

that in this size range, the addition or subtraction of a single atom can make all the difference.

Most industrial catalysis is now done with small metal particles held in place on a substrate, with sizes ranging from a few hundred angstroms down to as little as 20 angstroms. "The regime that is really unexplored is what happens when you go below this size," Kaldor says. The hope is that making the particles smaller and smaller will increase both the activity and the selectivity of their catalytic behavior. And experiments that test the reactivity of clusters with such simple molecules as hydrogen and methane encourage that hope.

Gold, for instance, is inert to most materials, but becomes very reactive with both hydrogen and methane when it is in the form of positively charged clusters with less than 15 atoms, Kaldor says. And as for selectivity, researchers have found one example after another of how a cluster's reactivity can depend closely on its size and composition.  $\text{Co}_9$  is almost completely inert to hydrogen or nitrogen gas, while  $\text{Co}_{10}$  reacts any time it comes in contact with either gas.  $\text{Co}_{13}$  is very reactive with hydrogen, but if one of the cobalt atoms is replaced with vanadium, a closely related element, it is not reactive at all.

Eventually, Cox notes, chemists will have to learn how to attach clusters to a surface, without breaking them up, if they are to be used in commercial catalysis, which normally involves running hot gases of reactants over a catalyst. But the work has a long way to go. Cox and his colleagues recently managed "soft landings" for platinum clusters on a silica surface and showed that clusters with up to six atoms remained intact after sticking to the surface. "After six, we got [so few clusters] that we couldn't see them on the surface," he says. The researchers don't know yet how much the presence of the surface deforms the structure of the clusters since they don't know what those structures are, and they don't know how putting clusters on a substrate will affect their reactivity with other chemicals. But they know that clusters have opened up a whole new field of science.

■ ROBERT POOL

#### ADDITIONAL READING

A. Alivisatos *et al.*, "Electronic states of semiconductor clusters: Homogeneous and inhomogeneous broadening of the optical spectrum," *J. Chem. Phys.* **89**, 4001 (1988).

O. Cheshnovsky *et al.*, "Ultraviolet photoelectron spectra of mass-selected copper clusters: Evolution of the 3d band," *Phys. Rev. Lett.* **64**, 1785 (1990).

W. Eberhardt *et al.*, "Photoemission from mass-selected monodispersed Pt clusters," *ibid.*, 780.

T. Klots *et al.*, "Magic numbers through chemistry: Evidence for icosahedral structure of hydrogenated cobalt clusters," *J. Chem. Phys.* **92**, 2110 (1990).

# Watching the Dietary Detectives

*Isotope ratios offer archeologists a firmer grip on prehistoric diets, helping to resolve key evolutionary questions*

IN A LABORATORY AT THE UNIVERSITY OF CAPE TOWN in South Africa, archeologist Julia Lee-Thorp spends some of her time carefully extracting carbon dioxide from the tooth enamel of a 1.5-million-year-old hominid tooth and then running the mineral through a mass spectrometer. Because the instrument measures the precise ratio of two carbon isotopes from a substance called apatite in the enamel, it can show Lee-Thorp just what this early hominid, *Australopithecus robustus*, was eating as it roamed the savanna in southern Africa. The answer, based on the ratio of carbon-13 to carbon-12: fruits, nuts, and grasses. The results are at odds with current thinking about the diet of *robustus*; if they hold up, they will contradict theories that the hominid was actually a vegetarian.

That dietary evidence in turn might provide an important clue about why *robustus* went extinct while its omnivorous contemporary, *Homo habilis*, survived to become the ancestor of modern humans. "The punch line is that the diet of early hominids can tell us about evolution—about their subsistence and why some species went extinct," says Lee-Thorp, a research archeologist in the lab of Nikolaas van der Merwe.

The use of isotope analysis to study the diet of hominids and early humans is among the latest applications of a technique that is rapidly becoming an important archeological tool. It was first tried in the early 1970s, when a few archeologists saw how geochemists used isotope ratios of carbon (and other elements) to date sediments. But only recently have archeologists begun to make full-scale use of such ratios to help answer central evolutionary questions, including which human groups were farmers and which remained hunter-gatherers, how different species coexisted at a single site, and how climate changes affected life on Earth.

This ambitious agenda for isotopy, as the field has come to be called, was described last week at the annual meeting of the International Council for Archaeozoology,



**Bone of contention?** Probably not. Marilyn Fogel (left) and Noreen Tuross are isotopists on excellent terms.

held at the Smithsonian Institution. At the meeting, two dozen or so isotopists (who also call themselves isotopeteers, isotopologists, or archeisologists) described the areas in which they are putting their methods to work. Many members of the little band present at the meeting are among the pioneers in the field.

Regardless of what they're called, these scientists are essentially dietary detectives. Their aim is to reconstruct ancient food webs, working with the scant evidence provided by isotopes found in bones, teeth, horns, and other human or animal tissues of dead humans or animals. The reason the method works, the isotopists are fond of saying, is because "you are what you eat, plus a few per mil" (a measurement of isotopes, equal to a few parts per thousand).

Every food leaves a distinctive isotopic signature in its consumer. The reason is that different types of plants metabolize carbon and nitrogen differently during photosynthesis; hence plants from different environments have distinct carbon and nitrogen isotope ratios. The animals that eat those plants—and the animals that in turn eat them—maintain similar ratios. Those isotopic differences make it possible to distinguish animals that ate seafood from those that grazed in savanna or browsed in woodlands.

Unfortunately, the process isn't perfectly straightforward, partly because the isotopic ratios are altered by a creature's metabolism

in a process known as fractionation. Last year biochemist Noreen Tuross of the Smithsonian's Conservation Analytical Laboratory showed just how complex fractionation can make things—by using herself as a guinea pig. Tuross ate a strict vegetarian diet that included no animal protein of any kind. When she sampled the nitrogen isotopes in her own fingernails, she found ratios that made it look as though she had been surviving largely on animal protein. She then warned her colleagues that an increase in nitrogen-15 can be a sign of protein deficiency—and not by any means a sure sign of a diet that is high in animal protein.

And there are other pitfalls. Isotope ratios can be altered by contamination in the lab or in soils where the bone was found or by decay after the animal has died. Different species may fractionate isotopes differently, and factors such as age, size, feeding behavior, and gut anatomy can influence the ratios. Even atmospheric nuclear tests and the industrial revolution have changed the carbon ratios in plants. Says isotope geochemist Marilyn Fogel of the Geophysical Laboratory of the Carnegie Institution of Washington: "When you start to think of all of that, you wonder why these methods work at all. Thank God, they do work."

Fogel's relief reflects the importance of the questions that isotopy is now capable of answering. "Diet is the key to some of the most important questions in evolution," says Paul L. Koch, a postdoctoral fellow at the Smithsonian. The question of what specific environmental niche a species occupied can in part be answered by some traditional archeological methods or by sampling fossilized seed and pollen associated with human and animal remains. But isotopic ratios are capable of providing a much more direct and definitive answer.

So far isotopes have provided an excellent window into diets of the relatively recent past—particularly where collagen is present. Collagen is the major protein in bone, and lab techniques for determining its isotopic ratios are well established. "In some of its applications, isotopy is becoming routine," says van der Merwe, who splits his time as a professor at Cape Town and Harvard University. "It's the kind of stuff that most archeologists working in the Americas use. As a matter of course, they deal with the collagen in skeletons to get dietary information about maize."

Using those methods, van der Merwe helped prove that hunter-gatherers in North American woodlands began to cultivate maize later than expected, at about A.D. 1000. He is using the technique to help settle a debate among archeologists about whether prehistoric people who lived along

the coast of Ecuador at about 3100 B.C. subsisted on seafood or on maize they had cultivated. Michael J. DeNiro at the University of California at Santa Barbara identified plants cooked by Indians living in the Upper Mantara Valley of Peru as early as 200 B.C. by measuring isotopes found in residues on the inside of their cooking pots.

Collagen, however, has its limitations as a material for isotopic analysis—and these have helped to determine the current limits for the technique. Collagen lasts only about 10,000 years in the tropics, making it useless for studying older specimens. As a result, much of the interest at last week's conference was sparked by new methods that could allow researchers to dig deeper into the past. "It is time to break out of the collagen bonds," van der Merwe said at the conference.

But efforts to break the collagen bonds are still highly experimental, and some in the field remain skeptical. Lee-Thorp's work with isotopes in apatite from tooth enamel in hominids and other primates is promising, but colleagues are waiting for more experiments to verify her findings before they can be fully accepted. Many in the field remember a disappointing earlier attempt to use apatite in determining isotope ratios that

was shot down by DeNiro and Margaret Schoeninger of the University of Wisconsin in a 1982 article.

But more researchers are beginning to test apatite, and some are trying to extract other isotopes, such as oxygen, hydrogen, and strontium, from noncollagenous sources. So far, their results have been mixed, and Koch of the Smithsonian reported that he'd had little success in trying to interpret oxygen isotope ratios from the apatite of humans who lived some 5000 years ago in Tennessee.

Nonetheless, it's inevitable that these methods will be tried on remains of early hominids in an attempt to reconstruct the world in which they lived, says van der Merwe. One of his postdocs at Cape Town is already using isotopy to study the climate at the time of a mass extinction in the Permian, more than 200 million years ago. This kind of work begins to change the entire scope of isotopy. "This takes us into global change," says Tuross. "It gives a way to study past ecosystems and how animals and humans interact with the environment. And that's just the beginning. These are complex signals, and they are giving us far more information than we ever anticipated."

■ ANN GIBBONS

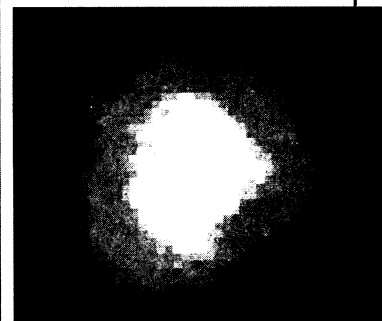
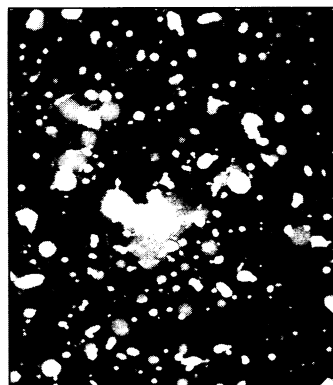
#### Seeing the Unseeable.

For two decades now, astronomers have been trying to comprehend a near-mystical substance known as "dark matter"—the invisible ectoplasm that seems to comprise at least 90% of the mass in the universe, and that makes itself known only by its gravitational effects on the visible stars and galaxies. Theorists have speculated that the stuff consists of intergalactic rocks, weakly interacting particles left over from the Big Bang, or even miniature black holes. But nobody has ever actually seen it.

Until now, that is: as the images shown here suggest, J. Anthony Tyson and his colleagues at Bell Laboratories have recently found a way to make rough maps of the dark matter that resides in clusters of galaxies. Their technique starts with a long, long telescopic exposure of the cluster—in this case, the cluster Abell 1689 (left). If the exposure is long enough, says Tyson, it will eventually reveal a dense patchwork of faint, irregular blue blobs behind the cluster, with each blob presumably being a very distant galaxy just bursting into life. But the blobs are not oriented at random, as they are in exposures of empty sky: the gravitational field of the cluster bends their light and distorts them into short arcs that are more or less concentric with the cluster center. A computer analysis of the arcs can therefore map out the mass in the cluster—and that mass must include the dark matter as well as the ordinary stars (right).

The resulting maps reveal that in most clusters the dark matter does indeed spread throughout intergalactic space, says Tyson. Moreover, it vastly outweighs the visible galaxies. He and his colleagues are now halfway through the analysis of some 14 clusters. And with the help of several international collaborators, they hope to have data from 30 clusters by the end of the year. The resulting images probably won't tell us what the dark matter actually is, says Tyson, "but they will certainly constrain the theoretical models."

■ M. MITCHELL WALDROP



J. Anthony Tyson