

Ancient clues help quantify modern methane

Natural geological emissions contributed little to the methane levels of the ancient atmosphere. The same could be true today.

Methane is a potent greenhouse gas. Although present in the atmosphere at less than 1% of the level of carbon dioxide, it strongly absorbs IR radiation, so it's responsible for between 15% and 30% of greenhouse warming. Its atmospheric concentration has more than doubled since the Industrial Revolution, from 700 to 1800 ppb, and continues to rise at a rate close to that of many worst-case projections.

Tracking down exactly where all the CH_4 is coming from has proven stubbornly tricky. The gas has many possible sources, some natural and some anthropogenic. And sources in each of those categories can be either biologically active (wetland bacteria, livestock) or fossil (natural seepage from underground deposits, leaks from the production and use of fossil fuels). Much of the overall emission comes from remote parts of the world, so it's difficult to quantify.

The University of Rochester's Vasilii Petrenko and colleagues may now have found an important piece of the puzzle by taking a look back in time to CH_4 that was trapped in Antarctic ice between 11 000 and 12 000 years ago.¹ By measuring the amount of carbon-14 in the trapped gas, the researchers found that essentially all of the ancient CH_4 was biogenic and that natural fossil emissions at the time were minimal. The result may mean that today's anthropogenic CH_4 emissions, particularly the anthropogenic fossil emissions, are higher than previously thought. If that's the case, we humans have more power than we'd realized to reduce our influence on climate change.

Carbon controversy

Assessments of the current CH_4 budget fall into two broad categories. Top-down studies measure the concentration, distribution, and isotopic composition of the CH_4 already in the air and use models to figure out where it came from. Bottom-



up studies measure emissions from known CH_4 sources, extrapolate them globally, and add them all up.

Both classes of studies are subject to large uncertainties, and even estimates of the same type can disagree substantially. Total global emissions are somewhere in the range of 500 to 700 teragrams per year, with bottom-up studies giving values some 20% higher than top-down ones.² The lion's share of that amount is biogenic, mostly from wetlands and agriculture. Only a minority—perhaps 100 to 150 Tg/yr—comes from fossil sources. But the CH_4 budget includes not only sources but also sinks, and CH_4 is generally removed from the atmosphere at more than 90% of the rate at which it's added. So even a small reduction in emissions could make a big difference.

The isotopic measurements in top-down studies often focus on carbon-13 and deuterium. Although those stable isotopes aren't created or destroyed on Earth in significant amounts, they're fractionated by various physical, chemical, and biological processes, so different sources of CH_4 have different isotopic

FIGURE 1. MINING ANCIENT METHANE.

At Taylor Glacier in Antarctica, Christo Buizert of Oregon State University helps to load ice cores into a melt-extraction chamber to measure their carbon-14 content. (Courtesy of Vasilii Petrenko.)

makeup. But stable isotope signatures are imperfectly known, overlap for different sources, and can even change over time for a single source.

Radioactive ^{14}C is different. It's created by cosmic rays in the stratosphere and upper troposphere, and it decays with a half-life of 5700 years. The atmosphere therefore has a steady-state concentration of ^{14}C , as do living organisms, which are constantly taking in and expelling carbon. When an organism dies, the carbon exchange stops, and the ^{14}C content declines.

That ^{14}C decay is the well-known basis for carbon dating. It also offers a way to distinguish between CH_4 sources. Biologically sourced CH_4 has the same ^{14}C level as the organisms that created it; the atmospheric lifetime of CH_4 , about 10 years, is too short for any appreciable decay to happen in the atmosphere. On

the other hand, fossil CH_4 , trapped underground for millions of years, has long lost all its ^{14}C . In principle, then, measuring the ^{14}C in a sample of CH_4 should reveal how much of it came from biological and how much from fossil sources.

In today's atmosphere, that measurement is hampered by the appreciable amount of $^{14}\text{CH}_4$ produced by nuclear power plants, and the biological-fossil breakdown of the modern CH_4 budget is still a matter of some controversy. The preindustrial atmosphere, as preserved in glacial ice, presents no such complication.

Cosmic correction

Petrenko and colleagues' first attempt to measure $^{14}\text{CH}_4$ in ancient ice was in 2009, when Petrenko was a graduate student with Jeffrey Severinghaus (also an author on the new paper) at the University of California, San Diego.³ They had several reasons for focusing on the period from 11 000 to 12 000 years before the present. It's well before the rise of any anthropogenic emissions, but recent enough—just two half-lives ago—that enough ^{14}C

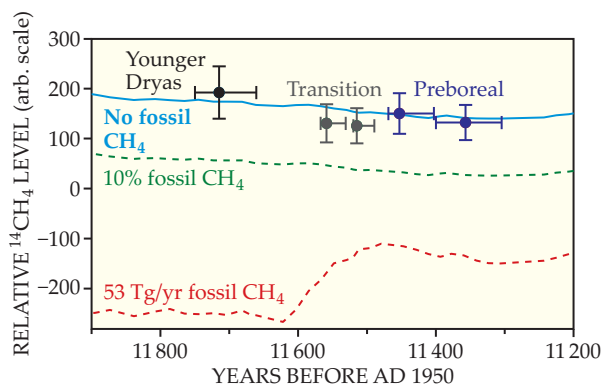


FIGURE 2. CARBON-14 IN METHANE from the Younger Dryas and Preboreal periods and the transition period between them. All measurements are most consistent with the conclusion that essentially all the atmospheric CH_4 came from biological, not fossil, sources. (Adapted from ref. 1.)

remains to measure. And it was a period of rapid change, both globally and regionally. The world was just emerging from the Younger Dryas period, which saw much of the Northern Hemisphere covered in ice, and entering the more hospitable Preboreal period. During the transition, many parts of the globe experienced abrupt climate change—parts of Greenland, in particular, warmed by as much as 10°C in just 20 years. And the global CH_4 level rose sharply—from 500 to 700 ppb—at an annual rate comparable to what we're experiencing today.

The researchers were interested in what sources drove that increase and how it was related to the regional warming.

Because CH_4 is a trace atmospheric gas and ^{14}C is a trace isotope, an accurate measurement requires about 1000 kg of ancient ice—a bit more than a cubic meter (see figure 1). That's too much to be feasibly obtained by the traditional method of drilling deep into a stratified ice sheet. Fortunately, certain locations in Greenland and Antarctica expose plenty of old ice at their surfaces. (Because the mixing time of the global atmosphere

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is about a year, an order of magnitude less than the CH_4 atmospheric lifetime, both Arctic and Antarctic ice record the same long-term trends.) The ice is dated through measurements of quantities, such as total CH_4 concentration and various stable-isotope levels, that changed in known ways over time.

In their 2009 study, Petrenko and colleagues analyzed several samples from across their period of interest. Surprisingly, all their ^{14}C values were far too high to be explained even by attributing all the ancient ^{14}C to biological sources. The discrepancy, they determined, was because ^{14}C creation by cosmic rays isn't limited to the upper atmosphere; the rays also penetrate near-surface ice to create ^{14}C *in situ*.

It took the researchers until 2016 to figure out how to correct for the cosmogenic ^{14}C . They travelled to Antarctica's Taylor Glacier, an extraordinary region where surface ice ranges from 8000 to more than 100 000 years old. They analyzed samples of 50 000-year-old ice—old enough that all its original ^{14}C was gone, and the only $^{14}\text{CH}_4$ remaining was cosmogenic.⁴

Then, for the present study, they moved 300 m along the glacier to col-

lect samples from the Younger Dryas–Preboreal period of interest. They used the 50 000-year-old samples to correct for cosmogenic $^{14}\text{CH}_4$ and estimate the true amount of $^{14}\text{CH}_4$ present in the atmosphere 11 000–12 000 years ago.

Figure 2 shows their results, along with a few model calculations based on different assumptions. As indicated by the light blue curve, the data are most consistent with the scenario in which all the CH_4 throughout the period was biological, not fossil. Even the case of 10% fossil CH_4 , shown by the green curve, is outside one standard deviation. Far outside the uncertainty limits is the red curve, which assumes a constant 53 Tg/yr of fossil CH_4 , a common estimate of today's nonanthropogenic fossil CH_4 from bottom-up and ^{13}C studies.⁵ In fact, Petrenko and colleagues found that at the 95% confidence limit, at most 15 Tg/yr of ancient CH_4 —about 7% of the total—came from fossil sources.

It's not impossible that geological CH_4 seepage could have increased threefold over 11 000 years. But it would be a puzzling rate to explain. Geological processes don't usually change that much over mere millennia, and if anything, the emissions should have decreased

over time. Sea levels have risen since then and covered up some potential CH_4 seeps (and it appears that CH_4 emitted deep underwater may be gobbled up by bacteria before it reaches the surface; see PHYSICS TODAY, August 2017, page 21). And as oil fields are drained of their natural gas, less remains to seep out naturally.

Petrenko and colleagues' work therefore suggests, but doesn't prove, that modern estimates of natural fossil CH_4 emissions may need to be revised downward—and thus that estimates of anthropogenic fossil CH_4 may need to be revised upward. The researchers plan to make similar measurements on ice from 200 to 250 years ago—much more recent but still largely preindustrial—to solidify their case.

Johanna Miller

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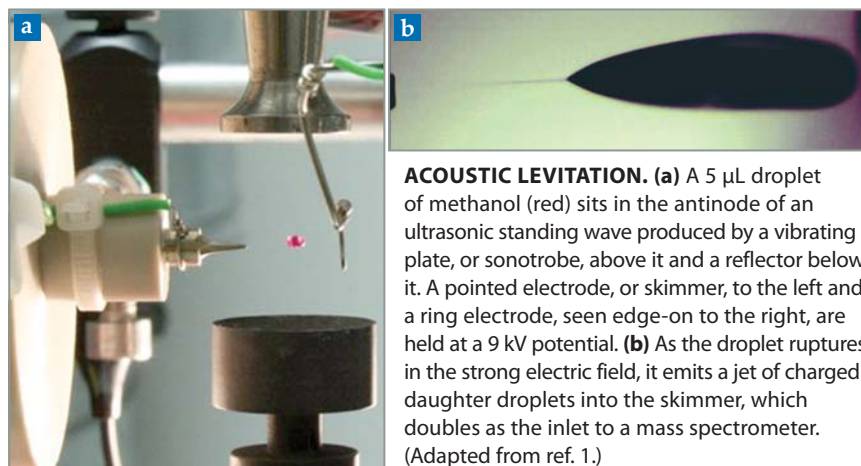
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Acoustic levitation widens the study of droplet jetting

To investigate the fission of charged droplets, a pair of chemists holds one stationary in electrified midair.

Thunderclouds, combustion chambers, and inkjet nozzles are among the many settings where droplets break up in an electric field. More than half a century ago G. I. Taylor identified the mechanism behind the fission. Above some field strength known as the Taylor limit, the coulombic repulsion of charges on a droplet's surface overcomes the attractive intermolecular forces that hold it together. As a result, the droplet ruptures and spews a fine jet of tiny daughter droplets.

Despite the natural and technological relevance of the phenomenon, some details remain murky. Macroscopic properties such as solute concentration, pH, and charge density are not uniform along a parent droplet's radius, and its surface



ACOUSTIC LEVITATION. (a) A 5 μL droplet of methanol (red) sits in the antinode of an ultrasonic standing wave produced by a vibrating plate, or sonotrode, above it and a reflector below it. A pointed electrode, or skimmer, to the left and a ring electrode, seen edge-on to the right, are held at a 9 kV potential. (b) As the droplet ruptures in the strong electric field, it emits a jet of charged daughter droplets into the skimmer, which doubles as the inlet to a mass spectrometer. (Adapted from ref. 1.)

and bulk compositions can differ dramatically. No one precisely understands the fluid dynamics that determine what molecular and ionic solutes the daughter droplets inherit from their parent. The dynamics of the rupture are complex,

and the mathematical singularity of the electric field at the sharp point that forms at the moment of breakup complicates numerical simulations.

Most research on droplet jetting is conducted with a 15-year-old technique