A MODEL FOR THE BIOLOGICAL PRECIPITATION OF PRECAMBRIAN
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As the major chemical sedimentary rock formed in the Archean and Early
Proterozoic, iron-formation has been widely used as a basis for geochemical
inferences about the chemistry of the early atmosphere and oceans. However,
the present mineralogy of iron-formation probably better reflects diagenetic
and metamorphic modifications rather than chemical attributes of the early
atmosphere and oceans. On the other hand, the existence of iron-formation
sequences, which may contain thousands of cubic miles of chemically precipi-
tated iron and silica, probably does reflect on the nature of the early
atmosphere and oceans. In this discussion I am restricting the term iron-
formation to rocks containing roughly equal proportions of silica and iron
minerals.

Today, under an oxygenated atmosphere and consequent oxygenated ocean,
the extreme insolubility of ferric iron precludes attaining significant con-
centrations in a water column. Therefore, widespread cherty iron-formations
do not form. A relatively oxygen-deficient atmosphere seems necessary to
allow sufficient ferrous iron in solution to produce widespread iron
precipitation. However, an oxygen-deficient atmosphere, with its associated
reducing water column and load of ferrous iron, poses the problem of a
mechanism in the Proterozoic and Archean to precipitate the iron. This
would be accomplished most readily by oxidizing the relatively soluble
ferrous iron to an insoluble ferric hydrate, which textural evidence and
geochemical models suggest is the main precipitate.

Because iron-formations range in age from 3,800 Ga to about 1,900 Ga,
and were formed in a wide variety of geological settings, it is not unreason-
able to suggest that their precipitation was controlled by local conditions.
These conditions would include local oxidizing conditions developed in dif-
ferent basins at different times and local availability of iron in these
basins. The fact that the major Proterozoic iron-formations range from about
2,500 Ga for the Hamersley Range of Western Australia to about 1,900 Ga for
the Lake Superior region suggests that iron-formation deposition was con-
trolled mainly by local basin chemistry, and that atmospheric influence was
minor. Furthermore, the widespread occurrence of iron-formations in the
Archean also points to local basin control. While it is possible to pro-
duce a locally reducing environment with an oxygenated atmosphere today, I
know of no way to produce a locally oxidizing environment with an oxygen-
deficient atmosphere except by biological activity. Therefore, precipitation
of the iron would be most readily accomplished by biological activity.

The precipitation of silica, the other major ingredient in iron-
formations, is especially problemmatical, including disagreement on whether
it is primary or secondary. While most workers assume that the chert is a
primary precipitate, some (1, 2) suggest that it is a replacement of earlier
calcite. Textural relations, including syneresis cracks (3), suggest that
the silica is a primary precipitate. However, the mechanism of precipitation
is not resolved. Although most Phanerozoic cherts are considered to be
biologically precipitated (by diatoms, radiolaria and sponges), Precambrian
cherts are generally considered to be inorganically precipitated because
Precambrian silica-secreting organisms have not been recognized. The
typical, ubiquitous association of iron and silica in iron-formations sug-
gests that the precipitation of the two must be related, even though the

chemistry of silica is very different from that of iron. I propose to show evidence that the silica as well as the iron in iron-formations was precipitated biologically.

One of the characteristic features of iron-formation cherts is the widespread occurrence of spheroidal structures about 30 um in diameter that consist of a central 20 um sphere surrounded by a variable number of 5 um spheroids (4). In most cases, the spheroids are revealed by a fine hematite "dust" that outlines the structures. Although the spheroids are not present in every layer, they are present in every Proterozoic and Archean iron-formation which has not been excessively metamorphosed and sheared that I have examined. As pointed out by LaBerge (4), the structures are remarkably similar in size and morphology to the organic-walled microfossil _Eosphaera tyleri_, and I suggest that the spheroids are best interpreted as relict forms of that organism. If so, the details of these structures may have
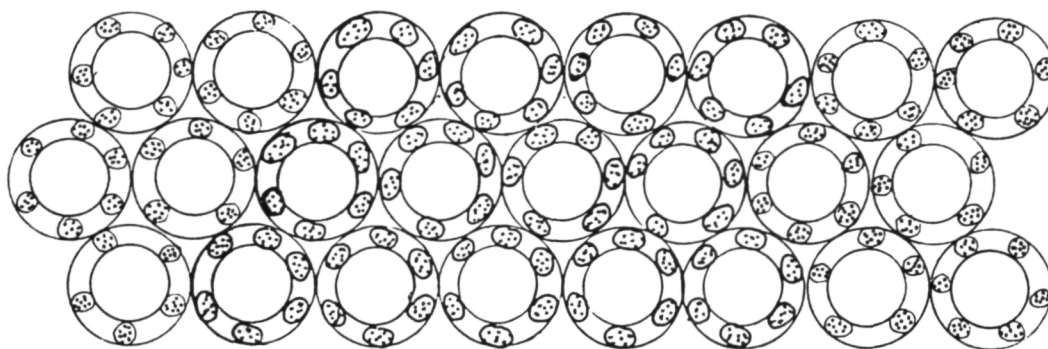

Sketch of hypothetical situation of what an accumulation of _Eosphaera tyleri_ might look like.
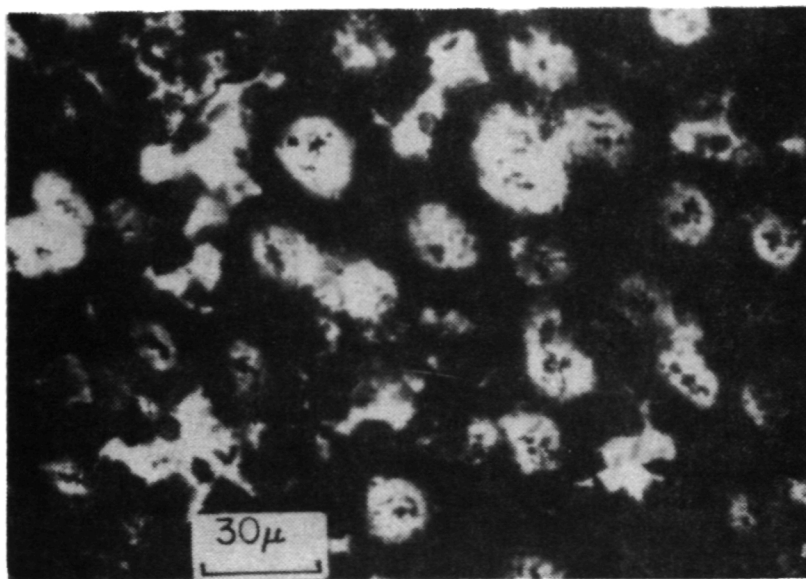
Photomicrograph of jasper with _Eosphaera_-like structures showing their abundance.

significant implications on the precipitation of iron-formation. First, the fact that these structures are abundantly preserved as spheroids in the cherty layers suggests that they had some rigidity, and were not simply an organic sheath, because a vast majority of organic matter in iron-formation does not retain its organic structure. Many jasper layers are virtually composed of spheroidal structures. Microscopically, the textural pattern of the Eosphaera-like structures suggests that the layers formed by accumulation of the spheroids. The fact that the spheroids appear to have had rigidity and to have formed the siliceous layers suggests that Eosphaera may have had a siliceous test. Similarly, the presence of similar structures within siliceous granules seems to attest to the durability of the spheroids. In addition, all Eosphaera-like structures are typically preserved by a fine hematite "dust" that colors the jasper red. The dust, then, may represent fine ferric hydrate that adhered abiotically to the organic walls of Eosphaera, or alternatively, it may indicate that Eosphaera was photosynthetic and the ferric hydrate accumulated on the membrane where oxygen was expelled (such as in modern Volvox), or it may be similar to the way the chemotrophic bacterium Leptothrix encases itself in a sheath of ferric hydrate. These two observations in the jaspers lead to the tentative interpretation that Eosphaera may have been a photosynthetic organism with siliceous frustules. If this interpretation is correct, it is significant regarding iron-formation and early life because these spheroids are present in Archean iron-formations including some from the 3,500 Ga old Pilbara block of Western Australia. Furthermore, the abundance of Eosphaera-like structures in laminated (deep water) jaspers may indicate that it was planktonic rather than benthic in life-style.

Several authors (4, 5, 6, 7) have reported that siderite in relatively unmetamorphosed iron-formations occurs as prominent spherical grains about 30 um in diameter. Microprobe examination of spherical siderites in Proterozoic iron-formation from the Gunflint district of Ontario reveals that they are double-walled structures remarkably similar to Eosphaera tyleri.
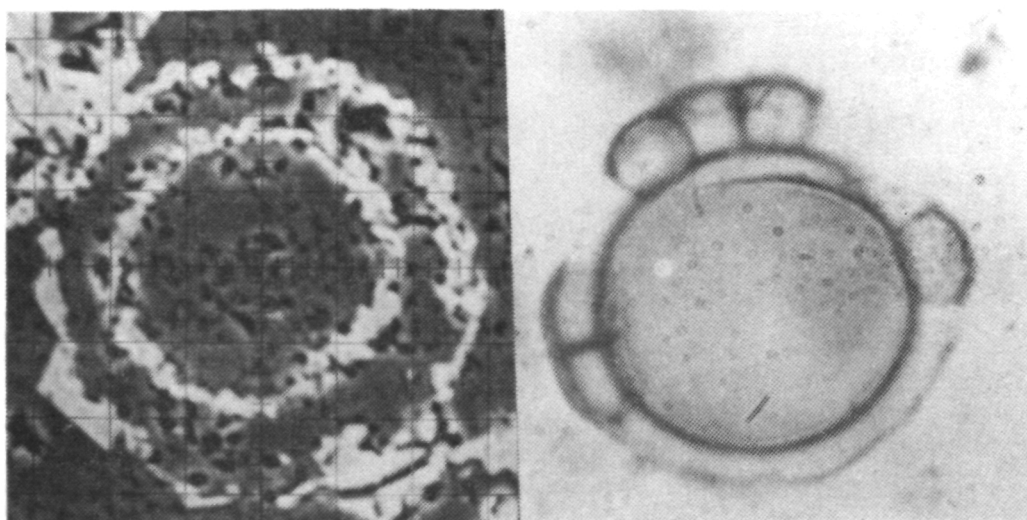
Comparison of double-walled spherical siderite (left) and Eosphaera tyleri (right). Siderite is white in the electron micrograph. Photos are approximately the same scale.
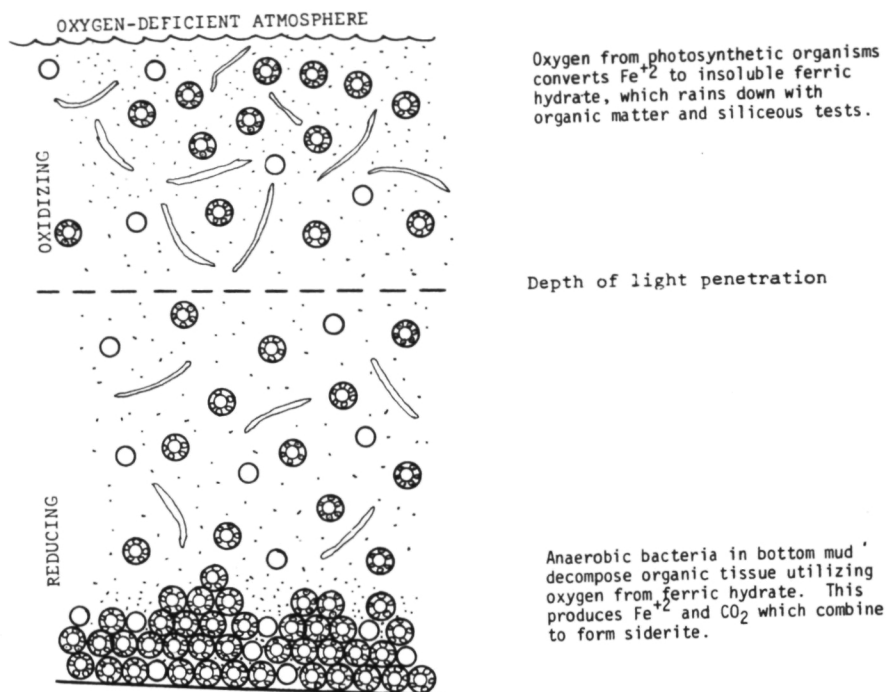
These double-walled, spherical siderite grains are interpreted to have formed by diagenetic alteration of primary hematite-coated varieties. Bacterial degradation of organic matter in the anoxic zone on the basin floor may have produced CO_2 and utilized ferric hydrate as an electron donor which reduced the iron to the ferrous state. The ferrous iron and CO_2 combined to form siderite "pseudomorphs" after hematite-pigmented forms involving progressive replacement of the silica. Siderite is a major mineral in some iron-formations, however, it appears to be primarily of early diagenetic origin, because siderite is part of the sedimentary fabric of the rock. The conversion of primary ferric hydrate to siderite is often incomplete, because hematite and siderite may co-exist in iron-formations. Perhaps this may be due to the amount of associated organic matter that was available for bacterial degradation on the basin floor. The net result seems to have been a primary precipitate containing a mixture of ferric and ferrous minerals in a metastable association.

Magnetite is the most abundant iron mineral in metamorphosed iron-formations, and I suggest that the hematite and siderite react to produce magnetite, which appears to be the equilibrium phase at elevated temperatures. In contrast to hematite and siderite, which were involved in the depositional fabric, magnetite typically forms crystal aggregates and veins that tend to obliterate primary features (6). Furthermore, Han (8) showed that much of the magnetite forms as overgrowths on earlier, rhombohedral hematite crystals. It may be appropriate to note here that these diagenetic (?) hematite crystals, which resemble monoclinic selenite crystals, may have been misidentified as pseudomorphs after gypsum (2, 9). If so, this may lead to erroneous interpretations about the oxygen content of the Precambrian atmosphere and oceans.

I suggest that the iron in iron-formations was precipitated as a ferric hydrate product by photosynthetic oxidation of iron in the photic zone. Presumably a variety of organisms were involved in the process, including planktonic iron-stripping bacteria such as Leptothrix and Metallogenium, which precipitated ferric hydrate in their sheaths from ferrous iron in the water. While some of the iron accumulated on the Eosphaera-like structures, most of it evidently formed as minute ferric hydrate particles that settled in the water column. The silica may have been precipitated largely as frustules of silica-secreting organisms, particularly Eosphaera tyleri. Thus, the "sediment rain" consisted of Eosphaera, ferric hydrate, and other organic materials, which accumulated on the basin floor. Incipient layering of iron and silica may have been produced by a relatively constant "rain" of ferric hydrate punctuated by periodic "blooms" of siliceous organisms. In the organic-rich ooze, anaerobic decay and chemoautotrophic bacteria may have flourished, giving off waste CO_2 and ferrous iron. These products reacted to form siderite, which may have been nucleated by the ferric hydrate on the Eosphaera or elsewhere. The notorious lack of sulfide minerals in cherty iron-formations suggests that sulfate was scarce in the basins, and that it did not serve as an oxygen source for organic delay. Continued accumulation of iron on the upper part of the siliceous layer, coupled with diagenetic formation of siderite would produce a marked density contrast between silica and ferruginous "grains". The layering would then be enhanced by currents separating the ferruginous and silica "grains". During periods of higher energy bottom currents, this laminated material might have been broken up to form granule-bearing units in shallower water as discussed by LaBerge (3). Subsequent metamorphism of the metastable siderite-hematite-chert rock would

result in widespread development of magnetite and/or iron-silicates.

OXYGEN-DEFICIENT ATMOSPHERE

Oxygen from photosynthetic organisms converts Fe^{+2} to insoluble ferric hydrate, which rains down with organic matter and siliceous tests.

Depth of light penetration

Anaerobic bacteria in bottom mud decompose organic tissue utilizing oxygen from ferric hydrate. This produces Fe^{+2} and CO_2 which combine to form siderite.

Sketch of the proposed model for the biological precipitation of Precambrian iron-formations.

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