Are there abiotically-precipitated iron-formations on Mars?

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Abstract—In early times, surface conditions on Mars and Earth were probably quite similar, however, the two planets took different paths in their evolution. Banded iron-formations (BIFs) were prevalent on Earth in the Archean, and the likelihood of their formation on Mars at the same time is investigated. There are several abiotic mechanisms for producing banded iron-formations on Earth. These are: (1) oxidation of ferrous iron by free oxygen, (2) photooxidation of ferrous iron, (3) oxidation of ferrous iron by hydrogen peroxide, and (4) anoxic precipitation of ferrous iron by changes in pH. Any of these mechanisms could have been active on Mars in its distant past, to produce BIFs there as well, which should be observable today. The minerals one would expect to observe on the surface of a BIF on Mars are indeed thought to exist on Mars, but unfortunately BIFs are not unique in containing these minerals, and confirmation of the existence of BIFs on Mars will have to wait for more data. Proof of the existence of BIFs on Mars would give us valuable information about the early history of the planet Mars as well as Earth. It would act to confirm models of Mars that include a warm, wet period, and the existence of bodies of standing water.

INTRODUCTION

IN THE SURFACE of Mars we see a relict of the early evolution of the planet. During the early history of the solar system, conditions were probably not dissimilar on the surface of Earth and Mars, but as time passed, the two planets diverged. Earth, larger and with a greater source of internal heating, stayed active and its surface kept evolving. Mars, on the other hand, smaller and with less internal heating, froze and its surface almost completely stopped evolving. Therefore, when we look at the surface of Mars, we have the opportunity not only to observe the early history of Mars itself, but also to observe a landscape perhaps more similar to that of early Earth than is the present terrestrial landscape.

The surface of Mars seems to have changed relatively little over the past several billion years. Processes that have acted on its surface in the past include meteorite bombardment, which was at its peak over 3.5 Gy ago; volcanism, which is thought to have largely ceased by about 1 Gy ago; and fluvial and glacial processes, about which there is active speculation (BAKER et al., 1991; BAKER et al., 1992; KARGEL et al., 1995), but which neither appear to have been active within the last 1 Gy (although periglacial processes may be active today (ROSSBACHER and JUDSON, 1981). The role of hydrothermal processes is as yet unknown, however they could be very important, both to the chemical evolution of the regolith and to the isotopic evolution of the atmosphere (JAKOSKY and JONES, 1996). Physical and chemical weathering, which is still active today, acts only to alter the characteristics of the uppermost surface layers (GOODING, 1978; GOODING et al., 1992).

It is likely that Earth and Mars were not dissimilar when they were first formed. By studying processes that occurred on the early Earth, we may gain insight into what processes might have been important on early Mars. And conversely, as we obtain more detailed information about the present surface of Mars, we will learn more about the early history of both planets. BURNS (1993) originally suggested that banded iron-formations (BIFs) could have occurred on Mars. The present paper discusses the likelihood of the occurrence of BIFs on Mars, and what their existence might imply about the early environment of Mars.

TERRESTRIAL BANDED IRON-FORMATIONS

Some of the oldest surviving sedimentary features on Earth are the banded iron-formations, chemically-precipitated sedimentary deposits containing layers of silica-rich and iron-rich bands. GROSS (1980) classifies banded iron-formations into two groups, based on associated types of rock, lithological features, and interpretation of their depositional environment. These two groups are Algoma-type and Lake-Superior-type. Both of these types exhibit cherty layers interbedded with iron in four facies: oxides, carbonates, silicates, and sulfides (JAMES, 1954). In addition to the banded iron-formations, there is another type of iron-formation called an oolitic ironstone. Oolitic ironstones are higher in aluminum than BIFs, and have a more clastic association. They are found in rocks of a variety of ages from Proterozoic to Pliocene (MAYNARD, 1983).

Although BIFs are agreed to be chemical precipitates of iron, the mechanism by which the precipita-

tion occurs is a controversial topic. Both biotic (CLOUD, 1973; GARRELS *et al.,* 1973; LABERGE, 1973; LABERGE *et al.,* 1987; ROBBINS *et al.,* 1987) and abiotic (BRATERMAN and CAIRNS-SMITH, 1987; CAIRNS-SMITH, 1978; EUGSTER and CHOU, 1973; FRANÇOIS, 1986; HOLLAND, 1973) mechanisms have been proposed.

The major idea behind both of these classes of theories is that the atmosphere of the early Earth was depleted in O_2, compared to the present atmospheric level (PAL). Under conditions of low oxygen fugacity, especially in an acidic environment, iron exists in the ferrous form, and is highly soluble in water. Thus any iron input into a lacustrine or oceanic system by weathering or other process will stay in solution in the water until it reaches saturation with respect some iron silicate or carbonate, or is oxidized to form ferric iron, which is relatively insoluble in water. Then, for any of a variety of reasons, depending on the model, the iron is oxidized, and precipitates out, forming the extensive deposits that still exist today.

In the classic biotic models the factor that causes this precipitation of iron is the increase in atmospheric O_2 caused by the development of photosynthetic organisms. However, it is not necessary to invoke the development of life to achieve oxidation of iron in Precambrian waters. Also, there is evidence that very little oxygen was present in the atmosphere during the formation of many of the deposits. The presence of detrital siderite in Lake-Superior-type deposits in Labrador and the occurrence of detrital grains of uraninite and pebbles of pyrite in the 2.5-Gy-old Witwatersrand conglomerate indicate a vanishingly low p_{O_2} content in the atmosphere at that time (GARRELS *et al.,* 1973). However, biotic models explain this by postulating procaryotic microorganisms that reduced CO_2 to CH_2O in the hydrosphere by taking electrons from ferrous iron (CLOUD, 1972, 1973).

ABIOTIC MECHANISMS OF MAKING IRON-FORMATIONS

There are four abiotic processes that are capable of forming BIFs. (1) *Oxidation of ferrous iron by dissolved oxygen.* Although this is also descriptive of what happens when photosynthesis produces oxygen, there are abiotic reactions that may produce free oxygen. (2) *Photooxidation of ferrous iron by ultraviolet irradiation.* Ultraviolet (UV) radiation is capable of directly oxidizing ferrous iron in solution. (3) *Oxidation of ferrous iron by hydrogen peroxide.* Hydrogen peroxide (H_2O_2) is a strong oxidant, and is also able to directly oxidize ferrous

iron in solution. (4) *Anoxic precipitation of ferrous iron.* Under anoxic conditions, it is possible to precipitate ferrous iron carbonates and silicates under the right conditions of pH and p_{CO_2}. These mechanisms are shown schematically in Fig. 1 and will be discussed in detail below.

The question of whether banded iron-formations on Earth formed primarily by a biotic or an abiotic mechanism is still an open question. Another open question is the likelihood of life ever having existed on Mars. The main thrust of the present paper is the discussion of abiotic mechanisms of making BIFs. Such mechanisms require fewer assumptions, when translated to Martian conditions, than do the biotic models. However, if life did exist on Mars and was instrumental in causing iron precipitation in bodies of water there, then the iron formations developed would be a likely place to look for fossil evidence of such life.

Dissolved oxygen

There is geological evidence that free oxygen was present in the early atmosphere (even as early as 3.8 Gy ago), although not in quantities approaching PAL (TOWE, 1983). HOLLAND (1973) demonstrated that neither subaerial weathering or volcanic emanations were likely to have been the immediate sources of soluble iron to form the Hamersley Basin BIF of Australia. He then proposed that upwelling of bottom waters in the ocean could
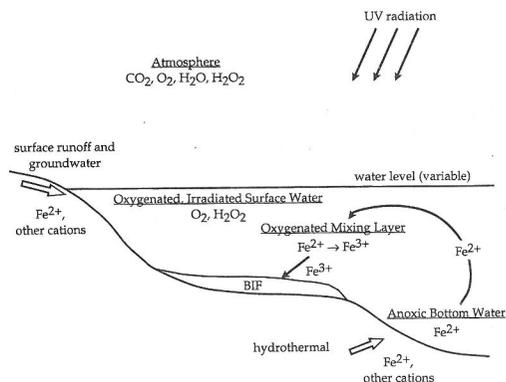

FIG. 1. Schematic diagram of the four abiotic mechanisms of BIF formation. Ferrous iron may be oxidized to ferric iron in the mixing layer by means of dissolved oxygen or hydrogen peroxide, or nearer the surface by UV radiation. Anoxic water (not necessarily bottom water, as in the figure, if the oxygen content of the atmosphere is low) may precipitate ferrous iron if the pH is very high (caused by evaporation) or very low (caused by an input of acidic ground or surface water).
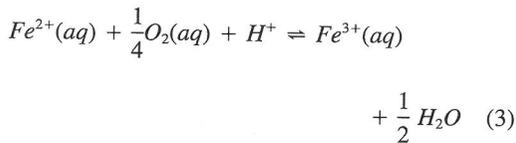
have provided the necessary quantities of dissolved iron to produce this deposit, and generalized this mechanism to explain other Lake Superior-type deposits where there is little clastic debris (HOLLAND, 1973). TOWE (1983) then finds a corollary to Holland's proposition, namely, that free oxygen does not have to be absent from the atmosphere to maintain the anoxic conditions necessary to transport large quantities of ferrous iron in solution, instead, that the deeper basins must remain stagnant and anoxygenic for reasonable periods of time.

In this model, anoxygenic bottom waters, carrying dissolved ferrous iron, circulate upwards to oxygen-rich surface layers in shallower regions of the ocean, where the iron is oxidized and deposited. It is not necessary to invoke photosynthesis here to produce the relatively oxygen-rich surface waters. In fact, there is evidence against photosynthesis being an important process here. BIF oxide facies are remarkably free of organic carbon (TOWE, 1983). Anoxic atmosphere models of BIF formation require that photosynthesis in the basin waters produce the dissolved oxygen necessary to oxidize the iron. However, if there were large algal communities living in these basins, one would expect to find evidence of them in the fossil record, which is not seen (TOWE, 1983). This observation is also supported by the very low contents of phosphorus in BIFs (BEUKES and KLEIN, 1992).

In the absence of photosynthesis to produce free oxygen in the atmosphere and dissolved in the surface waters, UV photolysis of water and CO_2 can become important processes:

$$H_2O \overset{h\nu}{\to} H_2 + \frac{1}{2}O_2 \tag{1}$$

$$CO_2 \overset{h\nu}{\to} CO + \frac{1}{2}O_2 \tag{2}$$
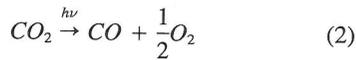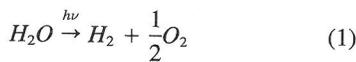
When this ferrous iron in solution is exposed to free oxygen, it will oxidize according to the following reactions (BURNS, 1993)

$$Fe^{2+}(aq) + \frac{1}{4}O_2(aq) + H^+ \rightleftharpoons Fe^{3+}(aq)$$
$$+ \frac{1}{2}H_2O \tag{3}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons FeO(OH)(s) \downarrow + 3H^+. \tag{4}$$

Measurements of UV radiation from T-Tauri stars (thought representative of the Sun at an early stage in its evolution) by the International Ultraviolet Explorer (IUE) spacecraft indicate that such stars produce far higher UV fluxes than originally thought (CANUTO et al., 1983). Although the Sun's total luminosity is thought to have been lower in the past, the UV flux was likely much higher (Table 1).

CANUTO et al. (1983) performed a detailed photochemical model of the Earth's early atmosphere to determine the abundance of free oxygen. They calculated that whereas the surface O_2 mixing ratio for an atmosphere containing 1 PAL CO_2 (2.8 $\times 10^{-4}$ bars), irradiated by the present solar UV flux, is about 10^{-15}, if an atmospheric abundance of 100 PAL is assumed, irradiated by a solar UV flux 4 times the present value (as would be appropriate at a solar age of about 1 Gy), the surface O_2 mixing ratio is a factor of over 10^3 greater (Fig. 2). This surface O_2 mixing ratio of 3×10^{-12} is within the range of O_2 values (10^{-13} to 10^{-3}) required to explain the simultaneous existence of oxidized iron and reduced uranium noted earlier in the oldest rocks (CANUTO et al., 1983). Even assuming the present solar UV flux, and an atmospheric partial pressure of 100 PAL (0.028 atm) CO_2, the CANUTO et al. (1983) model calculates a surface O_2 mixing ratio of about 10^{-12}, still within this range. The model of KASTING et al. (1984), on the other hand, calculated that the O_2 surface mixing ratio in an atmosphere containing 1000 PAL CO_2 under the present solar UV flux would be 10^{-11}, and that an increase in solar UV flux would act to reduce, not increase, the O_2 surface mixing ratio, due to the higher H_2 densities produced by more rapid H_2O photolysis. Clearly this is a complicated problem, but we seem close to understanding how surface O_2 levels in the atmosphere before the development of life could have been in the range

Table 1: *Stellar UV flux as a function of age, from* CANUTO *et al. (1983).*

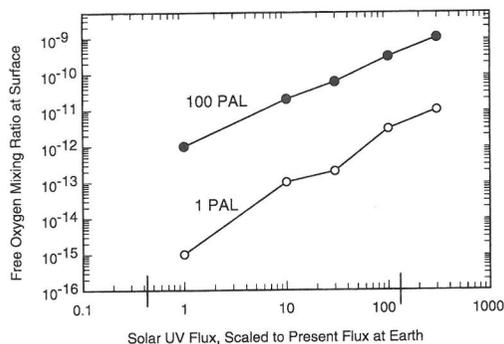| Age (years)	UV enhancement
10^6	10^4
10^7	500
5×10^7	100
10^8	32
5×10^8	8
10^9	4
5×10^9	1

FIG. 2. Free oxygen mixing ratio at the surface, *vs.* solar UV flux, from data in CANUTO *et al.* (1983). Two cases are given, an assumed p_{CO_2} of 1 PAL and one of 100 PAL. A range of solar UV fluxes from 1 to 300 times the present Earth value are shown. In addition, the two bars at about 0.4 and 130 present UV flux represent the corresponding fluxes at Mars, for this range of fluxes at Earth.

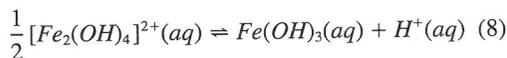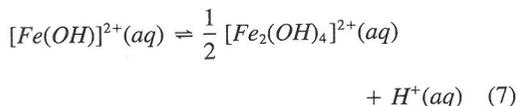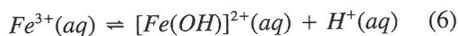necessary to explain the mineralogy of the sediments.

Ultraviolet irradiation

Another method of oxidizing iron in solution is by means of direct UV irradiation (WEISS, 1935; JORTNER and STEIN, 1962a and b; PAPP and VINCZE, 1980).

CAIRNS-SMITH (1978) originally proposed that BIFs were formed by the photochemical oxidation of iron, according to the reaction

$$Fe^{2+}(aq) + H^+(aq) \xrightarrow{h\nu} Fe^{3+} + \frac{1}{2}H_2 \uparrow. \quad (5)$$
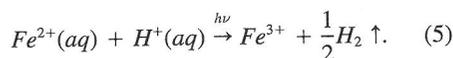
Further studies showed that photo-oxidation of iron is an important reaction in ferrous solutions with a wide range of pH values, 7.5 and less (BRATERMAN *et al.,* 1983 and 1984). At pH values less than about 3.5, hydrolysis and precipitation are not important, but in the pH range 6.2–4, goethite is precipitated according to the following reactions:

$$Fe^{3+}(aq) \rightleftharpoons [Fe(OH)]^{2+}(aq) + H^+(aq) \quad (6)$$

$$[Fe(OH)]^{2+}(aq) \rightleftharpoons \frac{1}{2}[Fe_2(OH)_4]^{2+}(aq) + H^+(aq) \quad (7)$$

$$\frac{1}{2}[Fe_2(OH)_4]^{2+}(aq) \rightleftharpoons Fe(OH)_3(aq) + H^+(aq) \quad (8)$$

$$Fe(OH)_3(aq) \rightarrow FeO(OH)(s) \downarrow. \quad (9)$$

The above scenario occurs in both saline and non-saline solutions, with UV irradiation at $\lambda < 300$ nm (BRATERMAN *et al.,* 1983 and 1984).

At pH values between 6.5 and 7.5, a different set of reactions becomes important (BRATERMAN *et al.,* 1983 and 1984; BRATERMAN and CAIRNS-SMITH, 1987):

$$Fe^{2+}(aq) \rightleftharpoons [Fe(OH)]^+(aq) + H^+(aq) \quad (10)$$

$$[Fe(OH)]^+(aq) \xrightarrow{h\nu} Fe(OH)_3 + H^+(aq). \quad (11)$$
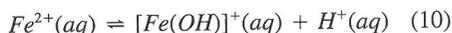
The $Fe(OH)_3$ then forms aggregates and eventually precipitates out as $FeO(OH)$, and the system evolves gaseous hydrogen. The reaction rate for this process is about 10 times greater than at lower pH, and longer wavelengths ($\lambda > 400$ nm) are still effective.
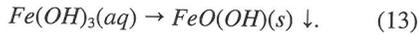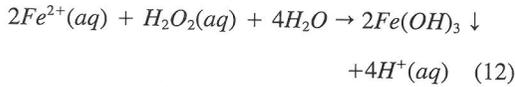
Using these reactions and assuming the present solar UV flux (with 50% loss through scattering and clouds), in terrestrial Fe^{2+}-containing waters having a pH > 6.5, a rate of photoprecipitation of $150–750$ mg cm^{-2} yr^{-1} at the tropics or $50–250$ mg cm^{-2} yr^{-1} at the poles can be calculated (BRATERMAN *et al.,* 1983). These are somewhat larger than estimates of iron deposition in the Hamersley BIFs of $9–43$ mg cm^{-2} yr^{-1} (TRENDALL and BLOCKLEY, 1970), indicating that photo-oxidation of iron is a sufficient explanation for their formation. The Precambrian ocean model of FRANÇOIS (1986, 1987), which also calculates deposition of iron formations based on the photo-oxidation of $[Fe(OH)]^+$, agrees with these results.

The work of ANBAR and HOLLAND (1992) on the photochemistry of manganese is also consistent with a photochemical model for the formation of BIFs. However, DES MARAIS (1994) points out that the absence of BIF deposition on shallow-water Archean platforms, even at water depths some distance below the photic zone, indicates that not only was the surface seawater oxidizing, but that a mobile oxidant such as dissolved O_2 must have penetrated below the photic zone to prevent the deposition of BIFs at those depths.

Hydrogen peroxide

KASTING *et al.* (1984, 1985) suggested that hydrogen peroxide (H_2O_2) could be formed in the early, carbon dioxide-rich atmosphere of Earth and then rain out to oxidize and precipitate the iron in the ocean. They determined that hydrogen peroxide is probably the dominant oxidant in rainwater at free oxygen levels less than $10^{-2}–10^{-3}$ PAL (about 2×10^{-3} to 2×10^{-4} bars), and was probably an important oxidant even in O_2-free atmospheres,

provided that the CO_2 levels were significantly higher than today. These results indicate that hydrogen peroxide is also a viable candidate for an inorganic oxidizer in the Precambrian ocean, that could have acted to precipitate the BIFs according to the reactions

$$2Fe^{2+}(aq) + H_2O_2(aq) + 4H_2O \rightarrow 2Fe(OH)_3 \downarrow$$

$$+4H^+(aq) \quad (12)$$

$$Fe(OH)_3(aq) \rightarrow FeO(OH)(s) \downarrow. \quad (13)$$

This oxidant, like dissolved oxygen gas, would not have had a problem penetrating below the photic zone to prevent the deposition of BIFs at such depths.

However, subsequent work by KASTING (1990) indicates that when sulfur chemistry is included in a low-O_2 atmosphere, the dominant photochemically-produced oxidant is sulfuric acid, and the hydrogen peroxide abundances are greatly reduced. In this case, the sulfuric acid would react with water in the atmosphere to form sulfate, which would then rain out into the ocean (KASTING, private communication). Sulfate is not nearly as powerful an oxidant as hydrogen peroxide, so this mechanism may not be sufficient to oxidize the ferrous iron to form iron formations.

In summary, there appear to be an abundance of adequate abiotic mechanisms to precipitate out iron in a largely anoxic Precambrian ocean, under a carbon dioxide-rich atmosphere. At our current level of knowledge, it is difficult to determine unequivocally which must have been the dominant process. Although certainly the development of living organisms radically changed the oxidation state of the early terrestrial environment, however, it is not necessary to invoke the origin of photosynthesis to begin the deposition of the banded iron formations.

Anoxic deposition and the banded nature of the iron-formations

In addition, the banded nature of the iron formations requires explanation, and the most common idea is that the iron supply is periodically variable (BUTTON *et al.,* 1982; DREVER, 1974; EUGSTER and CHOU, 1973; HOLLAND, 1973; MORRIS, 1993; TOWE, 1983).

EUGSTER and CHOU (1973) proposed that banded iron-formations were deposited in a playa-lake complex. They assumed that the atmosphere was free of oxygen, and that precipitation of iron occurred in response to changes in pH and f_{CO_2} at an

f_{O_2} level between that of the hematite + magnetite and magnetite + quartz + fayalite buffers. In their model, evaporative precipitation of carbonates occurs at the margins of a largely spring-fed lake, or barred lagoon, with magadiite ($NaSi_7O_{13}(OH)_3 \times 4H_2O$) and iron-silica gel precipitation occurring in the deeper parts of the lagoon. Occasional floods, which bring in fresh, low-pH waters, are invoked to precipitate the magadiite or sodium silica gel, and ferrous hydroxide ($Fe(OH)_2$), iron-silicate and sodium-iron-silicate gels and to wash the carbonates into the lake, producing bands. In addition, ferric hydroxide ($Fe(OH)_3$) precipitates if free oxygen should become available.

This model represents not a mechanism for oxidizing the iron, but a means of depositing it in the ferrous state. The presently-observed chert and ferric iron deposits are caused by the subsequent diagenesis of the primary precipitates mentioned above (EUGSTER and CHOU, 1973). This scenario is significantly different than the other models discussed here. The other models assume that the depths of the ocean were low in oxygen, but that ferric iron was oxidized and precipitated in an upper layer, either by dissolved oxygen or by some other means. The arguments for oxidization of the iron in solution are strong, and seem to preclude the likelihood of the EUGSTER and CHOU (1973) mechanism [developed over ten years earlier, before the work of Braterman, Cairns-Smith, Canuto, Kasting, Towe, and their co-workers (BRATERMAN *et al.,* 1983; BRATERMAN *et al.,* 1984; BRATERMAN and CAIRNS-SMITH, 1987; CAIRNS-SMITH, 1978; CANUTO *et al.,* 1983; KASTING *et al.,* 1984; KASTING *et al.,* 1985)] having been dominant. In addition, there is evidence from rare earth element (REE) analysis that Precambrian BIFs are the result of chemical precipitation from solutions that are mixtures of seawater and hydrothermal input (KLEIN and BEUKES, 1992). However, the thermodynamic calculations and predominance diagrams that they developed are still useful in determining what species are stable under given conditions of f_{O_2}, pH, and f_{CO_2}, particularly in the anoxic conditions prevalent deep in the ocean.

A more recent model for explaining the banded nature of the BIFs was developed by MORRIS (1993). This detailed model of the Hamersley BIF in Australia relies on the interaction of two major oceanic supply systems to produce bands of iron and silica: (1) surface currents and (2) convective upwelling from mid-ocean ridges or hot spots (MORRIS, 1993). The surface currents were saturated in silica, but relatively free of iron, either

because the system was oxidizing or because of photoprecipitation. Precipitation from these surface waters, possibly driven by evaporative concentration, formed the chert-rich layers. Periodically, upwelling from iron-rich deeper waters, driven by convective overturn, overwhelmed the deposition of silica to produce the iron-rich layers. This model includes a low-oxygen to anoxic atmosphere, higher heat flow under the oceans than at present, and a modest level of photosynthetic activity, but none of these conditions are essential to the model (MORRIS, 1993). Another factor considered in this model of the formation of the Hamersley deposits was the effects of surface volcanic activity.

The bulk of both ferrous and ferric iron presently in the Hamersley BIF is therefore attributed to oxidation in the surface zone of the ocean. The FeO(OH) precipitate eventually is transformed to (1) hematite, if oxidizing conditions are maintained in the sediments, or (2) magnetite, if partial reduction occurred due to the action of organic matter, or (3) siderite/silicate, if substantial reduction occurred in the photic zone (increasing its iron content) or in the sediment itself (MORRIS, 1993).

EARLY GEOCHEMISTRY OF EARTH AND MARS

When Mars and Earth were in their infancy, they were far more alike than they are at present. Both were rocky bodies, heated by their accretion, and with atmospheres dominated by carbon dioxide, nitrogen, and water vapor. Volcanic activity produced vast basalt plains, as well as volcanic edifices. The bombardment of the crust with meteorites also kept hydrothermal circulation systems active. In topographically low areas, lakes and oceans formed. Active weathering of the silicate crust by carbonic acid-rich waters provided a rich source of iron, silica, and other cations to supply the early oceans, and left behind it a clay and oxide-rich weathering profile, which might still be seen today on Mars (TOWE, 1983).

The existence of lakes or oceans on early Mars is still controversial. Values of total outgassed CO_2 from several to about 10 bars are consistent with present knowledge (POLLACK et al., 1987), and this amount of CO_2 implies an amount of water outgassed at least equal to an equivalent depth of 500 to 1000 meters (CARR, 1986). POLLACK et al. (1987) have made extensive calculations deriving the amount of carbon dioxide necessary to achieve a strong enough greenhouse effect to raise the surface temperature of Mars above the freezing point of water, and have determined that, for different values of surface albedo, latitude, and orbital position, pressures of from 0.75 to 5 bars are necessary. Work by KASTING, however (KASTING, 1991), indicates that CO_2 alone may not be sufficient to warm the surface of Mars above the freezing point of water. He finds that under Martian conditions carbon dioxide cannot be present in the atmosphere at such high pressures, but instead will condense out. There is recent work from FANALE and POSTAWKO (1995) and from YUNG et al. (1995) indicating that adding SO_2 to the models may eliminate the problem of CO_2 condensation. Even if a carbon dioxide atmosphere alone was not enough to cause a warm early Mars, there is still sufficient evidence that Mars outgassed large amounts of carbon dioxide (POLLACK et al., 1987), and there is much geological evidence of flowing water upon the surface, implying warm temperatures. In addition, PARKER and coworkers (PARKER et al., 1987; PARKER and GORSLINE, 1992; PARKER et al., 1993) have seen geomorphic evidence for ancient shorelines in the northern plains of Mars.

The existence of lakes or oceans on early Mars will therefore be assumed as a working hypothesis for this paper, but I will show that if BIFs do exist on Mars, their existence offers proof of the existence of large bodies of water on Mars at some time.

Mars is farther from the Sun, which means that it receives less radiation than Earth, and would have been cooler. More importantly, it is smaller than Earth, so that its internal heat was not enough to support plate tectonics, or to keep the crust from thickening and cutting off volcanic activity to the surface. As it lost volatiles from the atmosphere, both to the surface and to space, the surface cooled past the freezing point of water, and its geochemical evolution slowed and nearly ceased.

But before about 3500 million years ago, the two planets were relatively similar, and geochemical processes, such as the formation of BIFs, that we observe on Earth may have occurred on Mars as well. The second part of this paper investigates how one must modify the mechanisms discussed above to apply to Martian conditions, and discusses what implications the existence of BIFs on Mars would have for the history of the planet (such as confirmation of the warm, wet, early Mars hypothesis), and how we might determine their existence there today.

MECHANISMS OF MAKING IRON-FORMATIONS ON MARS

Dissolved oxygen

At present, the Martian atmosphere contains, on average, 0.13% O_2, in an atmosphere of about 7.5

$\times 10^{-3}$ bars CO_2, or about 10^{-5} bars of O_2 (OWEN, 1992). This oxygen is produced by the photolysis of water and CO_2, as it was described above for the prebiotic Earth. If there could be liquid water on the surface of Mars today, the upper layers, at least, would be oxygenated, and ferrous iron in solution could not exist. In the past, when there was more carbon dioxide and water vapor in the atmosphere of Mars, there might have been correspondingly more free oxygen as well. However, the oxygen produced in the atmosphere of Mars today is in contact with a highly-oxidized surface, whereas in the distant past it would not have been, and the oxygen in the atmosphere would have been decreased by its reactions with the surface materials and the cations in solution in water. The amount of oxygen in the atmosphere of Mars today is thought to be controlled by redox balance, such that the H escape rate is equal to twice the O escape rate (McELROY and DONAHUE, 1972) plus surface oxidation. Active volcanism in the past would have released H_2 and other reduced gases, which also would have lowered the p_{O_2} relative to present levels.

If an early Earth-type atmospheric model, such as that of CANUTO et al. (1983) or KASTING et al. (1984), is used to calculate the amount of oxygen in the atmosphere of Mars, it produces a much lower mixing ratio of oxygen than is presently seen. The CANUTO et al. (1983) model produces a surface oxygen mixing ratio for a solar UV flux of 1.7 times the present solar flux at Earth (appropriate for about 3.5 Gy ago, when the solar UV flux at Earth would have been about 4 times the present flux) and an atmosphere of 100 terrestrial PAL (2.8×10^{-2} bars) of approximately 10^{-13} (Fig. 2). If this model is further extrapolated to 10,000 terrestrial PAL, or 2.8 bars (a value that may have been necessary to produce enough of a greenhouse effect on Mars to raise the temperature above the freezing point of water), a mixing ratio of about 10^{-10} may be produced.

The KASTING et al. (1984) model, extrapolated in a similar fashion, also produces a surface oxygen mixing ratio of about 10^{-10} to 10^{-11}. It is not really a valid approximation to extrapolate either of these two models in this fashion, because there is a good deal of Earth-specific atmospheric chemistry in each of them, but it is useful to give us a vague approximation of the surface oxygen mixing ratio that might have been expected on early Mars.

Therefore, let us assume that the surface oxygen mixing ratio in the warm, wet period of early Mars may have been approximately 10^{-10} to 10^{-13}, based

on these two terrestrial models. This is more than enough oxygen to oxidize ferrous iron in solution so that it will precipitate out as ferric iron. [Note: There does appear to be a small stability field for siderite at f_{O_2} equal to 10^{-13} and below, and pH ≈ 6 (see Fig. 3, discussed in more detail later).] The problem with forming BIFs under these conditions, conversely, it that there must have been some mechanism for maintaining the ferrous iron in solution so that it could be transported. Possibly, any bodies of water on early Mars could have been deep enough and still enough (Mars, after all, can have had no tides) so that conditions near the bottom could have been anoxic.

Ultraviolet irradiation

Because Mars is only about 1.5 times as far from the Sun as is the Earth, the flux of UV (and other solar) radiation at its surface is only about a factor of 2.3 times less than that at the surface of the Earth. The yield of a photochemical process is di-
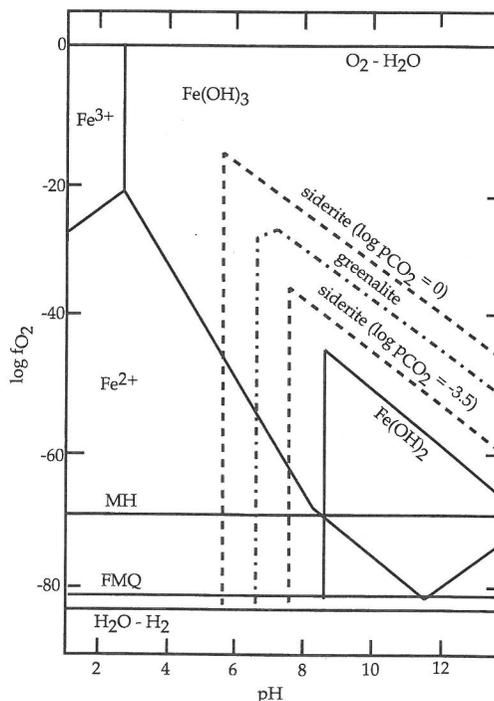

FIG. 3. Solubilities of $Fe(OH)_3$, $Fe(OH)_2$, greenalite (dot-dashes, in equilibrium with amorphous silica), and siderite (dashes, with a log p_{CO_2} of 0 and -3.5), at 25°C and a log total iron content of -4. The magnetite-hematite (MH) and fayalite-magnetite-quartz (FMQ) boundaries are also shown. Adapted from EUGSTER and CHOU (1973).

rectly proportional to the number of photons absorbed, so the efficiency of iron photoprecipitation on Mars at a given time should be about 2.3 times less than at the same time on Earth, if scattering and loss of UV flux through the atmosphere is disregarded. The range of iron photoprecipitation rates calculated by BRATERMAN *et al.* (1983) for Earth may be thus scaled to Mars, to get $65-320$ mg cm^{-2} yr^{-1} at the tropics or $22-110$ mg cm^{-2} yr^{-1} at the poles. These rates are still larger than the rate estimates for the terrestrial Hamersley BIF deposition ($9-43$ mg cm^{-2} yr^{-1} (TRENDALL and BLOCKLEY, 1979)), indicating that photoprecipitation of iron is a sufficient mechanism to produce BIFs on Mars as well.

Hydrogen peroxide

The same photochemical reactions that could have formed hydrogen peroxide in the early atmosphere of Earth could have acted in the early atmosphere of Mars. As a first approximation, one may look at the terrestrial model of KASTING *et al.* (1985), which determined that hydrogen peroxide is probably the dominant oxidant in rainwater at free oxygen levels less than $10^{-2}-10^{-3}$ PAL (about 2×10^{-3} to 2×10^{-4} bars). This model was also run with a mixing ratio of CO_2 of 100 PAL, and the H_2O_2 rain-out rate was found to decrease by only $5-30\%$. This implies that the crossover point between free oxygen or hydrogen peroxide as the major oxidant was probably the same, within an order of magnitude or so, on Mars as it was on Earth. The calculations for Mars above indicate that there may have been between 10^{-11} and 10^{-3} O_2 surface mixing ratio, or between 10^{-11} and 10^{-3} bars O_2, assuming a total atmospheric pressure of 1 bar. This range is from far less than the amount required to make free oxygen the dominant oxidant, to roughly the borderline between oxygen and hydrogen peroxide at the dominant oxidant. Based on this, hydrogen peroxide also was capable of precipitating BIFs on Mars.

Anoxic deposition

The anoxic model of terrestrial BIF formation developed by EUGSTER and CHOU (1973) attempts to explain not only iron-rich bands, but also the silica-rich chert bands. Their explanation of the formation of the chert bands is that these were originally deposited in the form of magadiite ($NaSi_7O_{13}(OH)_3 \times 4H_2O$). Magadiite, which is observed as the precursor to chert beds in Lake Magadi, in Africa, has a minimum in its solubility

curve at pH $= 8.6$ (EUGSTER and CHOU, 1973). This implies that magadiite can be precipitated by either evaporative concentration (raising the pH), or by flooding of silica-rich, high-pH brines by fresher, more acid waters. This mechanism is not dependent on any factors that are different on Mars than on Earth, and would therefore work equally well on Mars as it does on Earth.

The deposition of the iron-rich layers, in this anoxic model, is more complicated. The stabilities of various iron oxides, hydroxides, and iron carbonate relative to one another must be determined, to derive which species are stable under likely Martian conditions. The solubility of iron hydroxides and hydroxides depends on the f_{O_2} and the pH, and that of siderite ($FeCO_3$) depends as well on p_{CO_2}.

Figure 4 shows a predominance diagram (from EUGSTER and CHOU, 1973) for iron species in solution at 25°C. At low f_{O_2} the diagram is dominated by ferrous species, with Fe^{2+} being the most important at pH below 8. The pH of an early Martian ocean is likely to have varied between 5.4 (initially) and 10 (as the carbon dioxide in the atmosphere is reduced), over a time period of about 0.5 Gy, according to the model of SCHAEFER (1993). Therefore, at least at earlier times, ferrous iron should
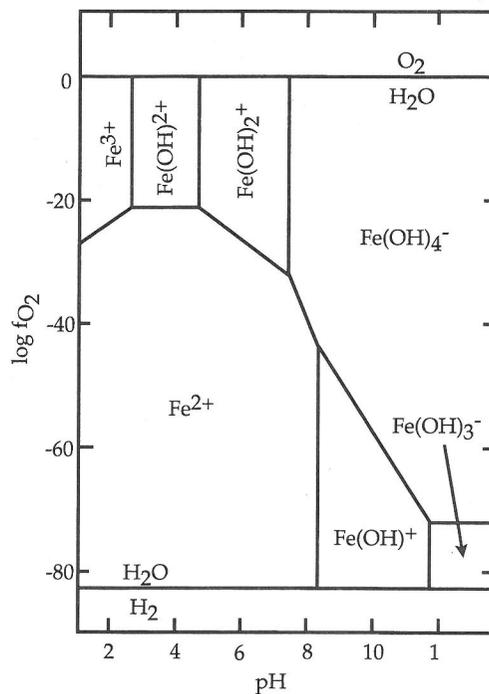

FIG. 4. Predominance diagram (adapted from EUGSTER and CHOU (1973) for iron species in solution at 25°C.
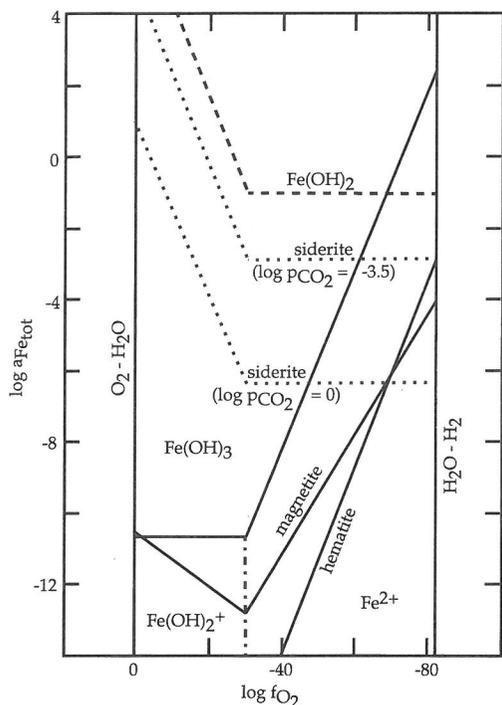
FIG. 5. The solubility of magnetite, hematite, siderite, and some iron hydroxides at a pH of 7 and 25°C, adapted from EUGSTER and CHOU (1973). The solubilities of $Fe(OH)_3$, magnetite, and hematite are shown as solid lines, $Fe(OH)_2$ as dashes, and siderite (at log f_{CO_2} of −3.5 and 0) as dots. The boundary between Fe^{2+} and $Fe(OH)_2^+$ is shown as dash-dot.

in Fig. 6. Under conditions of high p_{CO_2}, siderite will precipitate out at a much lower pH than calcite ($CaCO_3$). Siderite begins to precipitate at an iron concentration of only 0.5–0.05 ppm (log $a_{Fe^{2+}_{tot}}$ of 10^{-5}–10^{-6}) at low pH, and even lower at high pH.

Figure 3 is a log f_{O_2}-pH plot showing the comparative solubilities of $Fe(OH)_3$, $Fe(OH)_2$, greenalite ($Fe_3Si_2O_5(OH)_4$), and siderite, at 25°C and a log total iron content of −4, corresponding to about 5 ppm iron (after EUGSTER and CHOU (1973)). Under present terrestrial p_{CO_2} conditions, greenalite will precipitate preferentially to siderite at conditions of low f_{O_2} and moderate pH. However, in the higher pH regime thought to exist on early Mars, siderite will precipitate preferentially. If the log f_{O_2} is higher, above about −15 at a pH of 6, then $Fe(OH)_3$ is the preferential phase of iron in this system.

In summary, while the terrestrial anoxic model of EUGSTER and CHOU (1973) produces iron-rich layers that are dominated by calcite + greenalite, with some siderite present, the Martian version of this model strongly favors the precipitation of siderite. Both models produce chert bands, originally deposited as magadiite.

DISCUSSION

The application of abiotic models of producing terrestrial BIFs to the conditions likely on early

have been highly mobile in relatively anoxic waters (log f_{O_2} < ~ −20) on Mars. As was mentioned above, the atmosphere of Mars is now, and may always have been, oxidizing, but still waters may have been anoxic at depth. Also, groundwater that is not in direct contact with the atmosphere (*i.e.*, it has a long residence time in the aquifer) can be extremely anoxic, particularly if it is buffered by a redox buffer (such as Fe^{2+}–$Fe(OH)_3$ or Fe^{2+}–Fe_2O_3) (DREVER, 1988).

Figure 5 (after EUGSTER and CHOU, 1973) shows the solubility of magnetite, hematite, siderite, and some iron hydroxides at a pH of 7 and 25°C. The chief feature of interest here is the change in solubility of siderite with change in p_{CO_2}, it being far more stable under conditions of high p_{CO_2}, for any value of oxygen fugacity. At log f_{O_2} values of less than about −50, and a p_{CO_2} of 1 bar, siderite is preferentially precipitated over $Fe(OH)_3$.

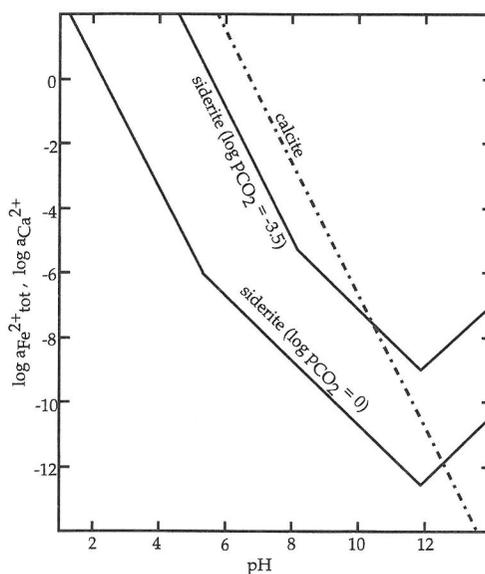The solubility of siderite relative to calcite for low f_{O_2} (after EUGSTER and CHOU (1973)) is seen

FIG. 6. Comparison of the solubilities of calcite and siderite, at low f_{O_2} and 25°C, adapted from EUGSTER and CHOU (1973). Siderite curves are drawn for log f_{CO_2} of −3.5 and 0.

Mars indicates that these deposits could have formed there, as they did on Earth. How can we determine if BIFs do indeed exist on Mars? And if they do, what implications does the existence of BIFs on Mars have for the evolution of the Martian atmosphere and hydrosphere?

Observations

The three mechanisms of BIF formation involving free oxygen, photoprecipitation, or hydrogen peroxide all produce deposits of FeO(OH). Under different formation conditions, FeO(OH) will precipitate in different crystal phases: α-FeO(OH) (goethite), β-FeO(OH) (akaganeite), γ-FeO(OH) (lepidocrocite), δ-FeO(OH), or δ'-FeO(OH) (feroxyhyte) (BURNS, 1993). Akaganeite may subsequently transform to either goethite or hematite (α-Fe$_2$O$_3$); lepidocrocite may revert to maghemite (γ-Fe$_2$O$_3$); feroxyhyte may transform to goethite, hematite, or mixtures of the two (BURNS, 1993). Many of these phases have been suggested as existing on the surface of Mars (*e.g.,* BURNS, 1980; HARGRAVES *et al.,* 1979; MORRIS *et al.,* 1989; MORRIS and LAUER, 1990; SINGER, 1982), but in the present Martian environment, hematite may be the only stable iron oxide (GOODING, 1978).

Under Martian conditions, the anoxic mechanism of BIF formation produces deposits of siderite. Siderite is unstable under present Martian conditions, and is converted via gas-solid decomposition into hematite (GOODING, 1978). Nanocrystalline hematite is a strong candidate to exist on the Martian surface (MORRIS *et al.,* 1989; MORRIS and LAUER, 1990), and a nanophase product could be expected as a result of gas-solid decomposition of siderite.

BURNS (1993) suggested that the bright deposits littering the Argyre and Hellas basins could be composed of dust derived from dessicated hydrous iron oxide-silica deposits that remained there after the water had evaporated from these deep depressions.

There is evidence, therefore, that one source for the iron oxides that are observed on Mars may be iron-formations. However, this is not the only possible source, because hematite and other iron oxides could have formed as weathering rinds on the rocks of the surface, without having been transported in solution, or could have formed by hydrothermal processes, in the presence of groundwater alone.

Spectroscopic data alone, whether ground-based or from a Mars-orbiting spacecraft, are not enough to determine the existence of BIFs on Mars, because the only surface expression of BIFs we expect is hematite.

As a result, in order to determine the existence of BIFs on Mars, we must see below the surface. A lander capable of penetrating past the uppermost weathered layer of the surface could, perhaps even by visual inspection alone, determine the existence of BIFs on Mars. Terrestrial BIFs form deposits of iron oxides and silica, with other associated minerals, which are quite distinctive in hand specimens. Adding to this simple visual inspection any spectoscopic measurements would enable easier identification, especially if the proposed Martian iron-formations do not have the same banded structure as the terrestrial ones. On Mars, one would wish to examine shallowly-buried impact debris in the northern plains or in large basins, such as Hellas or Argyre. It is in these localities that one might expect to find evidence of BIFs on Mars, should they exist. By examining impact debris we increase greatly the depth of sampling into the solid bedrock of the planet over what any feasible lander might be able to sample on its own. And by looking at shallowly-buried debris, such as might still be accessible to a lander, we allow the possiblilty of finding some material that has not entirely been altered to hematite.

The Mars Pathfinder, to be launched in 1996, is not likely to find evidence for iron-formations, because it will not be looking beneath the surface. The Mars Volatiles and Climate Surveyor, proposed for launch in 1998, has the necessary instumentation to search for iron-formations, but will be visiting the south polar cap region, which is not a likely place to find iron-formations on Mars. We will have to wait for one of the later Mars Surveyor missions to search for iron-formations on Mars.

Implications

If iron-formations are found on Mars, this will be confirmation of those models of the early environment of Mars that include the existence of a warm, wet atmosphere and bodies of liquid water. Their existence implies the existence of liquid water basins, probably of significant depth, and of a active weathering profile on the land, supported by a groundwater system and possibly rain as well. If it is possible to determine which of the different formation mechanisms produced the BIFs, at least between the oxidizing mechanisms (producing FeO(OH)) and the anoxic mechanism (producing siderite), then we can place limits on the oxygen fugacity of the early Martian atmosphere, or on the necessary depth of ocean basins.

In all the abiotic mechanisms of BIF formation discussed above, gaseous hydrogen is produced.

On Mars, this hydrogen will be lost from the upper atmosphere, contributing to the oxidation of the planet, and to the loss of its water to space. There is not likely to be a large isotopic effect due to banded iron formation, other than that resulting from preferential escape of D to space relative to H (Bruce Jakosky, personal communication).

Hydrothermal systems. The existence of hydrothermal systems could have a strong impact on the geochemical evolution of the surface and atmosphere of Mars (JAKOSKY and JONES, 1986). Hydrothermal systems could have relevance to the formation of BIFs on Mars as well. On Earth, hydrothermal plumes in the ocean have been suggested as a means of supplying the iron-rich fluids necessary to precipitate iron-formations (ISLEY, 1995; MORRIS, 1993). In the more volcanically-active environment of early Mars (compared to present-day Mars), such hydrothermal circulation systems could have existed as well, driven either by volcanism or by large impacts (NEWSOM, 1980). Such circulation cells below the lakes or oceans of Mars could have provided iron-rich fluids to these bodies of water. Martian hydrothermal systems in the crust could also provide additional cations to the groundwater, which would then flow into bodies of standing water.

Hydrothermal systems could have existed on Mars for a much longer time than the warm, wet period is likely to have existed. As these systems transported cations through the crust, they may also have deposited iron minerals there. If the groundwater was relatively anoxic, then ferrous iron would have been freely transported in it. If the water erupted onto the surface, as might have happened in the formation of the catastrophic outflow channels, and the atmosphere was relatively oxygen-rich, then ferric iron minerals could have been precipitated. One would expect, then, to find $FeO(OH)$ (now converted to hematite?) in the outwash plains of these channels. If the hydrothermal circulation systems remained below the surface, but gradually cooled and stopped circulating, the increase in pH of the fluid would drive the precipitation of siderite. Neither of these types of deposits are banded iron-formations, but the chemistry involved in their formation is the same.

CONCLUSIONS

There are several abiotic mechanisms for producing banded iron-formations on Earth. These are: (1) oxidation of ferrous iron by free oxygen, (2) photooxidation of ferrous iron, (3) oxidation of ferrous iron by hydrogen peroxide, and (4) anoxic precipitation of ferrous iron by changes in pH. Any of these mechanisms could have been active on Mars in its distant past, to produce BIFs there as well, which should be observable today.

The minerals one would expect to observe on the surface of a BIF on Mars are indeed thought to exist on Mars, but unfortunately BIFs are not unique in containing these minerals, and confirmation of the existence of BIFs on Mars will have to wait for more data. Proof of the existence of BIFs on Mars would give us valuable information about the early history of the planet, and about Earth. It would act to confirm models of Mars that include a warm, wet period, and the existence of bodies of standing water.

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