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Researchers develop a geothermometer for methane formation

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John Eiler (left) and Daniel Stolper (right) with the Caltech-led team's prototype mass spectrometer -- the Thermo IRMS 253 Ultra. This instrument is the first equipped to measure abundances of rare isotopic versions of complex molecules, even where combinations of isotopic substitutions result in closely similar masses. This machine enabled the first precise measurements of molecules of methane that contain two heavy isotopes -- 13CH3D, which incorporates both a carbon-13 atom and a deuterium atom, and 12CH2D2, which includes two deuterium atoms. Credit: Caltech

Methane is a simple molecule consisting of just one carbon atom bound to four hydrogen atoms. But that simplicity belies the complex role the molecule plays on Earth—it is an important greenhouse gas, is chemically active in the atmosphere, is used in many ecosystems as a kind of metabolic currency, and is the main component of natural gas, which is an energy source.

Methane also poses a complex scientific challenge: it forms through a number of different biological and nonbiological processes under a wide range of conditions. For example, microbes that live in cows' stomachs make it; it forms by thermal breakdown of buried organic matter; and it is released by hot hydrothermal vents on the sea floor. And, unlike many other, more structurally complex molecules, simply knowing its chemical formula does not necessarily reveal how it formed. Therefore, it can be difficult to know where a sample of methane actually came from.

But now a team of scientists led by Caltech geochemist John M. Eiler has developed a new technique that can, for the first time, determine the temperature at which a natural methane sample formed. Since methane produced biologically in nature forms below about 80°C, and methane created through the thermal breakdown of more complex organic matter forms at higher temperatures (reaching 160°C-220°C, depending on the depth of formation), this determination can aid in figuring out how and where the gas formed.

A paper describing the new technique and its first applications as a geothermometer appears in a special section about natural gas in the current issue of the journal *Science*. Former Caltech graduate student Daniel A. Stolper (PhD '14) is the lead author on the paper.

"Everyone who looks at methane sees problems, sees questions, and all of these will be answered through basic understanding of its formation, its storage, its chemical pathways," says Eiler, the Robert P. Sharp

Professor of Geology and professor of geochemistry at Caltech.

"The issue with many natural gas deposits is that where you find them—where you go into the ground and drill for the methane—is not where the gas was created. Many of the gases we're dealing with have moved," says Stolper. "In making these measurements of temperature, we are able to really, for the first time, say in an independent way, 'We know the temperature, and thus the environment where this methane was formed.'"

This is the ead author on the Caltech paper, Daniel Stolper, introducing a sample of methane into the mass spectrometer. Credit: Caltech

Eiler's group determines the sources and formation conditions of materials by looking at the distribution of heavy isotopes—species of atoms that have extra neutrons in their nuclei and therefore have different chemistry. For example, the most abundant form of carbon is carbon-12, which has six protons and six neutrons in its nucleus. However, about 1 percent of all carbon possesses an extra neutron, which makes carbon-13. Chemicals compete for these heavy isotopes because they slow molecular motions, making molecules more stable. But these isotopes are also very rare, so there is a chemical tug-of-war between molecules, which ends up concentrating the isotopes in the molecules that benefit most from their stabilizing effects. Similarly, the heavy isotopes like to bind, or "clump," with each other, meaning that there will be an excess of molecules containing two or more of the isotopes compared to molecules containing just one. This clumping effect is strong at low temperatures and diminishes at higher temperatures. Therefore, determining how many of the molecules in a sample contain heavy isotopes clumped together can tell you something about the temperature at which the sample formed.

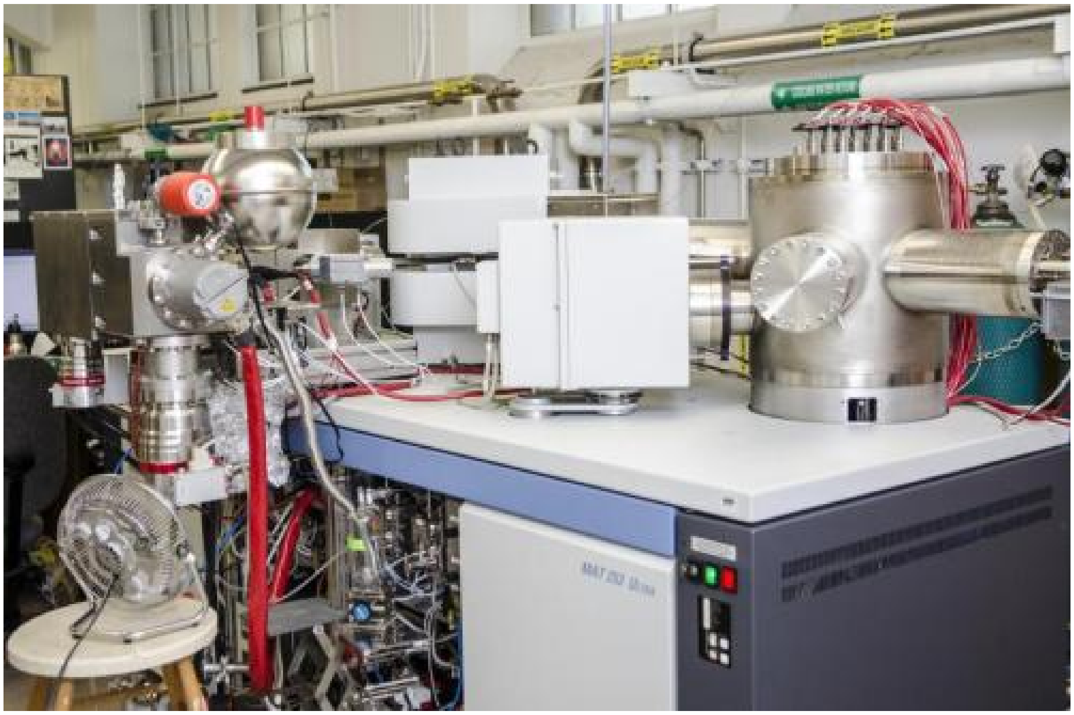
Eiler's group has previously used such a "clumped isotope" technique to determine the body temperatures of dinosaurs, ground temperatures in ancient East Africa, and surface temperatures of early Mars. Those analyses looked at the clumping of carbon-13 and oxygen-18 in various minerals. In the new work, Eiler and his colleagues were able to examine the clumping of carbon-13 and deuterium (hydrogen-2).

The key enabling technology was a new mass spectrometer that the team designed in collaboration with Thermo Fisher, mixing and matching existing technologies to piece together a new platform. The prototype spectrometer, the Thermo IRMS 253 Ultra, is equipped to analyze samples in a way that measures the abundances of several rare versions, or isotopologues, of the methane molecule, including two "clumped isotope" species: 13CH3D, which has both a carbon-13 atom and a deuterium atom, and 12CH2D2, which includes two deuterium atoms.

Using the new spectrometer, the researchers first tested gases they made in the laboratory to make sure the method returned the correct formation temperatures.

They then moved on to analyze samples taken from environments where much is known about the conditions under which methane likely formed. For example, sometimes when methane forms in shale, an impermeable rock, it is trapped and stored, so that it cannot migrate from its point of origin. In such cases, detailed knowledge of the temperature history of the rock constrains the possible formation temperature of methane in that rock. Eiler and Stolper analyzed samples of methane from the Haynesville Shale, located in parts of Arkansas, Texas, and Louisiana, where the shale is not thought to have moved much after methane generation. And indeed, the clumped isotope technique returned a range of temperatures (169°C-207°C) that correspond well with current reservoir temperatures (163°C-190°C). The method was also spot-on for methane collected from gas that formed as a product of oil-eating bugs living on top of oil reserves in the Gulf of Mexico. It returned temperatures of 34°C and 48°C plus or minus 8°C for those samples, and the known temperatures of the sampling locations were 42°C and 48°C, respectively.

To validate further the new technique, the researchers next looked at methane from the Marcellus Shale, a formation beneath much of the Appalachian basin, where the gas-trapping rock is known to have formed at high temperature before being uplifted into a cooler environment. The scientists wanted to be sure that the methane did not reset to the colder temperature after formation. Using their clumped isotope technique, the researchers verified this, returning a high formation temperature.



The Thermo IRMS 253 Ultra is Caltech's prototype mass spectrometer, which enables John Eiler and his team to determine formation temperatures for methane samples. Credit: Caltech

"It must be that once the methane exists and is stable, it's a fossil remnant of what its formation environment was like," Eiler says. "It only remembers where it formed."

An important application of the technique is suggested by the group's measurements of methane from the Antrim Shale in Michigan, where groundwater contains both biologically and thermally produced methane. Clumped isotope temperatures returned for samples from the area clearly revealed the different origins of the gases, hitting about 40°C for a biologically produced sample and about 115°C for a sample involving a mix of biologically and thermally produced methane.

"There are many cases where it is unclear whether methane in a sample of groundwater is the product of subsurface biological communities or has leaked from petroleum-forming systems," says Eiler. "Our results from the Antrim Shale indicate that this clumped isotope technique will be useful for distinguishing between these possible sources."

One final example, from the Potiguar Basin in Brazil, demonstrates another way the new method will serve geologists. In this case the methane was dissolved in oil and had been free to migrate from its original location. The researchers initially thought there was a problem with their analysis because the temperature they returned was much higher than the known temperature of the oil. However, recent evidence from drill core rocks from the region shows that the deepest parts of the system actually got very hot millions of years ago. This has led to a new interpretation suggesting that the methane gas originated deep in the system at high temperatures and then percolated up and mixed into the oil.

"This shows that our new technique is not just a geothermometer for methane formation," says Stolper. "It's also something you can use to think about the geology of the system."

More information: Formation temperatures of thermogenic and biogenic methane, by D.A. Stolper et al. www.sciencemag.org/lookup/doi/ … 1126/science.1254509

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