

is about a year, an order of magnitude less than the  $\text{CH}_4$  atmospheric lifetime, both Arctic and Antarctic ice record the same long-term trends.) The ice is dated through measurements of quantities, such as total  $\text{CH}_4$  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  $^{14}\text{C}$  values were far too high to be explained even by attributing all the ancient  $^{14}\text{C}$  to biological sources. The discrepancy, they determined, was because  $^{14}\text{C}$  creation by cosmic rays isn't limited to the upper atmosphere; the rays also penetrate near-surface ice to create  $^{14}\text{C}$  *in situ*.

It took the researchers until 2016 to figure out how to correct for the cosmogenic  $^{14}\text{C}$ . 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  $^{14}\text{C}$  was gone, and the only  $^{14}\text{CH}_4$  remaining was cosmogenic.<sup>4</sup>

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  $\text{CH}_4$  throughout the period was biological, not fossil. Even the case of 10% fossil  $\text{CH}_4$ , 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  $\text{CH}_4$ , a common estimate of today's nonanthropogenic fossil  $\text{CH}_4$  from bottom-up and  $^{13}\text{C}$  studies.<sup>5</sup> In fact, Petrenko and colleagues found that at the 95% confidence limit, at most 15 Tg/yr of ancient  $\text{CH}_4$ —about 7% of the total—came from fossil sources.

It's not impossible that geological  $\text{CH}_4$  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  $\text{CH}_4$  seeps (and it appears that  $\text{CH}_4$  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  $\text{CH}_4$  emissions may need to be revised downward—and thus that estimates of anthropogenic fossil  $\text{CH}_4$  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

## References

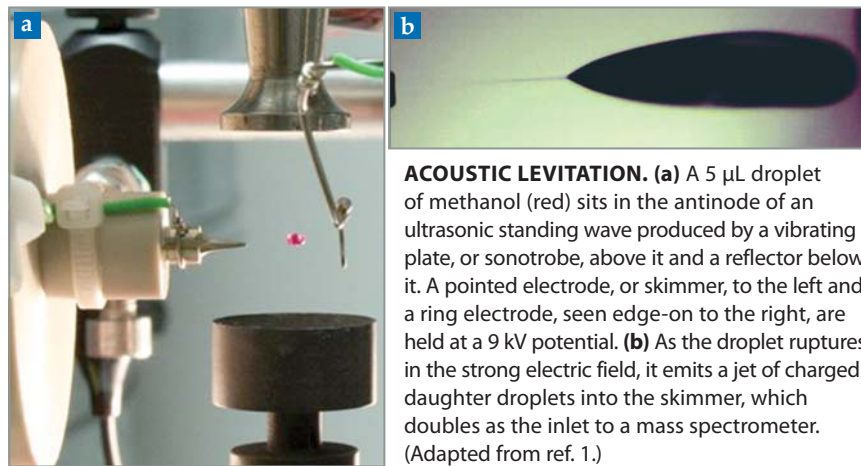
1. V. V. Petrenko et al., *Nature* **548**, 443 (2017).
2. S. Kirschke et al., *Nat. Geosci.* **6**, 813 (2013).
3. V. V. Petrenko et al., *Science* **324**, 506 (2009).
4. V. V. Petrenko et al., *Geochim. Cosmochim. Acta* **177**, 62 (2016).
5. G. Etiope et al., *Geophys. Res. Lett.* **35**, L09307 (2008); S. Schwietzke et al., *Nature* **538**, 88 (2016).

# 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.

**T**hunderclouds, 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  $\mu\text{L}$  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

known as field-induced droplet ionization, in which a series of parent droplets are dripped in air between the parallel plates of a charged capacitor. As they fall, the droplets become polarized in the capacitor's electric field, take on a lemon-like shape, and, depending on the droplets' net charge, squirt jets from one or both pointed ends toward the electrodes. But although the field strength and the net charge can be freely adjusted, experimenters can probe the droplets' dynamics only within the few milliseconds they remain in free fall.

Carsten Warschat and Jens Riedel from Germany's Federal Institute for Materials Research and Testing (BAM) have developed an acoustic technique that can probe those dynamics on the same droplet for as long as it lives—levitated in electrified midair.<sup>1</sup> As illustrated in the figure, their setup consists of a home-built levitator whose 40 kHz ultrasonic field produces a vertical standing pressure wave between two horizontal electrodes. A droplet placed at a pressure antinode can remain there for seconds to hours, limited only by its evaporation rate. What's more, the setup allows easy access to a nearby mass spectrometer that can capture the daughter droplets and analyze their composition.

Other researchers have studied jets from electrostatically held droplets, but in that approach the electric field has to both rupture the droplet and hold it up, so neither role could be controlled independently. Optical levitation is another option, but the energy to hold the droplet aloft risks overheating it. Acoustic levitation doesn't suffer either problem. Moreover, whereas free-falling, electrodynamic, and optical methods are restricted to droplets with diameters on the scale of tens of microns, an acoustic wave can levitate droplets two orders of magnitude larger—up to 5 mm using a 40 kHz field. (See also *PHYSICS TODAY*, March 2015, page 17.)

That freedom may come in handy in efforts to chemically synthesize relatively large amounts of material using a single droplet as a microreactor or to produce daughter droplets at low electric-field strengths. The Taylor limit depends inversely on the square root of the droplet radius  $r$ . That dependence offers experimental flexibility in cases where the dielectric breakdown of air occurs at field

strengths close to the Taylor limit. With their lower surface-to-volume ratio and slower evaporation, larger droplets also live longer.

In their demonstration, the BAM chemists used high-speed photography and mass spectrometry to image the rupture and chemically analyze the progeny of a methanol droplet roughly 2 mm in diameter. They found that the  $r^{-1/2}$  dependence on the critical threshold field at which fission occurs is still valid at the millimeter scale, says Riedel. More im-

portantly, the demonstration sets the stage for studies on the effects of a droplet's size, charge, and pH on the jet it emits. In preparation, Riedel and Warschat are currently building a controlled humidity chamber. Inside, a droplet's size will be an easily tunable knob and its lifetime effectively infinite.

Mark Wilson

## Reference

1. C. Warschat, J. Riedel, *Rev. Sci. Instrum.* (in press).

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