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On early Earth, iron may have performed magnesium's RNA folding job

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Jessica Bowman (left) and Loren Williams from the Georgia Tech School of Chemistry and Biochemistry assess a gel showing that RNA is not degraded by iron if oxygen is omitted. Based on these results, Williams hypothesizes that RNA evolved on the early earth in the presence of iron and is optimized to work with iron. Credit: Georgia Tech/Gary Meek

On the periodic table of the elements, iron and magnesium are far apart. But new evidence suggests that 3 billion years ago, iron did the chemical work now done by magnesium in helping RNA fold and function properly.

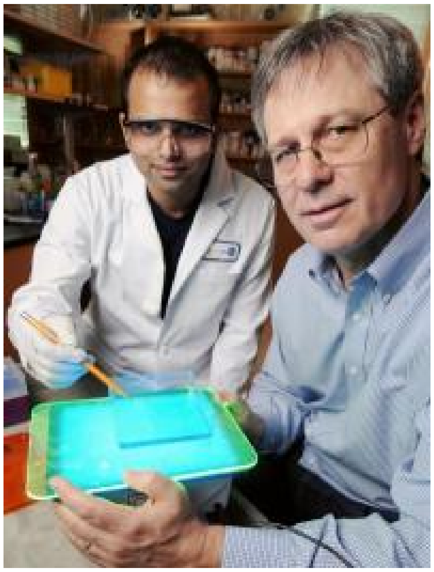
There is considerable evidence that the evolution of life passed through an early stage when RNA played a more central role before DNA and coded proteins appeared. During that time, more than 3 billion years ago, the environment lacked oxygen but had an abundance of soluble iron.

In a new study, researchers from the Georgia Institute of Technology used experiments and numerical calculations to show that iron, in the absence of oxygen, can substitute for magnesium in RNA binding, folding and catalysis. The researchers found that RNA's shape and folding structure remained the same and its functional activity increased when magnesium was replaced by iron in an oxygen-free environment.

"The primary motivation of this work was to understand RNA in plausible early earth conditions and we found that iron could support an array of RNA structures and catalytic functions more diverse than RNA with magnesium," said Loren Williams, a professor in the School of Chemistry and Biochemistry at Georgia Tech.

The results of the study were published online on May 31, 2012 in the journal PLoS ONE. The study was supported by the NASA Astrobiology Institute.

In addition to Williams, Georgia Tech School of Biology postdoctoral fellow Shreyas Athavale, research scientist Anton Petrov, and professors Roger Wartell and Stephen Harvey, and Georgia Tech School of Chemistry and Biochemistry postdoctoral fellow Chiaolong Hsiao and professor Nicholas Hud also contributed to this work.



Georgia Tech biology postdoctoral fellow Shreyas Athavale (left) and chemistry and biochemistry professor Loren Williams look at a gel showing the products of a ribozyme reaction that was run with iron instead of magnesium. Under identical anaerobic conditions, the activity of two enzymes was enhanced in the presence of iron, compared to their activity in the presence of magnesium. Credit: Georgia Tech/Gary Meek

Free oxygen gas was almost nonexistent more than 3 billion years ago in the early earth's atmosphere. When oxygen began entering the environment as a product of photosynthesis, it turned the earth's iron to rust, forming massive banded iron formations that are still mined today. The free oxygen produced by advanced organisms caused iron to be toxic, even though it was -- and still is -- a requirement for life.

This environmental transition triggered by the introduction of free oxygen into the atmosphere would have caused a slow, but dramatic, shift in biology that required transformations in biochemical mechanisms and metabolic pathways. The current study provides evidence that this transition may have caused a shift from iron to magnesium for RNA binding, folding and catalysis processes.

The researchers used quantum mechanical calculations, chemical footprinting and two ribozyme assays to determine that in an oxygen-free environment, iron, Fe^{2+}, can be substituted for magnesium, Mg^{2+}, in RNA folding and catalysis.

Quantum mechanical calculations showed that the structure of RNA was nearly identical when it included iron or magnesium. When large RNAs fold into native, stable structures, negatively charged phosphate groups are brought into close proximity. The researchers calculated one small difference between the activity of iron and magnesium structures: more charge was transferred from phosphate to iron than from phosphate to magnesium.

Chemical probing under anaerobic conditions showed that iron could replace magnesium in compacting and folding large RNA structures, thus providing evidence that iron and magnesium could be nearly interchangeable in their interactions with RNA.

Under identical anaerobic conditions, the activity of two enzymes was enhanced in the presence of iron, compared to their activity in the presence of magnesium. The initial activity of the L1 ribozyme ligase, an enzyme that glues together pieces of RNA, was 25 times higher in the presence of iron. Activity of the hammerhead ribozyme, an enzyme that cuts RNA, was three times higher in the presence of iron compared to magnesium.

"The results suggest that iron is a superior substitute for magnesium in these catalytic roles," said Williams, who is also director of the Center for Ribosomal Origins and Evolution at Georgia Tech. "Our hypothesis is that RNA evolved in the presence of iron and is optimized to work with iron."

In future studies, the researchers plan to investigate what unique functions RNA can possess with iron that are not possible with magnesium.

Provided by Georgia Institute of Technology

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