

CHEMISTRY

Supercritical Solvent Comes Into Its Own

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 demolition may turn out to be permanent.

—Robert F. Service

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.

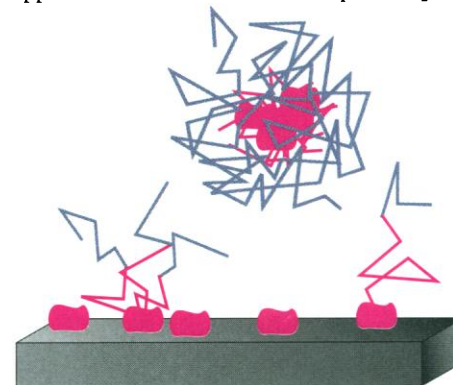
But today, long after chemists first pressurized CO₂ to convert it to a liquefied or near-liquid, "supercritical," form, industry still is using billions of kilograms of hazardous organic solvents a year. And the reason? Few substances will dissolve in CO₂. Now, however, new research may help jump-start CO₂'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 CO₂. At first, the answer seemed easy: Just find CO₂-loving surfactants—hybrid molecules that have one end that adheres to CO₂ and another end that sticks to whatever molecule it is chemists want dissolved in CO₂. But as a number of investigators came to discover, off-the-shelf surfactants didn't work. The big problem is that liquid CO₂ 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 CO₂ and water-soluble compounds (*Science*, 2 February, p. 624), opening the way to use CO₂ 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 CO₂ nonpolar, or water-hating, molecules, a category that includes grease, oils, machine-cutting fluids, and many polymers.

The researchers created a brand-new sur-

factant by linking a fluorinated, CO₂-loving acrylate compound with a strand of polystyrene, a nonpolar polymer. The team tested out their two-part compound by dumping it into a CO₂-filled vat containing a plate coated with polystyrene pieces, which, like grease, won't dissolve in CO₂ 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 CO₂-loving ends sticking out and polystyrene trapped in the middle. And in fact, the plate appeared to come clean in the liquid CO₂.



Washday miracle. Cleaning polystyrene (red pieces) from a plate with surfactant in CO₂.

SOURCE: J. DESIMONE

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 CO₂ 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