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Aqueous Iron Chemistry on Early Mars: Was it Influenced by Life?

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Introduction

The Thermal Emission Spectrometer on NASA's Mars Global Surveyor has detected deposits of crystalline hematite [1] in Sinus Meridiani, Aram Chaos and Vallis Marineris. These appear to be similar to terrestrial iron formations that formed in the Earth's Pre-cambrian oceans. The Sinus Meridiani deposit exceeds ~$10^5 km^2$ in size, and consists of coarse-grained, grey, schistose hematite [2]. Its age is ~4Ga or older based on counts of exhumed fossil craters [3]. Terrestrial Banded Iron Formations (BIFs) are laminated sediments deposited directly from solution. Pathological cases of crystalline hematite are particularly characteristic of the Late Proterozoic. These are associated with glaciomarine deposits and possibly formed when oceanic ice cover retreated. Iron oxides were precipitated when ferrous iron reacted with dissolved O_2. There is no question that the oxygen in the late Proterozoic atmosphere originated from photosynthetic organisms. Could iron formations that formed ~4 Ga ago on Mars also be related to oxygenic photosynthesis?

Iron in aqueous solution

Iron was transported in the ocean over large distances in its soluble ferrous form on early Earth. Iron was introduced by shallow hydrothermal exhalation or by upwelling from anoxic submarine sources to continental shelves [4]. On early Mars, in the absence of biology, net oxygen would only accumulate with loss of H to space. The oxygen sink from reduced volcanic gases can be estimated from thermal evolution and the oxygen source can be estimated assuming diffusion-limited loss of H to space. These estimates suggest an oxygen sink that exceeded the photochemical source. Consequently, the early Martian atmosphere had very low oxygen levels. Under such conditions, CO_2-containing liquid water dissolves iron from basalt to form partially dissociated iron (II) bicarbonate.

Formation of iron oxides

Martian iron oxides could form from Fe^{2+} oxidation a number of ways:

(1) In oxygenated surface waters, oxidation proceeds via an intermediate phase of ferrihydrite, "$Fe(OH)_3$", an insoluble red-brown gel [5] via: $4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+$ (1) Ferrihydrite is unstable and converts irreversibly to goethite (α-FeOOH) $Fe(OH)_3 = FeOOH + H_2O$ (2) This, in turn, may diagenetically convert to crystalline hematite $2FeOOH = Fe_2O_3 + H_2O$ (3) Hematite may also form directly from ferrihydrite at neutral pH and higher temperature, but can also be produced slowly in ice-cold waters. The oxidation rate increases 100 times per unit pH but is slower in more saline water.

(2) Iron (II) carbonate could be a precursor precipitate in surface waters [6]. Under an oxic atmosphere, this would oxidize in shallow waters to ferrihydrite, which then coverts to stable goethite or hematite.

(3) In principle, photo-oxidation can form iron oxides without molecular oxygen. However, the absence of BIF deposition on shallow-water Archean platforms suggests that this mechanism did not operate on early Earth.

(4) Another possibility is that Martian bacteria-like life oxidizes ferrous iron to goethite and hematite. Such biological processes are certainly observed in terrestrial waters and would demand a substantial biota for Mars.

(5) In reducing conditions (e.g., in the presence of organic matter) at pH>8, magnetite can form directly from solution or from a ferrihydrite precursor. Magnetite is a common primary precipitate in terrestrial BIFs. Magnetite on Mars could later be oxidized to hematite by dissolved oxygen.

Discussion

On early Mars several mechanisms could precipitate iron oxides from solution. However, these processes all stoichiometrically require oxygen. There are only two possibilities for an oxygen source:

(1) Small quantities of oxygen were slowly produced as hydrogen escaped to space and ferrous iron acted as a sink for this oxygen over an extended timescale.

(2) Early Mars had an oxygenic photosynthetic biosphere.

Simple calculations suggest that atmospheric oxygen was very scarce on a volcanically active early Mars. The exposed deposits of hematite, if they are deep, would require significant quantities of oxygen. Finally, although many of the findings suggestive of life in the ALH84001 meteorite have been disputed, the strongest piece of evidence has always been magnetite crystals of biogenic shape. It is interesting to note that magneto-tactic bacteria use magnetite for a specific purpose: to move along a redox gradient away from a surface environment dominated by oxygen.

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