may also play a role in the theft. So researchers have been trying to make model compounds with both nickel and iron, but the task is "extremely difficult," says Hembre. The reason, in part, is that nickel and iron have similar chemical reactivities, causing them to form clusters during synthesis and yield a variety of different compounds.

So Hembre and his colleagues J. Scott McQueen and Victor Day opted to use ruthenium, another transition metal, instead of nickel, because its chemical reactivity differs from that of iron. To better control the synthesis, they made their ruthenium-iron model compound by attaching each transition-metal atom to ring-shaped groups known as cyclopentadienes. These groups help stabilize the reactivity of the transition metals, making them easier to bring together. And because these models only have a pair of transition-metal atoms, while hydrogenase has many, it's much easier for researchers to use electrochemistry and spectroscopy to track changes in electronic behavior: The signal doesn't get lost in the noise.

First, the researchers determined how closely the models mimic hydrogenase. When placed in solution with hydrogen, both the enzymes and the new models grab electrons from H_2 and parcel them out one at a time to electron acceptors, such as methyl viologen, causing the viologens to change color from yellow to bright blue. The researchers were then able to get a closer look at the process using electrochemistry and nuclear magnetic resonance spectroscopy. The studies show that H_2 releases a proton after it binds to ruthenium. Next, the metal steals H_2's electron pair, and finally the remaining proton falls away.

"The final question is, does the real thing work that way?" asks Collman. To find the answer, Hembre and his colleagues are currently working to create new model compounds that contain nickel and iron in the core, hoping to see those compounds split H_2 in the same fashion as the real protein. They hope the stabilizing effects of the cyclopentadiene groups will make this synthesis easier.

Even if the strategy fails, some ruthenium-based compounds themselves may still prove useful. The hydrogen-splitting reaction is crucial in some fuel cells, which power things such as hospital generators. The cells strip the electrons from hydrogen to generate an electric current. At present, however, fuel cells typically perform this reaction with the help of a costly, but efficient, platinum catalyst. If Hembre's compounds based on ruthenium—a much less expensive metal—convert hydrogen to electricity just as efficiently, their relatively low cost may make these model compounds part of a model power source.

–Robert F. Service

MEETING BRIEFS

Geoscientists Contemplate a Fatal Belch and a Living Ocean

NEW ORLEANS—Paleontologists may deal with dusty fossils, but they also ponder some of the planet's greatest catastrophes. At last month's annual meeting of the Geological Society of America in New Orleans, one eye-opening presentation argued that the extinctions at the end of Permian period might have been triggered by a belch of deep-sea carbon dioxide. Another suggested that the scope of the Cretaceous-Tertiary catastrophe at the end of the age of the dinosaurs needs to be scaled back, at least in the oceans.

Another Killer Charged With Mass Extinction

No wonder life took a beating—its worst ever—250 million years ago at the end of the Permian period. Just months ago, researchers determined that the largest known volcanic eruption on land took place in present-day Siberia at the same geological moment as the extinctions, which wiped out 90% of all genera in the oceans. Now they've stumbled on evidence of another assault—a sudden surge of carbon dioxide from the deep sea that allegedly poisoned marine life.

Paleontologists studying the extinctions don't yet know how much to blame the eruptions or the gas belch—assuming it happened. And researchers in other fields aren't fully convinced by the scenario that paleontologists Andrew Knoll of Harvard University and Richard Bambach of Virginia Polytechnic Institute and State University and sedimentologist John Grotzinger of the Massachusetts Institute of Technology (MIT) have sketched out as the driving force behind their postulated carbon dioxide surge. But the idea, and the circumstantial evidence that Knoll and his colleagues are marshaling, is capturing imaginations. "It isn't as yet backed up by a tremendous amount of data," says paleontologist Douglas Erwin of the National Museum of Natural History, a leader in studies of the extinction, but "I think it's an interesting, even fascinating, hypothesis."

Knoll and his colleagues were drawn into the fray when a paleontologist colleague showed a slide of a layered rock from late in the Permian. The paleontologist assumed it was a fossil stromatolite, a mound of sediments glued together by primitive blue-green algae. But Knoll and Grotzinger immediately recognized it as an inorganic carbonate precipitate, a rock type that rarely formed in the past 500 million years but was common in earlier times. Carbonates are usually formed from the remains of once-living animals, but during five cycles of glaciation in the late Precambrian between 600 million and 800 million years ago, carbonates precipitated directly from seawater without any help from living things, presumably when the concentration of dissolved carbonate—that is, dissolved carbon dioxide—became exceedingly high. As it turned out, these anomalous carbonates are also relatively common at the time of the mass extinction, and Knoll and Grotzinger saw them as a sign of climate and geochemistry gone awry.

DOUGLAS ERWIN/NMNH

Trace of a killer? Did the high seawater carbon dioxide that precipitated this carbonate also trigger a mass extinction?

The ultimate cause, they propose, was a shutdown in the circulation of the deep ocean. Toward the end of the Permian, all the continents were huddled in a single supercontinent, Pangaea. That would have left a globe-girdling ocean with some narrow seas within the supercontinent. With no continental ice sheets to chill surface waters and send them diving into the deep sea, as they do today around Antarctica, the group argues, deep waters grew sluggish and even stagnant. As phytoplankton in surface waters continued to extract carbon dioxide from the atmosphere, converting it to organic matter that sank and oxidized to carbon dioxide, the deep sea's carbon dioxide content would have soared.

The deep ocean's gain was the atmosphere's loss, according to the Harvard-MIT scenario. As the "biological pump" of phytoplankton kept driving atmospheric carbon dioxide into deeper waters, the greenhouse effect weakened, sending Earth into a new ice age. Glaciation, in turn, would eventually have reinvigorated the circulation of the deep sea, churning the carbon dioxide–laden waters to the surface in an event something like the disastrous turnover of Lake Nyos in 1986 in Cameroon (*Science*, 1 April 1994, p. 26). The influx of carbon dioxide to shallow Permian waters could have precipitated the anomalous carbonates. And it could also have triggered the mass extinction by poisoning or smothering organisms in surface waters, where most marine species live.

Aside from the anomalous carbonates, Knoll and his colleagues point to other evidence supporting their scenario. Geologists have recently recognized signs of glaciation in the late Permian in northern Siberia. And the isotopic composition of the carbon locked in some of the carbonates hints at an oceanic turnover, say Knoll and his colleagues. Fluctuations in the ratio of heavy and light carbon isotopes imply that carbon was first stashed away in deep water, then swept up into the shallows.

The hand of carbon dioxide can also be recognized in the pattern of extinction at the end of the Permian, the group says. Those marine organisms that were already tolerant of higher concentrations of carbon dioxide—because their higher metabolic rates produced the gas in abundance or because they were accustomed to burrowing into bottom sediments, where carbon dioxide would accumulate—did relatively well in the mass extinction, losing less than 50% of their genera. But organisms having lower metabolic rates, like corals, or those that would have difficulty forming carbonate skeletons when high carbon dioxide levels boosted the acidity of ocean waters, like planktonic foraminifera, suffered greatly, losing 80% to 100% of their genera.

It will take more than circumstantial evidence to convince paleontologists like Erwin, however. "What we need is a much more precise idea of exactly when the extinctions occurred and how rapidly they occurred," he says. That would help distinguish the oceanic kill mechanism, which would have operated in the few million years leading up to the end of the Permian, from the effect of the eruption, which began only at the end of the Permian and was over within a million years or so (*Science*, 6 October, p. 27). Experts in other fields encompassed by the hypothesis also have their doubts. Says Steven D'Hondt of the University of Rhode Island, a paleoceanographer who heard Knoll's talk: "I have a hard time believing the ocean can be stagnant long enough or can hold enough carbon dioxide to do what I think he needs it to do."

But Knoll is optimistic for now: The death-by-carbon dioxide scenario "can stand or fall on things you can actually observe by careful field work. The best part of this it that it suggests about 10 years' worth of further research."

A Strangelove Ocean Comes Back to Life

The more researchers have speculated about conditions on Earth after a huge meteorite smashed into the Yucatán Peninsula 65 million years ago, the grimmer they have looked. Some proposed that debris hurled into space would have became red-hot as it re-entered the atmosphere, turning the surface into an oven for hours. Others said that the heat would have given way to months of cold as dust hurled into the stratosphere by the impact's blast shut out the sun. Acid rain, tidal waves, and global forest fires have all been included in the litany of destruction. But now one element of the scenario is actually looking less dire. Reports of the ocean's death, it seems, have been much exaggerated.

Geochemists analyzing microfossils from sea-floor muds had thought they saw evidence that the ocean was nearly devoid of life for tens of thousands of years after the impact—a Strangelove ocean, it was called, after the fictional movie character who builds a doomsday machine. Now Steven D'Hondt of the University of Rhode Island (URI) and his colleagues have traced the Strangelove signal a full 2 million years in a core of sediment from the southeastern South Atlantic. That's far too long for the ocean to have remained sterile, says D'Hondt, even in the direst scenarios. For all that time, he thinks, the ocean was not dead, only disturbed. "There's no reason to hypothesize a Strangelove ocean," he says. "The data don't require it."

D'Hondt and URI colleagues Danielle Luttenberg and Percy Donaghay monitored the ocean after the impact by analyzing the difference between the carbon isotopic compositions of surface and deep waters. In a normal, healthy ocean like today's, the carbonate dissolved in deep waters has more of the lighter isotope of carbon—carbon-12—than the heavier carbon-13. This difference is sustained by the so-called biological pump. Phytoplankton in surface waters preferentially extract the lighter carbon from carbon dioxide dissolved in seawater and incorporate it into their organic matter. When the plankton die, the carbon-12–rich organic matter can settle into the deep sea where it returns to dissolved carbon dioxide.

For an ancient ocean, these ratios have to be inferred by analyzing the carbonate fossils of microscopic animals that lived at shallow depths, forming their skeletons exclusively from surface-water carbonate, or those that lived on the ocean floor, drawing on deep waters. Earlier researchers had found that the isotope difference between surface and deep waters nearly vanished at the time of the impact and did not recover for tens of thousands of years. Together with the fossil evidence that nearly 50% of marine species went extinct at the Cretaceous-Tertiary boundary, the shift seemed to signal the worst sort of catastrophe, in which the oceans themselves became nearly lifeless under a pall of dust. In the mid-1980s, Kenneth Hsü of the Swiss Federal Institute of Technology in Zurich dubbed this bleak period the Strangelove ocean. Hsü imagined it lasting at most a few thousand years, says D'Hondt, but longer isotopic records deciphered later seemed to stretch it to 50,000 years and then to 500,000 years.

But now that the URI analysis extends the reduced carbon isotopic gradient to 2 million years, D'Hondt doesn't think a Strangelove ocean could be responsible. There's no plausible way to depress biological productivity for that long, he says. A Strangelove ocean, he says, "is okay as long as darkness persists following the impact, but once light returns, if you have any phytoplankton out there at all, it should be extraordinarily abundant very rapidly." Unconstrained phytoplankton populations can double once or twice a day, he notes, and he argues that nothing about the impact, including the acid rain it produced, could have held back the phytoplankton for more than a few decades.

Rather than invoking a dead ocean, D'Hondt and his colleagues explain the prolonged isotopic shift as a result of an ecological change due to the extinction of larger organisms. The amount of organic matter reaching the deep sea depends not only on phytoplankton productivity but also on how efficiently that organic matter is transported down from the surface. Large chunks sink fastest and are the least likely to be broken down in surface waters. As a result, the extinction of most larger phytoplankton as well as animals of all sizes, which package organic matter into pellets of feces as well as dead tissues, could have short-circuited the supply of isotopically light carbon to the deep sea, says D'Hondt. After a few million years, however, evolution reconstructed an efficient web of plankton grazers, and the system recovered.

The URI analysis "is moving in the right direction," says paleoceanographer James Zachos of the University of California, Santa Cruz. To test it, though, "we need some way to see what's happening higher in the food chain." Therein lies a challenge for paleontologists: Larger zooplankton leave no fossil record, and fossil fish are few and far between. Now that the Strangelove ocean has been pronounced alive, the problem is gauging the state of its health.

–Richard A. Kerr