Ready,

Set, Explore

by Jon Nalick

A restless experimenter, John Eiler cannot resist uncharted territory—even when that happens to be on another planet or billions of years back in time.

In recent years, the geochemist has partnered with colleagues in disparate scientific fields to make discoveries in paleontology, archaeobiology, atmospheric chemistry, climatology, martian geology, and more. Along the way, he has helped develop and refine instruments that reveal previously hidden facets of chemistry, and opened up new areas for scientific exploration.

"My inclination is to be constantly in motion and working in a segment of the scientific community where I can create something that really feels new to me," Eiler says. "So my career has been basically composed of episodes in which I pick something that interests me, then really burrow into it and try to create something substantial. I follow it up with support research, but pretty soon, I'm ready to pack my bags and go do something else."

Last year alone, "something else" included examining coral growth for hints about the connection between historical glacial cycles and changes in carbon dioxide (CO_2) levels in the deep ocean, and confirming the presence of sulfate-reducing microbes in 2.5-billion-year-old sediments.

The main tool in Eiler's kit that permits him to plumb new areas so effectively has been the analysis of isotopic clumping, a novel chemical analysis technique he developed to answer otherwise impenetrable questions. The technique exploits subtle differences in chemistry between the isotopes of a given element—such as carbon. (Isotopes are forms of the same element that differ only in the number of neutrons they contain).

For example, the most common form of carbon, carbon-12, contains six protons and six neutrons, while the rarer carbon-13 contains six protons and seven neutrons. Despite the differences in their number of neutrons, isotopes of a given element are generally thought to be chemically identical: any isotope of oxygen will behave exactly the same way as its peers in terms of what it will interact and combine with. Even so, the isotopes differ in mass, which makes their bonds with other atoms slightly more or less stable, subtly changing reaction rates and isotopic preferences for concentrating in one molecule or atomic site versus another.

The key phenomenon underlying Eiler's work on isotopic "clumping" is that heavier isotopes tend to bind to one another, or clump together, more strongly at lower temperatures and more weakly at higher temperatures. Thus, a measurement of the extent of "clumping" of oxygen, carbon, or hydrogen isotopes in a given sample often constrains the temperature at which a sample formed (though other sorts of chemical and physical effects might also change the proportions of "clumps").

The concept seemed so unlikely when he started talking about it in 2003 that at scientific conferences he was often met with blank stares from attendees. "I'd look out at an audience, which was totally quiet, and realize they didn't have any idea what I was talking about," he remembers. "They'd just

think I was talking about a measurement that sounds impossible."

But Eiler immediately comprehended the potential power of the technique: by focusing on the isotopic structure of compounds instead of simply tallying their total isotopic inventory (as is commonly done), he could glean hitherto inaccessible information. The difference is akin to that of seeing letters jumbled in a bowl of alphabet soup versus seeing the same letters arranged in a newspaper headline.

Much of Eiler's work was made possible by two Moore Foundation gifts. An $8.8 million gift in 2006 created the Center for Geochemical and Cosmochemical Microanalysis, which Eiler directs. The center's resources include two secondary-ion mass spectrometers for analyzing elemental and isotopic abundances, and a facility for developing highly sensitive new instruments to explore geochemistry. An earlier $13 million gift in 2004 created the Tectonics Observatory, which, though now closed, still houses the magnetic sector mass spectrometers he relies on for light-element isotopic analysis.

DINO TEETH AND METHANE FORMATION

Like many scientists, Eiler's fascination with the natural world began as a child. At age six, his curiosity about paleontology and history was apparent in a school report he titled "Dinosaurs—Roar!" Little did he know that 38 years later, his second attempt at a dinosaur paper would make headlines.

In 2011, Eiler led a team that, for the first time, provided hard physical evidence that dinosaurs, rather than being cold-blooded creatures as paleontologists long thought, maintained body temperatures that approximate those of contemporary mammals. For the study, which was published in *Science* and made a splash in the media, his team examined the rare isotopes carbon-13 and oxygen-18 in bioapatite, a mineral found in teeth and bone. Because carbon-13 and oxygen-18 bond to one another in bioapatite at a higher rate at colder temperatures, measuring the clumping of these isotopes directly shows the temperature of the environment in which the mineral formed. In this case, the body temperatures at which the minerals formed inside the dinosaurs studied—*Brachiosaurus brancai* and *Camarasaurus*—were found to be about 38.2 degrees Celsius and 35.7 degrees Celsius, respectively. Subsequent work applied the same tools to carbon-oxygen bonds in the eggshells of several dinosaurs, demonstrating that relatively small ones had significantly lower body temperatures, intermediate between those of modern reptiles and mammals, suggesting the apparent "warm bloodedness" of large dinosaurs may have been due to their great size rather than a metabolism resembling modern mammals.

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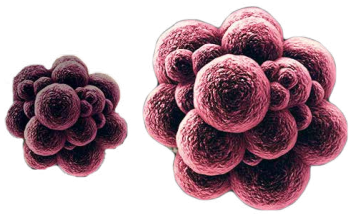
True to form, however, Eiler did not rest on his laurels. He jumped into several other projects that would lead to a flurry of papers in 2014. After tackling long-lost dinosaurs, Eiler teamed up with former Caltech graduate student Daniel A. Stolper (PhD '14) to develop a new technique for helping to determine how, and to some extent, where, a sample of natural methane was formed. Methane—a single carbon atom bound to four hydrogen atoms—forms through a variety of biological and nonbiological processes and under a wide range of conditions, but simply knowing its chemical formula provides no clues as to its origin.

Methane is produced by living organisms at temperatures below about 80 degrees Celsius, while methane created through the thermal breakdown of buried organic matter occurs at temperatures as high as 200 degrees Celsius. Being able to determine the temperature at which a methane sample formed can therefore reveal clues to its origin—an insight that served as a starting point for the study. Using a mass spectrometer that the team designed in collaboration with Thermo Fisher Scientific, the scientists examined the clumping of carbon-13 and deuterium (hydrogen-2) in gas samples created in the laboratory under known conditions to confirm the method's accuracy.

The team then analyzed samples of methane from the Haynesville Shale—a rock formation and methane reservoir that stretches across three Southern states—and found that their results closely matched the reservoir's temperature. They also found that methane formed biologically by oil-eating microbes returned temperatures within a few degrees of the temperatures—around 44 degrees Celsius—of the sampling locations. Additional tests validated the technique as an effective geothermometer, which Eiler says can have important applications in helping to determine, for example, the origin and migration of underground oil as a groundwater pollutant. Subsequent work by Stolper, Eiler, and other colleagues, published in April, demonstrated that this tool can determine mixing ratios of biogenic



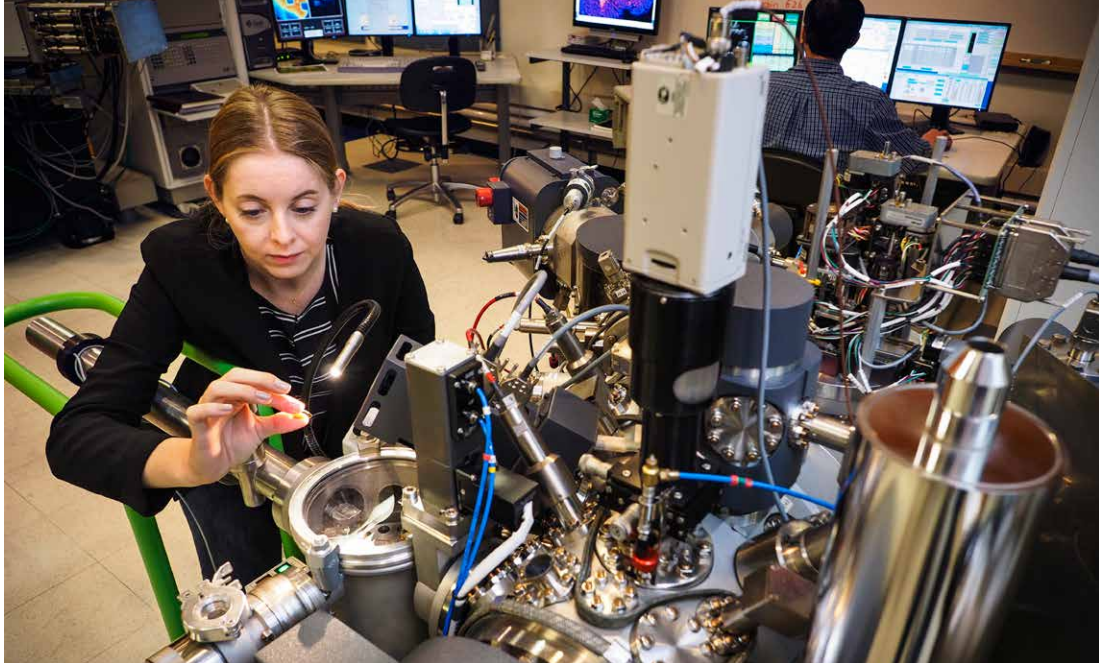
and thermogenic gas in places where the two sources mingle, and also found evidence that in some conditions biological methane-producing reactions can wildly violate the usual patterns of clumping, leading to distinctive isotopic fingerprints that may give clues to the mechanisms of microbial metabolism.

CORAL REEFS AND MARS MOLECULES

Eiler also contributed to a 2014 study concerning climate change, which examined the connection between historical glacial cycles and CO_2 levels in the deep ocean. Because ice sheets generally shrink as CO_2 levels rise, and vice versa, the team hypothesized that the deep ocean—which stores 60 times more inorganic carbon than does the atmosphere—must play a crucial role in these cycles.

Along with Professor of Geochemistry and Global Environmental Science Jess F. Adkins, leader of the project, and Dreyfus Postdoctoral Scholar in Geochemistry Nivedita Thiagarajan, Eiler analyzed the calcium carbonate skeletons of corals collected from one mile below the surface of the North Atlantic. The corals were built up from 11,000 to 18,000 years ago out of CO_2 dissolved in the ocean. Again using clumped isotope thermometry to look at carbon and oxygen isotopes in the calcium carbonate, the group was able to determine the temperature of the water in which the coral grew. The evidence showed that the deep ocean began to warm rapidly before the start of a major climatic shift 14,600 years ago when ice sheets—which had covered a large portion of the earth for about 100,000 years—retreated to their modern ranges. The results help elucidate the underlying mechanisms of climate change and may help us predict how climate may change in the future.

Looking to his prospective research plans, Eiler says he hopes to adapt what he has learned investigating the histories and origins of fairly large molecular structures.



Catherine Macris, a postdoctoral scholar working in Eiler's lab, inspects a polished slice of a tektite—a natural glass formed as a result of high-velocity impacts into Earth's crust—prior to loading the sample into one of Caltech's two secondary-ion mass spectrometers.

"Instead of measuring one special property, like a certain isotopic combination in methane that tells us its formation temperature, we'll try to make measurements where you observe 100 different combinations of isotopes in a single molecule and read back from it information of enormous complexity—maybe its conditions of formation, or the conditions it was stored at, or what substrate it was formed from, or the exact chemical reaction mechanisms by which it was synthesized," he says.

In the short term, he hopes to develop a measurement that can distinguish complex molecules made by life from those same molecules made by nonbiological processes.

"I know we're going to return materials from Mars, and I bet we will find at least one organic molecule in them," he explains. "And immediately we'll be faced with a difficult question—when you have a simple amino acid sitting on the table in front of you, how do you know what made it?"

According to Eiler, it's actually very difficult to tell because there are many processes that make what we normally think of as biomolecules—they occur in space, they get made in rocks, they get made in hydrothermal vents, and so on. But if there was a way of reading from the isotopic structure a very specific description of how that molecule was assembled and from what and under what conditions, that would be helpful.

"We'd have measurements that allow you to say, 'That is an amino acid that fell on Mars out of the sky on a meteorite,'" he says. "Or, 'That's an amino acid that was synthesized in a hydrothermal vent in the crust of the martian surface.' Or 'That was a monster that lived on Mars and this is its amino acid.'

"If we can reach that goal, we will have landed ourselves in a place where we can freely ask similar sorts of questions about all kinds of things: biomedically important compounds in your body, drug compounds, environmental forensics—all kinds of things that involved the history or origin of molecules of moderate complexity," he continues. "I don't know if we'll reach that goal, but it feels important to me. It's exciting to me. It's what I want to explore." E&S

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