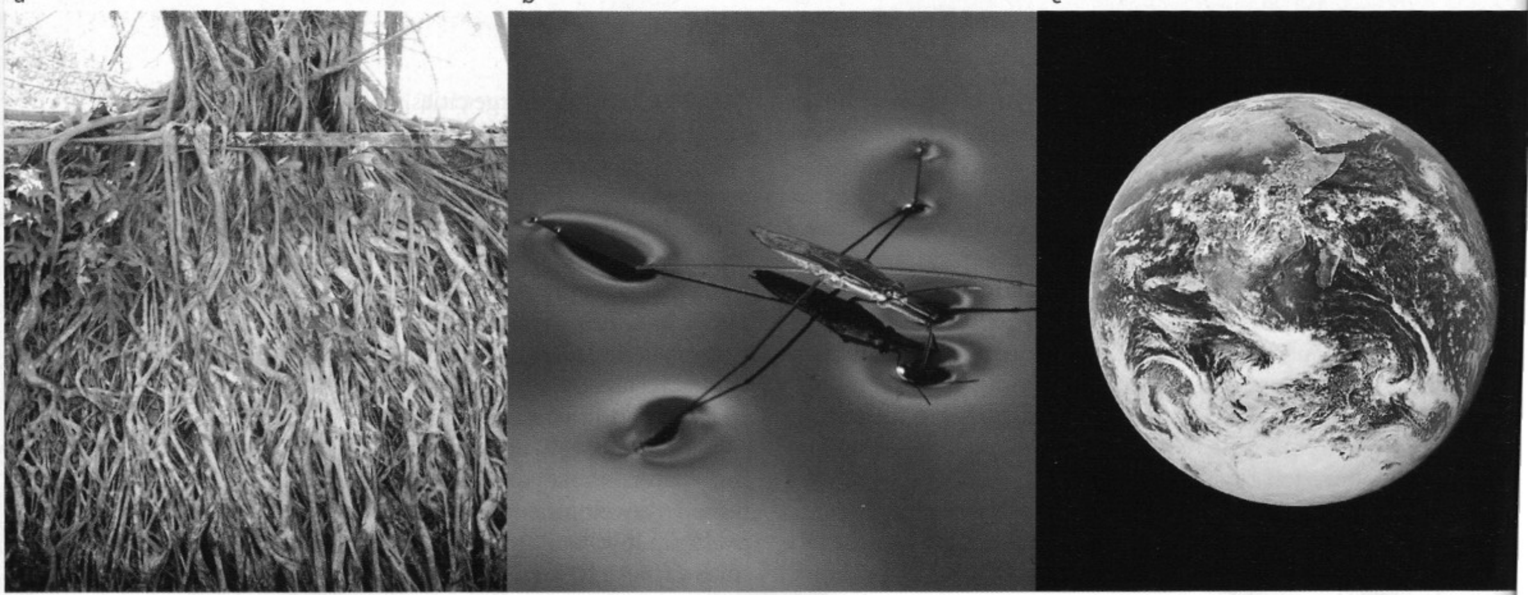

A SPECIAL BREW

Investigators still can't completely explain the strange molecular workings of water.

By Christopher J. Mundy, Shawn M. Kathmann, and Gregory K. Schenter

As children, we have all lain in the grass and looked up at the clouds. Sometimes they seemed to take on the shape of an animal, a favorite plaything, a familiar face. For many of us, such daydreaming segued into a deeper curiosity. What are the clouds? we wondered. What are they made of?

From an adult perspective, the answer seems obvious: water. Stand among the clouds on a mountaintop, and you can feel their moisture. Watch the plump white clouds of a sunny day transform into dark, daunting behemoths, and before long, sheets of water come pouring down. The common wisdom that clouds presage the weather is grounded in a less well known fact: the unique properties of water—in particular, its capacity to transport enormous quantities of energy—are what give the weather its variability, its energy, and its occasional violence.

Of course, our relationship with water goes far beyond the weather. We have fun with it whenever we go skiing or skating, boating, fishing, or swimming. The pleasure of a cold glass of thirst-quenching water on a hot summer day has a more serious basis, though. Without water, a human being can live only a few days. Every organism is made up mostly of water, and the substance covers nearly three-quarters of the Earth's surface.

Yet this commonplace, familiar, and essential stuff of life is also quite peculiar, as substances go. For example, if the water molecule (H_2O) acted in bulk like other small molecules—oxygen (O_2), carbon monoxide (CO), nitrogen (N_2)—it would be a gas under the conditions prevailing on Earth. Instead, water occurs in all three states of matter: solid, liquid, and gas. Furthermore, water reaches its maximum density in its liquid form, at 39.2 degrees Fahrenheit (four degrees Celsius), just a few degrees above the freezing point. Thus water stays at the surface as it starts to freeze, and ice floats—a rare property shared by very few other substances. If its nature were otherwise, all temperate-zone lakes, ponds, rivers, and even oceans would eventually freeze solid from the bottom up, and life as we know it could not exist. Instead, a floating skin of ice cocoons the life in the liquid water beneath a layer of insulation, enabling it to persist under the frozen surface.

Another unusual and related property of ice is that, for a given temperature, increasing the pressure decreases d

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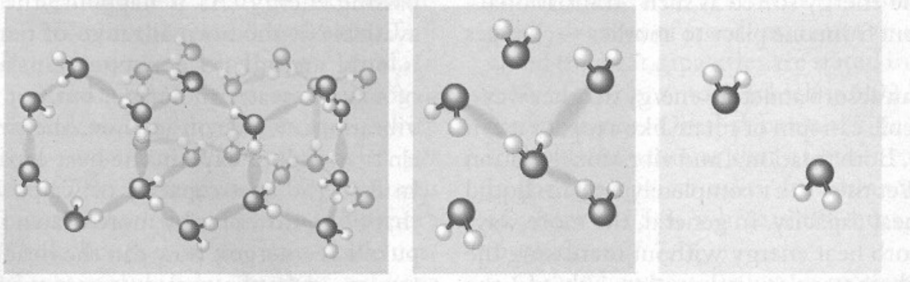
Strange properties of water: *(a) Cohesiveness enables water to travel upward from roots to leaves, against gravity. (b) High surface tension makes liquid water behave as if coated with an invisible film, which explains why insects can walk on it. (c) Water exists in all three phases—gas, liquid, and solid—at temperatures and pressures that are common on Earth. This familiar property is actually quite unusual. (d) Ice floats on liquid water; unlike most substances, water is most dense in its liquid phase. Lakes and even oceans would otherwise freeze solid in winter. (e) Water's abundance and heat capacity are, in part, responsible for the moderation of global temperature fluctuations and the gradual change of the seasons. (f) Water can dissolve a variety of substances, including acids, bases, and salts, earning it the moniker "universal solvent."*

the melting point. (Ordinary solids remain solid under pressure.) Even though these and other unusual bulk properties of water have been described in detail, a complete picture of how and why water acts the way it does is still lacking. It is not possible, for instance, to completely predict the properties of materials that incorporate water in their structure, either physically or chemically, or to design and tune their responses to various conditions. Perhaps the key to achieving that level of understanding and control is to study water on a molecular scale: how water molecules arrange themselves, how they interact, and how they dance with other kinds of molecules. We and our colleagues in the growing field of molecular science hope that by understanding exactly what happens at very small scales (around 10^{-10} meter, or a billionth of a meter), we can zoom out by a factor of a billion or so to understand and predict phenomena on a human scale.

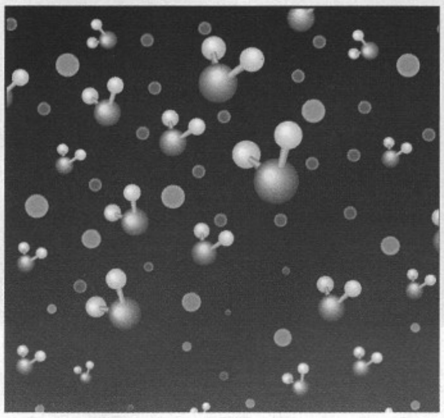


Ice (left) consists of a collection of hydrogen-bonded water molecules arranged in a pattern of hexagonal rings: oxygen atoms make up the vertices, and hydrogen bonds the edges. In liquid water (center), the water molecules are linked to their neighbors by three to four hydrogen bonds, which continually break and re-form. Water vapor (right), an important constituent of the atmosphere, consists of weakly interacting water molecules.

But we don't stop there. Because water is fundamental to all life on Earth, we also want to zoom out by another factor of 10 million to study its properties on a global scale.

Anyone who has visited the San Francisco Bay area has experienced local climate moderation. The city of San Francisco maintains a mild climate year-round, but just a few miles inland, where hills guard the bay, temperatures can soar to 90 degrees F (32.2 degrees C) in the summer and plummet to near freezing in the winter. The reason for this contrast, as most residents are well aware, is that the ocean moderates large temperature fluctuations. The same effect, on a global scale, is a factor in keeping seasonal temperature changes gradual rather than abrupt.

What governs the ocean's moderating effect is the large quantity and heat capacity of water. Heat capacity is the amount of heat energy that must be absorbed or released to raise or lower the temperature by a given amount. For example, it takes four times as much energy to warm a given mass



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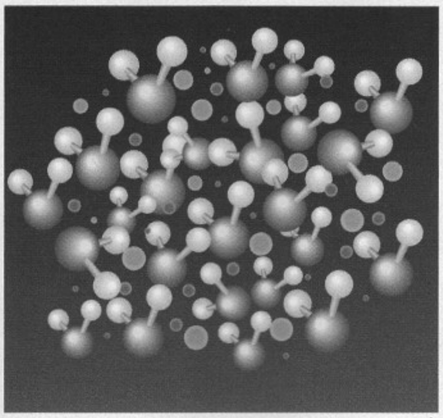

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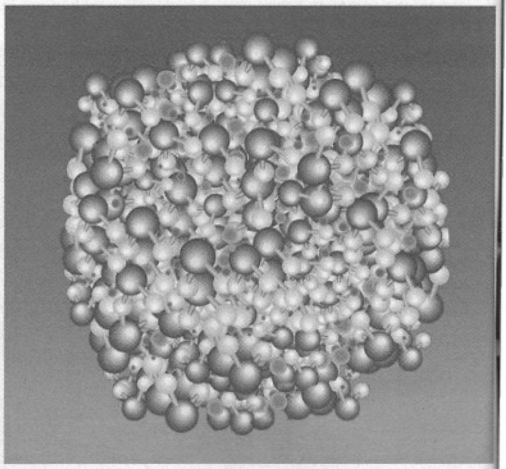

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of water by one degree Celsius as it does to warm the same mass of dry air by that amount. The heat capacity of water acts as a buffer, or perhaps a heavy flywheel, on climate, smoothing out what would otherwise be sharp changes in temperature.

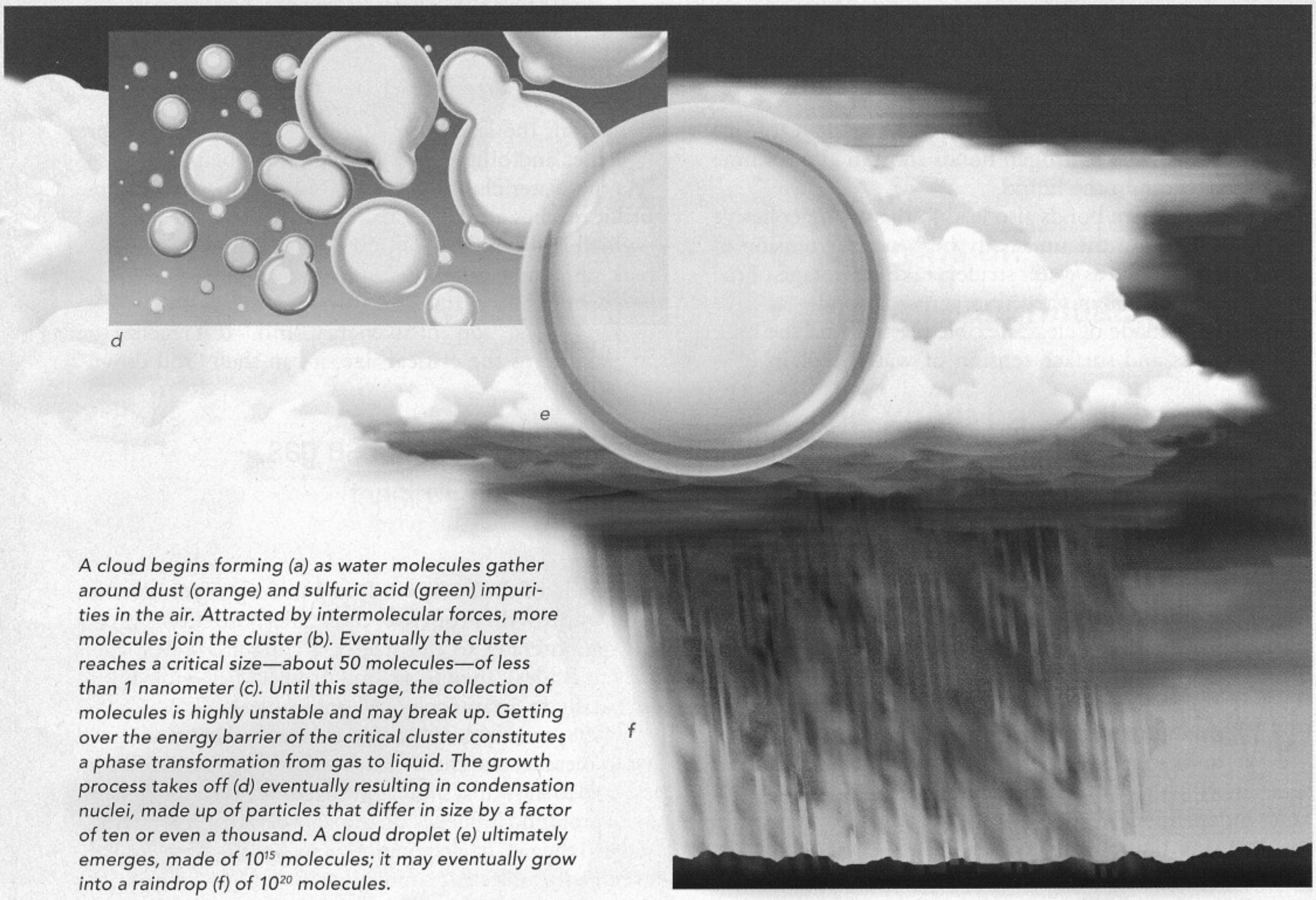
Heat capacity is a good example of a macroscopic property of water that can be explained by what takes place at a molecular level. The chemical formula H_2O, instantly recognized round the world, indicates that the water molecule is a bound system of three atoms, two of hydrogen and one of oxygen. When you add heat (a form of energy) to a macroscopic sample of water molecules, the molecules increase their average speed and collide more often. The temperature of the sample is simply a measure of their average speed. Any energy added to or subtracted from the energy stored as such "translational" motion—movement from one place to another—changes the temperature.

But molecules can absorb and store energy in other ways, too. A water molecule can spin or rotate like a top, or it can wiggle and vibrate. Both rotational and vibrational motion can store energy. Yet they can't completely explain liquid water's observed heat capacity. In general, the more ways molecules can absorb heat energy without increasing the average speed of their translational motion—that is, the greater the molecules' capacity to act as heat sinks without raising the temperature of a substance—the greater the heat capacity of that substance.

You might think that no matter how little energy a molecule may have stored, the energy would still spread more or less evenly among all the possible kinds of motions. In other words, the energy would be partitioned among all possible "degrees of freedom." Because virtually all molecules made up of three atoms have the same number of degrees of freedom, their heat capacity, too, should not differ substantially. And sure enough, the heat capacity of the water molecule is about the same as that of other triatomic molecules.

Although the conclusion to the preceding argument agrees with the observed result, the argument itself is faulty. In the world of atoms and molecules, energy cannot be absorbed by the various kinds of molecular motions in arbitrarily small amounts. Rather, atoms and molecules are subject to the laws of quantum mechanics. In the quantum world, all changes in the energy stored by an atom or molecule are *quantized*. Each kind of molecular motion—translational, rotational, and vibrational—can absorb energy only in discrete chunks, whose sizes depend on the details of a particular molecule and the kind of motion involved. Expose a water molecule to the right-size chunk of incident energy (from the Sun, for instance), and the molecule will suddenly rotate or vibrate faster. Expose it to the wrong-size chunk, and nothing will happen; the molecule will simply "disregard" the passing energy. As it happens, the amount of energy available at the normal range of temperatures on Earth is only enough to generate translations and rotations of a single water molecule, but not enough to generate vibrations. Thus, on its own, the single water molecule isn't enough to explain the heat capacity of liquid water. In fact, the heat capacity of water *vapor* is smaller than that of liquid water by more than a factor of two! So the puzzle reemerges: how can the heat capacity of water be explained from a molecular point of view?

The solution is to look beyond the properties of a single water molecule and consider the interactions among the vast number of molecules in a bulk sample. Begin by considering the interaction of two water molecules. Each molecule is shaped like a tetrahedron, with the oxygen atom at its center. Each of the two hydrogen atoms lies at one of the four corners of the tetrahedron, and each one acts as a center of positive electric charge. When it bonds with hydrogen, the oxygen atom acquires two complementary



A cloud begins forming (a) as water molecules gather around dust (orange) and sulfuric acid (green) impurities in the air. Attracted by intermolecular forces, more molecules join the cluster (b). Eventually the cluster reaches a critical size—about 50 molecules—of less than 1 nanometer (c). Until this stage, the collection of molecules is highly unstable and may break up. Getting over the energy barrier of the critical cluster constitutes a phase transformation from gas to liquid. The growth process takes off (d) eventually resulting in condensation nuclei, made up of particles that differ in size by a factor of ten or even a thousand. A cloud droplet (e) ultimately emerges, made of 10^{15} molecules; it may eventually grow into a raindrop (f) of 10^{20} molecules.

centers of negative electronic charge, which cluster at the opposite two corners of the tetrahedron.

When the two water molecules are brought together, opposite charges attract. One of the sites of positive charge—a hydrogen atom—in one molecule becomes attracted to one of the negatively charged sites associated with the oxygen atom in the second molecule. This attractive interaction is known as a hydrogen bond. In liquid water, each molecule often forms four hydrogen bonds. Two of them link the two hydrogen atoms with the oxygen atoms of two other water molecules [*see illustration on page 33*]. The other two hydrogen bonds link the oxygen atom with hydrogen atoms of two more water molecules. Those bonds give rise to a stable network of tetrahedral water molecules. In the liquid the network extends only locally, and the hydrogen bonds continually break and re-form. But in ice, the network of tetrahedrons extends over a long range and becomes a relatively unchanging lattice.

Within a network of tetrahedrons, the number of ways incident energy can create rotations, twists, vibrations, and suchlike significantly rises. Each new mode of motion provides an additional degree of freedom, and so the heat capacity of the network far exceeds the heat capacity of a single constituent molecule. Note, though, that many other molecules, including other triatomic molecules such as carbon disulfide (CS_2), also form linked networks whose heat capacity far exceeds the heat capacity of one of their constituent molecules.

In fact, although it is not widely appreciated, the heat capacity of water, even within a linked network having many degrees of freedom, is not unusually large—provided the heat capacities are stated in units of energy per molecule or per mole, which is 6.02×10^{23} molecules of the substance. On that basis, the heat capacity of water is about the same as that of other triatomic molecules. In the appropriate units, for instance, the heat capacity of water is 75.3, whereas the heat capacity of carbon disulfide is 75.7.

Only when heat capacity is measured in the amount of energy per unit mass does the heat capacity of water look anomalously large. The reason is that the molecular mass of water is small compared with that of other triatomic molecules. Expressed in those units, the heat capacity of H_2O is more than four times that of CS_2.

The study of the various configurations of the hydrogen bond has made it possible for molecular scientists to explain a number of other anomalies of water. For example, in ice, the hydrogen bonds tend to be slightly longer than they are in the liquid phase, resulting in a larger volume and thus the lower density of ice than of liquid H_2O. If ice is compressed, the hydrogen bonds shorten and become more like those in the liquid.

Stable hydrogen bonds also lead to the strong cohesive forces underlying the unusually high surface tension of water. Insects such as water striders take advantage of the surface tension when they skip across a pond—as if its surface were made of clear, flexible plastic. And the high cohesiveness and surface tension of water explain how long columns of watery suspensions can be drawn through extensive networks of blood vessels and even into tree canopies several hundred feet above the forest floor.

Water is the third most abundant chemical compound in the Earth's atmosphere, after nitrogen and oxygen. It is present there both as a vapor, or gas, in which the water molecules dart about randomly and independent of one another, and as an aerosol, a mist of tiny liquid droplets or solid ice crystals that are suspended in air because they're too fine to fall to earth as rain or snow. In its vapor form, water is the most important greenhouse gas, so it plays a major role in the climate of our planet.

But when water takes the form of an aerosol, it is crucial to cloud formation and to the reflection and absorption of radiation. Water aerosols act as condensation nuclei for clouds—after all, clouds themselves are made up of relatively large aqueous aerosols. And water aerosols transform radiation in ways that, in turn, feed the factors that shape cloud development. Reaching a better understanding of how water aerosols affect climate has become increasingly important in the past several decades.

Water aerosols enter the atmosphere when waves break in the ocean or when vapor turns to liquid. The latter process, condensation, is in essence a battle between entropy and energy, order and disorder. As water molecules condense into their liquid state, they gain order but lose kinetic energy. The kinetic energy given up by the phase change is dumped as heat into the surrounding air, giving rise to a pocket of thermal instability that will drive yet another change in the weather as it equilibrates.

The physical process of condensation is "seeded," or nucleated, around tiny molecular impurities or perhaps a dust particle in the air. Once an "embryo" of the new liquid phase forms, more molecules tend to gather around it and glom onto it, attracted by intermolecular forces [*see illustration on pages 34–35*]. The larger the surface area of the growing cluster, or the stronger the intermolecular interaction, the larger the target area onto which more molecules and other nearby droplets can be pulled.

As the water cluster grows, it remains highly unstable until it reaches a certain critical size—the critical cluster—which is about fifty molecules. Precritical clusters can break up at any time into single water molecules. As it approaches the critical size, though, the cluster is also climbing to the "top" of an energy "hill." If it reaches the top and attains the critical size, it can then "roll down" the far side of the energy hill and undergo spontaneous, runaway growth. From fifty molecules, the cluster grows and agglomerates to the size of a condensation nucleus (10^8 molecules), then to a cloud droplet (10^{15} molecules), and finally to a raindrop (10^{20} molecules).

In its vapor form, **water** is the most important **greenhouse gas**, so it plays a **major role** in the **climate** of our planet.

In 1998, members of our research team were among the first to measure the chemical identity of the nucleated particles and to show that the chemical interactions among them have a profound influence on the aerosol formation rate. We modeled the rate of evaporation of molecules from clusters, developed a molecular simulation strategy to compute the relevant kinetics, and applied the strategy to water. We found that the molecular interactions between water and the initial nucleating particles—whether dust, sea salt, sulfuric acid, ions, or some other substance—may significantly affect the rate of aerosol formation. That rate affects the distribution, duration, and precipitation processes in clouds, and thus their tendency to reflect, transmit, or absorb the Sun's radiant heat. All those properties in turn influence the reflectivity of the Earth and thus the global climate.

Atmospheric scientists have yet to determine the exact nature of that influence. One possibility is that if cluster droplets grow more quickly, more clouds may form, helping moderate global warming by providing more cloud cover. On the other hand, faster droplet growth could accelerate the production of rain, causing clouds to dissipate sooner. That would lead to a less cloudy world, and faster warming.

As we molecular scientists learn more about water, we are continually reminded that we have merely "scratched the surface" of its secrets. The mechanisms of its impact on life are still something of a mystery. Coaxing Mother Nature to reveal further secrets about water will require the full interdisciplinary sophistication of today's scientific toolbox. But since water is the wellspring of life, we owe it to ourselves—and everyone else—to explore all we can about its strange and intriguing properties. □