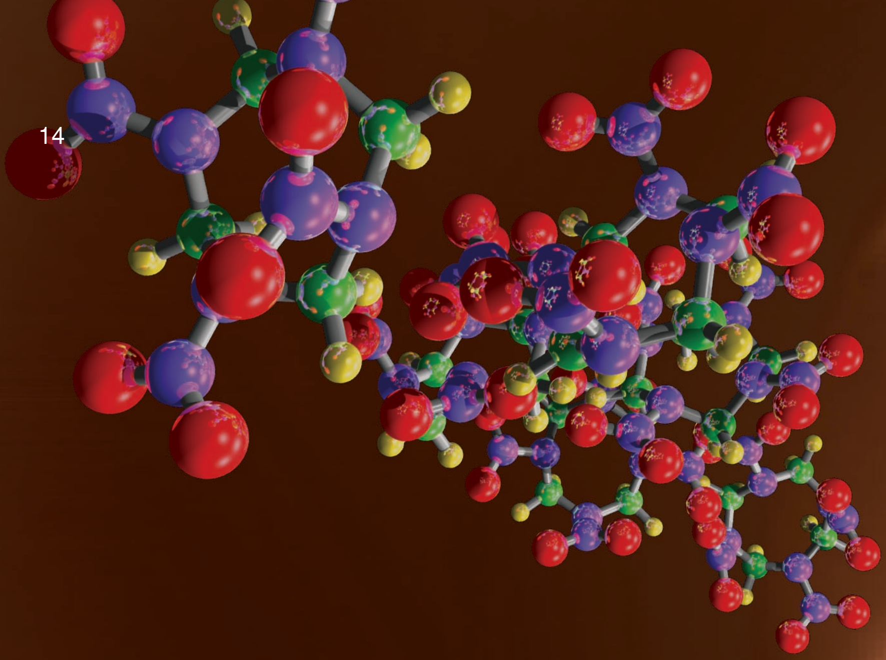


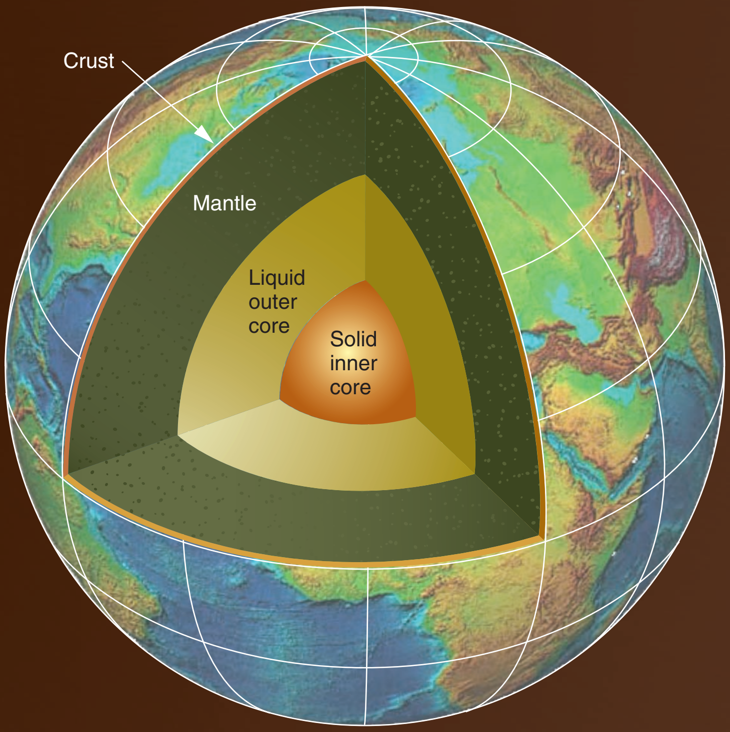
Going to Extremes

Researchers turn up the heat and pressure to understand chemical reactions under extreme conditions.

LITTLE is known about the chemistry that produces minerals in the deep regions of Earth or that creates the ammonia oceans of the outer planets and moons. What *is* known is that an element's fundamental properties—its optical, structural, electrical, and magnetic characteristics—can completely change when it is put under extreme conditions. In fact, when a material is exposed to pressures up to one million times the atmospheric pressure at Earth's surface and to temperatures above 6,000°C, its atoms can completely rearrange themselves, rendering an entirely new substance.

Similar conditions exist near Earth's core and in other planets, both inside and outside the solar system. They also occur in high-explosive reactions and impacts from meteorites and comets. Understanding chemical reactions at such extreme conditions is a critical research area for the National Nuclear Security Administration's (NNSA's) Stockpile Stewardship Program. To maintain the reliability and performance of the nation's nuclear weapon stockpile, scientists must be able to more accurately predict the performance of high explosives (HE). However, to refine the computer codes that simulate these reactions, they need more detailed information on the chemical, mechanical, and energetic properties of the water, carbon, and nitrogen produced by an HE detonation.

At Lawrence Livermore, much of this research is conducted by the Extreme Chemistry Group in the Chemistry and Materials Science (CMS) Directorate. According to chemist Larry Fried, who leads this group, the team's objective is to understand the physical and chemical processes at extreme conditions as well as scientists now comprehend those processes at ambient conditions.



Livermore's Extreme Chemistry Group studies chemical reactions that occur under high-pressure, high-temperature conditions—up to one million times the atmospheric pressure at Earth's surface and temperatures above 6,000°C. Similar conditions exist near Earth's core and in other planets.

The group's research applies not only to stockpile stewardship but also to emerging technologies in nanoscale and energetic materials. "We're finding answers to important technical questions regarding reaction chemistry," says Fried. "What we're learning can be applied to various phenomena, from planetary evolution to new states of matter." (See the box on p. 16.)

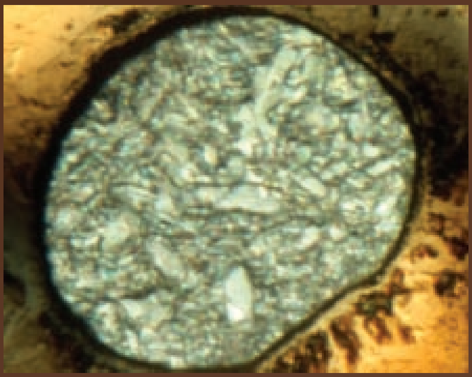
Achieving the Extreme

An essential element in studies of extreme chemistry is a material's equation of state—a mathematical expression showing the relationship of a material's pressure, temperature, and density. Many of the Laboratory's high-temperature, high-pressure experiments are designed to obtain more accurate data on the equation-of-state properties for various materials.

Measuring these properties takes ingenuity and a host of technologies. For example, two-stage gas guns at Livermore and at the Nevada Test Site have been instrumental in providing equation-of-state data. (See *S&TR*, September 2000, pp. 13–19; June 2004, pp. 4–11.) With gas guns, scientists can fire hypervelocity projectiles into highly instrumented targets, shocking matter to extreme conditions for a millionth of a second or less.

These experiments create pressures of a million-plus atmospheres, temperatures up to thousands of degrees, and densities several times that of a material's solid state. Shock-compression experiments have been used to evaluate liquefied gases such as hydrogen, nitrogen, carbon dioxide, and oxygen as well as solids such as aluminum, copper, tantalum, and carbon (graphite).

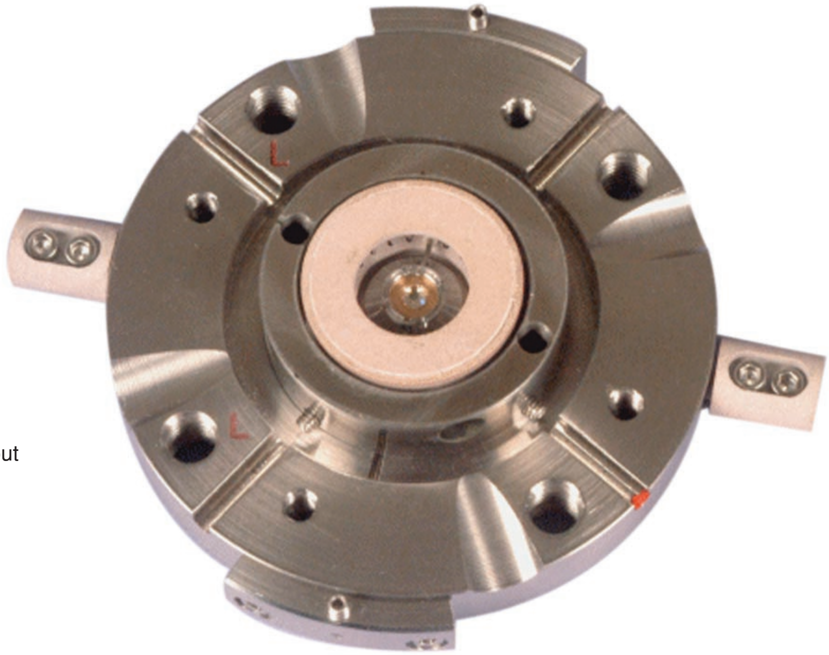
Mixtures of elements are more difficult to characterize. For those experiments, scientists use the diamond anvil cell, a device small enough to fit in the palm of one's hand. (See the figure on p. 16; also see *S&TR*, March 1996, pp. 17–27.) Diamond anvil cells can create the temperature–pressure conditions required to transform a substance: up to about 3.6 million atmospheres of pressure at room temperature and 1.7 million



Formic acid reacts to modest pressures and temperatures (about 2,000 atmospheres and 150°C).

atmospheres at about 3,000°C. Lasers can also be used to heat the samples in a diamond anvil cell, so that temperatures reach nearly 6,000°C at pressures below 1 million atmospheres. By comparison, the Sun's surface is about 5,500°C.

One advantage of the diamond anvil cell is that is does not necessarily destroy the sample being tested. "In shock experiments, the sample is destroyed, and the reaction occurs in less than a microsecond," says physicist Bill Nellis, who worked on some of the Laboratory's first gas-gun experiments and is now at the Harvard University Lyman Laboratory of Physics. (See *S&TR*, September 1996, pp. 12–18.) "With the diamond anvil cell, samples can be held under controlled extreme conditions long enough for us to observe the reaction."



The diamond anvil cell is small enough to fit in the palm of one's hand, but it can compress a sample to extreme pressures—up to about 3.6 million atmospheres at room temperature and 1.7 million atmospheres at about 3,000°C.

Predicting New Materials

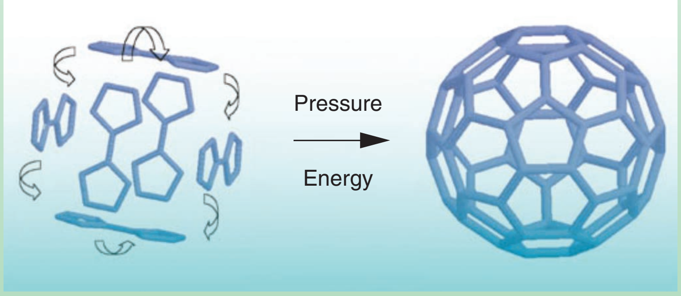
A few years ago, using computer simulations, theoretical chemist Riad Manaa predicted the possibility of a fullerene made of 60 purely single-bonded nitrogen atoms. (See *S&TR*, June 2001, pp. 22–23.) Although still strictly theoretical—no naturally occurring polymeric forms of nitrogen have ever been found—the calculations have shown that it may be possible to link together six molecules of N_{10}, or dipentazole, to create N_{60}, a fullerene expected to have unprecedented energetic potential. N_{10} has yet to be synthesized, but simulations show that linking two stable pentazole (N_5) ions could create the metastable building block needed to put together a nitrogen fullerene. (See the figure at right.)

Also necessary for the complex work would be extreme chemistry. Tremendous pressures would be needed to force the dipentazole molecules into the novel configuration.

The first fullerene, C_{60}, was synthesized in the laboratory nearly 20 years ago and named after R. Buckminster Fuller, whose geodesic dome is brought to mind by the shape of the fullerene molecule. The discovery of C_{60} is considered by many to be the beginning of nanotechnology. Says Livermore chemist Larry Fried, "This work on N_{60} may mark the beginning of the field of extreme nanotechnology."

The prediction of new forms of polymeric nitrogen is not new, however. More than 20 years ago, theoretical physicists Andy McMahan and Christian Mailhiot predicted that if squeezed hard enough, molecular nitrogen could be turned into a solid—a covalently bonded nonmolecular network like diamond. In 2002, Alexander Goncharov, now with Livermore, conducted experiments that confirmed the McMahan and Mailhiot prediction. "The calculations were not exactly in concert with the original prediction," says Fried, "but they did show that a nonmolecular state of nitrogen could be created with extreme chemistry."

Manaa hopes to see this same progression with his group's prediction of N_{60} and other nitrogen fullerenes. (See *S&TR*, December 2003, pp. 20–21.) And while scientific discovery rarely happens overnight, the past decade's advances in computing capabilities and the strides made in extreme chemistry are continually pushing theory to something more tangible.



Calculations show that six molecular units of N_{10} can be combined to form the nitrogen fullerene, N_{60}, which is expected to have unprecedented energetic potential.

Another option for extreme chemistry research is radiation technology. For example, Livermore researchers are conducting experiments on the new high-pressure x-ray beam line at the Advanced Light Source at Lawrence Berkeley National Laboratory. In the first experiment at the new facility, they observed the pressure-induced reactions of white phosphorous. (See the figure below.) They have also used Lawrence Berkeley's synchrotron infrared beam line to monitor chemical reactions in experiments with the diamond anvil cell.

To improve experimental capabilities for high-pressure materials studies, the Laboratory has joined the High Pressure Collaborative Access Team (HP-CAT). This collaboration is developing new beam lines at the Advanced Photon Source at Argonne National Laboratory for such research as characterizing materials at pressures greater than 500,000 atmospheres and improving x-ray diagnostics for shock-wave experiments.

Chemical kinetic studies are yet another way to look at reactions under extreme conditions. With an infrared system, scientists can monitor spectral features during a reaction, which allows them to study the process of product formation. From these observations, they can then determine the activation energy—the energy required for reactant A to become reaction product B. By better understanding activation energy, scientists can more accurately predict the pressure dependence of chemical reaction rates.

Tailored High Explosives

The Livermore team uses the data generated from experiments to refine the computer codes that simulate HE performance. Theoretical chemist Riad Manaa says, "We know how to engineer high explosives, but we don't know how they work on an atomic level—how and why they release energy. By improving our predictive capabilities, we can design HE materials that are safer and more energetic than the ones currently used."

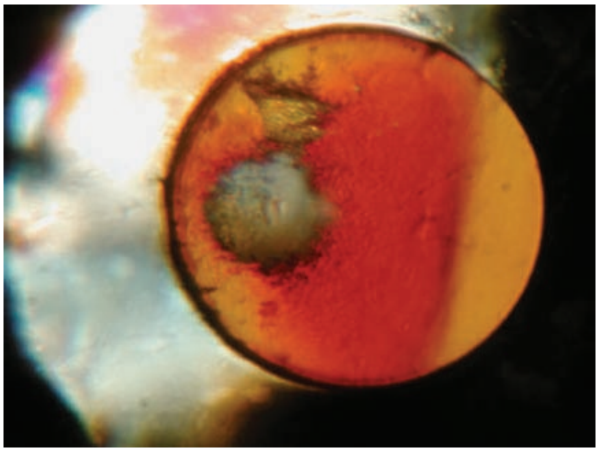
For example, a new trend in HE formulations is to add nanometer-scale metal particles to the mix. Metals make an HE reaction hotter but reduce its pressure. Very small metal particles react much more easily than large metal particles. In the right proportion, metals can almost double the energy content of an explosive, but the challenge is finding the optimal mix. A formulation with too much metal will not burn completely, so the pressure exerted in the explosion may be lower than needed. If metal levels are too low, the reaction may not produce the energy required for a specific application. Heavy metals such as tungsten, titanium, and zirconium can also be used to alter the energy delivery rate of a reaction.

"With computer simulations," says Fried, "we can better understand how to customize materials for a specific target or situation." This capability is of particular interest to the Department of Defense (DoD) because it will allow scientists to develop weapons systems that reduce collateral damage, say, when targets are near an enemy's weapons stockpiles or a civilian structure.

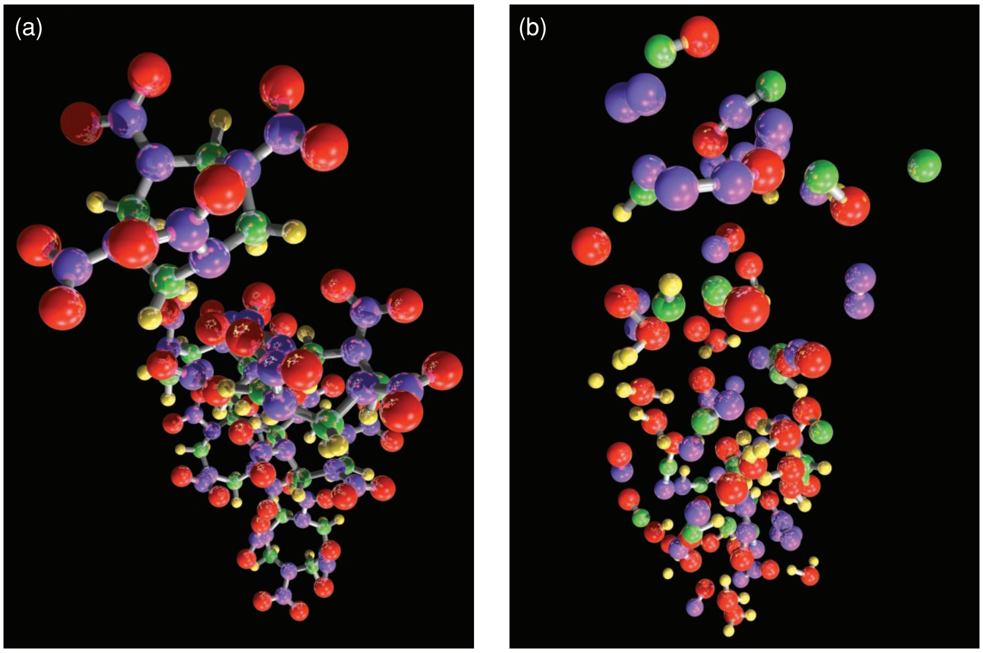
One code the team uses to model detonations is CHEETAH, which was begun in 1993 by Fried and his colleagues. (See *S&TR*, November 1997, pp. 21–23.) CHEETAH uses data from high-pressure experiments to simulate the performance of different HE formulations. Used by about 300 Department of Energy and DoD contractors, it allows scientists to determine how best to mix materials for various applications. For example, a shaped charge designed to penetrate armor must deliver its energy quickly, say, in 10 microseconds. By contrast, high explosives used in rock blasting are more effective if energy is delivered over tens of milliseconds. Researchers can use CHEETAH to tailor formulations for specific purposes and to examine several mix options without the time and expense involved in conducting small-scale experiments.

Fried is now linking CHEETAH to Livermore's hydrodynamic codes, so it can model the chemistry of entire systems of materials. "Historically, most chemical studies have examined individual materials in isolation," says Fried. "But with the advances in algorithms and computing power, we've moved from looking at elemental hydrogen to HE mixtures to whole explosives systems. These calculations, which were impossible to do 20 years ago, allow us to study systems such as warheads, reactive armor, or target effects."

Another series of calculations modeled the rapid decomposition of HMX, a commonly used propellant and explosive.



Pressure-induced reactions occur in white phosphorous during the first experiment on the new beam line at the Advanced Light Source at Lawrence Berkeley National Laboratory.



(a) A simulation of HMX under extreme conditions shows that stable molecules such as water form in less than 1 picosecond. (b) Slower chemical processes continue to change the chemical composition of HMX throughout the decomposition process.

These simulations showed how and in what order the molecules rearrange themselves as well as what intermediate products are formed.

At about 3,200°C and reaction times of up to 100 picoseconds, HMX decomposes through an initial step of nitro group elimination. Stable molecules such as water form rapidly—the first stable products appearing in less than 1 picosecond. But the transformation doesn't stop there. Slower chemical processes continue to change the chemical composition of HMX throughout the decomposition process. (See the figure above.)

According to chemist Joe Zaug, Livermore scientists are also beginning to examine in more detail the complex chemical systems on board weapon devices. "Moreover, the ultimate result of a detonated weapon is chemical species at extreme conditions," says Zaug. "If we can fully understand the behavior of a candidate species at relevant conditions, then we can work backward using the computational codes to better understand the detonation process."

Beyond Stockpile Stewardship

Understanding the stepwise changes that occur during these ultrafast reactions has far broader applications than high explosives. Data from HE experiments can be used to study the fundamental behavior of many materials under extreme conditions, from fossil fuels to water to the elements that form stars and planets.

One of these studies used laser-based ultrasonic technology to characterize iron, the main constituent of Earth's core. With this technique, the Livermore team recorded the precise sound velocity of iron under a pressure seven times greater than in previously reported experiments.

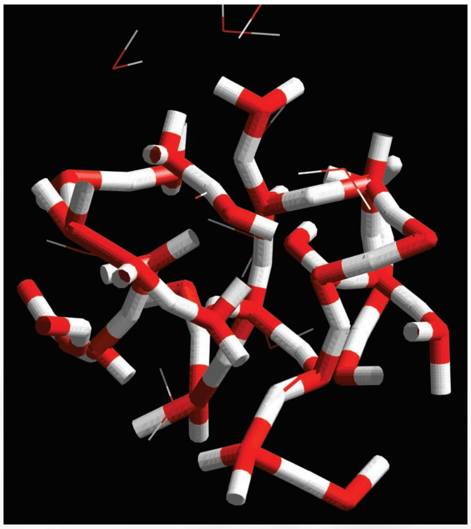
Other characterization techniques, which take less direct measurements, had led scientists to infer the makeup of Earth's internal structure, but those inferences were not borne out by the Livermore team's measurements. Instead, results indicate that the density of Earth's inner core is consistent with that of pure iron between 5,000 and 6,000°C, and the liquid outer core is less dense than pure iron. Such data help scientists better understand phenomena such as the strength of Earth's magnetic field and, in turn, begin to answer related questions—for example, by determining the role of the magnetic field in protecting Earth from solar flares.

Other experiments performed with diamond anvil cells or gas guns can mimic conditions similar to the atmospheres of giant planets and the outer envelopes of low-mass stars composed mostly from hydrogen. Data from these experiments can then be used to characterize the composition and evolution of the giant planets.

For example, scientists have learned that Neptune and Uranus are rich in methane gas, which transforms to hydrogen and various hydrocarbons under extremely high pressures and temperatures. Indeed, researchers have suggested that the methane in large planets may conceivably turn into diamond at shallow depths, about one-tenth of the way to the center.

Nearly two decades ago, Nellis led a project that shocked cooled, compressed liquid methane. "Francis Ree then ran a chemical equilibrium calculation with our data," says Nellis. "His simulation showed that methane at these conditions produced diamond and molecular hydrogen. So we have reason to believe the cores of Neptune and Uranus are most likely made of diamond."

Nellis adds that the project's findings were a spin-off result from the Laboratory's weapons research, which routinely used the single-carbon molecule methane in place of real explosives. "Hydrocarbons such as methane are a simple way to test an HE detonation," says Nellis. "Real explosives are complex, and testing with simpler species helps us



Applying extreme pressures and temperatures to water creates transient chains of oxygen–hydrogen–oxygen (O–H–O) molecules—a new phase of water.

understand the processes that occur during detonation." For example, some chemical reactions cause complex materials to rapidly decompose into simpler molecules, such as water, oxygen, nitrogen, carbon monoxide, and methane. The same reaction happens in giant planets.

"Uranus and Neptune are big balls of explosive materials," says Nellis. "Hydrogen accounts for 90 percent of all the atoms in the universe. The combination of hydrogen with oxygen gives us water, hydrogen with nitrogen gives us ammonia, and with carbon, we get methane. When all these accrete into one planet—collect in a snowballing effect—the planet gets bigger, and the materials deeper down are under even greater pressure. Because these materials are poor thermal conductors, the heat that's generated is trapped for millions of years, which leads to a very hot interior—much like the center of a detonated high explosive."

Fried's group also simulated water under high pressures and temperatures. In those calculations, the hydrogen atoms moved quickly, but the oxygen atoms were slower. As a result, short-lived transient chains of oxygen–hydrogen–oxygen (O–H–O) were being continually created and broken. Because the O–H bond is weak under these extreme conditions, the molecules exhibited a weak covalent character that is mostly ionic.

"We could say that we're turning water into salt by squeezing it really hard," says Fried. "What's important about our results is the information we acquire about the behavior of water under planetary conditions, which helps us better understand the magnetic properties of planets. We may find that the electrical conductivity of these molten salts is an important characteristic of giant planet interiors."

Extreme chemistry research has even challenged some of the most fundamental assumptions about the composition of fossil fuels. In 2003, a team of scientists from the Carnegie Institute of Washington re-created the conditions that exist more than 100 kilometers below Earth's surface.

The team compressed marble, iron oxide, and water at pressures about 50,000 times atmospheric pressure and at temperatures of about 1,500°C. Those experiments produced methane, the main constituent of natural gas. When the Carnegie data were modeled with the CHEETAH code, the simulations indicated that near the Earth's mantle—where temperatures and pressures are extremely elevated—petroleum may be forming inorganically.

Is It All So Extreme?

Hot outer planets, molten iron at the outer core of Earth, detonation processes—extreme conditions seem to be everywhere. But is it all really extreme? According to Zaug, the conditions at Earth's surface and within its delicate atmosphere are far from common. "The conditions we live under are unusual," says Zaug. "The conditions we create during so-called extreme chemistry experiments are not extreme—they're normal."

And as scientists learn more about the chemical reactions that can initiate a detonation sequence, they glimpse the balance of the universe.

—*Maurina S. Sherman*

Key Words: CHEETAH code, chemical kinetics, diamond anvil cell, equation of state, extreme chemistry, gas gun, high explosives (HE), planetary physics, shock physics, thermochemical code.

For further information contact Larry Fried (925) 422-7796 (fried1@llnl.gov).