The photochemistry of manganese and the origin of banded iron formations

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Abstract—The photochemical oxidation of Fe$^{2+}$-hydroxide complexes dissolved in anoxic Precambrian oceans has been suggested as a mechanism to explain the deposition of Banded Iron Formations (BIFs). Photochemical studies have not yet addressed the low levels of manganese in many of these deposits, which probably precipitated from solutions bearing similar concentrations of Fe$^{2+}$ and Mn$^{2+}$. Depositional models must also explain the stratigraphic separation of iron and manganese ores in manganiferous BIFs.

In this study, solutions containing 0.56 M NaCl and $\approx$180 $\mu$M MnCl$_2$ with or without 3 to 200 $\mu$M FeCl$_2$ were irradiated with filtered and unfiltered UV light from a medium-pressure mercury-vapor lamp for up to 8 hours. The solutions were deaerated and buffered to pH $\approx$ 7, and all experiments were conducted under O$_2$-free (< 1 ppm) atmospheres. In experiments with NaCl + MnCl$_2$, approximately 20% of the Mn$^{2+}$ was oxidized and precipitated as birnessite in 8 hours. Manganese precipitation was only observed when light with $\lambda < 240$ nm was used. In experiments with NaCl + MnCl$_2$ + FeCl$_2$, little manganese was lost from solution, while Fe$^{2+}$ was rapidly oxidized to Fe$^{3+}$ and precipitated as $\gamma$-FeOOH or as amorphous ferric hydroxide. The Mn:Fe ratio of these precipitates was $\approx$1:50, similar to the ratios observed in BIFs.

A strong upper limit on the rate of manganese photo-oxidation during the Precambrian is estimated to be 0.1 mg cm$^{-2}$ yr$^{-1}$, a factor of $10^3$ slower than the rate of iron photo-oxidation considered reasonable in BIF depositional basins. Thus, a photochemical model for the origin of oxide facies BIFs is consistent with field observations, although models that invoke molecular O$_2$ as the oxidant of Fe$^{2+}$ and Mn$^{2+}$ are not precluded. Apparently, oxide facies BIFs could have formed under anoxic, as well as under mildly oxygenated atmospheres.

INTRODUCTION

The extensive deposition of Superior-type Precambrian Banded Iron Formations (BIFs) between 3.8 and 1.9 Ga ago has long been used to place limits on the redox state and level of biological activity on the early Earth (see, for instance, JAMES, 1954; CLOUD, 1973; GARRELS et al., 1973). Today, oxide-facies BIFs are commonly taken as evidence that free oxygen existed in the atmosphere as early as 3.8 Ga ago; photosynthetically derived oxygen, on the order of $10^{-5}$-$10^{-2}$ times the present atmospheric level (PAL), is thought to have converted Fe$^{2+}$ dissolved in upwelling anoxic marine waters to Fe$^{3+}$, followed by the precipitation of flocculent Fe$^{2+}$/Fe$^{3+}$ hydroxides in restricted ocean basins (for reviews of the relevant literature, see TRENDALL and MORRIS, 1983; WALKER et al., 1983; HOLLAND, 1984; KASTING, 1987).

However, the conversion of ferrous to ferric iron does not require molecular oxygen. CAIRNS-SMITH (1978) has suggested that Fe$^{2+}$ could have been oxidized photochemically by solar UV radiation in the absence of O$_2$. The photo-oxidation of dissolved iron has been studied extensively (e.g., JORTNER and STEIN, 1962; BRATERMAN et al., 1983, 1984; SLOPER et al., 1983; BOROWSKA and MAUZERALL, 1987). In acidic solutions (pH < 6), the aqueous ferrous iron complex is the absorbing species:

\[ \text{2Fe}^{2+}(aq) + 2H^+ \rightarrow \text{2Fe}^{3+}(aq) + H_2 \]

($\lambda_{\text{max}} \approx 254$ nm). (1)

The quantum yield for the overall reaction is 0.06 $\pm$ 0.03 (SLOPER et al., 1983).

The pH of the oceans during the peak period of BIF deposition was probably ca. 7.0 (WALKER et al., 1983; HOLLAND, 1984). In dilute, near-neutral solutions, the rate of photo-oxidation of Fe$^{2+}$ is increased by the presence of the complex FeOH$^+$($aq$), which is sensitive to wavelengths > 300 nm. Quantum yields of 0.01-0.05 for Fe$^{2+}$ oxidation have been measured at 366 nm (BRATERMAN et al., 1984). BRATERMAN et al. (1983) and FRANCOIS (1986, 1987) have estimated that, in areas of vigorous upwelling, irradiation of waters containing $10^{-5}$-$10^{-2}$ M total dissolved iron by solar UV (300 nm < $\lambda < 450$ nm) could have precipitated iron at rates in excess of 100 mg cm$^{-2}$ yr$^{-1}$. This mechanism could therefore account for the precipitation of the 9-43 mg cm$^{-2}$ yr$^{-1}$ estimated for the Hamersley Basin BIFs (TRENDALL and BLOCKLEY, 1970).

We have studied the effect of UV radiation on dissolved manganese to determine if the photochemical model for BIF formation is consistent with the distribution of this element in BIFs. Manganese is of interest, because it was probably present in considerable concentrations in the solutions from which these deposits precipitated: the Mn:Fe molar ratios in the high-temperature "black smoker" vent solutions along mid-ocean ridges are typically 1:3 (see, for instance, EDMOND et al., 1982), and recent isotopic and REE studies suggest strongly that marine hydrothermal systems were major sources of iron in BIFs (DYMEK and KLEIN, 1988; JACOBSEN and PIMENTEL-KLOSE, 1988a,b; KLEIN and BEUKES, 1989; DERRY and JACOBSEN, 1990). Under anoxic conditions, Precambrian seawater saturated with respect to rhodochrosite...
and calcite could have supported on the order of 100 μM Mn²⁺ as aquo, organic, and inorganic complexes (Cerar et al., 1980b). This is consistent with the elevated manganese and iron contents observed in Archean carbonates (Veizer et al., 1990).

Oxide facies BIFs are typically Mn-poor. Their bulk Mn/Fe ratio is usually close to the crustal average of ~1:60 (Roy, 1980), and the manganese concentration of the Fe-rich bands is less than 1.0% by weight (Davy, 1983). When manganese ore deposits are present in BIFs, they are unevenly distributed; lenticular manganese oxide bands are conformably enclosed by Fe-rich strata. The manganese ores themselves may be banded, with layers of hausmannite, cryptomelane, braunite, and manganese carbonates alternating with Mn-poor cherts (Dorr, 1945; Cerar et al., 1980a).

The Hotazel formation of the Transvaal Supergroup in South Africa is the most spectacular example of a manganiferous oxide facies BIF (Reeves, 1973; Kleyenstuber, 1984; Nel et al., 1986). Interbedded iron and manganese oxide deposits also occur in the Morro de Urucum BIF in Brazil (Dorr, 1945; Hoppe et al., 1987). Carbonate and/or silicate facies formations containing manganese oxides include the meta- morphosed Brazilian Minas Series (Dorr, 1973), the Canadian Wabush Iron-Formation (Klein, 1966), and the Champion Mine, Marquette County, Michigan (Babcock, 1968).

Theories for the deposition of oxide facies BIFs must be consistent with the absence of manganese oxides from most BIFs, and with the separation of manganese ores from iron ores in manganiferous BIFs. Theories based on the oxidation of Fe³⁺ and Mn²⁺ by molecular oxygen meet this test, since the oxidation of Mn¹⁺ by atmospheric O₂ is known to be far slower than the oxidation of Fe²⁺ in the pH range 7–8 (Krauskopf, 1957; Stumm and Morgan, 1981). Iron oxides would therefore have precipitated well before manganese oxides from mildly oxygenated Precambrian seawater, and unoxidized Mn²⁺ might well have been flushed out of areas of BIF precipitation. Manganese might have accumulated within some BIF basins due to unusually long residence times of the Fe- and Mn-enriched seawater, or due to Eh/pH fluctuations, or due to microbial catalysis (e.g., Cerar et al., 1980b; Sundah and Huntsman, 1987). We have tried to determine whether photochemical models can account equally well for the observed distribution of manganese in Precambrian BIFs.

**MATERIALS AND METHODS**

Dilute solutions of FeCl₃ and/or MnCl₂ dissolved in deaerated, deionized water were prepared in a custom-built 750 mL Suprasil quartz reaction vessel (Fig. 1). Reagents were added through one of three inlets at the top of the reaction vessel. Fe⁴⁺ was introduced as 99% FeCl₃·4H₂O, and Mn²⁺ as 98% MnCl₂. Initial concentrations of these ions ranged from 3–200 μM (~0.1–10 ppm). Water was deaerated prior to the addition of these solutes by bubbling a deoxygenated O₂ < 1 ppm 2.0% CO₂ in Nz gas mixture through the water for 2–3 h. This procedure reduces oxygen concentrations to 1–10 μM (Conklin, 1986), low enough to prevent loss of a significant fraction of the dissolved Fe²⁺ and/or Mn²⁺ in these systems by reaction with O₂ (see runs C1–C4, Table 1). The oxygen content of the solutions was monitored continuously during preparation and following irradiation by a micro-oxygen electrode and digital meter (Microelectrodes, Inc. immersible MI-730 electrode and OM-2 meter). Positive pressure in the reaction vessel was maintained during all manipulations and irradiations to ensure that no oxygen entered the system.

Most reactions were run in 0.56 M NaCl. Solutions were buffered to pH 7.3 using approximately 1 × 10⁻² M NaHCO₃. NaCl and NaHCO₃ were the only reagents other than FeCl₃ and MnCl₂ that were added to the system. The NaCl and NaHCO₃ were both of analytical grade. pH measurements were made in situ using a semi-micro combination electrode (Orion 91-03 electrode and 407A meter), pH levels were measured before and after irradiation to ensure that pH had not changed.

A Canrad-Hanovia 450 W medium-pressure mercury-vapor lamp was used to illuminate the reaction vessel from one side. This lamp delivered output from roughly 180–1400 nm, with superimposed mercury emission lines. In some experiments, a Vycor glass filter with 5% transmission at ~240 nm and cutoff at 210 nm was used. The distance between the lamp and the reaction vessel was approximately 20 cm. Reaction mixtures were magnetically stirred during preparation and irradiation.

Glassware in contact with solutions containing Fe⁴⁺ accumulated acid-resistant iron oxide coatings as described by Brateman et al. (1984). Irradiated manganese solutions left acid-soluble residues. All glassware was rinsed with sodium dithionite solutions and deionized water between experiments.

Solution samples (2.0 mL) were collected before and after irradiation for later analysis. In some experiments, samples were taken at regular intervals during irradiation (e.g., runs C5, 11, 12, 14; see Table 1). Samples were drawn by purged syringe through 0.22 μm Gelman Acrodisc syringe-tip filters to separate dissolved Fe²⁺ and/or Mn²⁺ from particulate and colloidal iron and/or manganese species. All samples were mixed with 1.0 ml, 1.0 M HCl (analytical grade), and stored in glass vials for later analysis using standard graphite furnace techniques on a Perkin-Elmer 3030 atomic absorption spectrophotometer.

Precipitates were quantitatively recovered by filtering solutions through 0.22 μm Milipore GS membranes (37 mm diameter) in a sealed, anoxic filtration apparatus under positive pressure. Qualitative analysis of precipitates was carried out on a Cameca MBX electron microprobe using wavelength dispersive spectrometers (beam voltage: 15 keV; beam current: 15 namps; beam size: 120 μm). Fayalite and tephroite were used as standards for iron and manganese, respectively. Precipitates were also analyzed by X-ray powder diffractometry.

**RESULTS**

Our results are presented below and are summarized in Table 1, and in Fig. 2a,b.

**Control Experiments—No Irradiation: Runs #C1–C4**

In these control experiments, buffered, deaerated, saline solutions containing approximately 180 μM Fe²⁺ and 180 μM Mn²⁺ were stirred continuously for four hours under positive pressure. The solutions were shielded from all light. No significant changes were observed in the concentration of iron. The concentration of manganese in the final solutions was not determined.

**Manganese Experiments: Runs #1–7**

Irradiation of solutions containing ~180 μM manganese resulted in the formation of dark greyish-brown particles. These tended to clump into loose 1–2 mm agglomerates. An orange-brown film to which precipitate particles adhered formed on the irradiated side of the reaction vessel. Following irradiation, solutions were tinted slightly brown. Dissolved manganese concentrations fell approximately 20% during 450 min of irradiation (see Fig. 2a).
Origin of BIF's by photochemical oxidation of Fe\(^{2+}\)

No manganese precipitated when UV light was passed through a Vycor filter (50% transmission @ 240 nm, cutoff @ 210 nm) before entering the reaction vessel, and no change in the dissolved manganese concentration was detected (runs #4 and 5). Precipitate was observed following a second irradiation of the same solution with unfiltered light (see Table 1).

On filters, precipitates from manganese experiments formed dark brown/black layers. Upon drying, these layers cracked into warped platelets up to 1 mm across. Microprobe analysis revealed the presence of only trace amounts of iron. The precipitates showed strong XRD peaks at 7.17 Å and 3.55 Å. These d-spacings are diagnostic of birnessite (“7 Å manganite”), a hydrated manganese oxide (BURNS and BURNS, 1979).

Manganese Plus Iron Experiments: Runs #8–14

At the end of the irradiations, the solutions from these runs were tinted orange; and granular, yellowish-orange precipitates had formed. These were either XRD-amorphous or yielded peaks at 6.33 Å, 3.29 Å, 2.47 Å, and 1.94 Å, consistent with the presence of γ-FeOOH in the precipitates, as seen by BRATERMAN et al. (1983) following irradiation of solutions containing only iron.

In runs #11 and 12, no manganese was lost during the irradiation of the solutions initially containing ≈90 µM dissolved iron. However, some 85% of the iron precipitated from these solutions during irradiation (see Fig. 2b). A solution initially containing 202 ± 16 µM iron (run #8) lost nearly 40% of its dissolved iron during irradiation, but no drop in the manganese concentration was observed. Microprobe analysis showed that the precipitate from this run had a Mn:Fe ratio of approximately 1:50.

In run #14, the manganese loss was <10%, while the iron concentration fell by over 99% from an initial value of 28 ± 14 µM during the course of irradiation.

In runs #9 and 10, solutions containing ≈180 µM Fe\(^{2+}\) and 180 µM Mn\(^{2+}\) were irradiated with Vycor-filtered light. The precipitates from these runs were indistinguishable from those obtained by irradiation with unfiltered light, but the quantity of precipitate was somewhat smaller. Microprobe analysis showed that the Mn:Fe ratio in the precipitates from these runs was ≈1:50.

DISCUSSION

Analysis of Experimental Results

The formation of birnessite during irradiation of solutions containing Mn\(^{2+}\) indicates that Mn\(^{2+}\) can be oxidized photochemically. While birnessite is not found in association with BIFs, it may have altered diagenetically to hausmannite (Mn\(_3\)O\(_4\)) or to cryptomelane (KMn\(_8\)O\(_{16}\); FRENZEL, 1980), which are common phases in the Hotazel and Urucum BIFs, respectively (KLEYENSTUBER, 1984; HOPPE et al., 1987).

The oxidation probably proceeds by UV-stimulated electron transfer from Mn\(^{2+}\) to another dissolved species, followed by disproportionation of the resulting Mn\(^{3+}\) to form an oxide precipitate:

\[
Mn^{2+} + A^{x+} \rightarrow Mn^{3+} + A^{(x-1)+} \quad (2)
\]

\[
2Mn^{2+} + 2H_2O \rightarrow Mn^{2+} + MnO_2(s) + 4H^+ \quad (3)
\]

The photo-active species in Eqn. (2) are probably Mn\(^{2+}\)(aq), or chloride or carbonate complexes of Mn\(^{2+}\), as these were the major equilibrium species in our system. The identity of the electron receptor, A\(^{x+}\), is unknown. In our system, likely candidates are H\(^{+}\) (as observed in the case of iron photo-oxidation by BRATERMAN et al., 1983, and BOROWSKA and
TABLE 1. Results of photo-oxidation experiments

<table>
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<th>Run #</th>
<th>[NaCl] (mM)</th>
<th>Initial [Fe] (μM)</th>
<th>Initial [Mn] (μM)</th>
<th>Duration (minutes)</th>
<th>Final [Fe] (μM)</th>
<th>Final [Mn] (μM)</th>
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<td>164.5±1.5</td>
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<td>167.3±3.6</td>
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<td>0.2±0.2</td>
<td>165.5±2.7</td>
<td>A,D,E(1)</td>
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A = Solution turned orange-brown.  
B = Very fine, light-orange particles visible.  
C = Solution turned faintly brown.  
D = Dark grey-brown particles visible.  
E = Particles clumped together in agglomerations up to (1) mm across.  
F = No discoloration or precipitate observed.  
G = Particles adhered to side of reaction vessel facing lamp.  
H = Failure in lamp’s power supply invalidates this result.  
K = Fe/Mn ratio of (#), from microprobe analysis.  
{#} denotes Vycor-filtered radiation.  
N/A indicates that no measurement was made.  

Uncertainties are reported as ± 2σ.

Mauzerall, 1987) or dissolved CO2. In Precambrian waters, other dissolved metals or organic compounds could have been important electron acceptors. Dissolved organic compounds could also have inhibited photo-oxidation, via photo-reduction reactions similar to those observed in modern waters (e.g., Sundan et al., 1983; Zafriou et al., 1984). These processes are discussed below.
absorption by the Mn(H$_2$O)$_3^+$ complex has been observed in acidic solutions in the range 300–800 nm, with an extinction coefficient of 70 M$^{-1}$ cm$^{-1}$ at 470 nm (BAES and MESMER, 1976). However, this mechanism is unlikely at near-neutral pH, given the value of $K_{eq}$ for Eqn. 3 (BAES and MESMER, 1976). The possibility of photon absorption by Mn$^{3+}$ hydrolysis products or complexes of Mn$^{3+}$ with chloride, carbonate, or bicarbonate cannot be excluded. Oxidation of either Mn$^{2+}$ or Mn$^{3+}$ by photochemically generated chlorine radicals may occur but probably plays a minor role, since the rate of Mn$^{2+}$ oxidation seems independent of the Cl$^-$ concentration between 0.56 M and < 1 mM (compare runs #2 and 3 with runs #6 and 7).

Results from experiments using Vycor-filtered light (runs #4, 5, 9, and 10) showed that there is no detectable reaction of Mn$^{2+}$ with UV light of $\lambda$ > 240 nm. This observation is consistent with the 225 nm long-wavelength limit of the Mn$^{2+}$(aq) electron-transfer spectrum (DAINTON and JAMES, 1951) and the position of the peak of this transition (ORGEL, 1955). The absorption of Mn$^{2+}$-chloride complexes is weak beyond 240 nm in aqueous solutions (GOODKIN et al., 1975). No absorption data are available for manganese-carbonate complexes.

The intensity of radiation below 180 nm was minimal in our system due to the low output of the Mercury lamp in this range, and due to UV absorption by quartz. We therefore consider 180–240 nm to be the photo-active range for manganese photo-oxidation in our experiments. This also would have been the relevant range on the Earth’s surface under an O$_2$-free atmosphere, since photons below 180 nm are absorbed by atmospheric CO$_2$ and H$_2$O.

The experimental data show that the rate of oxidation of Mn$^{2+}$ in solutions that also contain Fe$^{2+}$ is much slower than the rate in Fe$^{2+}$-free solutions. In fact, little or no significant removal of manganese was observed in any solution that contained both cations, a result consistent with the observed low concentration of manganese in oxide facies BIFs. The reasons for the difference in the behavior of Mn$^{2+}$ in solutions containing Fe$^{2+}$ from that in Fe$^{2+}$-free solutions is at least partially due to reflection, absorption, and scattering of light by flocculent Fe$^{2+}$/Fe$^{3+}$ precipitates. Additionally, the thermodynamically favorable reaction

$$\text{Fe}^{2+}(aq) + \text{Mn}^{3+}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq)$$

($\Delta G^0 \approx -75 \text{ kJ mol}^{-1}$)

could have interfered with manganese photoprecipitation. However, the effect of dissolved Fe$^{2+}$ was probably small, since very little, if any, manganese was removed from solution even after the nearly complete removal of iron from the solution in run #14.

Precipitates from a solution containing iron and manganese in equal concentrations had a Mn:Fe ratio of $\approx 1:50$. Such low manganese concentrations are typical of oxide facies BIFs. TRENDALL and MOLLY (1983) reported Mn:Fe ratios $\leq 1:250$ in Hamersley Basin BIFs. DORR (1945) reported Mn:Fe ratios between 1:100 and 1:700 in the hematite layers of the Mooy de Urucum formation. The small amount of manganese in these BIFs and in the precipitates from our experiment is probably due to adsorption of manganese on hydrous iron oxides (e.g., VARENTSOV et al., 1980; DAVIES and MORGAN, 1989).

Implications for BIF Deposition

The experimental results and the observed distribution of manganese in oxide facies BIFs are qualitatively consistent. A quantitative analysis requires information on the relative rates of manganese and iron photo-oxidation. The experimental data are suggestive on this point; the rate of iron photo-oxidation was higher than that of manganese in our experiments, even when manganese was studied separately (compare $d[Mn]/dt$ in Fig. 2a with $d[Fe]/dt$ in Fig. 2b). However, this observation is uninterpretable because the intensity of the Mercury lamp between 180 and 240 nm is not known relative to the flux between 300 and 450 nm, which oxidizes FeOH$^+$. The relative intensity of the modern solar flux in this wavelength region is known: the 250–450 nm flux is $\approx$75 times greater than the flux below 250 nm (WEAST, 1982). The UV output of the sun between 2 and 3 billion years ago may have been greater than it is today (CANUTO et al., 1982), so the value of this ratio may have been smaller by a factor of two or three. Thus, it is tempting to suggest that the rate of manganese photo-oxidation was slower than that of iron photo-oxidation in the Precambrian oceans under an O$_2$-free atmosphere, even if the apparent inhibition of manganese photo-oxidation in the presence of iron is neglected. This is consistent with the distribution of manganese in oxide-facies BIFs, which demands that the oxidation of
iron was more rapid than that of manganese. It is also consistent with the apparent loss of Mn from clastic sediments and the precipitation of this Mn with carbonate sediments older than \( \approx 2 \) Ga (Kump and Holland, 1992). It is worthwhile, then, to attempt setting an upper limit on the rate of manganese photo-oxidation on an anoxic Earth, even though this requires a number of unproven assumptions.

The rate of Mn\(^{2+}\) photo-oxidation (\( \theta_{\text{Mn}} \), expressed as mg cm\(^{-2}\) yr\(^{-1}\)) can be modeled using the equation (Zafiriou et al., 1984; François, 1987):

\[
\theta_{\text{Mn}} = (3.15 \times 10^7 \text{ s yr}^{-1}) (5.49 \times 10^4 \text{ mg mol}^{-1})
\times \frac{0.5[\text{Mn}^{2+}]}{6.02 \times 10^{23} \int_0^{240 \text{ nm}} \int_{180 \text{ nm}} \phi_{\lambda} \varepsilon_{\lambda} F(\lambda, z) d\lambda dz},
\]

(4)

where

\[
F(\lambda, z) = F_0 10^{-k_{\lambda} z / \cos \omega},
\]

(5)

and

\[
k_{\lambda} = \sum_i \varepsilon_i [X_i].
\]

(6)

In these equations, \( \lambda \) is the wavelength; \( \phi \) is the quantum yield; \( \varepsilon \) is the molar absorptivity (M\(^{-1}\) cm\(^{-1}\)); \( F_0 \) is the photon flux at the Earth's surface (quanta cm\(^{-2}\) s\(^{-1}\) nm\(^{-1}\), West, 1982); \( z \) is the depth (we have considered the upper 100 m of the oceans); \( \omega \) corrects for the incident angle of the radiation (\( \omega = 35^\circ \), following François, 1987); and the factor 0.5 corrects for diurnal variations in the incident flux. The parameter \( k_{\lambda} \) accounts for the absorptivity for seawater. The \( X_i \) are the species contributing to absorption. In Eqn. (4), the concentration of Mn\(^{2+}\) is assumed to be constant with depth, representing a homogeneous mixed layer. This assumption is not entirely unrealistic, since BIFs were probably deposited in regions of strong upwelling, where advective velocities may be \( 10^3 \) times the global average value in the open oceans (François, 1986). In any case, this assumption is consistent with our goal of obtaining an upper limit.

In addition to Mn\(^{2+}\)-complexes, species such as Cl\(^-\), Br\(^-\), I\(^-\), HCO\(_3\)\(^-\), CO\(_3\)\(^{2-}\), Fe\(^{2+}\), FeOH\(^+\), NO\(_3\)\(^-\), and OH\(^-\), as well as a variety of trace metals and their complexes, absorb 180-240 nm radiation. Water also attenuates UV through absorption and scattering (Baker and Smith, 1982). In our calculations, we have included the effects of Cl\(^-\), Br\(^-\), HCO\(_3\)\(^-\), Fe\(^{2+}\), and FeOH\(^+\) on the radiation field, since these would have been the dominant UV-absorbing inorganic species in BIF depositional settings (although Fe\(^{3+}\) is a strong UV absorber, the solubility of Fe\(^{3+}\) hydroxides is too low to support significant quantities of dissolved ferric iron). The possible influence of dissolved organic matter is discussed below. The concentrations of Cl\(^-\), Br\(^-\), and HCO\(_3\)\(^-\) were set equal to their modern levels ([Cl\(^-\)] = 0.56 M; [Br\(^-\)] = 813 \( \mu \)M; [HCO\(_3\)\(^-\)] = 2400 \( \mu \)M), while iron and manganese were included at concentrations reasonable for an anoxic ocean ([Fe\(^{2+}\)] = 0.10 \( \mu \)M, as discussed above). The concentration of FeOH\(^+\) (0.32 \( \mu \)M) was calculated from [Fe\(^{2+}\)] and pH, using \( K_{\text{eq}} = 3.2 \times 10^{-10} \text{ mol dm}^{-3} \) (Baes and Messmer, 1976).

Figure 3a depicts the attenuation of 180-450 nm radiation in this simplified Precambrian ocean model. The wavelengths necessary for manganese photo-oxidation are dramatically attenuated with increasing depth, due to absorption by chloride, bromide, and bicarbonate. In contrast, the attenuation of radiation between 300 and 450 nm is much more gradual. The absorption data used in these calculations are shown in Fig. 3b. Absorption data for chloride, bromide, and bicarbonate are from Rabinowitch (1942). Fe\(^{3+}\) data are from Ehrenfreund and Leibenguth (1970) and are in agreement with Heinrich and Seward (1990). Absorption data for FeOH\(^+\) are those of Ehrenfreund and Leibenguth (1970) divided by 13 to match the more recent measurement at 366 nm by Brateman et al. (1983). Absorption data for manganese, which was assumed to be present as chloride complexes (discussed in the following text), are from Goodkin et al. (1975). Extrapolations from published data were necessary for iron species below 220 nm and for manganese species below 215 nm. In these extrapolations, the absorptivities at short wavelengths were assumed to be equal to the lowest wavelength published value. This procedure is no doubt inaccurate. However, since Cl\(^-\) and Br\(^-\) absorb very strongly at these wavelengths, our results are insensitive to errors in these extrapolations, even if the extrapolated absorptivities have been underestimated by factors of \( 10^2-10^3 \).

The attenuation of solar UV in the early Precambrian oceans was undoubtedly somewhat different from that in Fig. 3. However, it is likely that the Cl\(^-\) and Br\(^-\) concentrations in seawater were not very different from those in the modern oceans, as seen in seawater were not very different from those in the modern oceans (François, 1986). In any case, this assumption is consistent with our goal of obtaining an upper limit.
Origin of BIFs by photochemical oxidation of Fe$^{2+}$

The calculated manganese photo-oxidation rate is illustrated in Fig. 4. The manganese oxidation rate drops rapidly with depth due to the attenuation of 180 to 240 nm radiation by chloride, bromide, and bicarbonate, as shown in Fig. 3a. Thus, manganese photo-oxidation is confined to the uppermost part of the water column. Under these conditions, it is difficult to see how the rate of manganese photo-oxidation could have exceeded ≈10 mg cm$^{-2}$ yr$^{-1}$. A rate 10–100 times lower is obtained if we choose more likely values of the quantum yield. This is a high value for environmental photo-reactions in aquatic systems; a typical quantum yield is between 0.1 and 10$^{-4}$ (ZAFFRIOU, 1983).

The calculated manganese photo-oxidation rate for instance, is unlikely that iron photoreduction would have been important during the peak period of BIF deposition.

Because there is relatively little attenuation of light between 300 and 450 nm in our model, the rate of iron photo-oxidation decreases only gradually with depth in the upper 100 m, yielding a column-integrated rate of ≈200 mg cm$^{-2}$ yr$^{-1}$. This figure is consistent with previous estimates (BRATERMAN et al., 1983; FRANÇOIS, 1986). It should be noted that this value is sensitive to the depth of the layer in which photo-oxidation can occur; a rate less than half as large is calculated if a column only 10 m deep is considered. A "photo-oxidation zone" < 100 m deep could result from reflection and scattering of light in turbid waters, which might be expected in BIF depositional settings. Thus, the rate of iron photo-oxidation estimated in this study, and in previous work, may be somewhat exaggerated. However, even if photochemistry is confined to a water column only 10 cm deep, the iron photo-oxidation rate remains at least an order-of-magnitude higher than the upper limit of 0.1 mg cm$^{-2}$ yr$^{-1}$ estimated above for manganese.

These calculations, combined with the observed inhibition of manganese photo-oxidation in the presence of iron, lead us to conclude that the rate of manganese oxidation would have been much lower than that of iron in BIF depositional environments.
CONCLUSIONS

We have shown that Mn$^{2+}$ in 0.56 M Cl⁻ solutions is photo-oxidized by UV light between ca. 180 and 240 nm, and that the oxidized manganese precipitates as a constituent of himesite. No significant quantities of Mn$^{2+}$ were precipitated from irradiated solutions initially containing both Mn$^{2+}$ and Fe$^{2+}$. The low Mn:Fe ratio observed in precipitates from these solutions is similar to the ratios observed in oxide facies BIFs.

The far-UV dependence of the manganese photo-reaction, combined with the inhibition of manganese photo-oxidation in the presence of iron (due to refection and scattering of light by Fe$^{2+}$ precipitates and/or the reduction of Mn$^{2+}$ by Fe$^{2+}$), probably limited the manganese photo-oxidation rate to values < 0.1 mg cm$^{-2}$ yr$^{-1}$, several orders of magnitude smaller than the rate of iron photo-oxidation possible in BIF depositional environments on an anoxic Earth. Such a slow rate of Mn$^{2+}$ photo-oxidation is consistent with the low concentration of manganese in most oxide facies BIFs, and with the separation of iron and manganese in oxide facies BIFs as a whole.

Our data and calculations are consistent with the photo-chemical model for the origin of oxide facies BIFs first suggested by Cairns-Smith (1978), and extended by Brateman et al. (1983, 1984) and François (1986, 1987). Our data do not prove that this model is correct, since the oxidation of Mn$^{2+}$ by molecular O₂ is also very much slower than the oxidation of Fe$^{2+}$. Oxide facies BIFs could have formed both under anoxic and under mildly oxygenated atmospheres. It is possible, for instance, that the 3.8 Ga old BIF in the Isua area of West Greenland formed under an anoxic atmosphere, while the early Proterozoic BIFs formed under a mildly oxygenated atmosphere.

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