Deep biosphere research points to new methods for recovering petroleum

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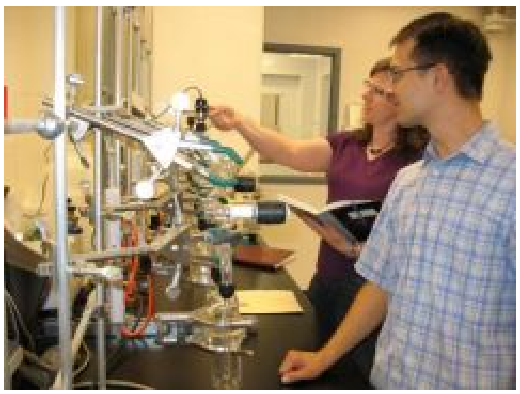

Graduate student Christopher Glein works with Assistant Professor Hilairy Hartnett to assemble testing equipment. Glein is currently the only student involved with the research, but the team anticipates having several more students working on both the experimental/analytical and the thermodynamical/mechanistic aspects of the project. Credit: Nikki Staab, ASU

Miles below us, deep within Earth's crust, life is astir. Organisms there are not the large creatures typically envisioned when thinking of life. Instead, thriving there are microbes, the smallest and oldest form of life on Earth. Although the biological diversity of these deep biosphere microorganisms may surpass that of the more familiar surface biosphere, much about them is still unknown, including the origin of the organic compounds they consume. Arizona State University researchers are using a novel approach that integrates physical organic chemistry with organic geochemistry and biogeochemistry to uncover the source of these organic compounds.

Carbon, the building block of organic matter, is one of the most dynamic elements on the planet; it responds to biological, physical and chemical processes in many ways and on many timescales. Understanding how carbon is formed, where it comes from, and how much of it exists, is important for a more detailed and coherent picture of the global carbon cycle. Yet a complete understanding of how carbon is produced and consumed in the environment still evades researchers because much of what is known is based on processes that act on short time-scales and at Earth's surface.

Deep biosphere microbes, like any living organism, require energy to survive; for many, their sustenance comes in the form of organic compounds. Over time, organic compounds are buried and pushed deeper into the Earth's crust. Harsh conditions on the journey to the deep Earth cause the organic compounds to become "recalcitrant," meaning they are no longer in a form that microbes can use. Some of the consumable organic compounds are produced by other subsurface microbes, but a large portion is most likely the end product of a mysterious geochemical process.

Theoretical biogeochemist Everett Shock, a professor in ASU's School of Earth and Space Exploration and the Department of Chemistry and Biochemistry in the College of Liberal Arts and Sciences, leads an interdisciplinary group of researchers who are investigating how this geochemical transformation from recalcitrant matter to usable organic compounds occurs deep in Earth's crust.

"The secret appears to lie in how temperature and pressure affect the reactivity of organic compounds, and, maybe more importantly, how the properties of water change deep in sediments and sedimentary rocks," says Shock. "The transformation in how water behaves is so enormous that we would hardly recognize it as the same stuff that comes out of our kitchen taps."

Most organic reactions at the Earth's surface do not work very well in water; either they need an organism that has evolved the mechanisms to promote organic reactions in water or they need an organic solvent, hexane or benzene, for example. The very deep Earth, below where microbial life has been shown to exist, has lots of rocks but no organic solvents. It does, however, have very hot water.

Hilairy Hartnett, an assistant professor in the School of Earth and Space Exploration and ASU's Department of Chemistry and Biochemistry, is part of Shock's interdisciplinary group examining the mechanisms of the sub-surface carbon cycle. The team hypothesizes that conditions deep in the Earth might be good for complex organic reactions.

"Evidence suggests that hot water at high pressures - conditions we'd find in the subsurface - is actually a very good solvent for organic reactions," Hartnett says. "It might be possible for these reactions to occur without biology if the conditions are right." She explains, "Biological processes can promote reactions to generate complex organic molecules even at unfavorable low temperatures and pressures - the difference for the deep Earth is the high-temperature and pressure."

Spurred by a $1.5M grant from the National Science Foundation, the team will apply new theoretical models of how water at high temperatures and pressures can transform organic compounds in unexpected ways. Through a series of high-temperature/pressure experiments involving organic compounds, water, and common minerals found in sedimentary rocks such as iron oxides and clays, the team plans to reveal how organic transformation reactions occur in natural geologic conditions.

Team member John Holloway, emeritus faculty in the School of Earth and Space Exploration and ASU's Department of Chemistry and Biochemistry, designed and built the hydrothermal reaction vessels necessary for testing. At ASU's new Omni-pressure Lab, simple compounds such as water and carbon dioxide are placed in the inert gold capsules and then tested.

"The samples are held at temperatures up to 300 degrees Celsius and pressures of 250 atmospheres, equivalent to the bottom of the ocean (2,500 meters) or slightly higher, for periods of hours to weeks," explains Holloway. "They are then quenched to ambient conditions and we analyze the products using gas chromatography and mass-spectrometry."

The results of past similar experiments have shown that the concentration, variety, and complexity of compounds all increase with time, and are strongly influenced by contact with minerals during the experiments.

"It will be important to find out if the mixture of compounds we make in the lab looks anything like the organic compounds that are found in the deep subsurface," says Hartnett. "If they do, then maybe this is how they formed - just rocks, hot water and simple carbon compounds. If they don't, well, we need to figure out what else is required."

"Lots of researchers have looked at individual aspects of the questions we're asking, but this is one of the first - or maybe the first - attempt to look at these high-temperature water-rock-organic processes from an integrated experimental and theoretical standpoint," Hartnett says.

A project of this caliber requires a team with a wide-range of expertise from thermodynamic modeling, reaction mechanisms, and organic characterization, to clay minerals and high-temperature/pressure experiments. Many different techniques and backgrounds are necessary to understand the complexities of the process.

"Some of the known organic reactions under hydrothermal conditions are fascinating to me as an organic chemist. But this is a not a research field that I can enter in my own, I don't know how to do the experiments and I don't know which are the important observations," says chemistry professor Ian Gould, "but I can bring expertise in the area of choosing useful and informative reactions to study."

"No one person is an expert in all aspects of the project. As a team, we all think about the same questions, but we each bring a different set of skills and ideas to the forum. That often means we can find answers more quickly, or find answers that come from a direction any one of us by ourselves might have overlooked," says Hartnett.

"What we're learning may be applied to hydrocarbon exploration, carbon dioxide sequestration, environmental reclamation, and microbial sustainability," says team member Lynda Williams, an associate research professor in the School of Earth and Space Exploration who focuses on the chemical composition of clay and sedimentary minerals. "It could also lead toward understanding primordial conditions on Earth and similar planets where carbon-based life has evolved," she adds.

This interdisciplinary approach to exploring organic reactions in hot water may also have important implications for "green" chemistry. By learning more about how to promote organic reactions in hot water, other researchers may be able to take that knowledge and develop new chemical processes that don't have to use environmentally unfriendly, toxic solvents.

Funded through NSF's Emerging Topics in Biogeochemical Cycles program, Shock and his team will be the first to link organic geochemical reactions deep in the Earth's crust to the support of microbes in the deep biosphere. In the process, the researchers plan to test new ideas about how petroleum forms from deeply buried organic matter, including the direct involvement of deep biosphere microbes. That deeply buried organic material is the precursor to petroleum, but it may also be the food that many microbes need to survive.

"By understanding organic synthesis reactions in the deep biosphere, we may find better organic and inorganic tracers to aid in finding petroleum resources and recovering them in more environmentally friendly ways," says Williams.

Source: Arizona State University

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