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Rocks Tell Tales of Earth Billions of Years Ago

By **KENNETH CHANG**

From just a few sulfur atoms trapped inside some diamonds from Botswana, scientists have inferred that there was almost no oxygen in the air until about 2.4 billion years ago. Meanwhile, a biology experiment looking at starved bacteria suggests that methane was in the air, perhaps explaining why the planet did not freeze over.



Associated Press

From diamond mines in Botswana, like this Debswana site in Jwaneng, scientists have found clues in trapped sulfur atoms suggesting that there was almost no oxygen in the earth's air until about 2.4 billion years ago.

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When scientists try to figure out what the earth was like billions of years ago, they do not have much to work with, mostly just rocks. But a rock can tell much about itself. Limestone is a remnant of ancient sea sediment. Basalt is a hardened lava flow. Granite is magma that slowly cooled underground into a hodgepodge of crystalline minerals.

And over the earth's history, the rocks have changed. Some mineral deposits like vast banded iron formations from ancient times cannot form today, because the oxygen in today's atmosphere and oceans now prevents iron from dissolving.

Scientists find even subtler clues in the weight of individual atoms within rocks. The earliest evidence of life on the earth is not a fossil — microbes rarely fossilize and when they do, they look like cracks or air bubbles — but rather, deposits of carbon dating back 3.8 billion years that almost completely lack a heavier version of carbon.

Ninety-nine percent of carbon atoms are carbon 12, containing six protons and six neutrons in their nuclei. Carbon 13, a rarer, heavier version, or isotope, contains seven neutrons. Living things prefer to be lazy if they can, eating compounds containing the lighter carbon 12 and leaving carbon 13 behind. Thus, clumps of graphite containing higher-than-normal levels of carbon 12 are believed to be the remains of ancient microbes.

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To deduce when oxygen entered the atmosphere, Dr. James Farquhar, a professor of geology at the University of Maryland, plays a similar game of chemical isotopes with sulfur. As sulfur compounds, spewed out by volcanoes, float in the air, ultraviolet light hits them and breaks them apart, producing a ratio of isotopes later preserved in rocks.

In work reported three years ago, Dr. Farquhar found that these sulfur ratios changed between 2.4 billion and 2.1 billion years ago, which he attributes to the advent of oxygen, in the form of ozone, that blocked out the ultraviolet radiation.

Dr. Farquhar has now found the same sulfur isotope signal in tiny specks, about one ten-thousandth of an inch wide, within diamonds. "It tells us it was sulfur from a volcano," he said. The new findings appeared in the Dec. 20 issue of the journal *Science*.

Besides confirming his earlier result, the findings also indicate that parts of the earth's crust were being pushed down and reheated and brought back up, much as they are today. "You can reconstruct this whole cycle," Dr. Farquhar said. "Volcano to atmosphere to sediments to mantle, back to surface."

Dr. Donald E. Canfield, a professor of ecology at the University of Southern Denmark, has taken an unusually modern approach in investigating the ancient earth. He and his colleagues grew bacteria, ones that eat sulfur compounds known as sulfates and produce another group of compounds known as sulfides as waste. The bacteria, lazy as always, tend to eat sulfates containing the lighter sulfur isotopes. "It's easier for them eat, basically," Dr. Canfield said.

Thus, the sulfates contain more of the heavier sulfur left behind by the bacteria, and their sulfide waste is richer in the lighter isotopes. But in rocks older than 2.5 billion years old, both sulfate and sulfide compounds contain roughly the same ratio of sulfur isotopes.

That, Dr. Canfield said, means that so little sulfate was in the oceans then that bacteria ate any sulfate they happened to find. In their experiments, they starved sulfate-eating bacteria to see at what point they stopped being picky eaters. Their conclusion, reported in the same issue of *Science*, is that sulfate levels then were at most one-hundredth of current levels.

With sulfate-eating bacteria limited by their food supply, that would have opened up an ecological niche for competing bacteria that produce methane, possibly solving the "faint sun paradox." The sun back then was about 20 percent dimmer, yet the earth was just as warm, so presumably the planet back then had a thicker blanket of so-called greenhouse gases.

Some scientists believe that high concentrations of carbon dioxide warmed the planet, but others believe that methane, which is more efficient than carbon dioxide at trapping heat, was the reason. "You have a possibility of making a methane greenhouse," said Dr. Uwe Wiechert, a geochemist at the Swiss Federal Institute of



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Technology in Zurich. "I like this idea very much."

Not everyone agrees with the stories deduced from the isotope data. Dr. Hiroshi Ohmoto, a professor of geochemistry at Penn State University, still believes that oxygen accumulated in the atmosphere soon after the advent of oxygen-producing bacteria at least 2.7 billion years ago.

Dr. Ohmoto points out that most of Dr. Farquhar's rocks and diamonds show an excess of the sulfur 34 isotope while experiments emulating the early atmosphere produce lower-than-average amounts of sulfur 34. "Until they come up with experimental data, it's awfully difficult for me to accept the explanation," he said.

Nonetheless, all the scientists agree that big changes were occurring in the earth's oceans and atmosphere about 2.4 billion years ago.

"We're just starting to understand how all these pieces correlate to this time interval," Dr. Canfield said.

If they can figure out what the rocks are telling them.

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