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Article in *Nature Reviews Earth & Environment* · February 2022

DOI: 10.1038/s43017-022-00271-2

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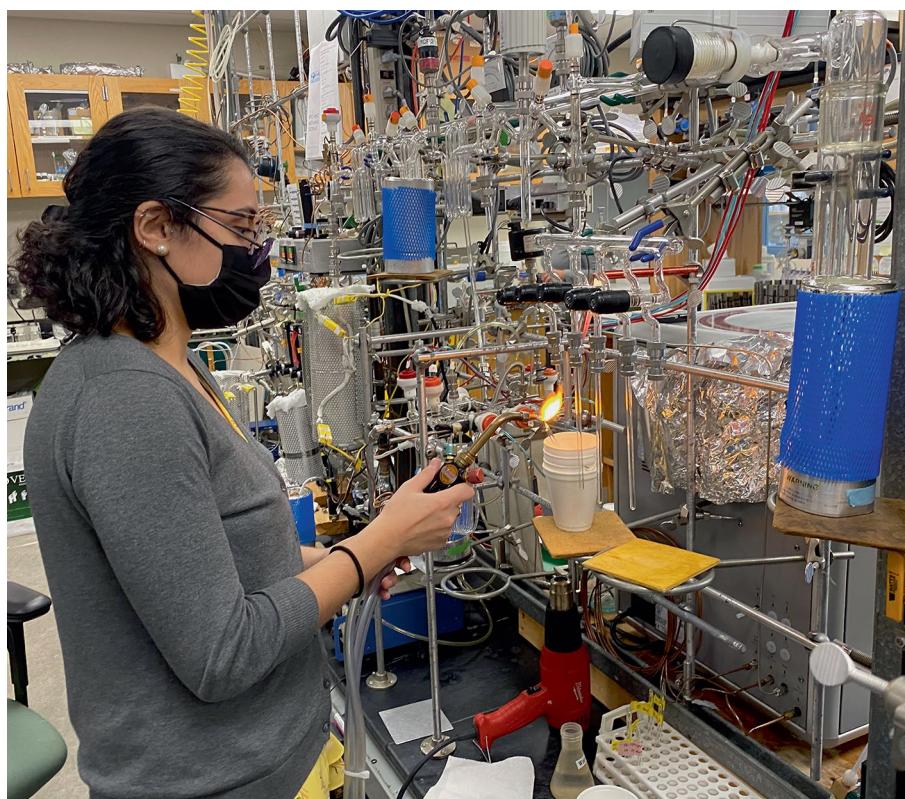
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Characterizing organic carbon with ramped pyrolysis oxidation

The burial and oxidation of organic carbon (OC) partially regulates global atmospheric CO₂ and therefore climate on both modern and geologic timescales. In order to understand fluxes in the carbon cycle, it is imperative to understand the chemical composition of OC, and in turn the fate of different OC sources and sinks. Bulk radiocarbon (¹⁴C) techniques are often used to understand environmental OC, but this method only reflects the average ¹⁴C age of all contributing C sources in a sample, providing no information on the composition of the OC and obscuring natural heterogeneity in OC ages.

Ramped pyrolysis oxidation (RPO) coupled to stable carbon ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) isotopic analyses of CO₂ is an analytical method that characterizes the chemical composition of OC, revealing more of the nuances of OC samples than isotopic analysis alone. In RPO, sequential heating is used to reveal the thermochemical stability of the organic matter, or the amount of energy needed to break the bonds. A sample, such as river or marine sediment, soil, or permafrost thaw water, is heated at a slow rate from room temperature to 1,000 °C in a dual oven coupled to a vacuum line. As the sample is heated, the OC oxidizes to release CO₂, which is passed to a flow-through infrared CO₂ gas analyzer (IRGA). At each time point, the concentration of CO₂ is converted to an instantaneous OC decay rate ($\mu\text{g C per second}$) using the measured gas flow rate and the ideal gas constant. Resulting ppm CO₂ versus temperature plots are referred to as thermograms. These thermograms can be transformed into activation energy distributions, which is an assessment of the overall chemical bonding environment of the OC. More labile



Credit: Mary Lardie Gaylord

OC is typically eluted at lower temperatures than more recalcitrant OC. Downstream of the IRGA, the CO₂ is cryogenically frozen at different temperature fractions based on the sample thermogram and later graphitized before being analyzed using mass spectrometry for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, which help further constrain the sources and ages of the OC.

The RPO thermographs, $\delta^{13}\text{C}$ values, and resulting $\Delta^{14}\text{C}$ ages can be used in tandem to resolve fundamental questions in the carbon cycle. For example, the combined data can be used to understand controls on the distribution

of ages and turnover rates of OC in soil; quantify the balance of modern versus aged OC that is mobilized in regions experiencing permafrost melting; or to constrain whether particulate river OC fluxes represent a potential sink or source of atmospheric CO₂ through the land–ocean continuum.

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Competing interests

The author declares no competing interests.