Hydrogen Sulfide Extinction

EARTH SCIENCE

Impact from the Deep

Strangling heat and gases emanating from the earth and sea, not asteroids, most likely caused several ancient mass extinctions. Could the same killer-greenhouse conditions build once again?
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Philosopher and historian Thomas S. Kuhn has suggested that scientific disciplines act a lot like living organisms: instead of evolving slowly but continuously, they enjoy long stretches of stability punctuated by infrequent revolutions with the appearance of a new species--or in the case of science, a new theory. This description is particularly apt for my own area of study, the causes and consequences of mass extinctions--those periodic biological upheavals when a large proportion of the planet's living creatures died off and afterward nothing was ever the same again.

Since first recognizing these historical mass extinctions more than two centuries ago, paleontologists believed them to have been gradual events, caused by some combination of climate change and biological forces such as predation, competition and disease. But in 1980 the understanding of mass extinctions underwent a Kuhnian revolution when a team at the University of California, Berkeley, led by geologist Walter Alvarez proposed that the famous dinosaur-killing extinction 65 million years ago occurred swiftly, in the ecosystem catastrophe that followed an asteroid collision. Over the ensuing two decades, the idea that a bolide from space could smite a significant segment of life on the earth was widely embraced--and many researchers eventually came to believe that cosmic detritus probably caused at least three more of the five largest mass extinctions. Public acceptance of the notion crystallized with Hollywood blockbusters such as Deep Impact and Armageddon.

Now still another transformation in our thinking about life's punctuated past is brewing. New geochemical evidence is coming from the bands of stratified rock that delineate mass extinction events in the geologic record, including the exciting discovery of chemical residues, called organic biomarkers, produced by tiny life-forms that typically do not leave fossils. Together these data make it clear that cataclysmic impact as a cause of mass extinction was the exception, not the rule. In most cases, the earth itself appears to have become life's worst enemy in a previously unimagined way. And current human activities may be putting the biosphere at risk once again.

After Alvarez

To understand the general enthusiasm for the impact paradigm, it helps to review the evidence that fueled it. The scenario advanced by Alvarez, along with his father, physicist Luis W. Alvarez, and nuclear chemists Helen V. Michel and Frank Asaro, contained two separate hypotheses: first, that a fairly large asteroid--estimated to have been 10 kilometers in diameter--struck the earth 65 million years ago; second, that the environmental consequences of the impact snuffed out more than half of all species. They had found traces left by the blow in a thick layer of iridium--rare on the earth but common in extraterrestrial materials--that had dusted the globe.

Within a decade of this prodigious announcement the killer's thumbprint turned up, in the form of the Chicxulub crater hiding in plain sight on the Yucat?Peninsula of Mexico. Its discovery swept aside most lingering doubts about whether the reign of the dinosaurs had ended with a bang. At the same time, it raised new questions about other mass extinction events: If one was caused by impact, what about the rest? Five times in the past 500 million years most of the world's life-forms have simply ceased to exist. The first such event happened at the end of the Ordovician period, some 443 million years ago. The second, 374 million years ago, was near the close of the Devonian. The biggest of them all, the Great Dying, at the end of the Permian 251 million years ago, wiped out 90 percent of ocean dwellers and 70 percent of plants, animals, even insects, on land [see "The Mother of Mass Extinctions," by Douglas H. Erwin;

Scientific American, July 1996]. Worldwide death happened again 201 million years ago, ending the Triassic period, and the last major extinction, 65 million years ago, concluded the Cretaceous with the aforementioned big bang.

The earth can, and probably did, exterminate its own.

In the early 1990s paleontologist David Raup's book Extinctions: Bad Genes or Bad Luck? predicted that impacts ultimately would be found to be the blame for all these major mass extinctions and other, less severe events as well. Evidence for impact from the geologic boundary between the Cretaceous and Tertiary (-K/T) periods certainly was and remains convincing: in addition to the Chicxulub crater and the clear iridium layer, impact debris, including pressure-shocked stone scattered across the globe, attests to the blow. Further chemical clues in ancient sediments document rapid changes in the world's atmospheric composition and climate that soon followed.

For several other extinction periods, the signs also seemed to point "up." Geologists had already associated a thin iridium layer with the end Devonian extinctions in the early 1970s. And by 2002 separate discoveries suggested impacts at the end Triassic and end Permian boundaries. Faint traces of iridium registered in the Triassic layer. And for the Permian, distinctive carbon "buckyball" molecules believed to contain trapped extraterrestrial gases added another intriguing clue [see "Repeated Blows," by Luann Becker; Scientific American, March 2002]. Thus, many scientists came to suspect that asteroids or comets were the source of four of the "big five" mass extinctions; the exception, the end Ordovician event, was judged the result of radiation from a star exploding in our cosmic neighborhood.

As researchers continued to probe the data in recent years, however, they found that some things did not add up. New fossil analyses indicated that the Permian and Triassic extinctions were drawn-out processes spanning hundreds of thousands of years. And newly obtained evidence of the rise and fall of atmospheric carbon, known as carbon cycling, also seemed to suggest that the biosphere suffered a long-running series of environmental insults rather than a single, catastrophic strike.

Not So Sudden Impact

The lesson of the K/T event was that a large-body impact is like a major earthquake leveling a city: the disaster is sudden, devastating, but short-lived--and after it is over, the city quickly begins rebuilding. This tempo of destruction and subsequent recovery is reflected in carbon-isotope data for the K/T extinctions as well as in the fossil record, although verifying the latter took the scientific community some time. The expected sudden die-off at the K/T boundary itself was indeed visible among the smallest and most numerous fossils, those of the calcareous and siliceous plankton, and in the spores of plants. But the larger the fossils in a group, the more gradual their extinction looked.

Slowly, paleontologists came to understand that this apparent pattern was influenced by the sparsity of large-fossil samples for most of the soil and rock strata being studied. To address this sampling problem and gain a clearer picture of the pace of extinction, Harvard University paleontologist Charles Marshall developed a new statistical protocol for analyzing ranges of fossils. By determining the probability that a particular species has gone extinct within a given time period, this analytical method teases out the maximum amount of information yielded by even rare fossils.

In 1996 Marshall and I joined forces to test his system on K/T stratigraphic sections and ultimately showed that what had appeared to be a gradual extinction of the most abundant of the larger marine animals, the ammonites (molluscan fossils related to the chambered nautilus) in Europe, was instead consistent with their sudden disappearance at the K/T boundary itself. But when several researchers, including myself, applied the new methodology to earlier extinctions, the results differed from the K/T sections. Studies by my group of strata representing both marine and nonmarine environments during the latest parts of the Permian and Triassic periods showed a more gradual succession of extinctions clustered around the boundaries.

That pattern was also mirrored in the carbon-isotope record, which is another powerful tool for understanding rates of extinction. Carbon atoms come in three sizes, or isotopes, with slightly varying numbers of neutrally charged particles in the nucleus. Many people are familiar with one of these isotopes, carbon 14 (14C), because its decay is often used to date specific fossil skeletons or samples of ancient sediments. But for -interpreting mass extinctions, a more useful type of information to extract from the geologic record is the ratio of 12C to 13C isotopes, which provides a broader snapshot of the vitality of plant life at the time.

That is because photosynthesis largely drives changes in the 12C-13C ratio. Plants use energy from the sun to split carbon dioxide (CO_2) into organic carbon, which they exploit to build cells and provide energy; happily for us animals, free oxygen is their waste product. But plants are finicky, and they preferentially choose CO_2 containing 12C. Thus, when plant life--whether in the form of photosynthesizing microbes, floating algae or tall trees--is abundant, a higher proportion of CO_2 remaining in the atmosphere contains 13C, and atmospheric 12C is measurably lower.

By examining the isotope ratios in samples from before, during and after a mass extinction, investigators can obtain a reliable indicator of the amount of plant life both on land and in the sea. When researchers plot such measurements for the K/T event on a graph, a simple pattern emerges. Virtually simultaneously with the emplacement of the so-called impact layer containing mineralogical evidence of debris, the carbon isotopes shift--13C drops dramatically--for a short time, indicating a sudden die-off of plant life and a quick recovery. This finding is entirely consistent with the fossil record of both larger land plants and the sea's microscopic plankton, which underwent staggering losses in the K/T event but bounced back rapidly.

In contrast, the carbon records revealed by my group in early 2005 for the Permian, and more recently for the Triassic, document a very different fate for plants and plankton during those two mass extinctions. In both cases, multiple isotope shifts over intervals exceeding 50,000 to 100,000 years indicate that plant communities were struck down, then re-formed, only to be perturbed again by a series of extinction events. To produce such a pattern would take a succession of asteroid strikes, thousands of years apart. But no mineralogical evidence exists for a string of impacts during either time span.

Indeed, further investigation of the evidence has called into question the likelihood of any impacts at those two times. No other research groups have replicated the original finding of buckyballs containing extraterrestrial gas at the end Permian boundary. A discovery of shocked quartz from that period has also been recanted, and geologists cannot agree whether purported impact craters from the event in the deep ocean near Australia and under ice in Antarctica are actually craters or just natural rock formations. For the end Triassic, the iridium found is in such low concentrations that it might reflect a small asteroid impact, but nothing of the planet-killing scale seen at the K/T boundary. If impacts are not supported as the cause of these mass extinctions, however, then what did trigger the great die-offs? A new type of evidence reveals that the earth itself can, and probably did, exterminate its own inhabitants.

Ghastly Greenhouse

About half a decade ago small groups of geologists began to team up with organic chemists to study environmental conditions at critical times in the earth's history. Their work involved extracting organic residues from ancient strata in search of chemical "fossils" known as biomarkers. Some organisms leave behind tough organic molecules that survive the decay of their bodies and become entombed in sedimentary rocks. These biomarkers can serve as evidence of long-dead life-forms that usually do not leave any skeletal fossils. Various kinds of microbes, for example, leave behind traces of the distinctive lipids present in their cell membranes--traces that show up in new forms of mass spectrometry, a technique that sorts molecules by mass.

This biomarker research was first conducted on rocks predating the history of animals and plants, in part to determine when and under what conditions life first emerged on the earth. But within the past few years scientists began sampling the mass extinction boundaries. And to the great surprise of those doing this work, data from the periods of mass extinction, other than the K/T event, suggested that the world's oceans have more than once reverted to the extremely low oxygen conditions, known as anoxia, that were common before plants and animals became abundant.

Among the biomarkers uncovered were the remains of large numbers of tiny photosynthetic green sulfur bacteria. Today these microbes are found, along with their cousins, photosynthetic purple sulfur bacteria, living in anoxic marine environments such as the depths of stagnant lakes and the Black Sea, and they are pretty noxious characters. For energy, they oxidize hydrogen sulfide ($H2S$) gas, a poison to most other forms of life, and convert it into sulfur. Thus, their abundance at the extinction boundaries opened the way for a new interpretation of the cause of mass extinctions.

Scientists have long known that oxygen levels were lower than today around periods of mass extinction, although the reason was never adequately identified. Large-scale volcanic activity, also associated with most of the mass extinctions, could have raised CO_2 levels in the atmosphere, reducing oxygen and leading to intense global warming--long an alternative theory to the impacts; however, the changes wrought by volcanism could not necessarily explain the massive marine extinctions of the end Permian. Nor could volcanoes account for plant deaths on land, because vegetation would thrive on increased CO_2 and could probably survive the warming.

But the biomarkers in the oceanic sediments from the latest part of the Permian, and from the latest Triassic rocks as well, yielded chemical evidence of an ocean-wide bloom of the H_2S-consuming bacteria. Because these microbes can live only in an oxygen-free environment but need sunlight for their photosynthesis, their presence in strata representing shallow marine settings is itself a marker indicating that even the surface of the oceans at the end of the Permian was without oxygen but was enriched in H_2S.

In today's oceans, oxygen is present in essentially equal concentrations from top to bottom because it dissolves from the atmosphere into the water and is carried downward by ocean circulation. Only under unusual circumstances, such as those that exist in the Black Sea, do anoxic conditions below the surface permit a wide variety of oxygen-hating organisms to thrive in the water column. Those deep-dwelling anaerobic microbes churn out copious amounts of hydrogen sulfide, which also dissolves into the seawater. As its concentration builds, the H_2S diffuses upward, where it encounters oxygen diffusing downward. So long as their balance remains undisturbed, the oxygenated and hydrogen sulfide-saturated waters stay separated, and their interface, known as the chemocline, is stable. Typically the green and purple sulfur bacteria live in that chemocline, enjoying the supply of H2S from below and sunlight from above.

Yet calculations by geoscientists Lee R. Kump and Michael A. Arthur of Pennsylvania State University have shown that if oxygen levels drop in the oceans, conditions begin to favor the deep-sea anaerobic bacteria, which proliferate and produce greater amounts of hydrogen sulfide. In their models, if the deepwater H2S concentrations were to increase beyond a critical threshold during such an interval of oceanic anoxia, then the chemocline separating the H2S-rich deepwater from oxygenated surface water could have floated up to the top abruptly. The horrific result would be great bubbles of toxic H2S gas erupting into the atmosphere.

Their studies indicate that enough H2S was produced by such ocean upwellings at the end of the Permian to cause extinctions both on land and in the sea. And this strangling gas would not have been the only killer. Models by Alexander Pavlov of the University of Arizona show that the H2S would also have attacked the planet's ozone shield, an atmospheric layer that protects life from the sun's ultraviolet (UV) radiation. Evidence that such a disruption of the ozone layer did happen at the end of the Permian exists in fossil spores from Greenland, which display deformities known to result from extended exposure to high UV levels. Today we can also see that underneath "holes" in the ozone shield, especially in the Antarctic, the biomass of phytoplankton rapidly decreases. And if the base of the food chain is destroyed, it is not long until the organisms higher up are in desperate straits as well.

Kump and Arthur estimate that the amount of H_2S gas entering the late Permian atmosphere from the oceans was more than 2,000 times the small amount given off by volcanoes today. Enough of the toxic gas would have permeated the atmosphere to have killed both plants and animals--particu-larly because the lethality of H_2S increases with temperature. And several large and small mass extinctions seem to have occurred during short intervals of global warming. That is where the ancient volcanic activity may have come in.

Around the time of multiple mass extinctions, major volcanic events are known to have extruded thousands of square kilometers of lava onto the land or the seafloor. A by-product of this tremendous volcanic outpouring would have been enormous volumes of carbon dioxide and methane entering the atmosphere, which would have caused rapid global warming. During the latest Permian and Triassic as well as in the early Jurassic, middle Cretaceous and late Paleocene, among other periods, the carbon-isotope record confirms that CO_2 concentrations skyrocketed immediately before the start of the extinctions and then stayed high for hundreds of thousands to a few million years.

But the most critical factor seems to have been the oceans. Heating makes it harder for water to absorb oxygen from the atmosphere; thus, if ancient volcanism raised CO_2 and lowered the amount of oxygen in the atmosphere, and global warming made it more difficult for the remaining oxygen to penetrate the oceans, conditions would have become amenable for the deep-sea anaerobic bacteria to generate massive upwellings of H_2S. Oxygen-breathing ocean life would have been hit first and hardest, whereas the photosynthetic green and purple H_2S-consuming bacteria would have been able to thrive at the surface of the anoxic ocean. As the H_2S gas choked creatures on land and eroded the planet's protective shield, virtually no form of life on the earth was safe.

Kump's hypothesis of planetary killing provides a link between marine and terrestrial extinctions at the end of the Permian and explains how volcanism and increased CO_2 could have triggered both. It also resolves strange findings of sulfur at all end Permian sites. A poisoned ocean and atmosphere would account for the very slow recovery of life after that mass extinction as well.

Finally, this proposed sequence of events pertains not only to the end of the Permian. A minor extinction at the end of the Paleocene epoch 54 million years ago was already--presciently--attributed to an interval of oceanic anoxia somehow triggered by short-term global warming. Biomarkers and geologic evidence of anoxic oceans suggest that is also what may have occurred at the end Triassic, middle Cretaceous and late Devonian, making such extreme greenhouse-effect extinctions possibly a recurring phenomenon in the earth's history.

Most troubling, however, is the question of whether our species has anything to fear from this mechanism in the future: If it happened before, could it happen again? Although estimates of the rates at which carbon dioxide entered the atmosphere during each of the ancient extinctions are still uncertain, the ultimate levels at which the mass deaths took place are known. The so-called thermal extinction at the end of the Paleocene began when atmospheric CO2 was just under 1,000 parts per million (ppm). At the end of the Triassic, CO2 was just above 1,000 ppm. Today with CO2 around 385 ppm, it seems we are still safe. But with atmospheric carbon climbing at an annual rate of 2 ppm and expected to accelerate to 3 ppm, levels could approach 900 ppm by the end of the next century, and conditions that bring about the beginnings of ocean anoxia may be in place. How soon after that could there be a new greenhouse extinction? That is something our society should never find out.

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MORE TO EXPLORE:

Rivers in Time: The Search for Clues to Earth's Mass Extinctions. Peter D. Ward. Columbia University Press, 2002.

Abrupt and Gradual Extinction among Late Permian Land Vertebrates in the Karoo Basin, South Africa. Peter D. Ward et al. in Science, Vol. 307, pages 709-714; February 4, 2005.

Photic Zone Euxinia during the Permian-Triassic Superanoxic Event. Kliti Grice et al. in Science, Vol. 307, pages 706-709; February 4, 2005.

Massive Release of Hydrogen Sulfide to the Surface Ocean and Atmosphere during Intervals of Oceanic Anoxia. Lee R. Kump, Alexander Pavlov and Michael A. Arthur in Geology, Vol. 33, No. 5, pages 397-400; May 2005.