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Article

Pyrogenic Carbon Degradation by Galvanic Coupling with Sprayed Seawater Microdroplets

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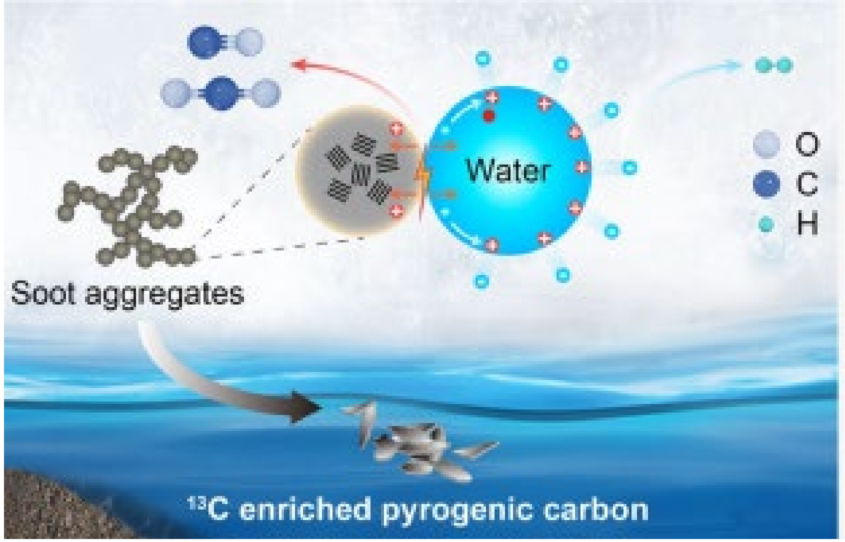
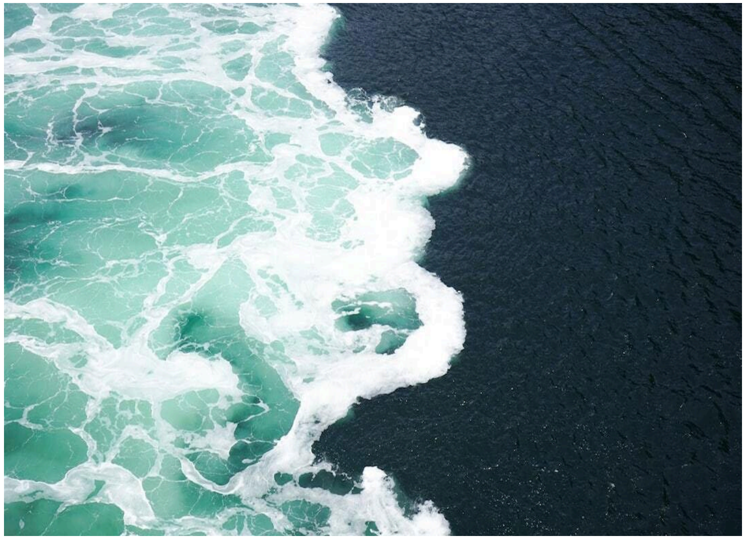


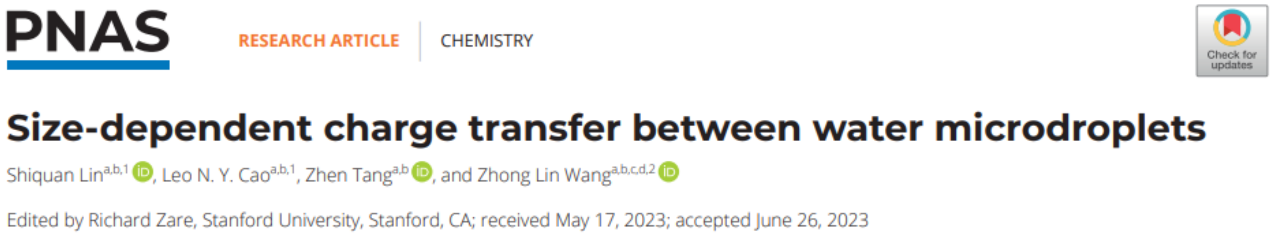
Keerthana Unni
27.04.2024

Introduction

- **Pyrogenic Carbon Overview:** Pyrogenic carbon (PyC), produced during incomplete combustion of biomass and fossil fuels, plays a critical role in carbon sequestration by acting as a long-term sink for atmospheric CO_2.
- **Oceanic Dynamics of PyC:** Approximately one-third of land-produced PyC is transported to the ocean via rivers, where it participates in complex mineralization and export pathways.
- **Significance in Climate Buffering:** Oceanic PyC, through its interaction with coastal and marine processes, significantly influences carbon cycling and potentially enhances climate change mitigation.



Background



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Size-dependent charge transfer between water microdroplets

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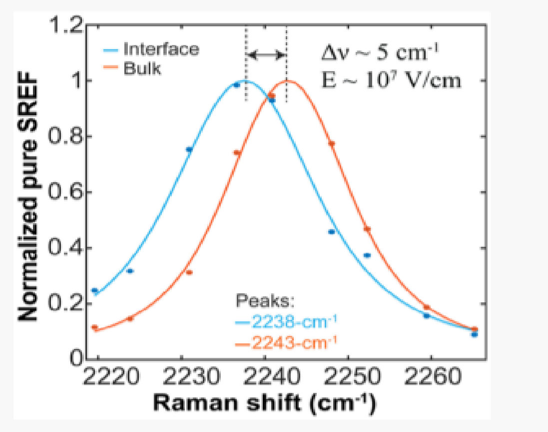


Water microdroplets – donate or accept electrons – three pathways

- High localized electric field on the water droplet
- Size-dependent charge separation exists between two separating water microdroplets known as Lenard effect.
- Contact electrification at water-hydrophobic interfaces leads to an electronic current across interfaces.

Xiong, H.; Lee, J. K.; Zare, R. N.; Min, W. Strong Electric Field Observed at the Interface of Aqueous Microdroplet. *J. Phys. Chem. Lett.*, ***2020***, 11, 7423−7428.

Overview

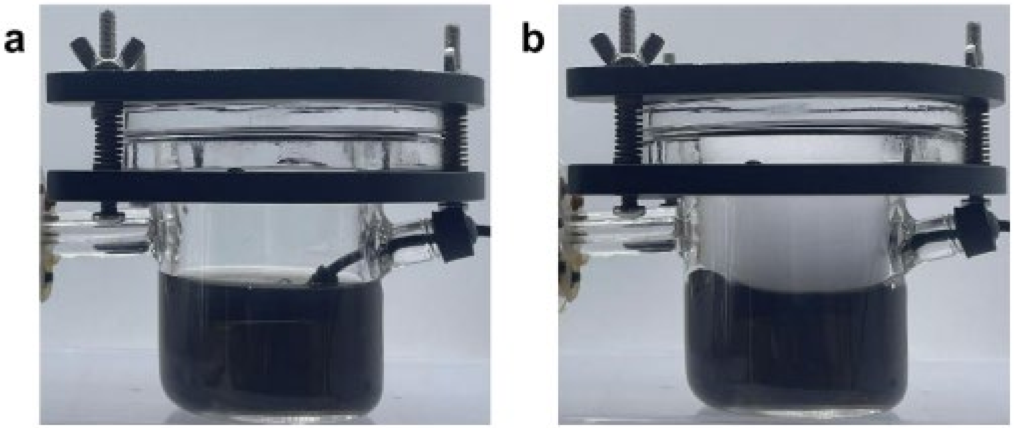
- Galvanic coupling between the contact electrification at microdroplet water−carbon interfaces and the Lenard effect at microdroplet water-vapor interfaces, which can enable refractory PyC to rapidly degrade.

- This electrochemical degradation process - large fractionation of stable carbon isotopes that far exceeds the previously known post-formation alteration of the carbon isotope composition of refractory PyC. This mechanism also accounts for the deposition of refractory PyC.

- A hypothesis is proposed, suggesting that the resuspension of such deposited refractory PyC could act as a source of ^{13}C-enriched PyC in the open ocean. This hypothesis provides a rationale for understanding the role of oceanic PyC in effectively sequestering atmospheric CO_2.

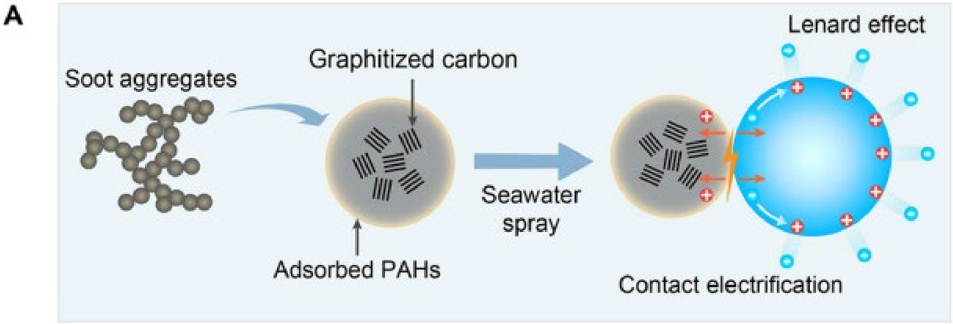
Results and discussion

Sprayed microdroplets – ultrasonic atomization system
Soot – combustion of bamboo pole in the ambient atmosphere
Ultrasonic atomization – homemade quartz reactor equipped with an atomizer of 1.7MHz ultrasonic frequency and 24 W of ultrasonic power.



2 mg soot and 75 mL simulated seawater solution (0.6 M NaCl) were added to the reactor. After removing air via repeated charging with 2 atm O_2 and discharging to 1 atm pressure for 10 times, the ultrasonic atomization was carried out in the dark for 9 h.

Spray process that breaks bulk-phase water into microdroplets- repeated contact and separation between the sprayed microdroplets and soot.



The charge separation between two separating water microdroplets, known as Lenard effect, shows a propensity of interfacial negative charges moving from large microdroplets to small microdroplets and vapor phase. The resultant positively charged seawater microdroplets can be investigated by measuring the accumulated charge of microdroplets collected on a nonconductive glass slide with an electrometer.

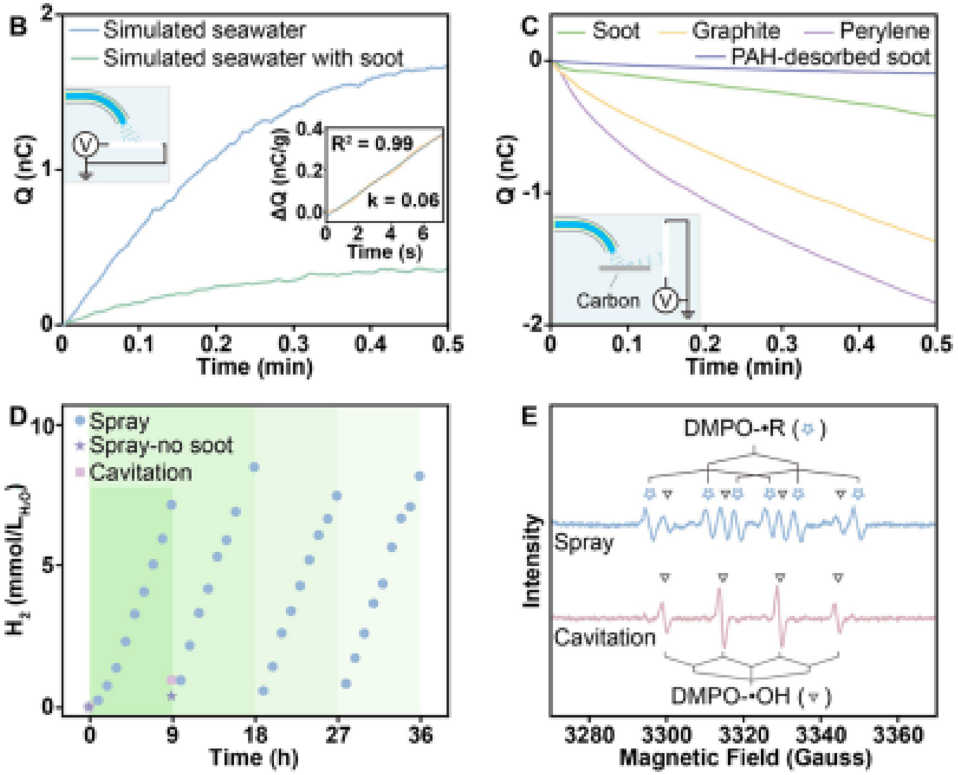


Figure 1. (B,C) Charge measurements of sprayed microdroplets and that after splashing on carbon. (D) Dependence of H_2 evolutions on time course of ultrasonic spray. (E) Measured EPR spectra under spray and cavitation conditions, and every peak is labeled by corresponding patterns.

- π-electron delocalization of carbon and the kinetics of its negative charge transfer to sprayed seawater microdroplets.

- Contact electrification between sp^2 carbon and water microdroplets should occur predominantly at the edge.

$$\Delta V = dQ/C$$

dQ - charge variation
C - interfacial electrical capacitance

- The water microdroplets can mediate an electronic current from carbon to water vapor; thus, a galvanic coupling between the microdroplet water−carbon interfaces and the microdroplet water-vapor interfaces can be established.

Electrochemical reaction driven by the galvanic coupling of the microdroplet water carbon interfaces and microdroplet water vapor interfaces

$$(\mathrm{H_2O})_i + e_{\mathrm{aq}}^{-} \rightarrow \mathrm{H_2} + \mathrm{OH^-}$$

$$(\mathrm{OH^-})_i \rightarrow (\cdot\mathrm{OH})_i + e_{\mathrm{aq}}^{-}$$

$$\text{Carbon or PAHs} + (\mathrm{H_2O})_i \rightarrow \text{Carbon centered radicals} + e_{\mathrm{aq}}^{-}$$

$$(\cdot\mathrm{OH})_i + e_{\mathrm{aq}}^{-} \rightarrow (\mathrm{OH^-})_i$$

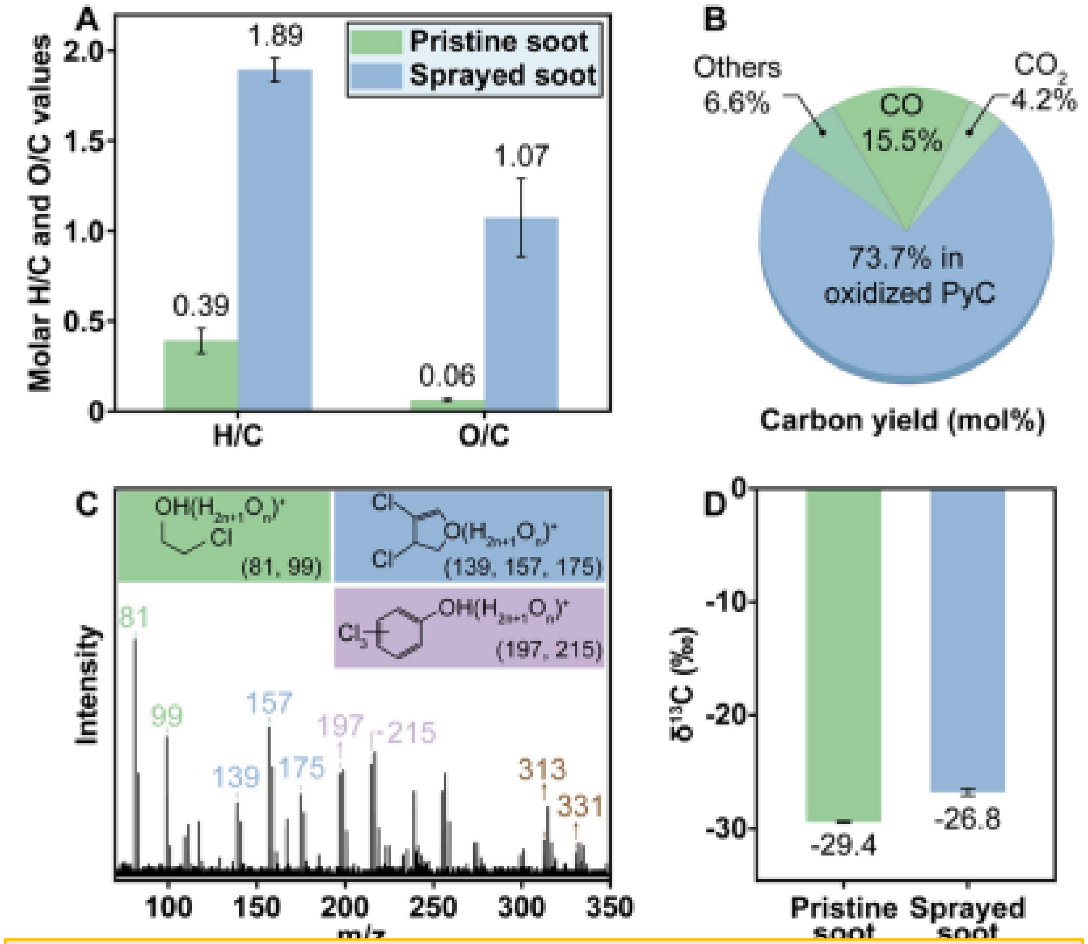


Figure 2. Seawater microdroplets increase the carbon-13 abundance of soot. (A) Elemental analyzer determined molar H/C and O/C values for pristine and sprayed soot. The error bars (standard deviation) were calculated from repeat measurements. (B) Distribution of carbon after ultrasonic spray. (C) Mass spectra of sprayed microdroplets in the absence of an external potential. (D) IRMS determined carbon isotope values for pristine and sprayed soot. The δ13C values are relative to those of Vienna Pee Dee Belemnite (VPDB)

- In contrast to the marked formation of H_2 and CO in sprayed simulated seawater, no H_2 and CO was observed upon substituting ultrapure water for seawater.
- Thus, the presence of ions to assist charge transport via forming electrolyte solution might be required to build up the galvanic coupling of the microdroplet water−carbon interfaces and microdroplet water-vapor interfaces.

- To investigate the intermediate of the oxidative cracking of soot - the sprayed microdroplets using MS operating in positive mode of detection.
- Detected hydrated protonated chloroethanol indicating the formation of epoxy intermediates derived from the epoxidation reaction of unsaturated groups in soot, such as aromatics and vinyl groups. These chloroethanol derivatives can be oxidatively degraded in the presence of microdroplet-bound ·OH, which might contribute to the mineralization reaction.
- This observation suggests that the mineralization reaction occurring at the interfaces of sprayed water microdroplets can induce isotopic fractionation of carbon.

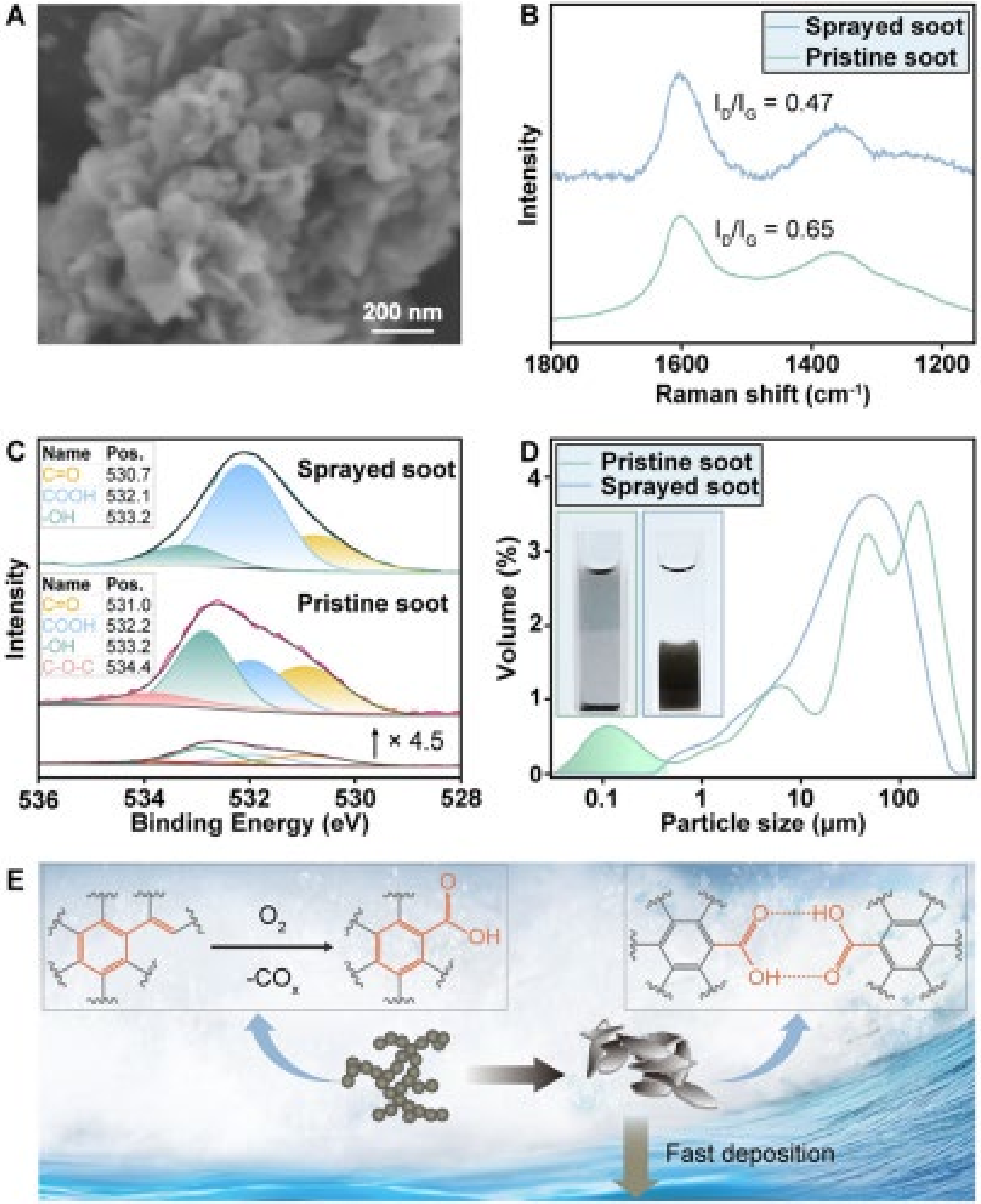
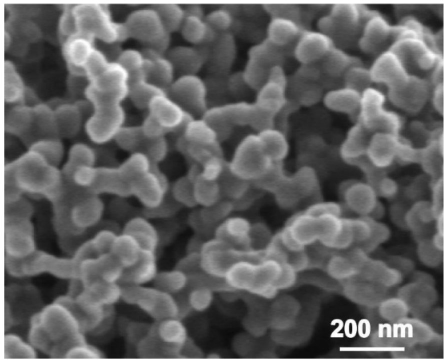
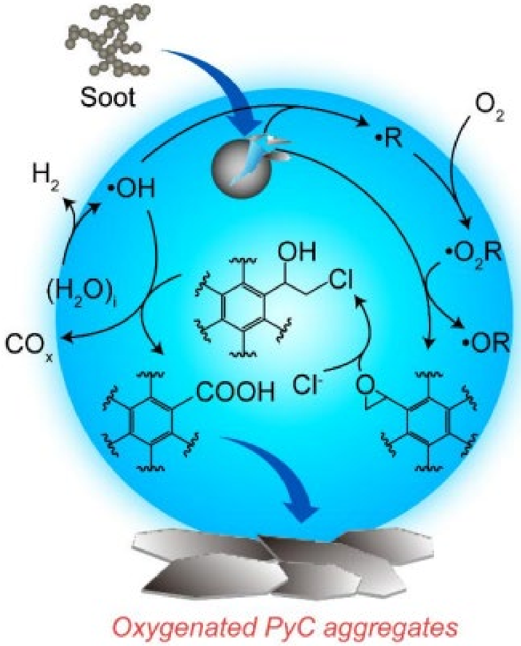


Figure 3. Deposition of soot after seawater spray. (A) Morphological characterization of soot after the reaction. (B) Raman spectra before and after ultrasonic spray. (C) O 1s X-ray photoelectron spectroscopy (XPS) spectra of soot before and after ultrasonic spray. (D) Particle size distribution and deposition of soot solution before and after ultrasonic spray. (E) Schematic representing the mechanism for the microdroplet mediated deposition of soot in seawater





- Initially, upon electron detachment from the interfaces of seawater microdroplets, H_2 evolution occurs, resulting in the accumulation of ·OH in seawater microdroplets.

- These microdroplets can lead to the formation of carbon-centered radical ·R from soot. Subsequently, ·R is oxidized to form ·O2R in the presence of molecular oxygen, which can then undergo addition reactions with unsaturated aromatic groups present in the soot, ultimately resulting in the generation of epoxides by the removal of ·OR.

- Considering the abundance of Cl^- in seawater, the epoxides are expected to readily undergo addition reactions with hydrated chloride ions, yielding chloroethanol derivatives.

- Finally, these chloroethanol derivatives are oxidatively degraded to carboxylic groups, and the process is facilitated by the presence of microdroplet-bound ·OH, which also contributes to the enrichment of ^{13}C in the remanent PyC.

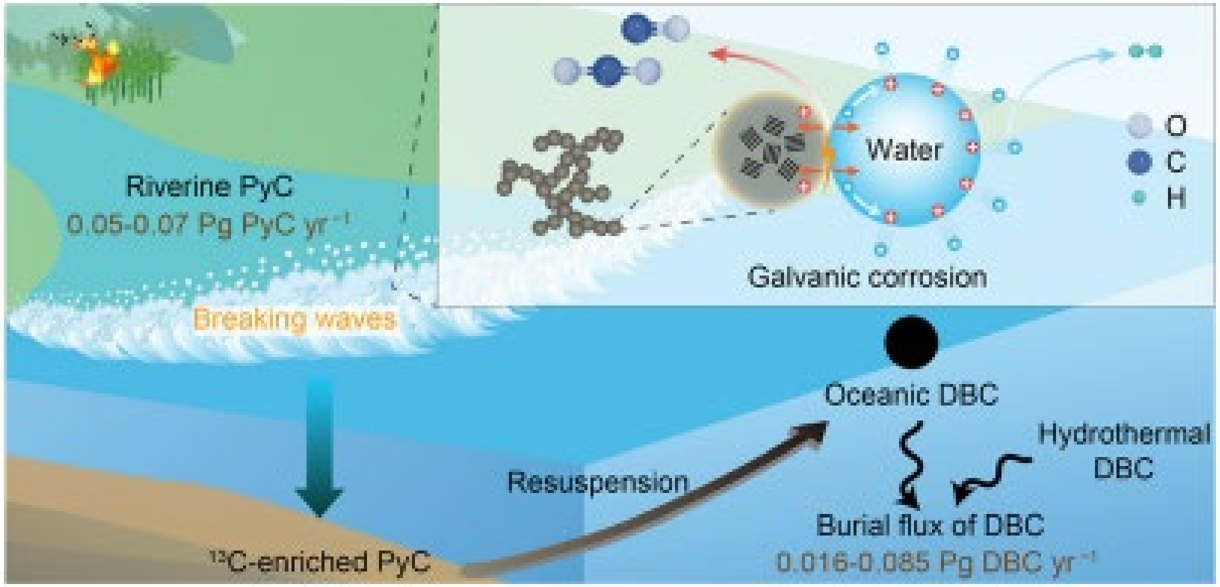


Figure 4. Concept model of PyC sequestering atmospheric CO_2 into the ocean driven by seawater microdroplets.

Summary

- Most riverine PyC derived from biomass may be quickly deposited and become enriched in ^{13}C in the coastal ocean by breaking waves.

- The subsequent resuspension of these deposited PyC in the coastal ocean can serve as a source of ^{13}C-enriched DPyC in the open ocean.

Ultrasonic atomization reaction experiment

Ultrasonic atomization reaction was conducted in a home-made quartz reactor equipped with an atomizer of 1.7 MHz of ultrasonic frequency and 24 W of ultrasonic power. Typically, 2 mg soot and 75 mL simulated seawater solution (0.6 M NaCl) were added to the reactor. After removing air via repeated charging with 2 atm O_2 and discharging to 1 atm pressure for 10 times, the ultrasonic atomization was carried out in the dark for 9 h.

Experimental procedure for the time-dependent curve of hydrogen production in the spraying reaction

The spraying reaction was carried out in a sealed quartz reactor containing simulated seawater solution and charged with 1 atm O_2. The detection of H_2 product was conducted every hour, and the atmosphere inside the reactor was replaced with 1 atm O_2 every 9 hours of atomization to inhibit the backward reaction caused by gas accumulation in the closed system, followed by the continuation of the reaction. A total of four replacements were performed until the accumulated reaction time reached 36 hours.