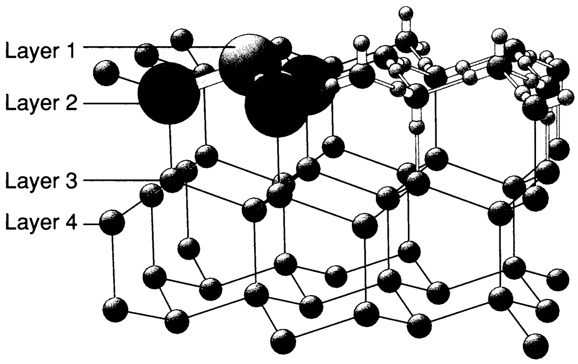
MATERIALS SCIENCE

On Ice's Surface, a Dance of Molecules

Ice has always been a slippery subject. As simple as an ice cube may seem, scientists have long been baffled about why its surface is so slick. But an upcoming paper in *Surface Science* may give researchers a firmer grasp of ice's surface subtleties by hinting that its outermost molecules behave like a liquid. This mobile layer could help explain mysteries from atmospheric chemistry to why it is more fun to skate on ice than on concrete.



Thin ice. A dynamic outermost layer of water molecules gives way to deeper rigid layers.

MICHEL VAN HOVE

Many people believe that ice's slipperiness comes from pressure-induced melting. Wrong, says Michel van Hove, a surface chemist at the Lawrence Berkeley National Laboratory. "It doesn't work out," says van Hove. "You put the data into the formula, and there's not enough pressure." The answer must lie elsewhere, he says.

Van Hove and a colleague, Gabor Somorjai, suspected that the properties of ice's surface might differ from those deeper inside the crystal. There was "very good circumstantial evidence that the surface of ice is molten," such as polarization measurements suggesting a thin surface film, says Somorjai, but "no real scientific evidence." To gather some, the two researchers probed the surface of thin layers of ice at –180°C with low-energy electron diffraction. This technique bounces electrons off the electron clouds of surface atoms and collects a diffraction pattern that holds clues to the surface structure. The results were a surprise.

The researchers expected to see the scattering signature of the first three layers of ice molecules, but they saw only two. Models of the two detected layers implied that an invisible top layer had to exist, so the researchers hypothesized that water molecules in the top layer were vibrating three or four times faster than those in the lower layers—blurring their diffraction pattern to the point of invisibility.

Although the water molecules in this outermost layer are bound in the lattice like a solid, "the vibrational amplitude is like a liquid," says Somorjai. "I believe this is the reason why we can ski and skate." Steve George, a chemist at the University of Colorado, agrees that "the surface of ice is extremely dynamic," although he's not convinced that vibrations of individual molecules are responsible. George speculates instead that the ice's surface is constantly being eroded and redeposited, like topsoil.

Either way, he and Somorjai note that a dynamic surface could help explain the rates of chemical reactions believed to take place on the surface of ice crystals in the upper atmosphere—including the chain of reactions that results in the destruction of ozone. These reactions should be extremely slow in the cold stratosphere, but the ice's changeable surface might accelerate them. It might also draw foreign molecules into the ice itself, affecting their chemical behavior, says Jeff Roberts, a chemist at the University of Minnesota. But most of all, says George, the finding "illustrates how we don't understand the simplest things we know about."

–Charles Seife

Charles Seife is a science writer in Scarsdale, New York.

PACIFIC ARCHAEOLOGY

Rock Chemistry Traces Ancient Traders

BOSTON—Archaeologists have long known that Captain James Cook was a Johnny-come-lately. By the time he ventured to the South Pacific in 1769, people of the region had been navigating—and trading—on the high seas for at least 3300 years. But now, Captain Cook may have fallen even farther behind. At a meeting of the Materials Research Society here earlier this month, a Malaysian and an American researcher presented a chemical analysis of flecks of volcanic glass that may push back the earliest dates for long-distance sea trading on the Pacific by another 2500 years, to 4000 B.C.

The analysis, by archaeologist Stephen Chia of the Universiti Sains Malaysia and chemist and archaeologist Robert Tykot of the University of South Florida, links volcanic glass found at a 6000-year-old archaeological site on Borneo to sources on islands 3500 kilometers to the east. It points to the longest sea trading network yet traced in the Stone Age. Other researchers are intrigued, although "there will be some skeptics about the dating," says Bennet Bronson, curator of Asian ethnology and archaeology at the Field Museum in Chicago. But if the claim holds up, Bronson says, it "is going to affect our whole understanding" of the migrations that peopled the islands of the western and central Pacific.

At the heart of the new findings are some 200 obsidian flecks, which Chia unearthed beginning in 1994 at the Borneo site, called Bukit Tengkorak. Because there are no obsidian sources nearby, Chia teamed up with Tykot to analyze the flecks and pinpoint their origin. At the meeting, Tykot reported that an analysis of the relative abundance of 11 different compounds, such as silicon dioxide and titanium oxide, in 30 of the flecks yielded several distinctive chemical fingerprints. For the majority of the flecks, these fingerprints matched well-known sources some 3500 kilometers away near New Guinea—on the island of New Britain and on one of the Admiralty Islands. A smaller percentage seemed to come from a source

SOURCE: R. TYKOT/UNIVERSITY OF SOUTH FLORIDA

Ancient mariners. Volcanic glass found at Bukit Tengkorak comes from sources on the Admiralty Islands and New Britain. It testifies to 3500-kilometer trade routes in 4000 B.C.

closer to the Philippines, Tykot reported.

The tightness of the matches makes it "almost impossible" that the flecks came from some as yet undiscovered obsidian source closer to the excavation site, says Tykot. Ron Hancock, a chemist and archaeologist at the University of Toronto who saw Tykot's presentation, agrees, saying that the chemical evidence tying the obsidian to distant sources "looks real," which "gives good credibility to the story" of early sea trading. And because materials in the sediment layers from which some of the obsidian was taken have been carbon-dated to 4000 B.C., Tykot and Chia conclude that the trading network was in place by that time.

The new results are "a tremendous surprise," says Bronson, and not just because of the early date. Widespread long-distance sea trading in the southwestern Pacific, he explains, has long been thought to have arisen around 1600 B.C., when seafarers pioneered trade routes extending Melanesian islands near New Guinea to Polynesia in the Central Pacific, leaving behind a trail of distinctive pottery, obsidian, and other ornaments known as the Lapita culture. The new obsidian flecks not only show that traders took to the open ocean much earlier than the people who made Lapita wares, but that their trading network extended far to the west of New Guinea, nearly to Southeast Asia. "This is revolutionary, because it offers apparent proof for a routine trading system in [a westward] direction," says Bronson.

The evidence that skilled navigators were roaming the western Pacific at such an early date also supports a new picture of how the Pacific islands were settled in the first place, says Bronson's Field Museum colleague John Terrell. In the standard picture, the people who settled Polynesia reached the central Pacific by island-hopping from Southeast Asia 3600 years ago—perhaps picking up some fellow travelers from Melanesia along the way (*Science*, 7 January 1994, p. 32). The new work, however, supports the idea that instead of setting out on a one-way eastward migration, the ancestral Pacific islanders opened up a "voyaging corridor" between Southeast Asia, Melanesia, and Polynesia, "with people and ideas flowing back and forth," says Terrell. The obsidian at Bukit Tengkorak, adds Bronson, "suggests that the early migrations come out of an early commercial system at a surprisingly early date capable of sophisticated navigation."

Because this picture demands that archaeologists reconsider some long-held notions, says Bronson, Chia and Tykot's claims are likely to come under intense scrutiny, especially the radiocarbon dating. Bronson says, however, that there's no reason at this point to doubt the early dates. Captain Cook's demotion may turn out to be permanent.

–**Robert F. Service**

CHEMISTRY

Supercritical Solvent Comes Into Its Own

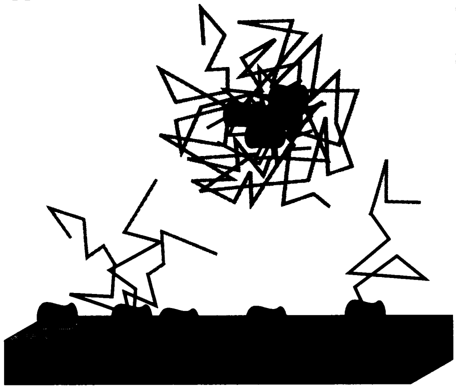
In the world of environmentally friendly chemistry, carbon dioxide has long been seen as a rising star—but one that has not made it very far above the horizon. When compressed, this ubiquitous gas becomes a liquid that at least in theory could be the perfect solvent: It's cheap, essentially harmless to living things, and at the end of a process, disposal is easy—just a matter of releasing the pressure in the reactor or cleaning vessel and allowing the gas to flow out. No wonder chemists have dreamed of using carbon dioxide for everything from degreasing computer chips and dry-cleaning clothes to dissolving ingredients in the manufacture of plastics and drugs.

But today, long after chemists first pressurized CO_2 to convert it to a liquefied or near-liquid, "supercritical," form, industry still is using billions of kilograms of hazardous organic solvents a year. And the reason? Few substances will dissolve in CO_2. Now, however, new research may help jump-start CO_2's stalled career. A U.S.–Italian team led by chemist Joseph DeSimone at the University of North Carolina, Chapel Hill, reports in this issue (p. 2049) that it has created a surfactant—a sort of soap—that should help carbon dioxide dissolve greasy molecules, including many compounds important in industry. "This is a leap ahead for using carbon dioxide as a solvent," says Al Sattelberger, a chemist at Los Alamos National Laboratory in New Mexico.

Soon after recognizing in the 1980s that carbon dioxide might have a future as a solvent, researchers began seeking ways to get a variety of molecules to mingle with CO_2. At first, the answer seemed easy: Just find CO_2-loving surfactants—hybrid molecules that have one end that adheres to CO_2 and another end that sticks to whatever molecule it is chemists want dissolved in CO_2. But as a number of investigators came to discover, off-the-shelf surfactants didn't work. The big problem is that liquid CO_2 is as inert as Teflon—nothing wants to stick to it.

But recently, researchers have begun to break the surfactant barrier. In the past year, DeSimone's group and, in a separate study, a team at the University of Texas, Austin, have devised surfactants that stick to CO_2 and water-soluble compounds (*Science*, 2 February, p. 624), opening the way to use CO_2 to process proteins and other water-loving biomolecules. And now, DeSimone's group and colleagues at Oak Ridge National Laboratory in Tennessee and at the University of Palermo in Italy appear to have found a way to dissolve in CO_2 nonpolar, or water-hating, molecules, a category that includes grease, oils, machine-cutting fluids, and many polymers.

The researchers created a brand-new surfactant by linking a fluorinated, CO_2-loving acrylate compound with a strand of polystyrene, a nonpolar polymer. The team tested out their two-part compound by dumping it into a CO_2-filled vat containing a plate coated with polystyrene pieces, which, like grease, won't dissolve in CO_2 without help. Their expectation was that the surfactant's polystyrene ends would pick up polystyrene from the plate, then slip into a ball-shaped configuration, called a micelle, with the CO_2-loving ends sticking out and polystyrene trapped in the middle. And in fact, the plate appeared to come clean in the liquid CO_2.


SOURCE: J. DESIMONE

Washday miracle. Cleaning polystyrene (red pieces) from a plate with surfactant in CO_2.

The researchers then confirmed that micelles had formed using an analytic technique called small-angle neutron scattering (SANS). To help verify that the micelles had dispersed the polystyrene, they had marked the polystyrene pieces on the plate with heavy hydrogen. And using SANS, the researchers showed that the pieces wound up inside the micelles. DeSimone says his group already has created a dozen other surfactants for compounds other than polystyrene.

The researchers also found that by adjusting the pressure inside the vat, they could control the micelles' size or break them up. Being able to vary the size could be extremely useful, DeSimone says, because it might allow industrial chemists to influence reactions occurring inside micelles. And by breaking up the micelles, chemists should be able to cause whatever is inside them—say, grease from a microchip—to drop out of solution.

With the new surfactants, it should be possible to carry out a wide range of processes in carbon dioxide, say CO_2 researchers. According to chemical engineer Eric Beckman of the University of Pittsburgh, "It was agonizing to get here. Lots of people gave up." But finally, supercritical carbon dioxide may be coming into its own.

–**Jocelyn Kaiser**