Organic carbon hides in sediments, keeping oxygen in atmosphere

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Lead author Jordon Hemingway holding a sample of Amazon river water rich in sediments. Credit: Chris Linder

A new study from researchers at the Woods Hole Oceanographic

Institution (WHOI) and Harvard University may help settle a long-standing question—how small amounts of organic carbon become locked away in rock and sediments, preventing it from decomposing. Knowing exactly how that process occurs could help explain why the mixture of gases in the atmosphere has remained stable for so long, says lead author Jordon Hemingway, a postdoctoral researcher at Harvard and former student at WHOI. The paper publishes June 14 in the journal *Nature*.

Atmospheric carbon dioxide (CO2), Hemingway notes, is an inorganic form of carbon. Plants, algae, and certain types of bacteria can pull that CO2 out of the air, and use it as a building block for sugars, proteins, and other molecules in their body. The process, which occurs during photosynthesis, transforms inorganic carbon into an "organic" form, while releasing oxygen into the atmosphere. The reverse occurs when those organisms die: microbes start to decompose their bodies, consuming oxygen and releasing CO2 back into the air.

One of the key reasons Earth has remained habitable is that this chemical cycle is slightly imbalanced, Hemingway says. For some reason, a small percentage of organic carbon is not broken down by microbes, but instead stays preserved underground for millions of years.

"If it were perfectly balanced, all the free oxygen in the atmosphere would be used up as quickly as it was created," says Hemingway. "In order to have oxygen left for us to breathe, some of the organic carbon has to be hidden away where it can't decompose."

Based on existing evidence, researchers have developed two possible reasons why carbon is left behind. The first, called "selective preservation," suggests that some molecules of organic carbon may be difficult for microorganisms to break down, so they remain untouched in sediments once all others have decomposed. The second, called the "mineral protection" hypothesis, states that molecules of organic carbon may instead be forming strong chemical bonds with the minerals around them—so strong that bacteria aren't able to pluck them away and "eat" them.

The mixing of organic-rich and sediment-rich waters of the Rio Negro and Solimoes River in the amazon basin. Credit: Chris Linder

"Historically, it's been hard to tease out which process is dominant. The tools we have for organic geochemistry haven't been sensitive enough," says Hemingway. For this study, he turned to a method called "ramped pyrolysis oxidation", or RPO, to test the hypotheses in sediment samples from around the globe. With a specialized oven, he steadily raised the temperature of each sample to nearly 1000 degrees Celsius, and measured the amount of carbon dioxide it released as it warmed. CO_2 released at lower temperatures represented carbon with relatively weak chemical bonds, whereas carbon released at high temperatures denoted strong bonds that took more energy to break. He also measured the age of the CO_2 using carbon dating methods.

"If organic molecules are being preserved because of selectivity—because microbes aren't able to break them down— we would expect to see a pretty narrow range of bond strength in the samples. Microbes would have decomposed the rest, leaving only a few stubborn types of organic carbon behind," he says. "But we actually saw that the diversity of bond strengths grows rather than shrinks with time, indicating that a wide range of organic carbon types are being preserved. We think that means they're getting protection from minerals around them."

Hemingway also saw a pattern in the samples themselves that supported his findings. Fine clays like those found at river outlets had a consistently higher diversity of carbon bonds than coarse or sandy sediments, suggesting that fine sediments provide more surface area on which organic carbon could attach itself.

"If you take, say, granite from New Hampshire and break it down, you'll get a sort of sand. Those grains are relatively large, so there's not that much surface available to interact with organic matter. You really need fine sediments created via chemical weathering at the surface—things like phyllosilicate clays," says Valier Galy, a biogeochemist at WHOI and co-author on the paper.

Although this work provides strong evidence for one hypothesis over another, Hemingway and his colleagues are quick to note that it doesn't provide a definitive answer to the organic carbon puzzle. "We were able to put our finger on the mechanism by which carbon is being preserved, but we don't provide information about other factors, like sensitivity to temperature in the environment, for instance. There are a lot of other factors to consider. This paper is intended as a sort of waypoint to direct biogeochemists in their research," says Galy.

More information: Mineral protection regulates long-term global preservation of natural organic carbon, *Nature* (2019). DOI: 10.1038/s41586-019-1280-6 , www.nature.com/articles/s41586-019-1280-6

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