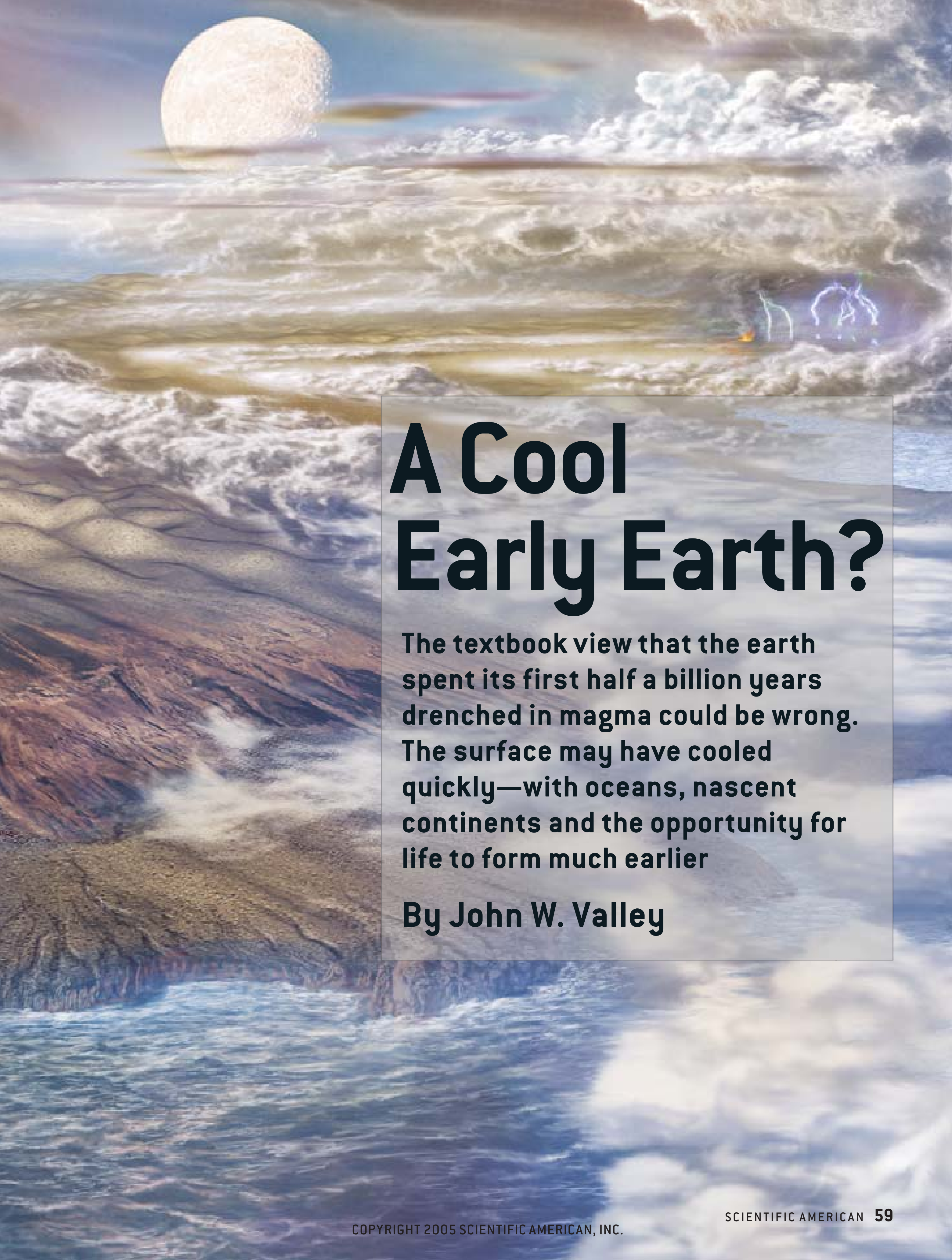
NEW VIEW of the young earth covered in oceans of liquid water as early as 4.4 billion years ago contrasts sharply with the hot, hostile world typically depicted in textbooks.



A Cool Early Earth?

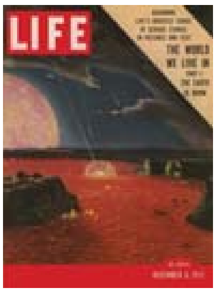
The textbook view that the earth spent its first half a billion years drenched in magma could be wrong. The surface may have cooled quickly—with oceans, nascent continents and the opportunity for life to form much earlier

By John W. Valley

In its infancy, beginning about 4.5 billion years ago,

the earth glowed like a faint star. Incandescent yellow-orange oceans of magma roiled the surface following repeated collisions with immense boulders, some the size of small planets, orbiting the newly formed sun. Averaging 75 times the speed of sound, each impactor scorched the surface—shattering, melting and even vaporizing on contact.

Early on, dense iron sank out of the magma oceans to form the metallic core, liberating enough gravitational energy to melt the entire planet. Massive meteorite strikes continued for hundreds of millions of years, some blasting craters more than 1,000 kilometers in diameter. At the same time, deep underground, the decay of radioactive elements produced heat at rates more than six times greater than they do today.



OLD VIEW of a hot young earth: *Life* magazine, December 8, 1952.

These fiery conditions had to subside before molten rock could harden into a crust, before continents could form, before the dense, steamy atmosphere could pool as liquid water, and before the earth's first primitive life could evolve and survive. But just how quickly did the surface of the earth cool after its luminous birth? Most scientists have assumed that the hellish environment lasted for as long as 500 million years, an era thus named the Hadean. Major support for this view comes from the apparent absence of any intact rocks older than four billion years—and from the first fossilized signs of life, which are much younger still.

In the past five years, however, geologists—including my group at the University of Wisconsin–Madison—have discovered dozens of ancient crystals of the mineral zircon with chemical compositions that are changing our thinking about the earth's beginnings. The unusual properties of these durable minerals—each the size of the period in this sentence—enable the crystals to preserve surprisingly robust clues about what the environment was like when they formed. These tiny time capsules bear evidence that oceans habitable to primitive life and perhaps continents could have appeared 400 million years earlier than generally thought.

Cooling Down

SINCE THE 19TH CENTURY, scientists have attempted to calculate how quickly the earth cooled, but few expected to find solid evidence. Although magma oceans initially glowed at temperatures exceeding 1,000 degrees Celsius, a tantalizing suggestion of a more temperate early earth came from thermodynamic calculations showing that crust could have solidified on the surface within 10 million years. As the planet hardened over, the thickening layer of consolidated rock would have insulated the exterior from the high temperatures deep within the interior. If there were suitably quiescent periods between major meteorite impacts, if the crust was stable, and if the early hothouse atmosphere did not trap too much heat, surface temperatures could have quickly fallen below the boiling point of water. Furthermore, the primitive sun was fainter and contributed less energy.

Still, for most geologists, an undisputed fiery birth and scant clues in the geologic record seemed to point instead to a prolonged ultrahot climate. The oldest known intact rock is the four-billion-year-old Acasta gneiss in Canada's Northwest Territories. This rock formed deep underground and bears no information about conditions on the surface. Most investigators assumed hellish conditions at the planet's surface must have obliterated any rocks that formed earlier. The oldest rocks known to have originated underwater (and thus in relatively cool environs) did not form until 3.8 billion years ago. Those sediments, which are exposed at Isua in southwestern Greenland, also contain the earliest evidence of life [see "Questioning the Oldest Signs of Life," by Sarah Simpson; SCIENTIFIC AMERICAN, April 2003].

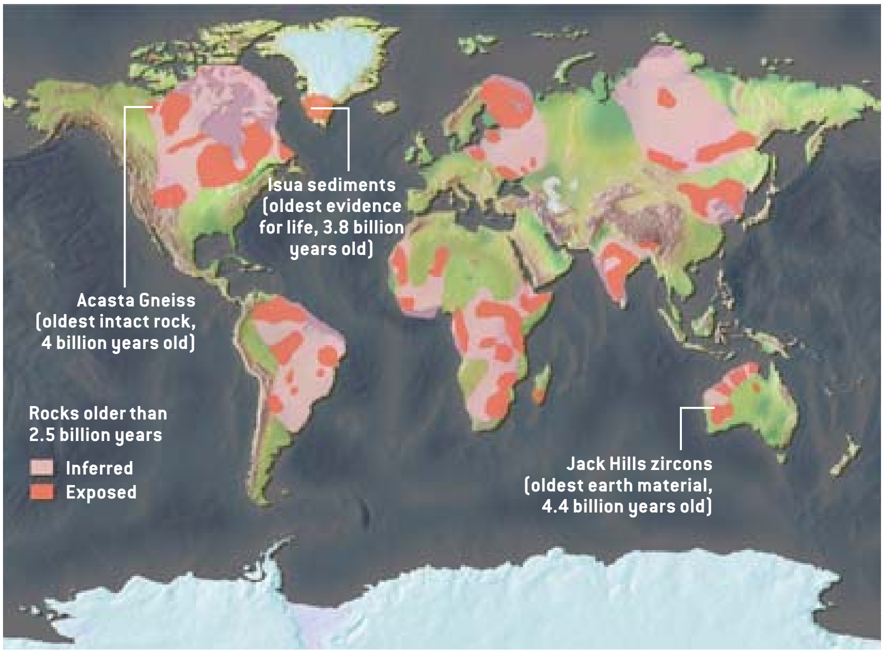
Single crystals of zircon began to add new information about the early earth in the 1980s, when a few rare grains from the Jack Hills and Mount Narryer regions of Western Australia became the most ancient terrestrial material known at that time—the oldest dating back almost 4.3 billion years. But the information these zircons carried seemed ambiguous, in part because geologists were unsure of the identity of their parent rock. Once formed, zircon crystals are so durable that they can persist even if their parent rock is exposed at the surface and destroyed by weathering and erosion. Wind or water can then trans-

Overview/*Zircon Time Capsules*

- Geologists have long thought that the fiery conditions of our planet's birth 4.5 billion years ago gave way to a more hospitable climate by about 3.8 billion years ago.
- Now tiny crystals of the mineral zircon, which retain clear evidence of when and how they formed, suggest that the earth cooled far sooner—perhaps as early as 4.4 billion years ago.
- Some ancient zircons even bear chemical compositions inherited from the cooler, wet surroundings necessary for life to evolve.

DON DIXON (*preceding pages*); TIME LIFE PICTURES/GETTY IMAGES (*this page*)

OLDEST PIECES OF THE PLANET



Ancient rocks older than 2.5 billion years crop out or lie just underneath the soil in many spots around the globe (*red*) and are probably hidden below younger rocks across even broader regions (*pink*). Zircon crystals as old as those discovered in the Jack Hills of Western Australia may eventually be discovered at another of these locations.

Fossilized gravel bed in the Jack Hills (*above*) contained the world's oldest zircons yet discovered. Geologists crushed and sorted hundreds of kilograms of this rock (*below*) to find the 20 crystals that bear signs of cool conditions more than four billion years ago.

LUCY READING-IKKANDA; SOURCE: WILLIAM H. PECK *Colgate University* (*map*); JOHN W. VALLEY (*photographs*)

port the surviving grains great distances before they become incorporated into deposits of sand and gravel that may later solidify into sedimentary rock. Indeed, the Jack Hills zircons—separated by perhaps thousands of kilometers from their source—were found embedded in a fossilized gravel bar called the Jack Hills conglomerate.

So, despite the excitement of finding such primeval pieces of the earth, most scientists, including me, continued to accept the view that the climate of our young planet was Hadean. It was not until 1999 that technological advances allowed further study of the ancient zircon crystals from Western Australia—and challenged conventional wisdom about the earth's earliest history.

Digging Deep

THE AUSTRALIAN ZIRCONS did not give up their secrets easily. For one thing, the Jack Hills and their surroundings are dusty barrens at the edge of vast sheep stations, called Berringarra and Mileura, situated some 800 kilometers north of Perth, Australia's most isolated city. The Jack Hills conglomerate was deposited three billion years ago and marks the northwestern edge of a widespread assembly of rock formations that are all older than 2.6 billion years. To recover less than a thimbleful of zircons, my colleagues and I collected hundreds of kilograms of rock from these remote outcrops and hauled them back to the laboratory for crushing and sorting, similar to searching for a few special grains of sand on a beach.

Once extracted from their source rock, individual crystals could be dated because zircons make ideal timekeepers. In addition to their longevity, they contain trace amounts of radioactive uranium, which decays at a known rate to lead. When a zircon forms from a solidifying magma, atoms of zirconium, silicon and oxygen combine in exact proportions ($ZrSiO_4$) to create a crystal structure unique to zircon; uranium occasionally substitutes as a trace impurity. Atoms of lead, on the other hand, are too large to comfortably replace any of the elements in the lattice, so zircons start out virtually lead-free. The uranium-lead clock starts ticking as soon as the zircon crystallizes. Thus, the ratio of lead to uranium increases with the age of the crystal. Scientists can reliably determine the age of an undamaged zircon within 1 percent accuracy, which for the early earth is about plus or minus 40 million years.

THE AUTHOR

JOHN W. VALLEY received his Ph.D. in 1980 from the University of Michigan at Ann Arbor, where he first became interested in the early earth. He and his students have since explored the ancient rock record throughout North America and in Western Australia, Greenland and Scotland. Currently Valley is president of the Mineralogical Society of America and Charles R. Van Hise Professor of Geology at the University of Wisconsin–Madison, where he founded a multimillion-dollar laboratory called WiscSIMS. The cutting-edge capabilities of the lab's new CAMECA IMS 1280 ion microprobe will enable a diverse range of research; besides zircons, Valley and his colleagues will probe many rare or extremely small materials ranging from stardust to cancer cells.

EXTRACTING EVIDENCE

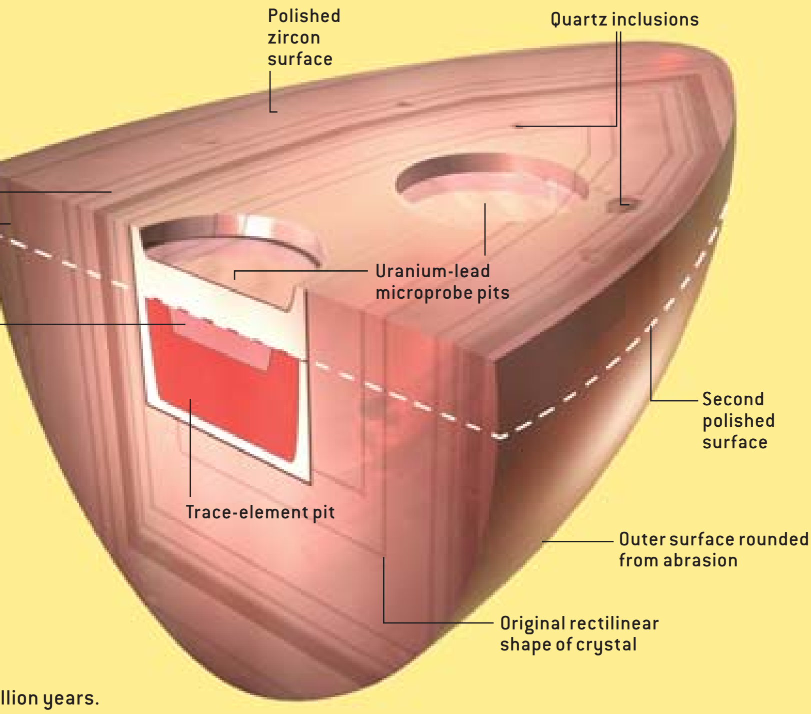
Scientists extract multiple clues about the earth's ancient environment from a single crystal of the mineral zircon (*main cutaway below*). They first embed the zircon in epoxy, then grind and polish the crystal to expose a pristine surface.

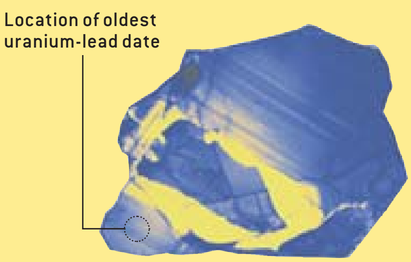
A scanning electron microscope identifies the zircon's growth patterns and any smaller fragments of minerals enclosed as it grew. Inclusions of quartz, for instance, occur most commonly in zircons that came from granite, a type of rock characteristic of continents.

An ion microprobe creates a small pit by sputtering atoms off this polished area using a narrow beam of ions and identifies those atoms by comparing their masses. To determine the age of the crystal, scientists measure atoms of uranium and lead, two impurities trapped within the zircon's atomic structure. Simply put, the constant radioactive decay of uranium to lead means that the more lead present relative to uranium, the older the crystal.

Investigators then grind down the surface to expose a deeper layer of the crystal and make a second microprobe pit in precisely the same location as the first one to measure atoms of oxygen, one of three elements that make up a zircon. The ratio of certain oxygen isotopes—atoms of oxygen with different masses—reveals whether the crystal records hot or cool conditions.

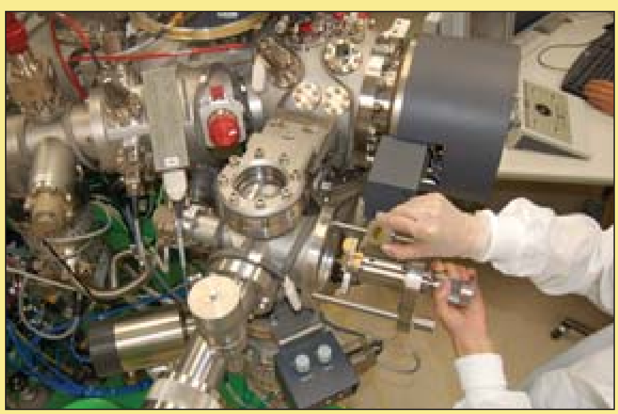
Researchers create a third pit to measure the abundance of certain trace elements—impurities known to make up less than 1 percent of the crystal's structure. Some of these elements are more common in continental crust.





The earth's oldest zircon, viewed as a cathodoluminescent image, dates back 4.4 billion years.

A CLOSER LOOK



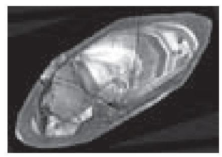
Red zircons (*right*), photographed near Roosevelt's nose on a U.S. dime for scale, come from the same rock sample that yielded the earth's oldest crystal. An ion microprobe, such as this one in the author's laboratory at the University of Wisconsin–Madison (*far right*), can analyze isotope ratios or trace elements from spots about 1/15 the diameter of the crystals themselves.

JOHN W. VALLEY (*laboratory*); SIMON A. WILDE *Curtin University of Technology* (*oldest zircon*);
ALFRED T. KAMAJIAN; SOURCE: AARON J. CAVOSIE *University of Wisconsin–Madison* (*zircon schematic* and *red zircons*)

Dating specific parts of a single crystal first became possible in the early 1980s, when William Compston and his colleagues at the Australian National University in Canberra invented a special kind of ion microprobe, a very large instrument they playfully named SHRIMP, short for Sensitive High-Resolution Ion Micro Probe. Although most zircons are nearly invisible to the naked eye, the ion microprobe fires a beam of ions so narrowly focused that it can blast a small number of atoms off any targeted part of a zircon's surface. A mass spectrometer then measures the composition of those atoms by comparing their masses. It was Compston's group—working with Robert T. Pidgeon, Simon A. Wilde and John Baxter, all then at Curtin University of Technology, also in Australia—that first dated the Jack Hills zircons in 1986.

Knowing this history, I approached Wilde. He agreed to reinvestigate the uranium-lead dates of Jack Hills zircons as part of the doctoral thesis of my student William H. Peck, who is now an assistant professor at Colgate University. In May 1999 Wilde analyzed 56 undated crystals using an improved SHRIMP at Curtin and found five that exceeded four billion years. To our great surprise, the oldest dated back to 4.4 billion years ago. Some samples from the moon and Mars have similar ages, and meteorites are generally older, but nothing of this vintage had been found (or expected) from our planet. Almost everyone assumed that if such ancient zircons had ever existed, the dynamic Hadean conditions destroyed them. Little did we know that the most exciting discovery was yet to come.

The tiny zircons from Western Australia did not GIVE UP THEIR SECRETS easily.



Evidence of Ancient Oceans

PECK AND I SOUGHT Wilde's zircons from Western Australia because we were looking for a well-preserved sample of the oldest oxygen from the earth. We knew that a zircon could retain evidence not only of when its host rock formed but also of *how*. In particular, we were using the ratios of different isotopes of oxygen to estimate the temperatures of processes leading to the formation of magmas and rocks.

Geochemists measure the ratio of oxygen 18 (^{18}O, a rare isotope with eight protons and 10 neutrons, which represents about 0.2 percent of all oxygen on the earth) to oxygen 16 (^{16}O, the common oxygen isotope with eight protons and eight neutrons, which comprises about 99.8 percent of all oxygen). These atoms are called stable isotopes because they do not undergo radioactive decay and thus do not spontaneously change with time; however, the proportions of ^{18}O and ^{16}O incorporated into a crystal as it forms differ depending on the ambient temperature at the time the crystal formed.

The $^{18}O/^{16}O$ ratio is well known for the earth's mantle (the 2,800-kilometer-thick layer immediately below the thin, five- to 40-kilometer-thick veneer of continents and ocean crust). Magmas that form in the mantle always have about the same oxygen isotope ratio. For simplicity, geochemists calibrate these ratios relative to that of seawater and express them in what is called delta (δ) notation. The $\delta^{18}O$ of the ocean is 0 by definition, and the $\delta^{18}O$ of zircon from the mantle is 5.3, meaning that it has a greater $^{18}O/^{16}O$ ratio than seawater.

That is why Peck and I expected to find a primitive mantle value of around 5.3 when we took Wilde's Jack Hills zircons, including the five oldest, to the University of Edinburgh in Scotland that same summer. There John Craven and Colin Graham helped us use a different kind of ion microprobe specially suited to measure oxygen isotope ratios. We had worked together many times over the preceding decade to perfect the technique and could analyze samples one millionth the size of those then possible in my laboratory in Wisconsin. After 11 days of round-the-clock analysis and little sleep (typical conditions for this difficult procedure), we completed the measurements—and found that our predictions were wrong. The zircons' $\delta^{18}O$ values ranged up to 7.4.

We were stunned. What could these high oxygen isotope ratios mean? In younger rocks the answer would be obvious, because such samples are common. A typical scenario is that rocks at low temperature on the earth's surface can acquire a high oxygen isotope ratio if they chemically interact with rain or ocean water. Those high-$\delta^{18}O$ rocks, if buried and melted, form magma that retains the high value, which is then passed on to zircons during crystallization. Thus, liquid water and low temperatures are required on the surface of the earth to form zircons and magmas with high $\delta^{18}O$; no other process is known to do so.

Finding high oxygen isotope ratios in the Jack Hills zircons implied that liquid water must have existed on the surface of the earth at least 400 million years earlier than the oldest known sedimentary rocks, those at Isua, Greenland. If correct, entire oceans probably existed, making the earth's early climate more like a sauna than a Hadean fireball.

Continental Clues

COULD WE REALLY BASE such far-reaching conclusions about the history of the earth on a few tiny crystals? We delayed publishing our findings for more than a year so we could double-check our analyses. Meanwhile other groups were conducting their own research in the Jack Hills. Stephen J. Mojzsis of the University of Colorado and his colleagues at the University of California at Los Angeles confirmed our results, and we published back-to-back technical articles describing our findings in 2001.

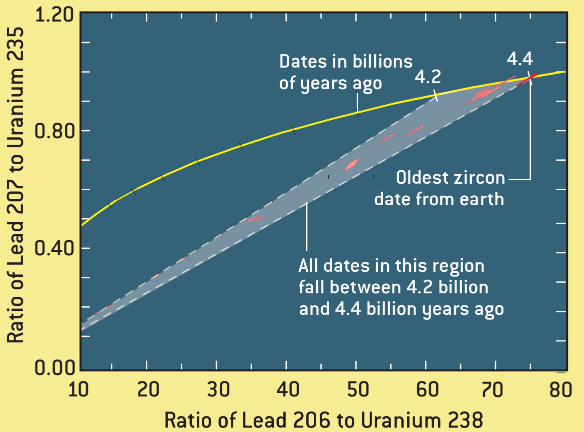
AARON J. CAVOSIE *University of Wisconsin–Madison*

THE TALES THEY TELL

Zircons from the Jack Hills of Western Australia have changed the way scientists think about the early history of the earth. These crystals are the oldest terrestrial materials yet discovered—hundreds of those identified formed more than four billion years ago. Many of these tiny timekeepers also bear clear chemical signs that oceans of liquid water and possibly even continents existed on the earth's surface at a time once thought to be molten and fiery.

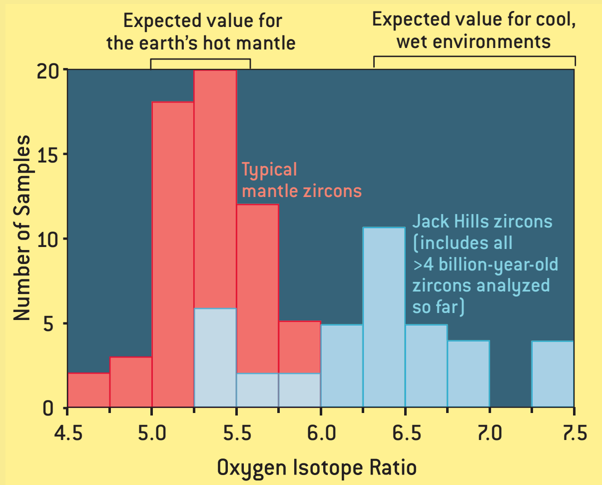
ANCIENT AGE

The oldest age for a Jack Hills zircon—4.4 billion years (*red*)—is an exact match of two geologic "clocks." Two pairs of isotopes—uranium 235–lead 207 (*vertical axis*) and uranium 238–lead 206 (*horizontal axis*)—form two radioactive timekeepers that start ticking when a zircon forms. If they are well preserved, their final ratios plot along a single line (*yellow*). Dates from other parts of the zircon (*pink*) fall off this line because some lead was lost from these areas, but scientists can correct for this damage.



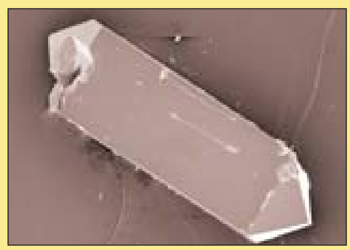
COOL OCEANS

Oxygen isotope ratios in Jack Hills zircon samples (*blue*), which range up to 7.5, are possible only if their source rock formed in a relatively cool, water-rich environment near the earth's surface. Had magma oceans covered the planet when these zircons formed, their values would have clustered near 5.3, as do those of all crystals from hot rock that originates in the planet's deep interior (*red*).



FIRST CONTINENTS?

Rounded surfaces of some Jack Hills zircons under a scanning electron microscope show that wind and possibly running water buffeted these crystals over long distances—possibly across a large continental landmass—before they were finally laid to rest (*right*). Zircons found near their place of origin retain their original sharp edges (*far right*). The large number of ancient, rounded Jack Hills zircons suggests their original source rocks were widespread.



As the possible implications of the zircon discoveries spread through the scientific community, the excitement was palpable. In the superheated violence of a Hadean world, no samples would have survived for geologists to study. But these zircons pointed to a more clement and familiar world and provided a means to unravel its secrets. If the earth's climate was cool enough for oceans of water early on, then maybe zircons could tell us if continents and other features of modern earth also existed. To find out, we had to look more closely into the interiors of single crystals.

Even the smallest zircon contains other materials that were encapsulated as the zircon grew around them. Such zircon inclusions can reveal much about where the crystal came from, as can the crystal's growth patterns and the composition of trace elements. When Peck and I studied the 4.4-billion-year-old zircon, for instance, we found that it contained pieces of other minerals, including quartz. That was surprising because quartz is rare in primitive rocks and was probably absent from the very first crust on the earth. Most quartz comes from granitic rocks, which are common in more evolved continental crust.

If the Jack Hills zircons came from a granitic rock, that evidence would support the hypothesis that they are samples of the world's first continent. But caution is warranted. Quartz can form in the last stages of magma crystallization even if the parent rock is not granitic, although such quartz is much less abundant. For instance, zircons and a few grains of quartz have been found on the moon, which never developed a granitic, continental-style crust. Some scientists have also wondered if the earth's earliest zircons formed an environment more like the early moon or by some other means that is no longer common, perhaps related to giant meteorite im-

LUCY READING-IKKANDA; SOURCE: SIMON A. WILDE *Curtin University of Technology* (*uranium-lead*); LUCY READING-IKKANDA; SOURCE: JOHN W. VALLEY (*oxygen isotope ratios*); AARON J. CAVOSIE *University of Wisconsin–Madison* (*zircon grains*) pacts or deep-sourced volcanism, but no one has found convincing evidence.

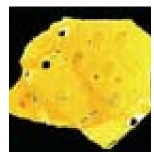
Meanwhile other clues for continental crust came from trace elements (those elements substituting in zircon at levels below 1 percent). Jack Hills zircons have elevated concentrations of these elements as well as patterns of europium and cerium that are most commonly created during the crystallization of crust, which means the zircons formed near the earth's surface rather than in the mantle. Furthermore, the ratios of radioactive isotopes of neodymium and hafnium—two elements used to determine the timing of continental-crust-forming events—suggest that significant amounts of continental crust formed as early as 4.4 billion years ago.

The distribution of ancient zircons provided additional evidence. The proportion of zircons older than four billion years exceeds 10 percent in some samples from Jack Hills. Also, the zircon surfaces are highly abraded and the originally angular crystal faces are rounded, suggesting the crystals were blown long distances from their source rock. How could these zircons travel hundreds or thousands of kilometers as windblown dust and still be concentrated together unless there had once been a lot of them? And how could these zircons escape burial and melting in the hot mantle unless thick continental-type crust was stable so as to preserve them?

These findings imply that the zircons were once plentiful and came from a widespread source region, possibly a continental landmass. If so, it is quite likely that rocks from this earliest time still exist, an exciting prospect because much could be learned from an intact rock of this age.

Furthermore, the age distribution of ancient zircons is uneven. Ages cluster in certain time periods, and no zircons have been found from other eras. My former graduate student Aaron J. Cavosie, now an assistant professor at the University of Puerto Rico, found such evidence even within single zoned zircons where the core formed early, say, 4.3 billion years ago, with a surrounding overgrowth that formed later, between 3.7 billion and 3.3 billion years ago. That the zircons get younger from core to rim is expected because zircon crystals grow concentrically by adding material to their grain boundary. But the great age difference with time gaps between the cores and rims of these particular zircons indicates that two distinct events took place, separated by a major hiatus. In more commonly available, younger zircons, this kind of core-to-rim age relation results from tectonic processes that melt continental crust and recycle the zircons within it. Many scientists are trying to test whether similar conditions produced the ancient Jack Hills zircons.

The Jack Hills zircons may be samples of the world's FIRST CONTINENT.



Most recently, E. Bruce Watson of the Rensselaer Polytechnic Institute and T. Mark Harrison of the Australian National University have reported lower-than-expected levels of titanium in these ancient zircons, suggesting that the temperatures of their parent magmas must have been between 650 and 800 degrees C. Such low temperatures would be possible only if the parent rocks were granitic; most nongranitic rocks melt at higher temperatures, and so their zircons should contain more titanium.

Zircons Are Forever

SINCE MY COLLEAGUES and I analyzed the oxygen isotope ratios in those five Jack Hills zircons in 1999, the data supporting our conclusions have grown rapidly. Investigators in Perth, Canberra, Beijing, Los Angeles, Edinburgh, Stockholm and Nancy, France, have now put tens of thousands of Jack Hills zircons into ion microprobes, searching for the relatively few that are older than four billion years, and other dating techniques have been applied as well.

Hundreds of newly discovered zircons have been reported from several localities with ages from 4.4 billion to four billion years old. David R. Nelson and his colleagues at the Geological Survey of Western Australia have found similarly ancient zircons as far as 300 kilometers south of the Jack Hills. Geochemists are scrutinizing other ancient regions of the earth, hoping to find the first pre-4.1-billion-year-old zircons outside Australia.

And the intensifying search is spurring improved technology. Cavosie has demonstrated much better accuracy of analysis and reported more than 20 Jack Hills zircons with the high oxygen isotope ratios that fingerprint cool surface temperatures and ancient oceans as early as 4.2 billion years ago. My colleagues and I are continuing the search using the first model of the newest generation ion microprobe, called the CAMECA IMS 1280, which was installed in my laboratory this past March.

Many questions will be answered if pieces of the original zircon-forming rock can be identified. But even if we never find that rock, there is still much to learn from the tiny zircon time capsules. SA

MORE TO EXPLORE

A Cool Early Earth. John W. Valley, William H. Peck, Elizabeth M. King and Simon A. Wilde in *Geology,* Vol. 30, No. 4, pages 351–354; April 2002.

Magmatic $\delta^{18}O$ in 4400–3900 Ma Detrital Zircons: A Record of the Alteration and Recycling of Crust in the Early Archean. Aaron J. Cavosie, John W. Valley, Simon A. Wilde and the Edinburgh Ion Microprobe Facility in *Earth and Planetary Science Letters,* Vol. 235, No. 3, pages 663–681; July 15, 2005.

The author's "Zircons Are Forever" Web site is at **www.geology.wisc.edu/zircon/zircon_home.html**

SIMON A. WILDE *Curtin University of Technology*