

## Taking a chemical look at the early Earth

Geologists believe that soon after Earth took shape some 4.6 billion years ago, it consisted of a conglomeration of minerals jumbled together. Later, molten material rose to the surface, altering the uniform composition of minerals below and forming Earth's first crust.

Until now, researchers had only been able to date this key evolutionary sequence to sometime during the first half-billion years of Earth's history. But last month, two Harvard University scientists presented evidence suggesting that the episode occurred very soon after the Earth formed—within the first 100 million years of our planet's existence. They base their finding on measurements of the relative abundances of neodymium isotopes in an ancient rock.

Geologist Richard W. Carlson of the Carnegie Institution of Washington (D.C.) cautions that the study relied on just one ancient rock sample and used a less-than-optimum reference sample for comparison. But, he adds, "What I find exciting about this work, if it proves true, is that the Earth was a very hot, chemically active body soon after its formation."

In providing a peek at very early geochemical processes, the new work suggests that Earth formed an extensive crust—some 40 percent of the volume of the present-day continents—more than 4 billion years ago, says study coauthor Charles L. Harper Jr. That primordial crust appears to have vanished long ago in the tumult of tectonic activity, so scientists cannot study it directly. But the ancient terrestrial rock examined by Harper and colleague Stein B. Jacobsen may represent a complement to the material that formed the ancient crust—a lost terrain of the early Earth, he asserts.

Harper reported the new findings in March at the annual Lunar and Planetary Science Conference in Houston.

The researchers measured the abundances of two isotopes of neodymium, a rare-earth element, in a Greenland rock that dates back about 3.8 billion years. One of the isotopes, neodymium-142, represents in part the radioactive decay product of a form of the element samarium, which was present only during Earth's earliest epochs. Because this form, known as samarium-146, has a half-life of only 103 million years and has essentially been extinct for billions of years, a relative excess of its decay product must reflect chemical changes that took place very early in Earth's history, Jacobsen and Harper assert.

Although other researchers have examined the amount of neodymium-142 in meteorites, Harper says he and Jacobsen are the first to report on its abundance in terrestrial rock.

Using a mass spectrometer, the researchers examined with unprecedented

precision the amount of the decay product neodymium-142 relative to a stable form of neodymium in the rock. They then compared that value with the abundance in a standard neodymium sample believed to have come from a rock formed long after initial chemical differentiation had taken place on Earth. Combining those data with measurements of neodymium-143, a decay product of a much longer-lived form of samarium, Jacobsen and Harper found that the ancient rock had a small excess of neodymium-142—33 parts per million—dating to within 100 million years of Earth's formation.

The researchers link the excess to early terrestrial evolution because neodymium, along with some other materials, binds to only a few other elements and would have left Earth's mantle readily during melting—the result of radioactive decay or the impact of a giant object. When a signifi-

cant amount of neodymium departed, it would have left behind a higher ratio of elemental samarium to elemental neodymium. As samarium-146 decayed, it would have produced a relative excess of neodymium-142 in the mantle—and a matching underabundance in the material that left the mantle, Harper says.

Although the new study pinpoints the time when parts of the Earth began to differentiate chemically, it doesn't prove that material that left a region of the mantle billions of years ago formed Earth's first continental crust. The material might have migrated elsewhere in the mantle, Harper notes. But earlier studies of neodymium in rocks from Mars and the moon support the crustal hypothesis, he says. Another possibility: Harper thinks the study may shed light on the conjecture that a Mars-size object once struck Earth, melting the mantle and blasting enough material to form the moon. The findings may indicate when this massive collision could have occurred.

—R. Cowen

### Steamed, gallium arsenide guides light

Sometimes, a little rust can do a lot of good. Electrical engineers have discovered that by steaming gallium arsenide chips they can oxidize the surface of this semiconductor and create microscopic patterns useful for guiding light, and possibly electrons, in lasers and other electronic and optical devices.

This finding puts gallium arsenide on a more equal footing with silicon, which reigns as the material of choice in electronics, in part because it forms a stable oxide. This allows engineers to etch circuits into the surface easily, says Nick Holonyak Jr. at the University of Illinois at Urbana-Champaign.

He and his colleagues made a similar oxide on gallium arsenide, then tapped this semiconductor's ability to emit light when subjected to an electrical current to create laser diodes. They report their work in the March 30 APPLIED PHYSICS LETTERS.

"The semiconductor is a [brighter] light source than any other light source, but we haven't had a good way to move photons," says Holonyak.

The Illinois team starts with a chip of pure gallium arsenide sandwiched between layers of gallium arsenide in which aluminum atoms have replaced some gallium atoms. "It's the aluminum that makes it possible for us to make a good oxide," Holonyak says. The researchers put a chemical mask with the desired pattern atop the chip surface, steam the chip, remove the mask and coat the chip with a thin conductor.

The oxidized parts insulate, so current reaches the light-emitting core only where the mask prevented oxida-

tion. The oxidized parts also have a lower index of refraction, so they deflect light, confining it to the pattern.

The researchers discovered they could make this smooth, hard oxide while studying the decade-long effects of exposure to air and moisture on aluminum gallium arsenide. In 1989, Holonyak and graduate student John M. Dallesasse tried to speed up decay by heating the material above 400°C in the presence of water vapor. But instead of crumbling, the chips formed a hard oxide. Since then, the group has made lines, rectangles and rings. They expect they can guide light along any pathway they want.

Because the oxide won't peel off, processing these chips into useful devices becomes relatively straightforward, says Holonyak. In addition, the technique appears to work for other compound semiconductors that contain aluminum in their top layers, says Russell D. Dupuis of the University of Texas at Austin.

He and Holonyak expect that companies using laser diodes in compact disk players, telecommunications and other applications will want to use this simpler approach. "And as we go toward integrated optoelectronic devices, this could be the enabling technology," Dupuis says.

Scientists first need to learn how well the oxide can channel electrons, as well as photons, and whether the oxide changes its characteristics over time, says Dupuis. "The snapshot we have now, though, is that it's working well," he adds.

—E. Pennisi