The Search for Methane in Earth's Mantle

PETROLEUM geologists have long searched beneath Earth's surface for oil and gas, knowing that hydrocarbons form from the decomposition of plants and animals buried over time. However, methane, the most plentiful hydrocarbon in Earth's crust, is also found where biological deposits seem inadequate or improbable—for example, in great ocean rifts, in igneous and metamorphic rocks, and around active volcanoes. Some scientists thus wonder whether untapped reserves of natural gas may exist in Earth's mantle.

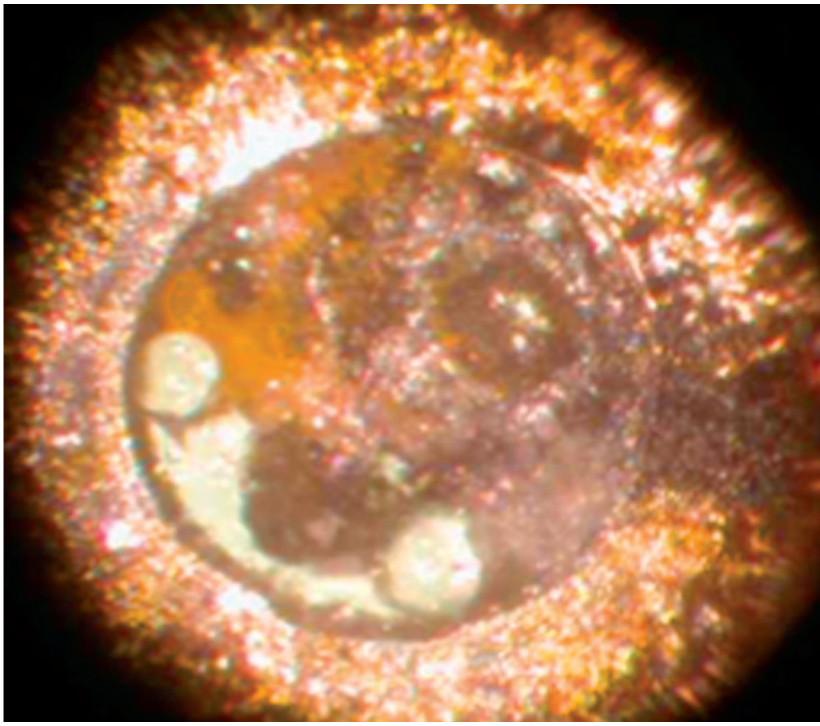
A collaboration of researchers from Lawrence Livermore and Argonne national laboratories, Carnegie Institution's Geophysical Laboratory, Harvard University, and Indiana University at South Bend is finding that methane may also be formed from nonbiological processes. Experiments and calculations conducted by the team indicate that Earth's mantle may provide the temperature and pressure conditions necessary to produce methane.

The idea that methane could be formed nonbiogenically came from observing the solar system. In the 1970s, astronomer Thomas Gold proposed that methane must form from nonbiogenic materials as well as from biological decomposition because large amounts of methane and other hydrocarbons could be detected in the atmospheres of Jupiter, Saturn, Uranus, and Neptune. In fact, in studying Titan, Saturn's largest moon, researchers found seven different hydrocarbons.

At the time Gold proposed this theory, conventional geochemists argued that hydrocarbons could not possibly reside in Earth's mantle. They reasoned that at the mantle's depth—which begins between 7 and 70 kilometers below Earth's surface and extends down to 2,850 kilometers deep—hydrocarbons would react with other elements and oxidize into carbon dioxide. (Oil and gas wells are drilled between 5 and 10 kilometers deep.) However, more recent research using advanced high-pressure thermodynamics has shown that the pressure and temperature conditions of the mantle would allow hydrocarbon molecules to form and survive at depths of 100 to 300 kilometers. Because of the mantle's vast size, its hydrocarbon reserves could be much larger than those in Earth's crust.

Simulating Thermochemical Conditions

Livermore's work on the methane research, led by chemist Larry Fried, uses a thermodynamics code called CHEETAH to simulate chemical reactions using data from the collaboration's experiments. Fried developed CHEETAH in 1993 for the Department of Defense (DoD) to predict the performance of different explosives formulations. Since then, Fried and his colleagues have continued to improve the code. (See *S&TR,* May 1999, pp. 4–11; June 1999, pp. 12–18; July/August 2003, pp. 20–22; July/August 2004, pp. 14–19.)

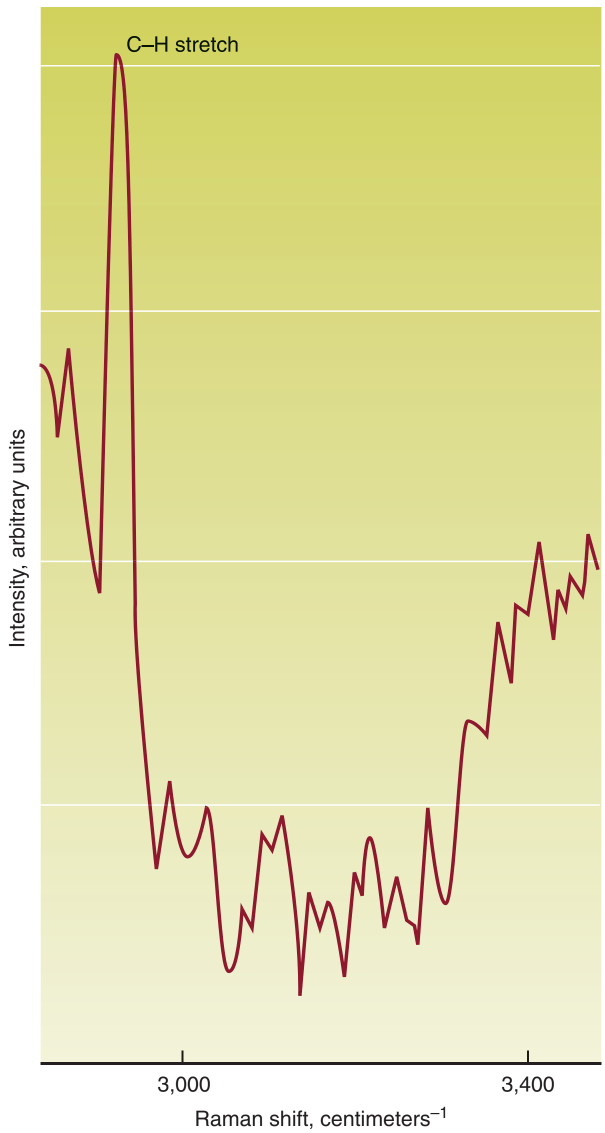


Research indicates that methane bubbles form when iron oxide, calcite, and water are heated to about 1,500°C at a pressure of 5.7 gigapascals and then decompressed at room temperature to 0.5 gigapascal.

One improvement was to include intermolecular interaction potentials. As a result, CHEETAH can model accurate equations of state, describing the relationship of a material's pressure, volume, and temperature at the molecular level, for a broad range of thermodynamic conditions. Because materials behave differently under extreme pressures than they do at normal atmospheric pressure, the equation-of-state data produced with CHEETAH help improve the precision of other computer codes used to model materials for stockpile stewardship.

With funding from the Laboratory Directed Research and Development Program, Fried's team is using CHEETAH to analyze the data from experiments conducted at the Geophysical Laboratory and at Argonne. "CHEETAH was designed for defense-related efforts," says Fried. "Our current studies for the methane collaboration are validating the code for work in high-pressure chemistry. These results will in turn help us better understand the processes occurring in a high-explosive detonation."

For the methane experiments, researchers at the Geophysical Laboratory used Argonne's diamond anvil cell (DAC)—a small mechanical press that forces together the tips of two diamond anvils and creates extremely high pressures on a sample of a material held within a metal gasket. DACs allow researchers to measure material properties under static pressure and at varying pressures and temperatures over many hours. (See *S&TR*, December 2004, pp. 4–11.) Diamonds are used because they can withstand these ultrahigh pressures. Also, their transparency permits diagnostic radiation, such as x rays and visible light, to pass unhampered through their crystalline structure.



In one experiment, a sample of iron oxide, calcite, and water is heated to 600°C at a pressure of about 2 gigapascals. Raman spectra of the sample show a carbon–hydrogen (C–H) stretching vibration at 2,932 centimeters^{-1}, which is the industry-standard signature for methane.

Comparing Experimental Results with Calculations

To determine the chemical reactions that might occur at the pressures and temperatures of Earth's upper mantle, the researchers used the DAC to squeeze a microgram sample of iron oxide, calcite, and water to pressures up to 11 gigapascals at temperatures of more than 1300°C. Then they analyzed the results using Raman spectroscopy, synchrotron x-ray diffraction, and optical microscopy.

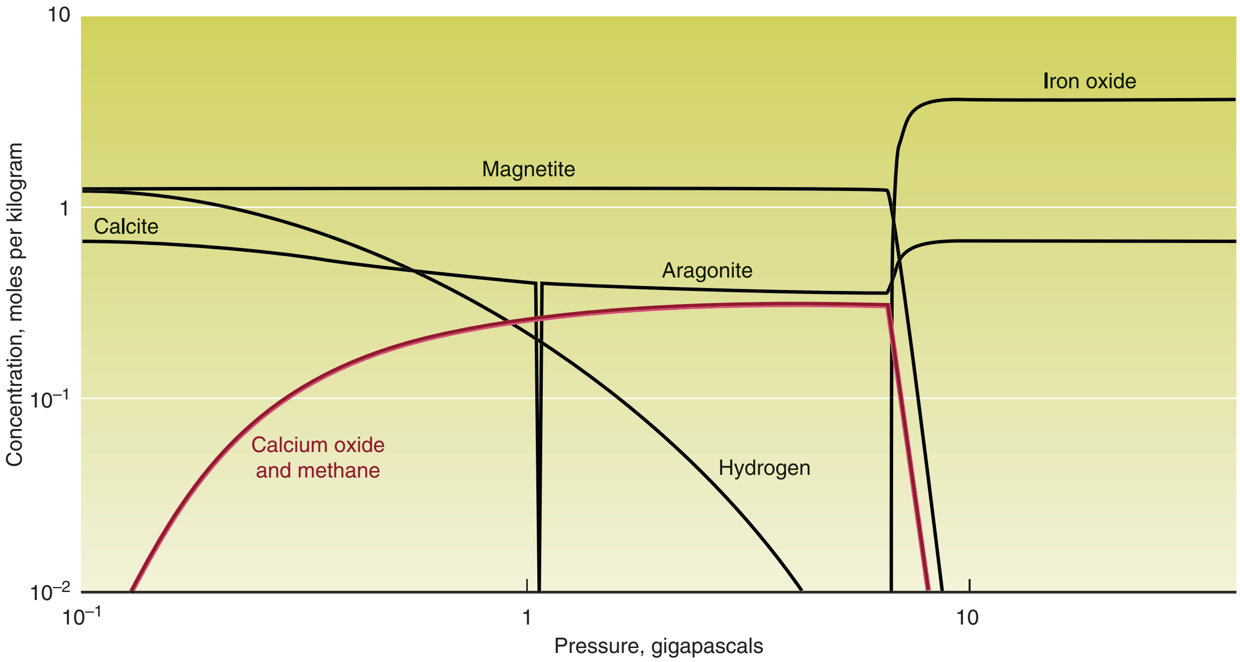
Raman spectroscopy measures the wavelength and intensity of scattered light from molecules as they vibrate about their bonds. These vibrations occur at certain frequencies. At normal pressures, electrons are tightly held within an atom's inner electron bands or shells. Squeezing a material under extreme pressures forces its atoms into a different orientation, which causes the delocalization of electrons and changes a material's properties and molecular structures.

By observing the frequency created when the electrons move or vibrate, scientists can tell how the elements are bonding to each other. Raman spectroscopy is highly sensitive to the stretching vibrations between carbon and hydrogen. The Raman spectra for the DAC samples showed hydrocarbon-rich regions. The bond vibration between carbon and hydrogen becomes apparent in the spectra when the sample temperature reaches 500°C and is very strong by 600°C.

The researchers used synchrotron x-ray diffraction to determine the principal reaction products that occur as the DAC squeezes the samples. With synchrotron x-ray diffraction, a beam of x rays passes through the sample, and the resulting diffraction pattern is recorded on an x-ray film or detector. Changes in the pattern reveal how much of each element is involved in the chemical reaction at different temperatures and pressures. Diffraction results on the team's samples showed the presence of calcium oxide and magnetite—a chemically reduced form of iron oxide. When researchers examined the samples using optical microscopy, they again found changes indicating the presence of methane. Most notable were bubbles, which Raman measurements confirmed to be methane.

The Potential for Unlimited Energy Reserves

The DAC experiments provided the researchers with accurate data on the chemical reactions occurring at the temperature and pressure conditions of Earth's mantle. Fried's team then



Thermochemical calculations for a mixture of iron oxide, calcite, and water heated to 500°C show that methane is produced at pressures up to almost 7 gigapascals.

simulated these reactions using CHEETAH. "Our goal," says Fried, "is to perform thermochemical calculations to determine which temperatures, heating mechanisms, and pressures are most favorable for methane formation." The CHEETAH calculations indicated that methane production is most likely to occur at temperatures near 500°C when pressure is less than 7 gigapascals. These conditions correspond to depths between 100 and 200 kilometers.

"According to our calculations, methane is thermodynamically stable at 500°C and at pressures up to 7 gigapascals," says Fried. "Those results indicate that methane reserves could possibly exist below Earth's surface with a half-life of millions of years." Although methane continued to form up to 1,500°C, the simulations showed that at higher temperatures, the carbon in calcite formed carbon dioxide rather than methane. The calculations also confirmed experimental results indicating the presence of magnetite.

Fried cautions that these findings are preliminary, and more research is needed to determine whether hydrocarbon reserves are indeed available in Earth's mantle. Nevertheless, the Livermore team is pleased with the results. "This work is a good example of collaborative success with groups outside the Laboratory, and it shows a successful dual-use of defense-related technologies," says Fried.

Livermore researchers plan to examine other simple molecular compounds under high pressure, for example, water under conditions that exist in the interiors of giant planets. They will use molecular dynamics and Raman spectroscopy to investigate the existence of a superionic phase of water. In this phase, oxygen atoms are fixed while hydrogen atoms diffuse freely. For Livermore researchers, the ability to study materials under extreme temperatures and pressures means that even the simplest substances may yield many surprises.

—Gabriele Rennie

Key Words: CHEETAH code, diamond anvil cell (DAC), hydrocarbon, methane, Raman spectroscopy, thermodynamics, x-ray diffraction.

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