

Ultraviolet photolysis of anthracene in H₂O interstellar ice analogs: Potential connection to meteoritic organics

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Abstract—The polycyclic aromatic hydrocarbon (PAH) anthracene was oxidized by exposure to ultraviolet (UV) radiation in H₂O ice under simulated astrophysical conditions, forming several anthracene ketones (9-anthrone, 1,4-anthraquinone, and 9,10-anthraquinone) and alcohols (1-anthrol and 2-anthrol). Two of the ketones produced have been detected in the Murchison meteorite but, to our knowledge, there has been no search for the alcohols or other oxidized anthracenes in meteorites. These results seem consistent with the possibility that interstellar ice photochemistry could have influenced the inventory of aromatics in meteorites. Since quinones are also fundamental to biochemistry, their formation in space and delivery to planets is relevant to studies relating to the habitability of planets and the evolution of life.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are found nearly everywhere in space (Allamandola et al. 1999), including along lines of sight that include cold (10–50 K) dense clouds and protostellar material (Sellgren et al. 1995; Brooke et al. 1999; Bregman et al. 2000; Chiar et al. 2000; Bregman and Temi 2001). In these cold environments, PAHs should condense into ice mantles, where they would come into contact with H₂O in the presence of radiation.

Aromatic compounds are also very common in carbonaceous chondrites (Basile et al. 1984; Cronin et al. 1988; Cronin and Chang 1993) and interplanetary (cometary/asteroidal) dust particles, or IDPs (Allamandola et al. 1987; Clemett et al. 1993). The aromatics in the carbonaceous (CM2) Murchison meteorite are enriched in deuterium (D) (Kerridge et al. 1987), and there is evidence that they may be one of the carriers of excess D in IDPs (Messenger et al. 1995).

Given that the D-enrichment of PAHs present in meteoritic materials suggests low-temperature chemistry (Sandford et al. 2000; Sephton and Gilmour 2000; Sandford et al. 2001) and is consistent with telescopic observations of dense clouds, we have studied the ultraviolet (UV)

photochemistry of PAHs and polycyclic aromatic nitrogen heterocycles (PANHs) under dense cloud conditions (Bernstein et al. 1999; Bernstein et al. 2001; Bernstein et al. 2002; Elsila et al. 2006). Meteoritic D-enrichments, lab reports of phenanthrene photo-oxidation and alkylation (Mahajan et al. 2003), and the UV photolytic formation of nitrogen-, carbon-, and oxygen-substituted aromatics (Bernstein et al. 2002; Elsila et al. 2006) similar to those in meteorites (Krishnamurthy et al. 1992; Sephton et al. 1999, 2001; Cody et al. 2002) suggest a link between energetic processing of ices and the substituted aromatics in meteorites.

We report here on the UV photolysis of anthracene (C₁₄H₁₀) in solid H₂O at low temperature to form anthracene ketones, compounds previously reported in meteorites (Basile et al. 1984; Krishnamurthy et al. 1992) and anthracene alcohols that, to our knowledge, have not been searched for in extraterrestrial samples.

These quinones, which can form abiotically in the dense cloud and protostellar conditions under which new stars and planetary systems form, also play important roles in biochemistry. Thus, our understanding of their extraterrestrial origins, formation mechanism, and distribution is also relevant to astrobiology.

MATERIALS AND METHODS

The preparation and UV photolysis of the H₂O/anthracene ices were performed on a Ni foil substrate held at 15 K in an evacuated sample chamber that is described in detail elsewhere (Allamandola and Sandford 1988; Bernstein et al. 1995; <http://www.astrochem.org/equipment.html>). The anthracene and H₂O were simultaneously vapor-deposited from separate glass source tubes under vacuum through a Swagelok heat exchanger tee in a manner such that the reactants did not mix until condensing onto the 15 K Ni substrate. The samples were deposited at a rate that in previous experiments was shown to produce an ice layer ~0.1 μm thick after 30 min of deposition (Bernstein et al. 2001). These conditions should produce ices with H₂O/anthracene ratios far in excess of 100, with the majority of the anthracene molecules isolated from one another. Residual pressure in the vacuum chamber during deposition was ~5 × 10⁻⁸ bar. Deposit times ranged from 2–7 days. Previous work with ices deposited under these conditions suggest that the H₂O in these ices is in its amorphous form, which is also believed to be representative of H₂O-rich ices in interstellar molecular clouds (Bernstein et al. 2005).

UV photolysis was performed simultaneously with sample deposition using a microwave-powered, flowing hydrogen discharge lamp (Warneck 1962). This lamp produces ~2 × 10¹⁵ photons cm⁻² s⁻¹, the flux being nearly evenly divided between the Lyman line at 121.6 nm and a molecular transition roughly 20 nm wide centered at 160 nm, with a lower level continuum extending beyond 300 nm. The lamp was operated at ~100 mbar of pressure for the H₂ gas. The flux of such lamps has been shown to vary with time and operating conditions, but in this work we have assumed a nominal flux of ~2 × 10¹⁵ photons cm⁻² s⁻¹ (Warneck 1962; Cottin et al. 2003; Loeffler et al. 2005). Based on the absorption cross section of H₂O ice, it has been estimated that 90% of the flux from this type of UV photolysis is absorbed within the first 0.1 μm of a pure water ice (Cottin et al. 2003).

Given the estimated lamp flux and expected absorption depth, the molecules in these ices should have received approximately 30 min of photolysis (~4 × 10¹⁸ photons cm⁻²). For an astrophysical comparison, the UV flux within a dense molecular cloud has been estimated in various literature reports as 1.4 × 10³ to 4.8 × 10³ photons cm⁻² s⁻¹ (Prasad and Tarafdar 1983; Mennella et al. 2003). At the edge of such a cloud, the flux can be approximated as ~10⁸ photons cm⁻² s⁻¹ (Mathis et al. 1983). Given this range, our typical UV dose corresponds to approximately 10² yr at the edge of the cloud, or about 10⁷ yr in the interior of a dense cloud, a reasonable time scale representing the lifetime of the cloud.

Although the conditions described above were used for the majority of these experiments, we modified the procedure for additional preliminary tests of some of our ices. These modifications included depositing/photolyzing samples at

150 K instead of 15 K to determine the effects of temperature, and photolyzing with a high-pressure Hg arc lamp (λ ≥ 200 nm) to test whether there was any wavelength dependence for observed photolysis effects.

Following deposition and photolysis, samples were warmed to 220 K at ~2 K per minute under dynamic vacuum. The Ni foil substrate onto which the ice was deposited was then quickly removed from the vacuum system under air and placed in a glass vial containing 250 μL of HPLC grade methanol; some frost from the room air condensed onto the foil during this process. This methanol extract was then analyzed using high-precision liquid chromatography (HPLC). HPLC was performed on a Hewlett-Packard 1100 series HPLC with tandem diode array UV/Vis and fluorescence detectors and a manual injector with a 5 μL loop. Separation was achieved using a Vydac C-18 4.6 × 250 mm 5 μm resin analytical column with a flow rate of 1 mL/min. The mobile phase was a binary gradient of a) a pH 5.5 50mM sodium acetate + 8% methanol buffer and b) methanol; the gradient ramped from 50% B to 67% B in 30 min.

Elution was monitored in the HPLC by simultaneously measuring the absorption at 238, 252, and 320 nm and the fluorescent emission at 450 nm when excited at 250 nm. Observed peaks were identified by comparing retention time and UV spectrum of unknown peaks with injections of standard solutions analyzed by the same method. The molar absorptivities of the standard compounds were determined from Beer's Law plots (linear fits through zero and the areas of the standard at five concentrations); these absorptivities were then used to determine absolute concentrations of detected compounds. Since our experience with standard solutions indicates that these products do not rapidly (i.e., in seconds to minutes) interconvert, these are taken as representative of the yields of the product molecules.

Control experiments performed with H₂O-anthracene mixtures that were not photolyzed did not produce any detectable products. These experiments indicate that the oxidized anthracene products described below were formed only when H₂O and anthracene are exposed together to UV photolysis. Thus, they are not the result of contamination or other non-photolytic reaction processes.

HPLC grade methanol (99.93% pure), sodium hydroxide (>97% pure), and acetic acid (>99% pure) used in the HPLC buffer were all obtained from Fisher. The water was purified via a Millipore Milli-Q water system to 18.2 MΩ. The anthracene (>99% pure) and the anthracene ketone standards 9,10-anthraquinone (>99% pure) and 9-anthrone (97% pure) were purchased from the Aldrich chemical company; 1,4-anthraquinone (94% pure) was purchased from Alfa Aesar. The anthracene alcohols 1-anthrol and 2-anthrol were not available for purchase; they were synthesized from the corresponding aminoanthracenes and recrystallized following the method of Fierz-David et al. (1946). The synthesized anthrols were purified by sublimation and analyzed by HPLC

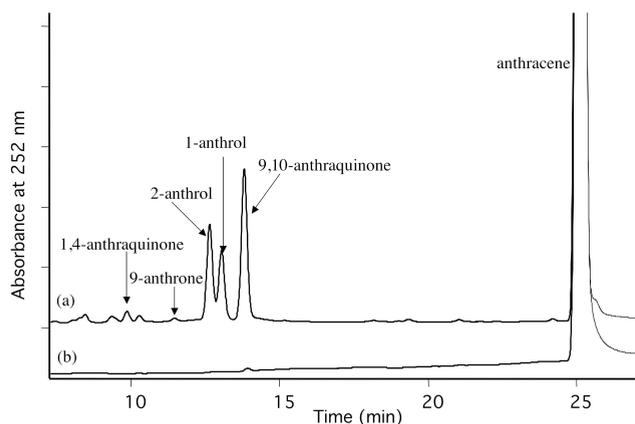


Fig. 1. The HPLC separation of the methanol extracts of the foils containing the residues remaining after warm-up of ices consisting of H₂O:anthracene (>100:1) ice deposited at 15 K, (a) with and (b) without UV photolysis. The peaks associated with unreacted anthracene and the photoproducts 1-anthrol, 2-anthrol, 9-anthrone, 9,10-anthraquinone, and 1,4-anthraquinone are labeled. The two chromatograms have been normalized to the peak height of anthracene.

with absorption and fluorescence detection as described above; the 2-anthrol could not be purified completely, so its absorptivity could not be calculated. Instead, we assumed that 1- and 2-anthrol have similar absorptivities at 252 nm (close to the λ_{max} for each compound) for the purposes of estimating yield.

RESULTS

Our HPLC analyses demonstrate that the vacuum UV (VUV) photolysis of anthracene frozen in solid H₂O followed by warmup yields a mixture of oxidized anthracene derivatives and unreacted anthracene. Figure 1 shows the HPLC results for the methanol extracts of both an anthracene: H₂O + VUV ice and a control ice (anthracene: H₂O, no VUV), both deposited onto substrates cooled to 15 K. The main products (represented structurally in Fig. 2) are two isomers of anthracene bearing two ketones (9,10-anthraquinone [B] and 1,4-anthraquinone [C]). Several singly oxidized species were also identified, including 1-anthrol (D), 2-anthrol (E), and 9-anthrone (F).

In typical experiments, 9,10-anthraquinone was the most abundant product and was produced with a $7.6\% \pm 0.6\%$ yield relative to the unreacted anthracene. The other quinone isomer seen, 1,4-anthraquinone, had a yield of $1.1\% \pm 0.5\%$. These two products were positively identified by comparison with commercial standards.

Three singly oxidized products were also identified. The 1-anthrol and 2-anthrol isomers were identified by comparison with our synthesized standards. The 1-anthrol was produced with a yield of $1.4\% \pm 1.1\%$ compared to unreacted anthracene. The estimated yield of 2-anthrol was

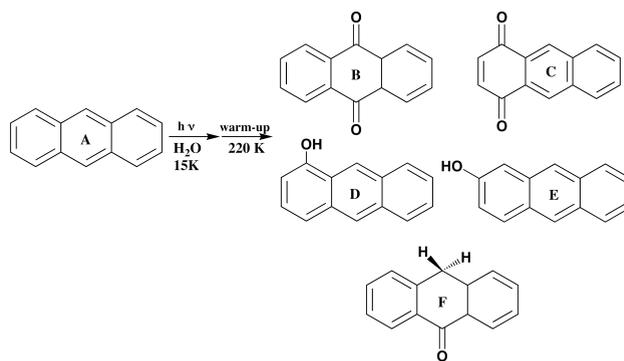


Fig. 2. A structural summary of our interstellar ice experiment depicting oxidation products observed from the in situ photolysis of the PAH anthracene isolated in solid H₂O at 15 K followed by warm-up. A fraction of the original anthracene (A) is converted to the quinones 9,10-anthraquinone (B) and 1,4-anthraquinone (C), the alcohols 1-anthrol (D) and 2-anthrol (E), and the ketone 9-anthrone (F). Molecules A, B, and F have been observed in the CM2 Murchison meteorite (Basile et al. 1984; Krishnamurthy et al. 1992), but we are not aware of any targeted search for the alcohols (D and E) or 1,4-anthraquinone (C) in meteoritic extracts.

the same as that of 1-anthrol ($1.9\% \pm 1.4\%$ relative to unreacted anthracene). The isomer with an oxygen atom added at the 9-position exists in an enol-keto tautomerism between 9-anthrone and 9-anthrol, leading to identification of both peaks in the standard solutions that we prepared with 9-anthrone. We positively identified the 9-anthrone isomer in the longer-running experiments (4–7 days deposition/photolysis), but not in the shorter ones (2–3 days), with a yield of $\sim 0.96\% \pm 0.05\%$ relative to unreacted anthracene.

There are additional peaks in the HPLC data (Fig. 1), indicating the presence of other products that we were unable to identify because we were not able to obtain authentic standards of most of the other possible oxidized and reduced anthracene variants. In a previous study involving naphthalene, where a much larger range of related oxidized standards are available, we identified di-alcohols and alcohol diketones among the products (Bernstein et al. 2001). By analogy to that previous study (and the hydrophilicity suggested by the short retention times), we propose that the unidentified peaks that elute at <10 min in Fig. 1 are probably other oxidized anthracene compounds. Peaks that elute between 18 and 24 min may represent partially reduced anthracene compounds by analogy with a similar experiment with quinolines (Elsila et al. 2006).

A few preliminary experiments were also performed in which certain experimental variables were changed. Photolysis with a high-pressure Hg lamp ($\lambda \geq 200$ nm) produced similar results to the H₂ lamp, with somewhat reduced yields. This indicates that the formation of these photoproducts does not require Lyman α photons or VUV photons, but that light with $\lambda \geq 200$ nm can also drive these

reactions. This is not what would be expected if the reactions were initiated by the photo-dissociation of H₂O (which only absorbs photons with $\lambda < \sim 190$ nm; Calvert and Pitts 1966), or the simple ionization of anthracene, which has an ionization potential (IP) of 7.41 eV, a value equivalent to 167 nm photons (Clar and Schmidt 1976). However, recent experimental work has shown that the IP for the PAH quaterrylene (QTR) is reduced by at least 2.11 eV when it is photolyzed in H₂O ice, a reduction which should hold for other PAHs trapped in H₂O-rich ices (Gudipati and Allamandola 2004; Woon and Park 2004). A 2 eV reduction of anthracene's IP places it at 5.4 eV. This is equivalent to a wavelength of about 230 nm, placing it near the center of one of the strongest absorption bands in anthracene (Birks 1970; Koch et al. 1973). Gudipati and Allamandola (2006) found no difference in the thermal stability and warm-up behavior of QTR⁺ when QTR/H₂O ices were photolyzed with defocused laser light at 266 nm or Ly radiation at 121.6 nm. Thus, it is likely that the anthracene cations react with the H₂O, and other species such as OH, OH⁻, H₂O⁻, etc., in the H₂O ice as the ice structure rearranges during warm-up, likely following the pathways discussed in Gudipati and Allamandola (2006). Thus, the first photolytic step in the creation of the anthracene products described here is probably the ionization of the anthracene to the cation, followed by ion mediated reactions with H₂O and related photofragments during warmup and subsequent H₂O sublimation (Bernstein et al. 1999, 2007; Gudipati and Allamandola 2004).

In another experiment, a sample of H₂O-anthracene ice was vapor deposited and photolyzed on a Ni substrate held at 150 K, rather than 15 K, to simulate possible planetary, rather than interstellar, conditions. At these temperatures, much of the H₂O is likely to be in its cubic and/or hexagonal crystalline forms (Jenniskens and Blake 1994), rather than being amorphous. This ice produced the same products as the 15 K amorphous ice, but the relative yields compared to unreacted anthracene changed; the yield of the quinones dropped substantially (to 0.6% for the 9,10-anthraquinone and 0.2% for the 1,4-anthraquinone), while the yields for the singly oxidized anthrols and anthrone remained approximately the same. The general similarity of products between the 15 K and 150 K ices and the overall lower yields for the 150 K sample are consistent with the possibility that the first photolytic reaction step is the ionization of the anthracene to the cation, with subsequent reaction with H₂O during warmup. The initial ionization of the anthracene should be relatively insensitive to the amorphous/crystalline nature of the H₂O matrix. However, rearrangement/crystallization of the amorphous 15 K ice during warming may promote more interactions of the ions with the ice than will occur when an already crystallized 150 K ice is simply warmed to its sublimation point.

DISCUSSION

Regiochemistry and Mechanism

To fully understand the photochemical processing of anthracene in H₂O-rich ices, it is not enough to just know what types and quantities of atoms are added to the molecule. One needs to determine the full regiochemistry of the process, i.e., determine where these atoms have been added and if there are preferred molecular sites for their addition (preferred isomers). Our previous studies of PAHs in H₂O ices focused on two compounds: the fully condensed PAH molecule coronene (C₂₄H₁₂), and the simple two-ring PAH naphthalene (C₁₀H₈). These compounds were chosen to restrict the range of possible products. Coronene allowed the study of a highly symmetric molecule with only one possible mono-alcohol and one mono-ketone isomer (Bernstein et al. 1999). Naphthalene has two aromatic rings and provides a more complex regiochemistry, with two mono-alcohol and 10 dialcohol isomers possible (Bernstein et al. 2001). Anthracene, which possesses three rings, has even more regiochemical possibilities, with three distinctly different sites for mono-oxidation and 15 possible isomeric combinations for double addition of oxygen. Of the three possible singly oxidized positions, two (the 1- and 2-sites) are most stable in the alcohol form and one (the 9-site) is most stable as the ketone (Notario et al. 2004). The 9,10-anthraquinone is more stable than the singly oxidized compounds based on enthalpy of formation (Ribeiro da Silva et al. 1989). To our knowledge, the corresponding data for the 1,4-anthraquinone is unavailable.

All three singly oxidized anthracene products were formed in these experiments, with the 1- and 2-anthrols formed in roughly equal yields; 9-anthrone was produced at approximately half that yield. The similar production of the two anthrols may be a reflection of their nearly equal thermodynamic stability (Notario et al. 2004). Previous laboratory and theoretical studies of naphthalene suggest a radical cation intermediate in the cryogenic water ice leading to the UV-driven formation of naphthols upon eventual warmup (Bernstein et al. 1999; Ricca and Bauschlicher 2000; Gudipati and Allamandola 2003). A similar radical intermediate mechanism could be responsible for formation of the oxidized anthracenes in the current experiment.

The low yield of the 9-anthrone and the high yield of 9,10-anthraquinone cannot be explained by thermodynamic stability alone, since the 9-anthrone is more thermodynamically favorable than the 1- and 2-anthrols (Notario et al. 2004). However, it is possible that the 9-anthrone, once formed, continues reacting under additional UV exposure to form the 9,10-anthraquinone, the most abundant product observed.

Possible Implications for Meteoritic Aromatics

Oxidized Aromatics

Although aromatics make up a large portion of meteoritic organics and many PAHs, including anthracene, have been detected in carbonaceous chondrites (Pering and Ponnampertuma 1971; Basile et al. 1984; Tingle et al. 1991; Kovalenko et al. 1992), little attention has been focused on oxidized aromatics in these meteorites. A handful of oxidized aromatics have been identified in the Murchison meteorite, including the aromatic ketones 9-fluorenone, 9-anthrone, 9,10-anthraquinone, and phenanthrenedione (Basile et al. 1984; Krishnamurthy et al. 1992). These identified oxidized aromatics include two of the major products formed in our current experiments (9-anthrone and 9,10-anthraquinone). Both Basile and Krishnamurthy also observed many other species that were not identified, in part because of a lack of standards for comparison. These unidentified species could include other oxidized anthracene compounds such as the anthrols and the 1,4-anthraquinone observed in the experiments described here. Any future study that reports the relative abundances of the anthrols and anthraquinone isomers in carbonaceous chondrites could be instructive regarding the possible role of ice photochemistry as a source of such species.

Implications of Ice Photolysis

Ice photolysis is only one means by which meteoritic oxidized PAHs could have formed. The Murchison meteorite, in which oxidized PAH compounds have been observed, experienced aqueous alteration on its parent body, as have numerous other carbonaceous chondrites (Bunch and Chang 1980; Zolensky and McSween 1988). It is possible that this aqueous alteration could form oxidized PAHs from parent aromatic compounds, creating aromatic alcohols and ketones similar to those produced in our ice photolysis experiments. Although the oxidation of anthracene in liquid water under meteoritic conditions has not been studied, there have been some investigations into anthracene oxidation under terrestrial conditions, including both photo-oxidation (Sigman et al. 1991; Beltran et al. 1995) and hydrous pyrolysis under hydrothermal conditions (McCullom et al. 1999). Hydrous pyrolysis of anthracene produced partially hydrogenated compounds, but no oxidized aromatic compounds (McCullom et al. 1999). Anthracene photo-oxidation under terrestrial conditions, however, formed the major product 9,10-anthraquinone (Sigman et al. 1991), which was also the major product in our ice photolysis experiments. Neither the anthrols nor 9-anthrone, significant products in the cryogenic ice irradiation experiments reported here, were observed in the terrestrial photo-oxidation in liquid water experiments. Of course, the conditions used in the terrestrial anthracene oxidation experiments are not

necessarily representative of those that would have occurred on meteoritic parent bodies. Nonetheless, these results suggest that the products formed in oxidation of PAHs in liquid water could be qualitatively different than those formed via ice photolysis and that these different products may provide a means of determining the relative contribution of these formation mechanisms to meteoritic organic inventories. Further work to study the oxidation of PAHs under meteoritic aqueous alteration conditions is needed to test this hypothesis more fully.

The potential connection between ice photochemistry and meteoritic oxidized PAHs also has implications for the D-enrichments observed in many meteoritic organic compounds (Kerridge et al. 1987). In ice photochemistry, D-enrichment should be produced concurrently with photochemical oxidation, producing D-enrichment that should correlate with specific functional groups such as alcohols and ketones (Sandford et al. 2001). Thus, searches for a correlation of D-enrichment with PAH size and oxidation state in meteoritic organics are of particular interest for future studies of oxidized meteoritic aromatics and the potential link with ice photochemistry.

Astrobiological Implications

Oxidized aromatic compounds play a key role in terrestrial biochemistry, where they participate in electron transport, pigmentation, and other important biological functions. For example, the naphthoquinone structure is found in K vitamins, and is found in some electron transporters and oxidative phosphorylation co-enzymes. Oxidized anthracene compounds, such as the 9,10-anthraquinone that was the most abundant product in our UV-photolyzed anthracene:H₂O ices, are also present in life on the Earth. For example, 9,10-anthraquinone is found in plants, including aloe, senna, and rhubarb, and is also produced in fungi, lichens, and insects, serving most commonly as a pigment skeleton. Admittedly, these are not deep-branching forms of life, nor are the roles of 9,10-anthraquinone in these organisms necessarily biochemically ancient. However, it is plausible that 9,10-anthraquinone, if available, could have been used by early life until the enzymatic machinery evolved to create more sophisticated photocenters. Thus, if oxidized aromatic compounds such as 9,10-anthraquinone are formed via ice chemistry in the ISM and are then incorporated into meteorites or other potential planetary impactors, they could be delivered to planetary surfaces and thus could be potentially important ingredients in the prebiotic environments from which life could emerge. Substituted aromatics such as the anthraquinones described here, like other abiotic molecules that resemble those in living things, could act as false biomarkers if detected on the surfaces of solar system objects.

CONCLUSIONS

The main products of the UV photolysis of the PAH anthracene in H₂O at 15 K under astrophysically relevant conditions are (with yields relative to unreacted anthracene in parentheses): 9,10-anthraquinone (7.6%), 1,4-anthraquinone (1.1%), 9-anthrone (1.0%), and the 1- and 2-anthrols (1.4% and 1.9%, respectively). A number of other minor photoproducts remain unidentified.

The production of anthrols in these ices is distinctive compared to the expected products from aqueous alteration under terrestrial conditions; with further study of aqueous alteration under meteoritic conditions, this observation might be used to determine relative contributions of ice photochemistry and parent body aqueous alteration to meteoritic oxidized aromatics. In addition, the type of photochemistry described here is also expected to lead to deuterium enrichment and an expected correlation between D-enrichment and the presence of functional groups such as alcohols and ketones. There have been few reports of oxidized aromatic compounds in meteorites; a systematic search for this class of molecules and an examination of their abundance, D-enrichment, and regiochemistry could shed light on the potential link between interstellar ice chemistry and meteoritic organic compounds. In addition, the astrobiological significance of these oxidized aromatic compounds is another compelling reason to further study the presence of these molecules in extraterrestrial sources and the means by which they could have been delivered to the early Earth.

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