Iron was life's 'primeval' metal, say scientists

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Close-up photo of magnetite-banded iron formation from South Africa. Credit: Jena Johnson, University of Michigan

Every living organism uses tiny quantities of metals to carry out biological functions, including breathing, transcribing DNA, turning food into energy, or any number of essential life processes.

Life has used metals in this way since single-celled organisms floated in Earth's earliest oceans. Nearly half of the enzymes—proteins that carry out chemical reactions in cells—within organisms require metals, many of which are transition metals named for the space they occupy in the periodic table.

Now, a team of scientists from the University of Michigan, California Institute of Technology and University of California, Los Angeles, argue that iron was life's earliest, and sole, transition metal. Their study, titled "Iron: Life's primeval transition metal," is published in the *Proceedings of the National Academy of Sciences.*

"We make a radical proposal: Iron was life's original and only transition metal," said Jena Johnson, assistant professor in the U-M Department of Earth and Environmental Sciences. "We argue that life only relied on metals that it could interact with, and the iron-rich early ocean would make other transition metals essentially invisible."

To probe this idea, Johnson joined UCLA professor Joan Valentine and Caltech researcher Ted Present.

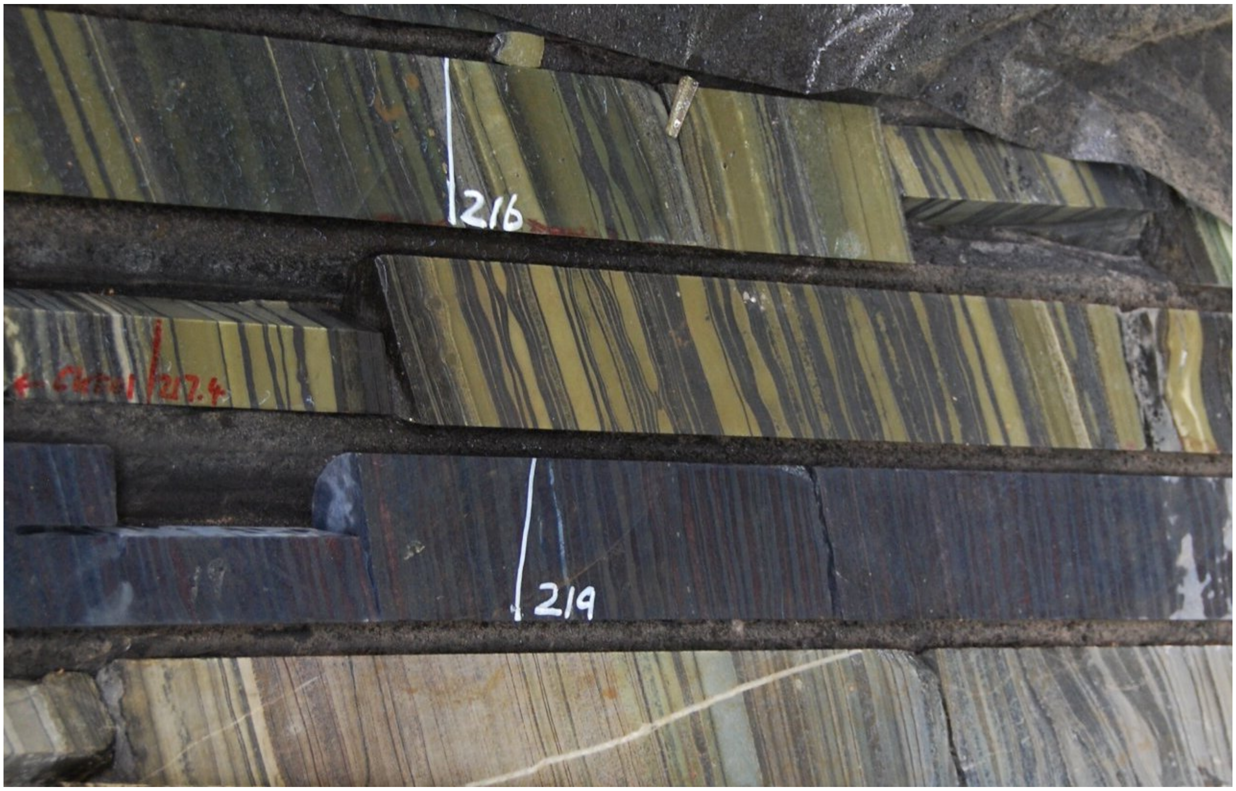
A bioinorganic chemist, Valentine became interested in how the earliest life evolved from being microscopic to the proliferation of complicated organisms there are today. Specifically, she wondered what metals were incorporated into enzymes during early life so that organisms could carry out necessary life processes. Repeatedly, she heard other researchers say that for the first half of Earth's history, the oceans were full of iron.

"You have to understand that in my field of biochemistry and bioinorganic chemistry, in medicine and in life, iron is a trace element. These are elements that are present only in small amounts," Valentine said. "When these guys told me that iron wasn't a trace element, that blew my mind."

Johnson, whose group studies iron formations and early ocean biogeochemistry, and Ted Present were familiar with geologic evidence suggesting that early oceans were rich in iron—specifically, an ion of iron called Fe(II). Fe(II) can be readily dissolved in water and would have been the primary metal found in oceans during the Archean Eon, a geologic time period that began about 4 billion years ago and ended about 2.5 billion years ago.

The end of the Archean Eon was marked by something called the Great Oxygenation Event. At this time, life evolved the ability to perform oxygen-producing photosynthesis. Over the next billion years, Earth's ocean transformed from an iron-rich, anoxic sea to today's oxygenated body of water, according to the researchers. This also oxidized Fe(II) into Fe(III), rendering it insoluble.

While Johnson and Present said geologists knew of iron's ubiquity on Earth during this time, it wasn't until they began talking with Valentine that they realized how great an impact iron might have had on early life.



Drill core of Archean iron formation from South Africa. Credit: Jena Johnson, University of Michigan

To examine the potential impact, Present designed a model that updated predictions of the concentrations of certain metals, including iron, manganese, cobalt, nickel, copper and zinc, that could have been available in Earth's oceans when life began. The group was able to estimate the maximum concentration and availability of these elements for earliest life, he said.

"The thing that changed most dramatically as the Great Oxygenation Event occurred was not really the concentration of these other trace elements," Present said. "The thing that changed the most dramatically was a decrease in dissolved iron concentrations. The implications for what that meant for life and how it 'sees' elements in water hadn't really been wrestled with."

Once the group had determined what metals were available in early oceans, they explored which metals that simple biomolecules would bind to in these iron-rich solutions.

"We realized iron would have to do almost everything," Johnson said.

"Biomolecules could capture magnesium and iron, but zinc's not getting in—maybe nickel can get into some biomolecules in the right circumstances, but zinc's not competitive. Cobalt is invisible. Manganese is pretty invisible. This order of magnitude difference in the concentration of iron in oceans had this really tangible effect on what biomolecules can 'see' and bind from the environment."

To determine whether iron would work in metalloenzymes that currently rely on other metals, Valentine and Johnson dug into scientific literature to find out how life uses certain metals today.

In each instance, they found examples of how iron or magnesium could be substituted instead. While a metalloenzyme might use a certain kind of metal, such as zinc, they found that doesn't mean it's the only metal the enzyme can use.

"Zinc and iron is a really dramatic example because zinc is absolutely essential for life now," Valentine said. "The idea of life without zinc was really hard for me to think about until we dug into this and realized that as long as you have no oxygen around to oxidize your iron from Fe(II) to Fe(III), iron is often better than zinc in these enzymes."

Present said that once iron oxidized and was no longer as biologically available as it was before the Great Oxygenation Event, life had to find other metals to plug into its enzymes.

"Life, in the face of orders of magnitude more iron than other metals, couldn't know to evolve toward such a sophisticated way of managing them," Present said. "The fall of the abundance of iron forced life to manage these other metals to survive, but that also enabled new functions and the diversity of life we have today."

More information: Johnson, Jena E., Iron: Life's primeval transition metal, *Proceedings of the National Academy of Sciences* (2024). DOI: 10.1073/pnas.2318692121. doi.org/10.1073/pnas.2318692121

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