

Figure 4 displays the compositional ranges, with abundanceweighted DBE and H:C ratios, for precursor compound classes in native maltenes and the photoproducts. For example, abundant HC and O₁ classes in native maltenes serve as precursors for the O_x species (x = 1-8) detected in PPA and oxidized maltenes. Similarly, S₁ and N₁ classes produce SO_x and NO_x compounds upon solar irradiation. O_x and SO_x maltenic photooxidation products remain in the compositional range of the precursor material; however, PPA species exhibit slightly higher abundance-weighted DBE values and some pubs.acs.org/EF



Figure 5. Combined DBE vs. carbon number plots for N_1 , O_1 , and S_1 precursor ions and IRMPD fragments for a) native maltenes, b) native asphaltenes, c) oxidized maltenes, and d) PPA species. Fragmentation mass spectra highlight single-core and multicore motif fragmentation pathways by a green arrow and a blue dashed line.

compounds closer to the PAH limit. It is important to note that the shift toward the PAH limit could be attributed to the increased oxygen content of PPA compounds: it is known that ketones are formed upon petroleum photooxidation; that functionality adds a double bond to the hydrocarbon structure without increasing hydrogen content.^{15,48,58-61} Future work, with model compounds, could point to other reasons for this behavior, including aromatization of naphthenic rings and ringclosing reactions. Moreover, photooxidation can also introduce carboxylic acids and aldehydes, which increase the DBE by a factor of 1 per additional carbonyl. Thus, the increase in DBE of the PPA species could be attributed either to the addition of carbonyl groups during photooxidation or the formation of aromatic species. Conversely, the compositional range for Ncontaining species drastically changes after solar irradiation. Native maltenes reveal abundant homologous series with DBE values of 8, 9, 12, 13, 15, and 16, which suggest pyrrole and pyridine moieties accompanied by fused aromatic cores with different structural motifs, i.e., single-core and multicore, as shown in Figure S6. We hypothesize that solar irradiation induces fragmentation of N-containing multicore compounds to yield low DBE oxidized maltenes. Photofragmentation of petroleum-derived products has also been observed in previous studies.¹⁸ Conversely, single-core N-containing species can oxidize, become slightly more aromatic, and exhibit a solubility behavior consistent with asphaltenes.^{62,63}

Most species for native/oxidized maltenes and PPA present a compositional range below DBE 15 (gray dashed line), whereas native asphaltenes have a compositional range at higher carbon number ($\sim 20-50$) and much higher DBE ($\sim 15-35$), indicating that native asphaltenic species are far more aromatic (DBE > 15) than asphaltenes produced by photooxidation. Reports by Czarnecki⁶⁴ and Stanford et al.^{65,66} indicate that alkane-insoluble compounds (asphaltenes) with low aromaticity and several oxygen atoms per molecule are interfacially active. Thus, the compositional trends shown in Figure 4 and the significant ionization as protonated species in APPI (Figure 3) imply that PPA compounds likely enhance emulsion stability,^{55,64,67,68} which is of great environmental concern in oil spills.

Figures S7 and S8 of the Supporting Information demonstrate that the other two crudes follow, in general, similar trends. The photoproducts compositional ranges feature carbon number and DBE values similar to those of the maltenic precursor material, and the native asphaltenes exhibit much higher DBE. However, the photoproducts from each crude oil clearly present a different molecular composition, which demonstrates that photochemical changes, and thus PPA chemistry, are sample-dependent.

Structural Comparison of Native Compounds and their Photoproducts. We performed gas-phase fragmentation by IRMPD with FT-ICR MS to understand the structure of the photoproducts (PPA and oxidized maltenes) and compare it with native asphaltenes and maltenes. High-DBE precursor ions were isolated by stored-waveform inverse Fourier transform (SWIFT) prior to fragmentation by IRMPD. Thus, loss of both DBE and carbon number upon IRMPD suggests the dissociation of covalent bonds between the aromatic cores of multicore structures. Conversely, singlecore species can lose only carbon number because of fragmentation of alkyl-side chains; their DBE remains somewhat constant because the IR laser cannot fragment across the aromatic cores.⁴⁵

Figure 5a displays the composition of multinotch SWIFTisolated N₁, O₁, S₁ high-DBE, low mass defect precursor ions (m/z 452–455), the compound class distribution of which can be found in Figure S9, and their IRMPD fragments for Wyoming native maltenes, along with the fragmentation mass spectrum. The leftmost DBE versus carbon number plot contains mostly high DBE precursor ions (circled in red). The IRMPD fragments (class distribution presented in Figure S10) are shown in the DBE plot to the right and suggest the production of abundant fragment ions with DBE > 20, demonstrating that single-core compounds are dominant. Native asphaltenes (Figure Sb) show a similar trend: only high DBE precursors are isolated, and most of the fragments remain in the same DBE range. For both samples, the mass spectra display fragment ions with m/z close to the precursors; small mass losses are indicative of single-core compounds.

Figure 5c,d displays the structural analysis for the photoproducts. For both samples, only high-DBE precursor ions (DBE > 20, left plots) were isolated and fragmented. The DBE vs carbon number plots to the right demonstrate a dramatic loss in both DBE and carbon number, which is possible only if multicore motifs are dissociated (Figure S11). The mass spectra reveal dealkylation (green arrow) and a low-molecularweight distribution (blue line) comprising ions with lower carbon number and DBE. Thus, significant mass losses upon IRMPD suggest the presence of multicore compounds formed through photooxidation. Similar results can be seen in the IRMPD fragments for the polyheteroatomic classes (e.g., S1O2, O_3 , N_1O_1) displayed in Figure S12. Collectively, the results indicate that oxidized maltenes and PPA are a mixture of single-core and abundant multicore motifs. Moreover, Figures S9 and S10 demonstrate a concurrent increase in the relative abundance of monoheteroatomic ions and a decrease of the poly heteroatomic species after IRMPD, suggesting the existence of archipelago poly-heteroatomic ions in which the various heteroatoms may be contained in separate aromatic cores. Such compounds fragment into ions comprised of fewer aromatic cores with lower numbers of heteroatoms or lose polar/pendant functionalities. We hypothesize that the photooxidative weathering of single-core maltenic species can yield multicore structures, which may suggest the occurrence of photoinduced polymerization reactions (Figure 6). Specifically,



Figure 6. General mechanism for proposed photoinduced polymerization of single-core structured starting material (top panel). The subsequent photofragmentation and photooxidation is shown in the bottom left and the new multicore structure produced by photoinduced polymerization is shown in the bottom right. Addition of oxygen by photooxidation is indicated with blue text (i.e., $+ 4(^{\circ}OH)$) indicates addition of 4 oxygen groups to the structure).

low-molecular-weight alkyl-substituted aromatic cores (1-3 rings) undergo photooxidation and photofragmentation (loss of alkyl-side chains induced by sunlight). These species may undergo addition reactions (polymerization) to produce multicore compounds with higher carbon number, DBE, and oxygen content. Thus, the results point to photoinduced polymerization as a possible pathway to produce newly formed asphaltenes in the environment. It is important to point out

that the proposed transformation route in Figure 6 highlights only one of the many possibilities for pathways of phototransformation. Ring opening/closing have not been considered here and are part of future work supported by model compounds.

Comprehensive Knowledge of Asphaltene Composition. Structural/compositional knowledge of petroleumderived samples can also be attained with extrography separation followed by FT-ICR MS analysis. In extrography, petroleum samples are adsorbed onto a polar adsorbent, e.g., SiO₂, and extracted with solvents that feature varying polarity or different intermolecular interactions. In this work, the extraction begins with acetone in which predominant dipoledipole interactions facilitate the isolation of aromatic compounds with a single-core dominant structure. The subsequent extraction with Hep/Tol enables the separation of alkyl-aromatic compounds. Finally, Tol/THF/MeOH assists the extraction of molecules with abundant polar functionalities that interact via hydrogen bonding with the SiO₂ silanol groups.³⁷ Previous works demonstrate that the ionization efficiency of the acetone fraction is ~50-fold higher than that of the Tol/THF/MeOH fraction. Thus, MS analyses of whole/ unfractionated samples preferentially reveal the compounds extracted with acetone. A more complete insight into asphaltenes is achieved by the separate MS characterization of the extrography fractions.³⁷

Figure 7 shows the combined compositional ranges for SO_x classes. The plots also include the gravimetric yields (wt %) for the extrography separation. Whole native Wyoming asphaltenes and its acetone fraction present almost identical compositional ranges, and reveal abundant compounds close to the PAH limit (red dashed line) with DBE values above 20 and short homologous series (species with the same DBE span a 15 carbon atom range). The Hep/Tol and Tol/THF/MeOH extrography fractions exhibit compounds with DBE values between 10 and 40 that were not accessed in the analysis of the whole sample because of selective ionization. The combined compositional ranges for the NO_x and O_x classes demonstrate trends consistent with the SO_x species and can be found in SI Figure S13.

The compositional ranges for whole PPA and its acetone fraction are almost identical (DBE = 5-25, carbon number = 10-40) in agreement with previous reports that MS characterization of whole asphaltenic samples preferentially reveals the compounds extracted in the acetone fraction.^{37,45} The later-extracted fractions, Hep/Tol and Tol/THF/MeOH, remain in the low carbon number (<30), low DBE (<20)compositional range. However, the compressed DBE distributions of the PPA (10 < DBE < 20) relative to the native asphaltenes (10 > DBE > 40) confirm that they are much less aromatic. Their solubility behavior, consistent with asphaltenes, is likely due to their higher oxygen content, which enables heteroatom-based interactions such as hydrogen bonding. Such interactions would lead to aggregates that are insoluble in both alkane solvents and water; however, it is important to keep in mind that high-oxygen content could also cause molecular insolubility in alkanes.

The gravimetric yields for the extrography separation suggest that both asphaltene samples are depleted in nonpolar compounds (i.e., Hep/Tol, < 2.5 wt %) and contain abundant polarizable species (i.e., acetone and Tol/THF/MeOH fractions): consistent with known asphaltene science.⁶⁹ The results indicate that the amount of desorbed material from the



Figure 7. Compositional ranges for the combined SO_x classes from whole samples and extrography fractions (acetone, Hep/Tol, and Tol/THF/MeOH) for Wyoming crude native asphaltenes (upper panel) and PPA species (lower panel).

silica gel, by Soxhlet extraction, is ~73 wt % for native asphaltenes and ~88 wt % for PPA. In general, asphaltenes are known for their strong and, in many cases, irreversible adsorption onto polar surfaces. We hypothesize that comprehensive molecular knowledge of polar asphaltene compounds with strong adsorption on SiO₂ (i.e., Tol/THF/MeOH and irreversibly retained species) is paramount to understand the impact of oil spills in coastal ecosystems (e.g., beaches and salt marshes). Our future studies will therefore focus on those fractions and their phototransformation products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c02654.

Heteroatom compound class distribution reported separately for protonated molecules and radical cations (Figures S1, S2, and S4) for Wyoming, NIST Vanadium Standard, and Venezuelan extra heavy crude oils; combined heteroatom compound class distribution (Figure S3) and relative abundances for protonated molecules and radical cations (Figure S5) for (+) APPI FT-ICR MS analysis of Venezuelan extra heavy crude oil; (Figure S6) molecular structures of common N₁ class compounds that exist in petroleum including combined isoabundance color-contoured plots of DBE versus carbon number for (+) APPI FT-ICR MS analysis of precursor material and photoproducts for NIST Vanadium Standard (Figure S7) and Venezuelan extra heavy (Figure S8) crude oils; heteroatom compound class distribution of the SWIFT-isolated precursor ions used for IRMPD and the resulting high DBE, low mass defect IRMPD fragments (Figures S9 and S10); general mechanism for Infrared Multiphoton Dissociation (IRMPD) fragmentation of single-core and multicore

structural motifs (Figure S11); combined DBE vs carbon number plots of the polyheteroatomic classes of precursor ions and IRMPD fragments (Figure S12); compositional ranges of NO_x and O_x classes of the extrography fractions from Wyoming crude oil (Figure S13) (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Martha L. Chacón-Patiño Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, United States; orcid.org/0000-0002-7273-5343; Phone: +1 850-644-1319; Email: chacon@magnet.fsu.edu; Fax: +1 850-644-1366
- Alan G. Marshall Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory and Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32310, United States; o orcid.org/0000-0001-9375-2532; Phone: +1 850-644-0529; Email: marshall@magnet.fsu.edu; Fax: +1 850-644-1366
- Ryan P. Rodgers Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory and Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32310, United States; orcid.org/0000-0003-1302-2850; Phone: +1 850-644-2398; Email: rodgers@magnet.fsu.edu; Fax: +1 850-644-1366

Author

Taylor J. Glattke – Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory and Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32310, United States; Occid.org/0000-0003-2934-0749

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.0c02654

Notes

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