

1 **Banded iron formation to iron ore: a record of the evolution**
2 **of Earth environments?**

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9 **ABSTRACT**

10 Banded iron formations (BIF) are the protolith to most of the world's largest iron
11 ore deposits. Previous hypogene genetic models for Paleoproterozoic "Lake Superior"
12 BIF-hosted deposits invoke upwards, down-temperature flow of basinal brines via
13 complex silica and carbonate precipitation/dissolution processes. Such models are
14 challenged by the necessary SiO₂ removal. Thermodynamic and mass balance constraints
15 are used to refine conceptual models of the formation of BIF-hosted iron-ore. These
16 constraints, plus existing isotope and halogen ratio evidence, are consistent with removal
17 of silica by down- or up-directed infiltration of high-pH hypersaline brines, with or
18 without a contribution from basinal brines. The proposed link to surface environments
19 suggest that Paleoproterozoic BIF-ore upgrade may provide a record of a critical time in
20 the evolution of the Earth's biosphere and hydrosphere.

21

22 **INTRODUCTION**

23 Banded iron formations (BIFs) record changing environmental conditions and are
24 a precursor to the world's largest iron ore deposits. Vast volumes of BIFs were deposited
25 on passive margins from ca. 2.6 Ga to the Great Oxygenation Event (GOE) at ca. 2.4 Ga
26 (e.g., Beukes and Gutzmer, 2008). After 1.85 Ga, formation of iron formations essentially
27 ceased until a restricted resurgence in the late Neoproterozoic (Young, 1976; Klein and
28 Beukes, 1993) and more recent minor occurrences.

29 The temporal distribution of BIFs records a complex interplay between a cooling
30 Earth and changes in mantle plume events, continental growth and tectonics, evolution of
31 the biosphere and an increased flux of iron to the hydrosphere, which in turn had a
32 fundamental control on the oxygen contents of the hydrosphere and redox state of the
33 oceans (Isley and Abbott, 1999; Holland, 2005; Bekker et al., 2010). In most giant
34 Paleoproterozoic BIF-hosted iron ore deposits (~35 wt% Fe) the formation of high-grade
35 (>58 wt% Fe) iron ore from Lake Superior-type BIF is thought to have occurred post 2.2
36 Ga, after the GOE (Taylor et al., 2001; Rasmussen et al., 2007; Thorne et al., 2009), so
37 the BIF-ore upgrade provides a record of the changing chemistry of the hydrosphere and
38 atmosphere in the Paleoproterozoic.

39 In the Hamersley province, Western Australia, the BIF-ore upgrade is proposed to
40 involve basinal brines, meteoric fluids, and supergene enrichment (e.g., Morris et al.,
41 1980; Barley et al., 1999; Taylor et al., 2001; Thorne et al., 2004, 2008). Silica removal is
42 proposed to occur by upward, down-temperature flow of basinal brines (e.g., Thorne et
43 al., 2004; Gutzmer et al., 2006; Thorne et al., 2008), and it is this stage of the BIF-ore
44 upgrade that is explored in this paper.

45 The challenge for models that involve removal of SiO₂ from BIF by down-
46 temperature flow is that quartz solubility decreases with decreasing temperature (e.g.,
47 Manning, 1994), so fluid that moves down-temperature is a poor agent for quartz
48 removal, unless large volumes of fluids enter the BIF in a silica-undersaturated state.
49 Here, we combine numerical constraints with petrological, geochemical and isotopic
50 characteristics of BIF-hosted iron ore from the Hamersley province, Western Australia, to
51 constrain the conditions associated with silica loss and carbonate precipitation, and
52 discuss the findings in the context of the temporal evolution of the world's atmosphere
53 and oceans.

54 **DEPOSIT SCALE PARAGENESIS**

55 The mineralogy of BIF, hydrothermally altered BIF and iron ore varies (e.g., Thorne
56 et al., 2004; Rosiere et al., 2008; Mukhopadhyay et al., 2008; Angerer and Hagemann,
57 2010) but some features are sufficiently common to allow generalisation. BIF protolith
58 (Figs 1a;1b1;1b2) consists of magnetite- and chert-rich bands, iron silicates ± diagenetic
59 carbonates. Initial hydrothermal alteration (Figs 1a;1b3;1b4), which may be gradational,
60 involves conversion of some of the silicates to carbonates. Subsequently, chert and quartz
61 are replaced by iron-bearing carbonate with, in some, cases conversion of magnetite to
62 hematite, often with no apparent change in volume. Reaction fronts may be gradual
63 (millimeter to decimeter scale) or knife-sharp on the scale of individual bands. Quartz
64 may be precipitated locally in fault zones within shear veins (e.g., Hagemann et al., 1999;
65 Thorne et al., 2010).

66 The carbonate-bearing alteration assemblage (Figs 1a;1b5;1b6) is separated from
67 almost pure (hypogene) hematite iron ore (Figs 1a;1b7;1b8) by a sharp or gradational

68 reaction front. Carbonate loss is thought to occur without iron mobility on a scale greater
69 than a few cm (Taylor et al., 2001). Carbonate dissolution continues in the weathering
70 environment.

71 Upgrade of BIF in the Hamersley province, Western Australia, is thought to have
72 occurred from 2.15 Ga onwards during the waning stages of the Ophthalmian orogeny
73 (Rasmussen et al., 2007). There is evidence for extensional faulting and orogenic collapse
74 at the proposed time of ore upgrade (Müller et al., 2005) and it has been suggested that
75 topographic relief drove circulation of surface-derived waters through the fault system at
76 this time (e.g. Hagemann et al., 1999; Oliver and Dickens, 1999).

77 Constraints on ore upgrade in the Hamersley are provided by fluid inclusion,
78 isotopic, and halide concentration measurements. Fluid inclusions in carbonates are
79 hypersaline, up to 24 wt% CaCl₂ equivalent, which were trapped at temperatures between
80 150 and 400 °C (Thorne et al., 2004; Brown et al., 2004), mainly at the lower end of this
81 range. Quartz-hosted fluid inclusions (e.g. Brown et al., 2004) records periods of quartz
82 growth, not quartz removal, so such inclusions may record either a different event, or a
83 later stage of the silica dissolution event that is of interest here.

84 Iron oxide oxygen isotopes in unaltered BIF have $\delta^{18}\text{O}_{\text{VSMOW}}$ (Vienna Standard
85 Mean Ocean Water) between 4 and 13‰, whereas hematite and magnetite in altered and
86 mineralized rocks have $\delta^{18}\text{O}_{\text{VSMOW}}$ between -9 to -2.9 ‰ (Thorne et al., 2009). Carbon
87 isotopes of carbonate minerals lie between -10‰ and 0‰, relative to Vienna Peedee
88 belemnite (VPDB). The lower values are typical of unaltered BIF. Values in altered rocks
89 could record equilibrium with either Paleoproterozoic ocean water or dolomite in the
90 underlying Wittenoom formation. Fluid inclusion Na/Br and Cl/Br ratios record

91 overlapping populations of fluids: (1) seawater that has evaporated to halite saturation;
92 and (2) meteoric waters that interacted with evaporites (Thorne et al., 2010).

93 **CONSTRAINTS ON SILICA REMOVAL AND CARBONATE PRECIPITATION**

94 **Fluids in Equilibrium with BIF**

95 Quartz solubility is sensitive to pressure, temperature (e.g., Manning, 1994), pH
96 (Busey and Mesmer, 1977), and salinity (e.g., Shmulovich et al., 2006). Quartz and
97 carbonate solubilities were calculated as a function of pressure, temperature and salt
98 content (Fig. 2) using the methods outlined in the GSA Data Repository¹. Calcite, rather
99 than iron carbonate was used for the models because data for iron carbonates is sparse,
100 but similar trends for iron carbonates are expected. Temperature is the first order control
101 on quartz solubility, whereas calcite solubility depends strongly on pressure (Fig. 2a).
102 Salinity-driven mineral precipitation/dissolution is minor for geothermal gradients <50
103 °C km⁻¹ (Fig. 2b). There is no geothermal gradient for which silica dissolution is
104 accompanied by carbonate precipitation in the observed quantities, so it is necessary to
105 consider infiltration of out-of-equilibrium fluids.

106

107 **Fluid out of Equilibrium with BIF**

108 Infiltration of high-pH, out-of-equilibrium fluid can drive quartz removal via up-
109 or down-temperature flow, because quartz is 4 orders of magnitude more soluble at pH 9
110 than it is at pH 6 (Busey and Mesmer, 1977). The desilicification/carbonation and
111 oxidation fronts observed in BIFs are sufficiently sharp that they can be treated as
112 advective chromatographic fronts; broadening by diffusion, dispersion and kinetic

113 broadening can be neglected. The ratio of the distance traveled by a fluid to that of
114 associated reaction front is given by

$$115 \quad \frac{d_{\text{fluid}}}{d_{\text{rock}}} = \frac{c_{i,\text{rock,final}} - c_{i,\text{rock,initial}}}{\theta(c_{i,\text{fluid,initial}} - c_{i,\text{fluid,final}})}, \quad (1)$$

116 (adapted from Evans et al., 2003). d is the position of the front relative to the infiltration
117 horizon in meters, c_i is the concentration of the reactant of interest in moles m^{-3} , and θ is
118 porosity.

119 Relative positions of carbonation, desilicification, and oxidation fronts were
120 calculated using the values given in Table DR1 (in the Data Repository), which are based
121 on the assumption of infiltration an out-of-equilibrium, pH 9, SiO_2 -free, CO_2 -rich, O_2 -
122 bearing fluid (O_2 at 10% of present-day values). Front positions were normalized to that
123 of the most advanced carbonation front (Fig. 1b). The oxidation front is predicted to
124 proceed the smallest distance, as observed, though the position of this front is modified
125 by post-hypogene meteoric fluid and supergene processes. The carbonation front is
126 predicted to advance further than the desilicification front for any reasonable combination
127 of input parameters. In reality, the desilicification front coincides with a sharp increase in
128 carbonate content, which suggests a reaction-induced porosity control on fluid
129 infiltration.

130 **Volumes of Fluid Flow**

131 The relationship between time-integrated fluid flux and silica removal for
132 hydrothermal alteration where pressure, temperature and fluid composition gradients are
133 fixed, and for constant fluid flow rates is given by

$$134 \quad Q = \frac{\Delta n_{\text{SiO}_2}}{\left(\frac{dc_{\text{SiO}_2}}{dl} \right)}, \quad (2)$$

135 (c.f. Evans and Bickle, 1999, their equation 6). Q is the time-integrated fluid flux, in
136 cubic meters of fluid per square meter of rock, Δn_{SiO_2} is the SiO_2 removed from the
137 volume (moles m^{-3}), c_{SiO_2} is the concentration of SiO_2 in the fluid in (moles m^{-3}), and l is
138 distance along the flow path (m). This expression is based on mass balance and can be
139 applied to in- or out-of-equilibrium situations. Calculations were made for flow up- or
140 down-temperature of a pH 9, silica-undersaturated fluid, such as might be derived from
141 an ultramafic lithology or hypersaline evaporite-derived fluid. pH is assumed to drop
142 from 9 to 5 during equilibration. dc_{SiO_2}/dpH was calculated from Busey and Mesmer
143 (1977) and checked against HCh output (Shvarov and Bastrakov, 1999).

144 Flow volumes were calculated for a single cubic meter of rock undergoing pH-
145 driven quartz dissolution and scaled to estimate the volume needed to produce the
146 observed SiO_2 depletion on a scale comparable to observed small iron ore deposits ($3 \times$
147 10^8 m^3). The volume of fluid required is approximately $\sim 10^9 \text{ m}^3$.

148 **DISCUSSION AND CONCLUSIONS**

149 The observed silica removal and carbonate precipitation needed for formation of a
150 kilometer-scale BIF-hosted Fe deposit is inconsistent with in-equilibrium fluid flow (Fig.
151 2), but could be produced by pervasive infiltration of $\sim 10^9 \text{ m}^3$ of a high pH ($\text{pH} > 9$) fluid
152 flowing up- or down- temperature.

153 Density- or topography-driven infiltration (McLellan et al., 2004) of dense
154 hypersaline brines evolved on continental margins (Fig. 3) provides a plausible source of
155 high-pH fluid. The pH of hypersaline lakes today is up to 10, and the CO_2 content is
156 high; reported alkalinities exceed $10,000 \text{ mg liter}^{-1}$ (Gosselin et al., 1994). These brines
157 form on marginal platforms (Leach et al., 2010) and were present on the north Yilgarn

158 margin in the Palaeoproterozoic (El Tabakh et al., 1999) and in Mesoproterozoic
159 dolomitic argillites in the western United States (Gonzalez-Alvarez and Kerrich, 2011).
160 The Yilgarn and Pilbara cratons may not have been adjacent at the time of ore formation,
161 and the latitude of the Pilbara margin at that time is poorly known but existing constraints
162 place the latitude within the range of those required for evaporite formation (Li, 2000).
163 Fault zones in similar environments today are sufficiently permeable that proposed
164 volumes could have flowed on a geologically reasonable timescale (Jones et al., 2002).

165 Carbon and oxygen isotopes of early carbonate and iron oxides in mineralised BIF
166 are consistent with seawater derivation from Palaeoproterozoic seawater. High salinities
167 and Na/Br and Cl/Br ratios record fluids typical of seawater that has evaporated to halite
168 saturation (Thorne et al., 2010), which is also consistent with an involvement of
169 evaporite-derived fluids. Temperatures of up to 250 °C are consistent with fluid inclusion
170 evidence, and with other environments where voluminous quantities of surface-derived
171 fluids infiltrate basement rocks (e.g. Gleeson and Yardley., 2003). However,
172 temperatures >300 °C recorded by early assemblages at Mt. Tom Price require a separate
173 high-temperature alteration stage. SiO₂ deposition in outflow zones from the flow system
174 described have not been recorded, to date, but may prove difficult to recognize given that
175 chert was a common sedimentary rock at this time.

176 Some geometric constraints in mineralized Pilbara BIFs favour an upwards
177 flowing fluid (e.g. Dalstra and Rosiere, 2004). The Wittenoorn formation underlies many
178 of the ore-bearing units, and has been proposed as a way for basinal brines to access the
179 BIF (e.g. Taylor et al., 2001). Dolomite in the Wittenoorn formation contains numerous
180 shale bands (Davy, 1975), and is separated from the BIF by the Si-bearing Mt McRae

181 shale and Sylvania Formation, so fluids from this unit would be at, or close to, SiO_2
182 saturation, unless fluids were focused solely within shale-free regions of the dolomite,
183 such as the Paraburdoo Member (Thorne and Tyler, 1997). If this were the case then the
184 dolomite in the Wittenoom formation could have acted as an aquifer that supplied
185 overlying iron formations with fluids derived either from faults that focused either down-
186 flowing evaporitic brines with or without a contribution from upwards-flowing basinal
187 brines, as suggested by previous workers (e.g. Taylor et al., 2001).

188 Mafic and ultramafic rocks are present in the Pilbara (e.g., Barnes and Hoatson,
189 1994) and can equilibrate with water to provide high pH fluids, but such fluids are
190 unlikely to have reached the BIF without interacting with Si-bearing rocks such as the Mt
191 McRae shale.

192 Oxidized, sulfur-bearing, hypersaline brines produced on basin margins since 2.0
193 Ga have been linked to base metal sulfide deposition, including MVT (Mississippi Valley
194 type) and SEDEX-Pb-Zn deposits (Leach et al., 2010). Such deposits older than 2.02 Ga
195 have not been found; Archaean and Paleoproterozoic oceans were reduced and largely
196 sulfur-depleted (e.g., Farquhar et al., 2010), so marginal hypersaline brines at 2.2 Ga, at
197 the time of ore upgrade, could have had a significantly different composition to those
198 today. It is interesting to speculate whether redox controls related to mobilization,
199 transport, and deposition of Pb and Zn by Palaeoproterozoic evaporite-derived brines,
200 such as a lack of sulfur (Leach et al., 2010) lack of oxidized source rocks and aquifers, or
201 reduction of sulfate via rock-buffering in the immediate sub-surface, may have prevented
202 formation of these deposit types prior to 2.02 Ga.

203

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355 **FIGURE CAPTIONS**

356 Figure 1. (a) Commonly observed banded iron formation (BIF) alteration stages related to
357 the formation of iron ore and their characteristics. (b1–8) Polished blocks and
358 photomicrographs of the typical alteration stages (mplH—microplaty hematite, mar—
359 martite). (c) Results of mass balance calculations to determine the relative distances
360 moved by decarbonation, desilicification and oxidation fronts. Values indicate distance
361 traveled by front relative to the carbonation front for a solution with 1 mol liter⁻¹ CO₂.

362

363 Figure 2. Results of thermodynamic calculations of SiO₂ and calcite solubility as a
364 function of pressure and temperature (a), and temperature and salt concentration (b).

365

366 Figure 3. Proposed genetic model for desilicification of banded iron formation (BIF) by a
367 density-driven, hypersaline, high-pH brine.

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371 Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.