

New Colors of Hydrogen from the Depths

By John Benson

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1. Introduction

The title of this paper actually describes its content very well, although I'm sure it will leave most readers confused. That is, most readers that are not members of the American Association for the Advancement of Science, and/or don't regularly read their weekly issue of *Science*. But now at least you know where my main lead came from.

Would you believe there are vast amounts of relatively pure hydrogen underground, and we can drill wells to extract this? Read on.

2. Mali

In the shade of a mango tree, Mamadou Ngulo Konaré recounted the legendary event of his childhood. In 1987, well diggers had come to his village of Bourakébougou, Mali, to drill for water, but had given up on one dry borehole at a depth of 108 meters.

"Meanwhile, wind was coming out of the hole," Konaré told Denis Brière, a petrophysicist and vice president at Chapman Petroleum Engineering, in 2012. When one driller peered into the hole while smoking a cigarette, the wind exploded in his face.¹

"He didn't die, but he was burned," Konaré continued. "And now we had a huge fire. The color of the fire in daytime was like blue sparkling water and did not have black smoke pollution. The color of the fire at night was like shining gold, and all over the fields we could see each other in the light. ... We were very afraid that our village would be destroyed."

It took the crew weeks to snuff out the fire and cap the well. And there it sat, shunned by the villagers, until 2007. That was when Aliou Diallo, a wealthy Malian businessman, politician, and chair of Petroma, an oil and gas company, acquired the rights to prospect in the region surrounding Bourakébougou. "We have a saying that human beings are made of dirt, but the devil is made of fire," Diallo says. "It was a cursed place. I said, 'Well, cursed places, I like to turn them into places of blessing.'"

In 2012, he recruited Chapman Petroleum to determine what was coming out of the borehole. Sheltered from the 50°C heat in a mobile lab, Brière and his technicians discovered that the gas was 98% hydrogen. That was extraordinary: Hydrogen almost never turns up in oil operations, and it wasn't thought to exist within the Earth much at all. "We had celebrations with large mangos that day," Brière says.

Within a few months, Brière's team had installed a Ford engine tuned to burn hydrogen. Its exhaust was water. The engine was hooked up to a 300-kilowatt generator that gave Bourakébougou its first electrical benefits: freezers to make ice, lights for evening prayers at the mosque, and a flat-screen TV so the village chief could watch soccer games. Children's test scores also improved. "They had the lighting to learn their lessons before going to class in the morning," Diallo says. He soon gave up on oil, changed the name of his company to Hydroma, and began drilling new wells to ascertain the size of the underground supply.

¹ Eric Hand, *Science*, "Hidden hydrogen," Feb 17, 2023 Issue, Pg. 630.

<https://www.science.org/content/article/hidden-hydrogen-earth-may-hold-vast-stores-renewable-carbon-free-fuel>

The Malian discovery was vivid evidence for what a small group of scientists, studying hints from seeps, mines, and abandoned wells, had been saying for years: Contrary to conventional wisdom, large stores of natural hydrogen may exist all over the world, like oil and gas—but not in the same places. These researchers say water-rock reactions deep within the Earth continuously generate hydrogen, which percolates up through the crust and sometimes accumulates in underground traps. There might be enough natural hydrogen to meet burgeoning global demand for thousands of years, according to a U.S. Geological Survey (USGS) model that was presented in October 2022 at a meeting of the Geological Society of America.

3. The Science

“When I first heard about it, I thought it was crazy,” says Emily Yedinak, a materials scientist who devoted a fellowship at the Advanced Research Projects Agency-Energy (ARPA-E) to drumming up interest in natural hydrogen. “The more that I read, the more I started to realize, wow, the science behind how hydrogen is produced is sound ... I was kind of like, ‘Why is no one talking about this?’”

*Since 2018, however, when Diallo and his colleagues described the Malian field in the *International Journal of Hydrogen Energy*, the number of papers on natural hydrogen has exploded. “It’s absolutely incredible and really exponential,” says geologist Alain Prinzhofer, lead author on the Mali paper and scientific director of GEO4U, a Brazil-based oil and gas services company that is doing more and more hydrogen work. Dozens of startups, many in Australia, are snatching up the rights to explore for hydrogen. Last year, the American Association of Petroleum Geologists formed its first natural hydrogen committee, and USGS began its first effort to identify promising hydrogen production zones in the United States. “We’re in the very beginning, but it will go fast,” says Viacheslav Zgonnik, CEO of Natural Hydrogen Energy. In 2019, the startup completed the first hydrogen borehole in the United States, in Nebraska.*

The enthusiasm for natural hydrogen comes as interest in hydrogen as a clean, carbon-free fuel is surging. Governments are pushing it as a way to fight global warming, efforts that were galvanized when Russia invaded Ukraine last year and triggered a hasty search, especially in Europe, for alternatives to Russian natural gas. At the moment, all commercial hydrogen has to be manufactured, either in a polluting way, by using fossil fuels, or in an expensive way, by using renewable electricity. Natural hydrogen, if it forms sizable reserves, might be there for the taking, giving the experienced drillers in the oil and gas industry a new, environ-mentally friendly mission. “I believe that it has the potential to replace all fossil fuels,” Zgonnik says. “That’s a very large statement, I know.”

Critically, natural hydrogen may be not only clean, but also renewable. It takes millions of years for buried and compressed organic deposits to turn into oil and gas. By contrast, natural hydrogen is always being made afresh, when underground water reacts with iron minerals at elevated temperatures and pressures. In the decade since boreholes began to tap hydrogen in Mali, flows have not diminished, says Prinzhofer, who has consulted on the project. “Hydrogen appears, almost everywhere, as a renewable source of energy, not a fossil one,” he says.

It is still early days for natural hydrogen. Scientists don't completely understand how it forms and migrates and—most important—whether it accumulates in a commercially exploitable way. “Interest is growing fast, but the scientific facts are still lacking,” says Frédéric-Victor Donzé, a geophysicist at Grenoble Alpes University. Big Oil is hanging back, watching while wildcatters take on the risky exploratory work. Commercialization of the Mali field has run into snags, and elsewhere only a few exploratory wells have been drilled. Donzé, who has sworn off accepting industry money, worries about hype.

Yet some scientists have become true believers. Eric Gaucher, a geochemist at the University of Bern, left a career at French oil giant Total because it wasn't moving fast enough on hydrogen. He believes the Mali discovery might end up in the history books alongside one that happened 163 years ago in Titusville, Pennsylvania. At the time, the world knew about seeps of oil in places such as Iraq and California but was blind to the vast deposits that lay underground. Then on 27 August 1859, a nearly bankrupt prospector named Edwin Drake, working in Titusville with a steam engine and cast-iron drill pipes, struck black gold at a depth of 21 meters, and began collecting it in a bathtub. Before long, U.S. companies were harvesting millions of bathtubs of oil every day.

“I am thinking we are not very far from that with hydrogen,” Gaucher says. “We have the concept, we have the tools, the geology. ... We only need people able to invest...”

But what about the “new colors?” Below are some of the old and a couple of new colors.

The hydrogen rainbow

Researchers use colors to distinguish between different kinds of hydrogen.

Gray hydrogen: Made from fossil fuels, which release carbon dioxide and adds to global warming.

Blue hydrogen: Same as gray hydrogen, but the carbon is captured and sequestered.

Green hydrogen: Made without carbon emissions by using renewable electricity to split water.

Gold hydrogen: Tapped from natural subsurface accumulations.

Orange hydrogen: Stimulated by pumping water into deep source rocks...

Green hydrogen costs about \$5 per kilogram, more than twice as much as gray hydrogen, which tends to track the price of natural gas. Cheaper electrolyzers will help—DOE is sponsoring a “moonshot” to reach \$1 per kilogram within a decade...

Pumping hydrogen out of the ground should be much cheaper, which is why proponents sometimes call the natural stuff “gold.” Brière² says extraction at the Mali site, which benefits from shallow wells and nearly pure hydrogen, could be as cheap as 50 cents per kilogram. Ian Munro, CEO of Helios Aragon, a startup pursuing hydrogen in the foothills of the Spanish Pyrenees, says his break-even costs might end up between 50 and 70 cents. “If it does work, it could revolutionize energy production,” he says. “There’s a big ‘if’ there. But you’re not going to get that with green hydrogen, right? To me, that’s a bottomless pit.”

² Denis Brière, a petrophysicist and vice president at Chapman Petroleum Engineering.

4. Why Now?

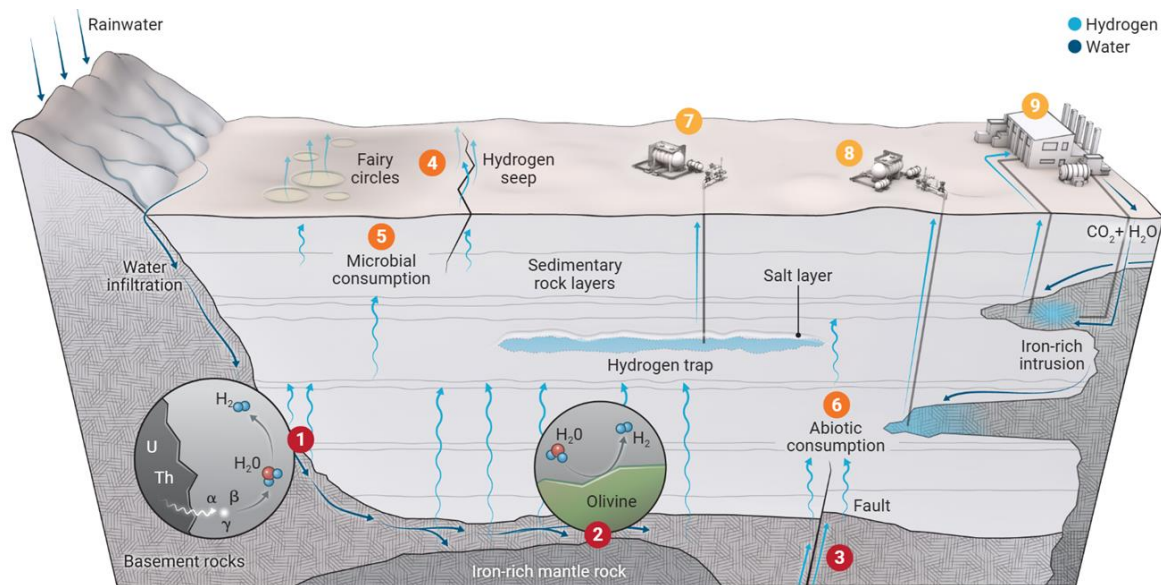
The oil and gas industry has punctured Earth with millions of wells. How could it have overlooked hydrogen for so long? One reason is that hydrogen is scarce in the sedimentary rocks that yield oil and gas, such as organic-rich shales or mudstones. When compacted and heated, the carbon molecules in those rocks consume any available hydrogen and form longer chain hydrocarbons. Any hydrogen the oil encounters as it migrates to a porous “reservoir” rock such as a sandstone tends to react to form more hydrocarbons. Hydrogen can also react with oxygen in rocks to form water or combine with carbon dioxide to form “abiotic” methane. Microbes gobble it up to make yet more methane.

Even if the hydrogen survives, geologists thought, it should not accumulate. Hydrogen is the smallest molecule of all: It can leak through minerals and even metals. If Earth were producing hydrogen, it seemed unlikely to hang around.

And so, historically, when well loggers cataloged their borehole emanations, they rarely bothered to measure for hydrogen. “The bottom line—they weren’t really looking for hydrogen,” says Geoffrey Ellis, an organic geochemist at USGS. “We weren’t looking in the right places with the right tools.”

Earth’s hydrogen factories:

Hydrogen is a carbon-free fuel, but manufacturing it is dirty and expensive. Some researchers believe cheap, vast, and potentially renewable sources of natural hydrogen sit underground.



Generation

- 1. Radiolysis:** Trace radioactive elements in rocks emit radiation that can split water. The process is slow, so ancient rocks are most likely to generate hydrogen.
- 2. Serpentinization:** At high temperatures, water reacts with iron-rich rocks to make hydrogen. The fast and renewable reactions, called serpentinization, may drive most production.

3. **Deep-seated:** Streams of hydrogen from Earth's core or mantle may rise along tectonic plate boundaries and faults. But the theory of these vast, deep stores is controversial.

Loss mechanisms:

4. **Seeps:** Hydrogen travels quickly through faults and fractures. It can also diffuse through rocks. Weak seeps might explain shallow depressions sometimes called fairy circles.
5. **Microbes:** In shallower layers of soil and rock, microbes consume hydrogen for energy, often producing methane.
6. **Abiotic reactions:** At deeper levels, hydrogen reacts with rocks and gases to form water, methane, and mineral compounds.

Extraction:

7. **Traps:** Hydrogen might be tapped like oil and gas—by drilling into reservoirs trapped in porous rocks below salt deposits or other impermeable rock layers.
8. **Direct:** It might also be possible to tap the iron-rich source rocks directly, if they're shallow and fractured enough to allow hydrogen to be collected.
9. **Enhanced:** Hydrogen production might be stimulated by pumping water into iron-rich rocks. Adding carbon dioxide would sequester it from the atmosphere, slowing climate change.

Yet the hints were there for those who did look. According to Zgonnik, a geochemist who recently published a review of natural hydrogen, the first scientific discussion of it dates to 1888, when Dmitri Mendeleev, the father of the periodic table, reported hydrogen seeping from cracks in a coal mine in Ukraine. Zgonnik, who was born and raised in Ukraine, says reports of hydrogen are relatively common throughout the former Soviet Union—because Soviet researchers were looking for it. They held to a now discredited theory that would have required significant amounts of natural hydrogen to produce oil from nonliving processes rather than from ancient life.

For Barbara Sherwood Lollar, a University of Toronto geochemist, the hydrogen revelation came in the 1980s, when she was a graduate student. She was taking data in mines in Canada and Finland, following up on evidence they sometimes contained flammable gases. She measured the expected hydrocarbons—some methane, some ethane—but they didn't add up to the total mass in her samples. Finally, she realized that some contained as much as 30% hydrogen. "We didn't even measure for it, because nobody expected hydrogen in the system," she says.

Hundreds of hydrogen seeps have now been documented around the world. Zgonnik has come to believe hydrogen can explain even more common features: hundreds of thousands of shallow, circular depressions in the land, tens or hundreds of meters across, that go by names like fairy circles, witch rings, or water basins. "They're widespread and very mysterious," he says. Surveying several of these features along the U.S. East Coast, where they are called Carolina bays, Zgonnik and his colleagues found they were leaking hydrogen, and that its concentration grew with depth. Zgonnik thinks that hydrogen dissolves away minerals in underlying rocks, leading to slumping at the surface.

Vegetation within the circles can sometimes be suppressed, notes Isabelle Moretti, a geologist at the University of Pau and the Adour Region who has documented hydrogen seeping from fairy circles in Brazil, Namibia, and Australia. She speculates it might have something to do with hydrogen-loving microbes consuming other nutrients. “Maybe there is nothing left,” she says...

5. Gold (hydrogen) is Where You Find It

The main engine of natural hydrogen production is now thought to be a set of high temperature reactions between water and iron-rich minerals such as olivine, which dominate Earth’s mantle. One common reaction is called serpentinization, because it converts olivine into another kind of mineral called serpentinite. In the process the iron oxidizes, grabbing oxygen atoms from water molecules and releasing hydrogen.

Scientists diving in submersibles have seen this process up close at the volcanic Mid-Atlantic Ridge, where tectonic plates are tugged apart and mantle rocks rise up to create fresh slabs of ocean crust. At a site known as Lost City (for the towering “white smoker” chimneys gushing mineral-rich hot water), researchers measured high amounts of hydrogen spewing from the sea floor. And on Iceland, which straddles the Mid-Atlantic Ridge, Moretti and her colleagues have recorded comparable hydrogen flows at some of the hot springs and geothermal wells that dot the country.

But the hope for commercial natural hydrogen lies closer to potential customers on the continents. Prospectors are looking in cratons, the ancient cores of continents, says Owain Jackson, exploration director at H2Au, a U.K.-based hydrogen company. Trapped within them are bands of iron-rich rock, called greenstone belts, which are the remnants of ocean crust that got squeezed between the cratons in ancient continental collisions. Where olivine and other minerals are buried deep enough to be hotter than 200°C, and yet still exposed to water percolating from the surface, they can produce hydrogen. Jackson, who once helped evaluate lease blocks in a region of Mali several hundred kilometers away from Bourakébougou, believes greenstone belts deep in the West African craton are driving the hydrogen production there. “We’re just a bit annoyed we gave the blocks back,” he says.

Cratons hold a second major source of iron with hydrogen-producing potential, Prinzhofer says—one that dates to an evolutionary turning point about 2.4 billion years ago. At the time, the oceans were anoxic and saturated in dissolved iron. But then, in a revolution known as the Great Oxidation Event, ocean-living microbes evolved the ability to photosynthesize. The oxygen they emitted caused the iron to fall as rust to the ocean floor, where it eventually turned to stone. Like greenstone belts, some of these deposits wound up surviving in the cratons and are known today as banded iron formations. They’re thought to hold some 60% of the world’s iron reserves.

In a 2014 paper, Sherwood Lollar and colleagues considered the makeup of Earth’s cratons and found that serpentinization should produce as much as 80% of Earth’s hydrogen. A second mechanism, radiolysis, may generate the rest. As radioactive elements in the crust such as uranium and thorium decay, they emit beta particles, aka helium nuclei, along with other radiation that can split water molecules underground and generate an extra trickle of hydrogen...

What matters for the natural hydrogen industry is simply whether there is enough of the stuff to go after. At USGS, Ellis³ is working on answering that question. He thinks Earth produces orders of magnitude more hydrogen each year than the 90 million tons that humans manufacture. But it's not only that flow that matters—it's the size of the underground stock. "How much can be trapped in the subsurface that we can actually go after?" Ellis asks. "That's a much more difficult question to answer."

He and his USGS colleague Sarah Gelman gave it a try using a simple "box" model borrowed from the oil industry. The model accounted for impermeable rock traps of different kinds, the destructive effect of microbes, and the assumption—based on oil industry experience— that only 10% of hydrogen accumulations might ever be tapped economically. Ellis says the model comes up with a range of numbers centered around a trillion tons of hydrogen. That would satisfy world demand for thousands of years even if the green-energy transition triggers a surge in hydrogen use...

³ Geoffrey Ellis, an organic geochemist at USGS.