Mineral Remains of Early Life on Earth? On Mars?

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Abstract The oldest sedimentary rocks on Earth, the 3.8-Ga Isua Iron-Formation in southwestern Greenland, are metamorphosed past the point where organic-walled fossils would remain. Acid residues and thin sections of these rocks reveal ferric microstructures that have filamentous, hollow rod, and spherical shapes not characteristic of crystalline minerals. Instead, they resemble ferric-coated remains of bacteria. Modern so-called iron bacteria were therefore studied to enhance a search image for oxide minerals precipitated by early bacteria. Iron bacteria become coated with ferrihydrite, a metastable mineral that converts to hematite, which is stable under high temperatures. If these unusual morphotypes are mineral remains of microfossils, then life must have evolved somewhat earlier than 3.8 Ga, and may have involved the interaction of sediments and molecular oxygen in water, with iron as a catalyst. Timing is constrained by the early infall of planetary materials that would have heated the planet's surface.

Because there are no earlier sedimentary rocks to study on Earth, it may be necessary to expand the search elsewhere in the solar system for clues to any biotic precursors or other types of early life. Evidence from Mars shows geophysical and geochemical differentiation at a very early stage, which makes it an important candidate for such a search if sedimentation is an important process in life's origins. Not only does Mars have iron oxide-rich soils, but its oldest regions have river channels where surface water and sediment may have been carried, and seepage areas where groundwater may have discharged. Mars may have had an atmosphere and liquid water in the crucial time frame of 3.9-4.0 Ga. A study of morphologies of iron oxide minerals collected in the southern highlands during a Mars sample return mission may therefore help to fill in important gaps in the history of Earth's earliest biosphere.

Keywords: Bacteria, ferrihydrite, hematite, iron, Isua Iron-Formation, Mars, oxygen, prebiotic, sampling.

Introduction

The earliest known sedimentary rocks on Earth are a suite of 3.8-Ga amphibolites, quartzites, schists, and gneisses in the Isukasia region of southwestern Greenland (Appel, 1980; Nutman et al., 1984). Interbedded within this sequence, the Isua Iron-Formation can be subdivided into the oxide, carbonate, silicate, and sulfide facies, as

defined by James (1954). Magnetite dominates the oxide facies of the Isua Iron-Formation (Appel, 1980).

Amphibolite-facies rocks are not considered useful for paleontological studies because graphite is the stable carbon phase under such high temperatures; microfossils should be totally eliminated (Pflug, 1990). The next oldest rocks, 3.5 Ga, occur in Mt. Goldsworthy, Australia. These are the Warrawoona Group, a lower greenschist facies assemblage that contains a hematitic iron-formation (Robbins, LaBerge, and Schmidt, 1987) and actual fossils of bacteria including morphotypes resembling 13 modern-day photoautotrophic, 8 chemoautotrophic, and 14 chemoorganotrophic bacteria (Schopf and Walter, 1983).

Constrained by metamorphism and the lack of earlier sedimentary rocks, many researchers have chosen the strategy of continuing the search for earlier or earliest life by studying different layers in the Isua Iron-Formation and applying sophisticated geochemical techniques to the rocks. Nagy, Zumberge, and Nagy (1975), Pflug (1978, 1981), and Weber (1987, 1988) found rounded and bifurcating microremains. McKirdy and Hahn (1982) and Pflug (1986) characterized the geochemical spectra as biotic. Schidlowski (1988) found biogenic carbon isotopic ratios. Others disagreed with biotic interpretations, and called Pflug's pictured forms abiotic microstructures (Bridgwater et al., 1981; Roedder, 1981; Schopf, 1983). Robbins (1987) and Robbins, LaBerge, and Schmidt (1987) took the approach of studying the modern iron-rich environment to learn the types of mineral remains left behind by bacteria, particularly the oxidized metastable minerals that retain the shape of iron bacteria.

The rationale for studying living iron-oxidizing bacteria as a modern analog for ancient iron-oxidizing life leads in many directions. These include explanations in fields as diverse as evolution, microbiology of iron bacteria, geochemistry of the Archean ocean, and origins of life. The complexity of evolution ensures that organisms that lived 3.8 billion years ago no longer exist. Furthermore, molecular analyses have not been undertaken to learn if the precipitation of hematite precursors implies antiquity for the iron bacteria. However, the generalized response by bacteria to high metal loads in the environment—adapt, coat, escape, detoxify, change the microenvironment, or encyst and wait it out—probably is an ancient behavior (Robbins, LaBerge, and Schmidt, 1987). Many of these processes leave behind mineral coatings on bacteria.

Many consider that the Archean ocean was completely devoid of oxygen (Holland, 1984; Walker, 1987). This interpretation is grounded in the fact that some of the uranium and pyrite grains in the 2.7–2.9 Ga Witwatersrand gold fields of South Africa are rounded as if they had been subjected to subaerial erosion in an anoxic atmosphere (Hallbauer, 1986). However, some of the rounded uraninite is muffin shaped (Schidlowski, 1970) and some of the rounded buckshot pyrite is microlaminated in the manner of oncolites (A. Cadle, University of Witwatersrand, personal communication, 1990). A microbial origin rather than an anoxic atmosphere may therefore be indicated. The presence of reduced iron in the form of magnetite in an iron formation has also been cited as a rationale for a reduced ocean chemistry (Maynard, 1983). But Han (1988) showed that the magnetite of several different iron formations resulted from a secondary, probably thermal phenomenon because the magnetite surrounds elongated hematite crystals.

The fact that oxidized iron in the form of hematite is ubiquitous in Archean and Proterozoic iron-formations has always been a puzzle to the anoxic ocean paradigm (LaBerge, Robbins, and Han, 1987). LaBerge, Robbins, and Han (1987) suggested that the early ocean had patches of localized oxygen and these places were the loci of hematite-bearing iron-formations. Kasting (1987) and Towe (1990) have also questioned the anoxic paradigm. Using Berner's (1981) conservative definition of anoxia as $O_2 \le 1$

 μ M (present-day atmosphere is around 250 μ M or 1.5 \times 10²⁰ molecules/L of sea water), an anoxic ocean would still hold a finite amount of free molecular oxygen (around 6 \times 10¹⁷ molecules; J. J. Morgan, CIT, personal communication, 1991). This amount would be well within the field of stability of ferric oxide and ferric hydroxide (Pourbaix, 1966). No reasonable change in the pH of the ocean is likely to change this interpretation (Scott and Morgan, 1990). For early bacteria, therefore, oxygen cannot be ruled out as an electron acceptor, particularly in regions where other electron acceptors may not have been present.

Many different scenarios have been proposed for the beginning of life on Earth. Organic-rich soups (Haldane, 1928; Oparin, 1924, 1938), prebjotic associations of preproteins (Fox and Dose, 1977) making homogeneous catalysts in the ocean (Orgel, 1986; Schuster, 1986; Watson et al., 1987), clay minerals as templates and protected environments (Cairns-Smith, 1982; Cairns-Smith and Hartman, 1987), zeolite substitution for proteins (Gilbert, 1986; Nisbet, 1986), and pyrite formation as an energy source (Waechtershaeuser, 1988a, 1988b, 1990) have been invoked. These processes can be organized plausibly, according to Iberall and Soodak (1987) and Iberall (1988, 1989a, 1989b, 1989c), in the following schema: the creation of cellular forms took place in a sedimentary bed within which an autonomous chemistry gradually evolved heterogeneously from external catalysts, leading to onboard power, growth, and reproduction. Such a schema does not confine life's origin only to Earth. Indeed, extraterrestrial origins have also been considered (Arrhenius, 1908; Chyba et al., 1990; Hoyle and Wickramasinghe, 1981; Pflug, 1984a, 1984b). Tonks and Melosh (1989) showed that ejecta material could have been transported from Earth to Mars or from Mars to Earth, which means that spore-forming life might have originated on either planet and been carried to the other.

This paper focuses on the morphologies of diagnostic iron oxide minerals in the Isua Iron-Formation and explains why life could have been present by 3.8 Ga. It explores the possibility that life originated earlier, for example, 3.9 to 3.8 Ga, on Earth or elsewhere. It focuses on Mars as a possible alternative, discussing sampling strategies and methods to use during a sample return mission.

The Soils, Water, and Early Climate of Mars

Mars would be an ideal place to look for precursor processes (Iberall, 1989a) or remains of early life (McKay, 1986; McKay and Stoker, 1989; Newsom and Brittelle, 1989; Oberbeck et al., 1989). Liquid water existed on the surface of Mars during the early stages (Fig. 1), and the early history of Mars appears to have been similar to that of Earth.

The iron content of Martian soils is about 18 wt% as shown by x-ray fluorescence during the two Viking lander experiments (Sherman, Burns, and Burns, 1982; Toulmin et al., 1977). These data, along with spectrophotometric data, are consistent with the presence of various ferric oxides, including hematite, maghemite, feroxyhyte, and hydrated phases such as ferrihydrite (Morris, 1987; Sherman, Burns, and Burns, 1982).

Both the Martian surface and atmosphere have some water today; the water ice cap of the north pole expands and contracts seasonally (Carr, 1981, 1987; Squyres and Carr, 1986). Early Mars probably had running water, a warmer climate, and an atmosphere possibly composed of water, carbon dioxide, and nitrogen (Baker, 1982; Carr, 1986; Carr and Clow, 1981; Melosh and Vickery, 1989). Heavily cratered, dendritic features that look like gravity-driven river systems and stratified deposits that resemble lake deposits have been identified (Lucchitta, 1982; Lucchitta and Ferguson, 1983; McCauley, 1978; Nedell, Squyres, and Andersen, 1987). Of major interest is the fact that



Figure 1. Dense drainage network in the southern highlands of Mars (NASA image 63A09, 48 °S 98 °W).

the dendritic features may have been fed by groundwater discharge rather than by rainfall (Carr, 1979, 1981; Masursky et al., 1977). Water is part of the evidence showing that Earth and Mars had comparable early histories, which also would include similar prebiotic surface geochemistries (Iberall, 1989a).

Sampling strategies for early life in a Mars sample return mission (Greeley, 1990) undoubtedly will focus on the terrains of early Mars that had water. Macroscopic structures, such as stromatolitic associations, and endolithic bacteria and algae that live in cracks in rocks on Earth are among the possibilities for early life on Mars (Des Marais, 1988; McKay, 1986; Schopf and Walter, 1983). Environments that would have precipitated cold-water carbonates and other aquatic settings also are targeted (McKay and Nedell, 1988; McKay and Stoker, 1989).

Modern-Day Iron Bacteria That Precipitate Metastable Iron Oxide Minerals

Bacteria from diverse groups oxidize iron (Ehrlich, 1990). Those that coat sheaths with iron oxide and that live in circumneutral pH conditions have been lumped by some into

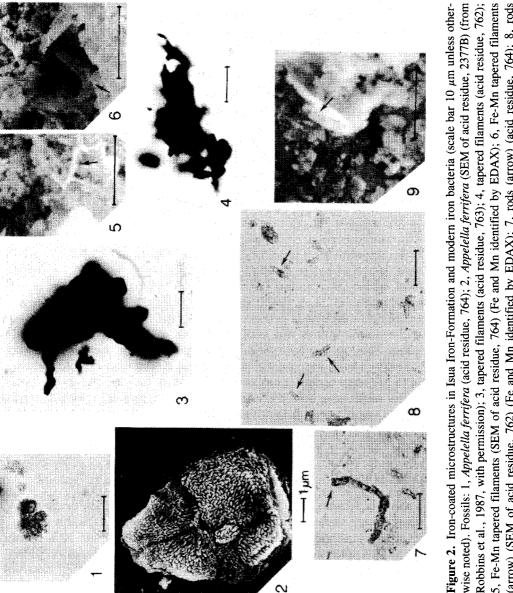
the iron bacteria (Pringsheim, 1947). Other microbiologists prefer to call such bacteria the iron- and manganese-precipitating bacteria (Staley et al., 1989), to exclude the acidophilic iron-oxidizing bacteria and archaebacteria. Some iron bacteria are microaerophiles that thrive where oxygen concentrations are in the microoxic range (around 1 or 2 mg/L); others are aerobes that require near-saturation of oxygen in the water (Staley et al., 1989). Some are chemoautotrophs, able to use electrons from ferrous iron in a chain of reactions from which they derive energy and to use oxygen as the electron acceptor, thereby precipitating ferric iron oxides on their stalks (Nealson, 1982, 1986a, 1986b). Others are heterotrophs, using organic compounds as energy sources and passively precipitating ferric oxides on their sheaths. In all these instances, such bacteria can be thought of as natural-process catalysts (Emerson et al., 1982). The form of iron oxide precipitated by them is ferrihydrite, a mineral that dehydrates to hematite (Chukrov et al., 1973; Ferris, Tazaki, and Fyfe, 1989).

Many of the iron bacteria have distinct morphologies that produce distinct mineral forms. Once coated with iron oxides, sheathed bacteria such as *Leptothrix* (Fig. 2, photos 10 and 11) abandon their sheaths. When they colonize a new area, some secrete new sheaths (Frobisher, 1953; Mulder and Deinema, 1981). The abandoned sheaths become further mineralized with time, causing freshwater iron springs and iron-rich marine embayments to become bright red (Harder, 1919; Puchelt et al., 1973). In response to available iron in the water, other iron-depositing bacteria such as *Gallionella* will secrete large masses of iron-oxide encrusted stalks as they grow (Hanert, 1981a) Cells of *Ochrobium* become so heavily encrusted that they can sink back into anoxic bottom waters (Jones, 1981). When their iron-oxide crusts dissipate by iron reduction, the cells can migrate back up into the water column. *Metallogenium*-like forms (Fig. 2, photo 12) are thought to become more and more encrusted with iron and manganese oxides until visible filaments are rare (Kuznetsov, 1970; Fig. 2, photo 12c).

Iron bacteria can be abundant in freshwater (Harder, 1919; Jones, 1986; Pringsheim, 1947) and marine environments (Hanert, 1981b; Puchelt, 1973; Puchelt et al., 1973; ZoBell, 1946). Puchelt et al. (1973) studied the water chemistry in the iron-rich embayments of the Santorini Islands in the Aegean Sea, and showed that CO₂ bubbling from underwater volcanic springs was available for use as a carbon source by Gallionella ferruginea. These are the environments on Earth where iron bacteria proliferate today. If similar environments were present on Mars, and if conditions evolved in directions favorable to life, then certain places could be searched on Mars for specific iron oxide minerals that might have been precipitated by ancient iron-precipitating bacteria, or at least precursor environments in which such iron redox processes could have taken place.

Materials and Methods

Acid residues and thin sections of oxide, silicate, carbonate, and sulfide facies of the Isua Iron-Formation were studied (Table 1). Samples were processed through a palynological procedure (Robbins and Traverse, 1980) that uses 10% HCl and 50% HF to eliminate carbonate and silicate minerals and to concentrate the residue of oxide minerals and carbonized organic tissues, if present. Optical microscopy, scanning electron microscopy (SEM), energy-dispersive x-ray analysis (EDAX), and x-ray diffraction (XRD) were used for the analysis.



(arrow) (SEM of acid residue, 762) (Fe and Mn identified by EDAX); 7, rods (arrow) (acid residue, 764); 8, rods (arrows) (acid residue, 764); 9, hollow rod (SEM of acid residue, 764).

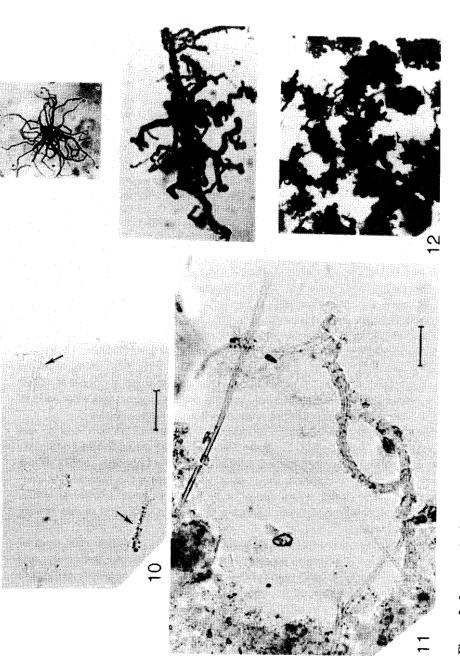


Figure 2. Iron-coated microstructures in Isua Iron-Formation and modern iron bacteria (scale bar 10 μm unless otherwise Leptothrix/Sphaerotilus intact iron-coated filaments (same locality); 12, stages in the life cycle of Metallogenium (from Kuznetsov, 1970, with permission), (a) trichospherical stage (photograph by G. A. Dubinina), (b) radially lobate stage (micrograph by noted) (Continued). Modern: 10, Leptothrix broken filaments (arrows) (Huntley Meadows wetland, Fairfax County, VA); 11, B. V. Perfilev), and (c) rounded-tuberose stage.

 Table 1

 Lithology and Microstructure Content of Samples from Isukasia

Lab No.	Field No.	Lithology and $\operatorname{Bedding}^a$	Microstructures		
			Iron Oxide Rods	Appelella	Tapering Filaments
761	3378	bk sulfide, lam	_	+	?
762	3379	bk sulfide, lam	_	+	+
763	3381	bk & wt carbonate, lam	_	+	+
764	3444	bk, wt, & yw gn silicate, lam	+	+	+
765	3445	bk & wt oxide, mass	+	+	?
766	3446	bk, wt, & yw gn silicate, lam	+	+	?
767	3451	bk & wt oxide, lam	+	+	?
768	3456	bk & wt oxide, lam	+	+	?
769	3470	bk & wt oxide, lam	+	+	?

^aAbbreviations: -, not present; +, present; ?, presence uncertain; bk, black; gn, green; lam, laminated; mass, massive; wt, white; yw, yellow.

Results and Discussion

Possible Microbial Minerals of the Isua Iron-Formation

Red and black iron oxide minerals were distinct in the resulting acid-resistant residue of the Isua Iron-Formation. Magnetite was the dominant iron oxide mineral identified by XRD. Red iron oxide minerals were only a minor part of the residues and were not present in large enough concentrations to be identified by XRD. They were identified as hematite by their characteristic lustrous appearance in reflected light and hematite's known stability in amphibolite-grade rocks (Robie, Hemingway, and Fisher, 1979).

Thin sections and acid residues of the samples contained three morphologies of red and black iron oxides that are not characteristic of metamorphic minerals, most of which are planar or botryoidal. The unusual iron oxide morphologies in the rocks were balls or spheres, elongate filaments having tapered ends, and hollow rods.

One iron oxide morphotype, red balls or spheres, averaged 13 μ m in diameter and was present in all facies (Table 1; Fig. 2, photos 1 and 2). These structures had complex, clavate wall structures and have been named *Appelella ferrifera* (Robbins, 1987). While no evolutionary relationship is implied, they can be compared to the modern encapsulated iron bacterium *Siderocapsa*, which can grow to 30 μ m in width (Robbins, 1987). Unlike *Siderocapsa*, *Appelella* had linear elements that resemble fission planes cutting across the length and width.

Another morphotype consisted of black filaments, around $1 \mu m$ wide, that taper to points (Fig. 2, photos 3-6). These structures were present in silicate, carbonate, and sulfide facies rocks (Table 1). EDAX showed that these filaments contained manganese and iron. They can be compared to the morphology produced during the rounded-tuberose stage of the manganese-precipitating *Metallogenium* (Fig. 2, photo 12). Modern-day *Metallogenium* is a subject of much discussion, because if it exists it may not grow in pure culture, it may be a strict symbiont, or it may require collecting

procedures that are not commonly used (Emerson, Garen, and Ghiorse, 1989; Gregory, Perry, and Staley, 1980; Kuznetsov, 1970; Sly, Hodgkinson, and Arunpairojana, 1988).

The third morphology was red rods (Fig. 2, photos 7–9); they were of variable length, but are around 1 μ m in width. These structures were present in oxide- and silicate-facies rocks (Table 1). They were hollow (Fig. 2, photo 9) and were composed of iron. They can be compared to the rod- or drinking straw-shaped microbial minerals made today by filamentous sheath-abandoning *Leptothrix/Sphaerotilus* (Fig. 2, photos 10 and 11) or perhaps *Gallionella* (Robbins, LaBerge, and Schmidt, 1987).

Can Minerals Be Fossils?

We interpret these three morphologies—balls/spheres, tapered filaments, and hollow rods—to be microbial minerals, minerals that retained the shape of the microorganisms that precipitated them. How can iron oxide minerals in the Isua Iron-Formation be the remains of organisms? After all, the rocks at Isukasia have been heated to temperatures in excess of 500 °C; such temperatures would change organic carbon to graphite.

Only an organism that coated itself with a mineral phase stable under amphibolite-grade temperatures would leave remains under these conditions. Interestingly, modern iron bacteria become coated with a metastable mineral that converts under low temperatures to a stable mineral. *Leptothrix* is among the modern iron bacteria coated with the hematite precursor ferrihydrite, a hydrated ferric oxide mineral having the structural formula 5Fe₂O₃ · 9H₂O (Chukhrov et al., 1973). This metastable ferrihydrite can dehydrate to stable hematite under conditions typical of those that might be expected in the mud or during diagenesis. At 40 °C, the conversion took 10–14 days in the laboratory; at 80 °C, the conversion took a few hours (Chukhrov et al., 1973). Such data show that the ferrihydrite-coated remains of modern iron bacteria would result in hematite having such an unusual morphology that it could be called a biologically precipitated mineral. Furthermore, these data may imply that iron-formations represent oxygen detoxification by early iron-oxidizing bacteria.

The Hierarchy of Processes That Led to Life

These data from the Isua Iron-Formation show that bacteria could have precipitated the iron and manganese oxide micrometer-sized minerals. However, the presence of life at 3.8 Ga requires quite a leap in understanding why Earth or Mars could have been ready for living organisms by this time.

Actually, galaxies are quite suited for life during most of the stage of cold chemistry below the recombination temperature for ionized hydrogen. All elements used for life processes are abundant. Relative to Si, and ignoring H and the noble gases, the abundant elements are (number density) O (20), C (12), N (2.5), Mg (1.1), Si (1.0), Fe (0.9), S (0.5), Al (0.08), Na and Ca (0.06), Ni (0.05), and P and Cr (0.01) (Anderson, 1989). These elements are organized in a manner useful to organisms; there are donor–acceptor atoms (H, C, Si), water-bearing carbonaceous (C, O, H, N) and silicic (SiO) compounds, gases (H, O, C, N, S), metallic oxide complexes (MgO, Al₂O₃, CaO, FeO, SiO₂), and metallic ions such as Fe.

Given such universal element abundances and the fact that all physicochemical processes undergo evolutionary changes, there are both powerful physical constraints and theoretical reasons why life probably started around 3.8 Ga in our planetary history. These include the presence of water in liquid form, which is only one in the list of

conditions that had to occur before Earth could provide a suitable substrate for organisms. At least seven major stages in our planetary system had to be in operation before life could begin on any planet (Iberall and Soodak, 1987; Taylor, 1987). These stages include an early high-temperature condensing event forming a primitive nebula around 4.56 Ga, followed by segregative loss of volatiles and selective accretion of such condensed matter into planets from rings of material or from planetesimals. This fairly wellestablished time scale leaves 0.7 or 0.8 Ga for all the next stages, which include (1) planetary degassing at temperatures lower than 1000 K, (2) physicochemical segregation and separation into layers within the planets, (3) water condensation, and (4) formation of a complex atmosphere related to both water condensation and volcanism. After that point, the histories of Earth and Mars apparently diverged. On Earth, volcanism was followed by continuing plate-tectonic motions, repetitive hydrological erosion of continents, and, apparently, the origins of life as a heterogeneous catalysis within the earliest sedimentary material at the triple interface of land, atmosphere, and water (Iberall and Soodak, 1987; Iberall, 1989c). As a first approximation, these individual processes must have taken no more than about 100 million years each, in order to lead up to life on Earth by 3.8 Ga.

The timing of a similar number of the early events could not have been any faster on Mars because of the common natural physical evolution involved within the planetary system, for example, with powerful infalls of heated materials as late as 3.9 Ga (Maher and Stevenson, 1988; Melosh and Vickery, 1989; Sleep et al., 1989). While Mars lacks evidence for continuing plate-tectonic motions, it did have at least a brief hydrological cycle and sedimentation before its atmosphere was lost; therefore, there is potential for at least a prebiotic chemistry.

The steps from prebiotic to biotic are constrained in time by physical but not yet by biophysical processes. Biochemical evolution is not a unique step, because all complex systems evolve by using chemical bonding within matter and other known forces. The beginning of independent life required a scaling and entwining of electrical and gravitational forces and the development of thermodynamic engine processes that could exploit gradient instabilities to create life's required cyclic processes, such as transport of matter, metabolism, and reproduction. The electrical forces would include chemical bonding, chemical potentials, surface tension, catalysis, and transport processes, as well as flux and potential boundary conditions (Iberall and Soodak, 1987). The building blocks had to be the cosmically abundant elements, unique elements such as H, C, and Si that can bond in many simple and complex forms, and strongly polar water that could serve as a solvent but also coexist in three states or phases, gas, liquid, and solid. A basic step in cellular autonomy must have been the taking on board of an internal thermodynamic engine, which could not have been very complex at first. Among other elements and energy transducing processes, an element such as iron could have provided a very efficient thermodynamic engine because of its ability to switch redox states from 2+ to 3⁺ and back again to 2⁺. Therefore, even without the existence of organic-rich soups, catalytic preproteins, clay templates, or specific organometallic complexes on Earth or Mars, an element having bistable ionic states could provide a primitive organic physicochemical energy source at redox boundaries for autonomous, fluid, cell-like units.

An argument can be made that metals must have been important at the inception of life. Metals such as Fe, Mn, Co, Ni, Ca, and Mg are in metalloorganic complexes that have enzymatic properties, and metals are easily precipitated on the simplest microbial cells and sheaths (Beveridge and Murray, 1976). Lead and zinc have been studied for their catalytic potential in early enzymes (Eigen and Schuster, 1982), but other organo-

metallic molecules such as those containing reversibly oxidizable iron could have served as switches in the same manner (Iberall, 1989c).

Such catalytic reactions could have taken place either on Earth or on Mars. It is not possible to test ideas of early or prebiotic evolution on Earth because the earliest sedimentary rocks already contain putative evidence for life. Mars may be an ideal environment to search for primitive life processes or precursors because of several factors. Almost 66% of its old cratered highland surface is preserved from its earliest history (Carr, 1981). Mars probably was subjected to the same processes that built Earth, but these may have slowed down or stopped when the atmosphere was lost (Carr, 1981; Iberall, 1989a). Last, the presence of water, which is a critical phase for life, focuses research for early life on Mars.

Mars had all the required elements for life, including liquid water. Experiments designed for the Viking Lander biology mission to discover life studied aeolian drift material by using gas exchange, labeled release, carbon assimilation, and molecular analyses; the results were negative or inconclusive (Horowitz, 1986; Klein, 1979; Moore et al., 1987). None of these techniques, however, would have revealed minerals left by metal-precipitating bacteria. The sediment would have to be scanned with a microscope to reveal mineral evidence for past life.

Collecting Methods and Localities on Mars

Localities to collect samples for mineral remains of iron-oxidizing bacteria exist on Mars. Because deoxygenated groundwater may have discharged at the heads of dendritic channels, ironstone at suspected discharge points should be collected. Such localities are at the heads of narrow sinuous channels in the Southern Highlands and at the base of valley walls of Valles Marineris. Iron accumulations along channels should be collected, along with any red sediment that appears to have been deposited in lakes.

Samples need not be kept cool or be collected using aseptic techniques. Once samples are back on Earth, a subsample of sediment could be wet-mounted on microscope slides and scanned for unusual iron oxide morphologies by using both light and scanning electron microscopy. Another subsample could be subjected to HCl and HF treatment to remove carbonate and silicate minerals, thereby concentrating the iron oxide fractions and increasing the likelihood of finding mineral remains of bacteria. Carbon compounds rather than graphite could also be present in such minerals because Mars has not been subjected to the high temperatures of metamorphism.

Living iron bacteria are probably not present on the surface of Mars; temperatures are too cold (Carr, 1981), so the methods used on Earth to collect living iron bacteria will not be of use on Mars. On Earth, iron bacteria living in surface waters can be collected in jars of water, as films on glass slides, or as flocculent masses with medicine droppers (Robbins et al., 1992). Those in muds and organic-rich soils are sampled with medicine droppers, shovels, and coring devices. On Earth, only a few micrograms of sample is required to determine the presence and morphology of iron bacteria. For Mars, half a gram of weakly cemented ironstone placed in a paper envelope and returned to Earth would suffice.

Conclusions

The study of iron oxide morphologies in the earliest sedimentary rocks on Earth provides new strategies for sampling on Mars for the remains of early or prebiotic life. The

morphologies of micrometer-sized iron and manganese oxide minerals in the Isua Iron-Formation are hollow rods, tapering filaments. and round balls or spheres having complex surface structures. Such microstructures are typical of the precipitates of modern iron-encrusted bacteria, and it would be easy to scan for them from very small amounts of water-borne sediment deposited in Martian paleochannels or former lakes.

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References

- Andersen, D. 1989. Physics of the Earth. Blackwell Scientific, Boston.
- Appel, P. W. U. 1980. On the Early Archaean Isua Iron Formation, West Greenland. *Precambrian Res.* 11:73-87.
- Arrhenius, S. 1908. Worlds in the Making, The Evolution of the Universe. Harper, New York.
- Baker, V. R. 1982. The Channels of Mars. University of Texas Press, Austin.
- Berner, R. A. 1981. A new geochemical classification of sedimentary environments. *J. Sed. Petrology* 51:359-365.
- Beveridge, T. J., and R. G. E. Murray. 1976. Uptake and retention of metals by cell walls of *Bacillus subtilis*. J. Bacteriol. 127:1502-1518.
- Bridgwater, D., J. H. Allaart, J. W. Schopf, C. Klein, M. R. Walter, E. S. Barghoorn, P. Strother, A. H. Knoll, and B. E. Gorman. 1981. Microfossil-like objects from the Archaean of Greenland: A cautionary note. *Nature (Lond.)* 289:51-53.
- Cairns-Smith, A. G. 1982. Genetic Takeover and the Mineral Origin of Life. Cambridge University Press, Cambridge.
- Cairns-Smith, A. G., and H. Hartman. 1987. Clay Minerals and the Origin of Life. Cambridge University Press, Cambridge.
- Carr, M. H. 1979. Formation of Martian flood features by release of water from confined aquifers. *J. Geophys. Res.* 84(B6):2995-3007.
- Carr, M. H. 1981. The Surface of Mars. Yale University Press, New Haven, CT.
- Carr, M. H. 1986. Mars: A water-rich planet. Icarus 68:187-216.
- Carr, M. H. 1987. Water on Mars. *Nature (Lond.)* 326:30–35.
- Carr, M. H., and G. D. Clow. 1981. Martian channels and valleys: Their characteristics, distribution, and age. *Icarus* 48:91–117.
- Chukhrov, F. V., B. B. Zvyagin, A. E. Gorshkov, L. P. Termilova, and V. V. Balachova. 1973. Ferrihydrite. *Int. Geol. Rev.* 16:1131-1143.
- Chyba, C. F., P. J. Thomas, L. Brookshaw, and C. Sagan. 1990. Cometary delivery of organic molecules to the early Earth. *Science* 249:366-373.
- Des Marais, D. J. 1988. Search for Martian fossil communities: Sediment sites and sample handling. In M. J. Drake, R. Greeley, and G. McKay (Eds.), Mars Sample Return Science Workshop, pp. 67-68. Lunar and Planetary Institute, National Aeronautics and Space Administration, Johnson Space Center Technical Report 88-07, Houston, TX.
- Ehrlich, H. L. 1990. Geomicrobiology, 2nd ed. Marcel Dekker, New York.
- Eigen, M., and P. Schuster. 1982. Stages of emerging life—Five principles of early organization. J. Mol. Evol. 19:47-61.
- Emerson, S., R. E. Garen, and W. C. Ghiorse. 1989. Formation of *Metallogenium*-like structures by a manganese-oxidizing fungus. *Arch. Microbiol.* 151:223-231.
- Emerson, S., S. Kalhorn, L. Jacobs, B. M. Tebo, K. H. Nealson, and R. A. Rosson. 1982.

- Environmental oxidation rate of manganese(II): Bacterial catalysis. *Geochim. Cosmochim.* Acta 46:1073-1079.
- Ferris, F. G., K. Tazaki, and W. S. Fyfe. 1989. Iron oxides in acid mine drainage environments and their association with bacteria. *Chem. Geol.* 74:321-330.
- Fox, S. W., and K. Dose. 1977. Molecular Evolution and the Origin of Life, rev. ed. Marcel Dekker, New York.
- Frobisher, M., Jr. 1953. Fundamentals of Microbiology. Saunders, Philadelphia.
- Gilbert, W. 1986. The RNA world. Nature (Lond.) 319:618.
- Greeley, R. 1990. Mars Landing Site Catalog. National Aeronautics and Space Administration Reference Pub. 1238, Washington, DC.
- Gregory, E., R. S. Perry, and J. T. Staley. 1980. Characterization, distribution, and significance of *Metallogenium* in Lake Washington. *Microbial Ecol.* 6:125-140.
- Haldane, J. B. S. 1928. The origin of life. Rationalist Ann. 45:3-9.
- Hallbauer, D. K. 1986. The mineralogy and geochemistry of Witwatersrand pyrite, gold, uranium, and carbonaceous matter. In C. R. Anhaeusser and S. Maske (Eds.), Mineral Deposits of Southern Africa, pp. 731-752. Geological Society South Africa, Johannesburg.
- Han, T.-M. 1988, 18-22 August. Origin of magnetite in Precambrian iron-formations of low metamorphic grade. *Proc. 7th Quadrennial International Association of the Genesis of Ore Deposits Symposium*, Lulea, Sweden, pp. 641-656.
- Hanert, H. H. 1981a. The genus Gallionella. In M. P. Starr, H. Stolp, J. G. Treuper, A. Balows, and H. G. Schlegel (Eds.), The Prokaryotes, A Handbook on Habitats, Isolations, and Identification of Bacteria, pp. 509-515. Springer-Verlag, New York.
- Hanert, H. H. 1981b. The genus Siderocapsa (and other iron- or manganese-oxidizing Eubacteria). In M. P. Starr, H. Stolp, J. G. Treuper, A. Balows, and H. G. Schlegel (Eds.), The Prokaryotes, A Handbook on Habitats, Isolations, and Identification of Bacteria, pp. 1049–1059. Springer-Verlag, New York.
- Harder, E. C. 1919. Iron-depositing bacteria and their geologic relations. U.S. Geological Survey Professional Paper 113, Washington, DC.
- Holland, H. D. 1984. The Chemical Evolution of the Atmosphere and Oceans. Princeton University Press, Princeton, NJ.
- Horowitz, N. H. 1986. To Utopia and Back: The Search for Life in the Solar System. W. H. Freeman, New York.
- Hoyle, F., and C. Wickramasinghe. 1981. In C. Ponnamperuma (Ed.), Comets and the Origin of Life, p. 227. Reidel, Dordrecht.
- Iberall, A. S. 1988. Possible correlation between species extinction, evolution, and plate adjustments to continental erosion. *GeoJ.* 16:229-232.
- Iberall, A. S. 1989a. A planet-bound model for origins of life, including pre- and retrodiction. *GeoJ.* 19:207-220.
- Iberall, A. S. 1989b. How many species? GeoJ. 18:133-139.
- Iberall, A. S. 1989c. What's Wrong with Evolution? Desk-Top Publication, Los Angeles.
- Iberall, A. S., and H. Soodak. 1987. A physics for complex systems. In F. E. Yates (Ed.), Self-Organizing Systems, pp. 499-520. Plenum, New York.
- James, J. L. 1954. Sedimentary facies of iron-formation. Econ. Geol. 49:235-293.
- Jones, J. G. 1981. The population ecology of iron bacteria (genus *Ochrobium*) in a stratified eutrophic lake. *J. Gen. Microbiol.* 125:85-93.
- Jones, J. G. 1986. Iron transformations by freshwater bacteria. Adv. Microbial Ecol. 9:149-185.
- Kasting, J. F. 1987. Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian Res.* 34:205-229.
- Klein, H. P. 1979. The Viking mission and the search for life on Mars. Rev. Geophys. Space Phys. 17:1655-1662.
- Kuznetsov, S. I. 1970. The Microflora of Lakes and Its Geochemical Activity (Translation). University of Texas Press, Austin.

- LaBerge, G. L., E. I. Robbins, and T.-M. Han. 1987. A model for the biological precipitation of Precambrian iron-formations—A. Geological evidence. *In P. W. U. Appel and G. L. La-Berge (Eds.)*, *Precambrian Iron-Formations*, pp. 69–96. Theophrastus, Athens.
- Lucchitta, B. K. 1982. Lakes or playas in Valles Marineris. National Space and Aeronautics Administration Technical Memorandum 85127, Reports of Planetary Geology Program, pp. 233-234, Washington, DC.
- Lucchitta, B. K., and H. M. Ferguson. 1983. Chryse basin channels: Low gradients and ponded flows. J. Geophys. Res. 88(Suppl):A553-A568.
- Maher, K. A., and D. J. Stevenson. 1988. Impact frustration of the origin of life. *Nature (Lond.)* 331:612-614.
- Masursky, H., J. M. Goyce, A. L. Dial, G. G. Schaber, and M. E. Stobell. 1977. Classification and time of formation of Martian channels based on Viking data. *J. Geophys. Res.* 82:4016–4038.
- Maynard, J. B. 1983. Geochemistry of Sedimentary Ore Deposits. Springer-Verlag, New York.
- McCauley, J. F. 1978. Geologic map of the Coprates Quadrangle of Mars. U.S. Geological Survey Miscellaneous Inventory Series Map I-897, scale 1:5,000.000.
- McKay, C. P. 1986. Exobiology and future Mars missions: The search for Mars' earliest biosphere. Adv. Space Res. 6:269-285.
- McKay, C. P., and S. S. Nedell. 1988. Are there carbonate deposits in the Valles Marineris, Mars? *Icarus* 73:142-148.
- McKay, C. P., and C. R. Stoker. 1989. The early environment and its evolution on Mars: Implications for life. *Rev. Geophys.* 27:189-214.
- McKirdy, D. M, and J. H. Hahn. 1982. Composition of kerogen and hydrocarbons in Precambrian rocks. In H. D. Holland and M. Schidlowski (Eds.), Mineral Deposits and the Evolution of the Biosphere, pp. 123-154, Springer-Verlag, Berlin.
- Melosh, H., and A. Vickery. 1989. Impact erosion of the primordial atmosphere of Mars. *Nature* (*Lond.*) 338:487-489.
- Moore, H. J., R. W. Hutton, G. D. Clow, and C. R. Spitzer. 1987. Physical properties of the surface materials at the Viking landing sites on Mars. U.S. Geological Survey Professional Paper 1389, pp. 117-120, Washington, DC.
- Morris, R. V. 1987. What ferric oxide/oxyhydroxide phases are present on Mars? In M. J. Drake, R. Greeley, and G. McKay (Eds.), Mars Sample Return Science Workshop, pp. 96-97. Lunar and Planetary Institute, National Aeronautics and Space Administration/Johnson Space Center Technical Report 88-07, Houston, TX.
- Mulder, E. G., and M. H. Deinema. 1981. The sheathed bacteria. In M. P. Starr, H. Stolp, J. G. Treuper, A. Balows, and H. G. Schlegel (Eds.), The Prokaryotes, A Handbook on Habitats, Isolations, and Identification of Bacteria, pp. 425-441. Springer-Verlag, New York.
- Nagy, B., J. E. Zumberge, and L. A. Nagy. 1975. Abiotic, graphitic microstructures in micaceous metaquartzite about 3760 million years old from southwestern Greenland: Implications for early Precambrian microfossils. *Proc. Natl. Acad. Sci.* (USA) 72:1206–1209.
- Nealson, K. H. 1982. Microbiological oxidation and reduction of iron. In H. D. Holland, and M. Schidlowski (Eds.), Mineral Deposits and the Evolution of the Biosphere, pp. 51-66. Springer-Verlag, New York.
- Nealson, K. H. 1986a. The microbial iron cycle. *In* W. E. Krumbein (Ed.), *Microbial Geochemistry*, pp. 159-190. Blackwell Scientific, Boston.
- Nealson, K. H. 1986b. The microbial manganese cycle. In W. E. Krumbein (Ed.), Microbial Geochemistry, pp. 191-221. Blackwell Scientific, Boston.
- Nedell, S. S., S. W. Squyres, and D. W. Andersen. 1987. Origin and evolution of the layered deposits in the Valles Marineris, Mars. *Icarus* 70:409-441.
- Newsom, H. E., and G. E. Brittelle. 1989. Impact cratering on Mars and the formation of crater lakes: A possible environment for the origin of life. *Lunar and Planetary Science Conference XXI*, pp. 877-878. National Aeronautics and Space Administration, Houston, TX.

- Nisbet, E. G. 1986. RNA, hydrothermal systems, zeolites, and the origin of life. *Episodes* 9:83-90
- Nutman, A. P., J. A. Allaart, D. Bridgwater, E. Dimroth, and M. Rosing. 1984. Stratigraphic and geochemical evidence for the depositional environment of the early Archaean Isua supracrustal belt, southern west Greenland. *Precambrian Res.* 25:365-396.
- Oberbeck, V. R., J. R. Marshall, D. E. Schwartz, and R. L. Mancinelli. 1989. Search for life: A science rational for a permanent base on Mars. *Lunar and Planetary Science Conference XXI*, pp. 907-908. National Aeronautics and Space Administration, Houston, TX.
- Oparin, A. I. 1924. Proiskhozhdenie Zhizni [Origin of Life]. Izd. Moskov. Rabotchii, Moscow.
- Oparin, A. I. 1938. The Origin of Life. Macmillan, New York.
- Orgel, L. E. 1986. Molecular replication and the origins of life. In J. de Boer, E. Dal, and O. Ulfbeck (Eds.), The Lesson of Quantum Theory, pp. 283-294. Elsevier, New York.
- Pflug, H. D. 1978. Yeast-like microfossils detected in oldest sediments of Earth. *Naturwissenschaften* 65:611-615.
- Pflug, H. D. 1981. Equidensitometry and spectrometry in the analysis of Archean microfossils. *Microsc. Acta* 84:25-36.
- Pflug, H. D. 1984a. Microvesicles in meteorites, a model of pre-biotic evolution. *Naturwissenschaften* 71:531-532.
- Pflug, H. D. 1984b. Ultrafine structure of the organic matter in meteorites. *In C. Wickramasinghe (Ed.)*, *Fundamental Studies and the Future of Science*, pp. 24-37. University College Press, Cardiff.
- Pflug, H. D. 1986. Morphological and chemical record of the organic particles in Precambrian sediments. System. Appl. Microbiol. 7:184-189.
- Pflug, H. D. 1990. History of Life in the Precambrian—A Review. Geological Institute Special Publication 70, Cologne University Press.
- Pourbaix, M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions, p. 312. Pergamon, New York.
- Pringsheim, E. G. 1947. Iron bacteria. Biol. Rev. 24:1-200.
- Puchelt, H. 1973. Recent iron sediment formation at the Kameni Islands, Santorini, Greece. In
 G. C. Amstutz and A. J. Bernard (Eds.), Ores in Sediments, pp. 227-245. Springer-Verlag,
 New York.
- Puchelt, H., H. Schock, E. Schroll, and H. Hanert. 1973. Rezente Marine Eisenerze auf Santorin, Griechenland. *Geol. Rundsch.* 62: 786-813.
- Robbins, E. I. 1987. Appelella ferrifera, a possible new iron-coated microfossil in the Isua Iron-Formation, southwestern Greenland. In P. W. U. Appel and G. L. LaBerge (Eds.), Precambrian Iron-Formations, pp. 141-154. Theophrastus, Athens.
- Robbins, E. I., J. P. D'Agostino, J. Ostwald, D. S. Fanning, V. Carter, and R. L. Van Hoven. 1992. Manganese nodules and microbial oxidation of manganese in the Huntley Meadows wetland, Virginia, USA. *Catena*, suppl. 21.
- Robbins, E. I., G. L. LaBerge, and R. G. Schmidt. 1987. A model for the biological precipitation of Precambrian Iron-Formations—B. Morphological evidence and modern analogs. *In* P. W. U. Appel and G. L. LaBerge (Eds.), *Precambrian Iron-Formations*, pp. 97-139. Theophrastus, Athens.
- Robbins, E. I., and A. Traverse. 1980. Degraded palynomorphs from the Dan River (North Carolina)-Danville (Virginia) basin. In V. Price, Jr., P. A. Thayer, and W. A. Ranson (Eds.), Geological Investigations of Piedmont and Triassic Rocks, Central North Carolina and Virginia. Carolina Geological Society Field Trip Guidebook, pp. BX-1-11. E. I. du Pont de Nemours, Aiken, SC.
- Robie, R. A., B. S. Hemingway, and J. R. Fisher. 1979. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures. U.S. Geol. Survey Bull. 1452.
- Roedder, E. 1981. Are the 3800-Myr-old Isua objects microfossils, limonite-stained fluid inclusions, or neither? *Nature (Lond.)* 293:459-462.

- Schidlowski, M. 1970. Untersuchungen aur Metallogenese im Suedwestlichen Witwatersrand Becken (Oranje-Freistaat Goldfeld, Suedafrika). Beih. Geol. Jb. 85.
- Schidlowski, M. 1988. A 380-million-year isotopic record of life from carbon in sedimentary rocks. *Nature (Lond.)* 333:313-318.
- Schopf, J. W. (Ed.). 1983. Earth's Earliest Biosphere, Its Origin and Evolution. Princeton University Press, Princeton, NJ.
- Schopf, J. W., and M. R. Walter. 1983. Archean microfossils: New evidence of ancient microbes. *In J. W. Schopf (Ed.)*, *Earth's Earliest Biosphere, Its Origin and Evolution*, pp. 214-239. Princeton University Press, Princeton.
- Schuster, P. 1986. The interface between chemistry and biology—Laws determining regularities in early evolution. *In G. Pifat-Mrzljak (Ed.)*, *Supramolecular Structure and Function*, pp. 154–185. Springer-Verlag, Berlin.
- Scott, M. J., and J. J. Morgan. 1990. Energetics and conservative properties of redox systems. In
 D. C. Melchior and R. L. Bassett (Eds.), Chemical Modeling of Aqueous Systems II, pp. 368-378. American Chemical Society, Washington, DC.
- Sherman, D. M., R. G. Burns, and V. M. Burns. 1982. Spectral characteristics of the iron oxides with application to the Martian bright region mineralogy. *J. Geophys. Res.* 87(B12):10,169-10,180.
- Sleep, N. H., K. J. Zahnle, J. F. Kasting, and H. J. Morowitz. 1989. Annihilation of ecosystems by large asteroid impacts on the early Earth. *Nature (Lond.)* 342:139–142.
- Sly, L. I., M. C. Hodgkinson, and V. Arunpairojana. 1988. Effect of water velocity on the early development of manganese-depositing biofilm in a drinking-water distribution system. FEMS Microbiol. Ecol. 53:175-186.
- Squyres, S. W., and M. H. Carr. 1986. Geomorphic evidence for the distribution of ground ice on Mars. *Science* 231:249–252.
- Staley, J. T., M. P. Bryant, N. Pfennig, and J. G. Holt (Eds.). 1989. Bergey's Manual of Systematic Bacteriology, Vol. 3, pp. 1873-1989. Williams & Wilkins, Baltimore.
- Taylor, S. 1987. The origin of the moon. Amer. Sci. 75:468-477.
- Tonks, W. B., and H. J. Melosh. 1989. Mass exchange among the terrestrial planets: Implications for life exchange between Earth and Mars. *Eos* 70:1173.
- Toulmin, P., A. K. Baird, B. C. Clark, K. Keil, H. J. Rose, R. P. Christian, P. H. Evans, and W. C. Kelliher. 1977. Geochemical and mineralogical interpretation of the Viking inorganic chemical results. J. Geophys. Res. 82:4625-4634.
- Towe, K. M. 1990. Aerobic respiration in the Archaean? Nature (Lond.) 348: 54-56.
- Waechtershaeuser, G. 1988a. Before enzymes and templates: Theory of surface metabolism. *Microbiol. Rev.* 52:452-484.
- Waechtershaeuser, G. 1988b. Pyrite formation, the first energy source for life: A hypothesis. *System. Appl. Microbiol.* 10:207-210.
- Waechtershaeuser, G. 1990. Evolution of the first metabolic cycles. Proc. Natl. Acad. Sci. USA 87:200-204.
- Walker, J. C. G. 1987. Was the Archaean biosphere upside down? Nature (Lond.) 329:710-712.
- Watson, J., N. Hopkins, J. Roberts, J. Steitz, and A. Weiner. 1987. Molecular Biology of the Gene, 4th ed., Vol. 2, pp. 1098-1161. Benjamin/Cummings, Menlo Park, CA.
- Weber, B. 1987. Mikrofossilien aus dem Archaikum Groenlands. Biol. Rundsch. 25:263-266.
- Weber, B. 1988. Isuasphaera isua Pflug 1978: Zur Kenntinis einer problematischen Mikrostruktur aus archaischen Metasedimenten Groenlands. Z. Geol. Wiss. Berlin 16:253-266.
- ZoBell, C. E. 1946. Marine Microbiology. Chronica Botanica, Waltham, MA.