

A Better Atmosphere for Life

Thirty years ago, geochemists took away the primordial soup that biologists thought they needed to cook up the first life on Earth. Now, some atmospheric chemists are trying to give it back. They're suggesting that the early Earth could have held onto much more of its volcanic hydrogen—a key ingredient in the recipe for making the organic compounds that may have led to the first life.

Creating the primordial organic goo used to be easy. If you combined the methane and ammonia seen in the still-primordial atmosphere of Jupiter, passed lightninglike sparks through the mixture, and added some water, voilà, complex organic compounds such as amino acids formed. But then in the 1970s geochemists spoiled the party by insisting that Earth's earliest atmosphere was nothing like Jupiter's. Earth's carbon would have been part of oxygen-rich carbon dioxide, and its nitrogen part of inert nitrogen gas, they said. And hydrogen seeping from the planet's interior would have quickly escaped to space. That left chemists with a thin gruel indeed. It had far too much oxygen, which destroys organics, and not enough of the hydrogen that enables carbon atoms to link up to form the complex polymers needed for life. In the lab, such mixtures yielded few organics, and simple compounds at that.

Now, atmospheric chemist Feng Tian of the University of Colorado, Boulder, and his colleagues argue that hydrogen on early Earth would have escaped much more slowly than has been assumed (*Science*, 13 May, p. 1014). Lacking the oxygen that absorbs solar energy, they point out, the outer fringes of the early atmosphere would have been far colder than they are today. With less energy jittering its atoms, much less lightweight hydrogen would have "boiled" away into space.

The researchers also figured out how to calculate the rate at which hydrogen would have been lost as wisps of the atmosphere flowed away into space. The mathematics of such supersonic flow had frustrated all previous attempts. Overall, hydrogen would have escaped at 1/100 the rate previously assumed, the group says. Rather than building to concentrations of just 0.1%, hydrogen might have reached 30%. That would make for a far more productive atmosphere than chemists have been coping with for 30 years. "The end result is you drop vast amounts of organic compounds into the ocean to make a soup," says the group's Brian Toon of the University of Colorado, Boulder.

"On the face of it, what they have produced is quite reasonable," says atmospheric chemist Yuk Yung of the California Institute of Technology in Pasadena. "It's a nice piece of work. It's going to make the biologists a lot happier." Astrobiologist David Catling of the University of Bristol, U.K., isn't so sure. "It would be rather premature," he says, to shift emphasis back to the prebiotic chemistry of a hydrogen-rich atmosphere and organic-goo-laced ocean. Tian and his colleagues "haven't dealt with all the factors that lead to hydrogen escape," says Catling. He suspects that a more sophisticated model would show that hydrogen escaped the early Earth at least as fast as it does today. Time will tell whether too many cooks spoil the primordial broth.

—R.A.K.



Deep roots. A buildup of volcanic hydrogen may have helped form life's ingredients.

p. 1104). The atmospheric oxygen, they noted, would have weathered sulfur off the land, dosing the ocean with deadly sulfides, which would have chemically removed the iron and molybdenum from seawater. The algae needed these elements to form enzymes essential to taking up nutrients; without them, they were malnourished and therefore evolutionarily listless.

The Canfield Ocean, and thus the Malnourished Earth hypothesis, has since gained ground. Several groups have extended Canfield's sulfur isotope analysis across the mid-section of the Proterozoic era (2.5 billion to

0.54 billion years ago), confirming signs of anoxia. But those studies drew on marine rocks deposited from waters that were at least partially isolated from the open ocean, like today's Red Sea. Perhaps their anoxia was not typical of the ocean at large.

Last year Anbar, geochemist Gail Arnold, then at the University of Rochester, New York, and colleagues allayed many of those doubts. In *Science* (2 April 2004, p. 87), they reported on their analysis of molybdenum isotopes preserved in mid-Proterozoic rocks. The ratio of two molybdenum isotopes depends on the amount of oxygen in the ocean. And unlike

many other dissolved elements, molybdenum remains in seawater so long before being removed to the sediment that it has a chance to mix throughout the ocean, even its backwaters. Samples from one place in the Proterozoic ocean, then, should reflect the amount of oxygen in the ocean as a whole. Arnold and colleagues found signs that far more of the ocean floor was anoxic 1.4 billion and 1.7 billion years ago than today. So, almost 4 billion years after the world began, the team of life and Earth that boosted oxygen from nothing to detectable levels still had a ways to go.

Breakout

What locked a billion years of the Proterozoic in geochemical and evolutionary stasis remains a mystery. But the bigger, more enticing mystery may be how oxygen finally rose to something like modern levels toward the end of the Proterozoic, 0.6 billion or 0.7 billion years ago. That's when multicellular animals first appeared, and then large animals such as the enigmatic Ediacara, creatures that must have required higher levels of oxygen. Canfield's sulfur isotopes hint that oxygen levels did in fact rise about then.

This second oxidation event is proving far more elusive than the great one. Most scientists agree that it hinged on some major change that started locking up more organic matter in sediments before it could decay. Instead of being consumed in the chemistry of decomposition, oxygen built up in the atmosphere and ocean.

As to what triggered the mass carbon burial, explanations fall into two camps: geological and biological.

Proposed geological shifts capable of driving up oxygen levels include a jump in the production of clays able to adsorb organic matter and preserve it beneath the sea floor, and the assembly of a supercontinent whose weathering could stimulate ocean life and subsequent carbon burial by adding nutrients to the seas. Biological shifts include the arrival of lichens on land, which would have accelerated rock weathering as well, and the evolutionary innovation among zooplankton that produced dense, organics-laden fecal pellets able to sink into the deep sea.

Before the oxygen historians can sort out the truth from the just-so stories, they'll have to come to grips with the nature of the ancient record of life as well as oxygen. "There's less data the older you go [in the geologic record]," says Kirschvink, "so there's less chance of being proven wrong right off" if you're working 2 billion or 3 billion years in the past. That can make spinning yarns about the early days more fun, but it puts a premium on collecting what data can be retrieved from the oldest rocks.

—RICHARD A. KERR