

Extraterrestrial demise of banded iron formations 1.85 billion years ago

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ABSTRACT

In the Lake Superior region of North America, deposition of most banded iron formations (BIFs) ended abruptly 1.85 Ga ago, coincident with the oceanic impact of the giant Sudbury extraterrestrial bolide. We propose a new model in which this impact produced global mixing of shallow oxic and deep anoxic waters of the Paleoproterozoic ocean, creating a suboxic redox state for deep seawater. This suboxic state, characterized by only small concentrations of dissolved O₂ (~1 μM), prevented transport of hydrothermally derived Fe(II) from the deep ocean to continental-margin settings, ending an ~1.1 billion-year-long period of episodic BIF mineralization. The model is supported by the nature of Precambrian deep-water exhalative chemical sediments, which changed from predominantly sulfide facies prior to ca. 1.85 Ga to mainly oxide facies thereafter.

INTRODUCTION

Significant global changes in marine mineral deposits occurred between 1.9 and 1.8 Ga (e.g., Groves et al., 2005). We focus here on two changes: the end of an ~1.1 billion-year-long period during which massive amounts of iron accumulated episodically in banded iron formation (BIF) deposits (Klein, 2005), and a shift in the character of deep-marine exhalative chemical sediments (Slack et al., 2007). Prior explanations for changes in these and other types of Paleoproterozoic marine mineral deposits all involve gradual modifications to environmental or tectonic conditions on Earth. In contrast, we propose a catastrophic cause in which a giant extraterrestrial bolide, the Sudbury impactor, produced global alteration of the redox state of deep seawater, fundamentally changing the character of marine sedimentation. This hypothesis is based on a recently discovered relationship between the giant BIF deposits of the Lake Superior region (United States and Canada) and a directly overlying layer of ejecta-bearing rocks produced by the Sudbury impact event at 1.85 Ga (Cannon et al., 2010, and references therein).

In this paper, for simplicity, we include granular iron formation (GIF; see Klein, 2005) with BIF. Algoma-type iron formation, which is mainly restricted to volcanic sequences, is not considered in our study because this mostly smaller type of iron deposit, relative to Superior-type BIF, does not inform the redox state of deep seawater on a large scale (Huston and Logan, 2004). We use the terms shallow, mid-depth, and deep seawater as indicating depths of <200 m, 200–600 m, and >600 m, respectively: the 200 m depth corresponds to the base of the photic zone in most modern oceans, whereas the 600 m depth discriminates deep seawater from shallower settings that characterize modern continental margins.

BANDED IRON FORMATIONS

BIFs consist of chert interlayered with iron oxide, iron carbonate, or iron silicate minerals, and occur nearly exclusively in marine sedimentary strata of Precambrian age (e.g., Klein, 2005). Formation of BIF is generally interpreted to reflect the dispersal of aqueous Fe(II) from seafloor hydrothermal vents or plumes (Slack et al., 2007, and references therein), followed by Fe(II) transport in anoxic deep seawater to mainly shallow continental-margin settings, where insoluble Fe(III) oxyhydroxides precipitated by abiological photochemical oxidation of Fe(II) or by activity of anoxygenic phototrophic Fe(II)-oxidizing bacteria (e.g., Konhauser et al., 2007). Mafic rocks may be additional sources of Fe(II), produced during anoxic weathering. Iron silicate and iron carbonate minerals in BIF likely formed in anoxic seawater, either by inorganic or bacterially mediated processes (Klein, 2005; Ohmoto et al., 2006; Johnson et al., 2008). Some late Paleoproterozoic BIF deposits consist predominantly of GIF or reduced facies (iron silicates and carbonates), but Fe(III)-rich chemical hematite and/or magnetite laminae also occur in these deposits.

Previous studies (e.g., Klein, 2005) concluded that major BIF deposition ended at ca. 1.8 Ga. Diverse explanations have been offered for this global termination of BIF mineralization, including changes in the redox state of the deep ocean from anoxic to oxic or anoxic to sulfidic; both processes had removed dissolved Fe(II) from seawater by the formation of insoluble Fe(III) oxyhydroxides or insoluble iron sulfides, respectively (see Holland, 2006). Some workers have argued for deepening of mid-ocean ridges and decreased heat flow after 1.8 Ga (Isley, 1995), or greatly decreased Fe/H₂S ratios of hydrothermal vent fluids due to higher seawater sulfate concentrations (Kump and Seyfried, 2005) following initial oxygenation of the atmosphere during the Great Oxidation Event (GOE) at ca. 2.4 Ga. A more recent

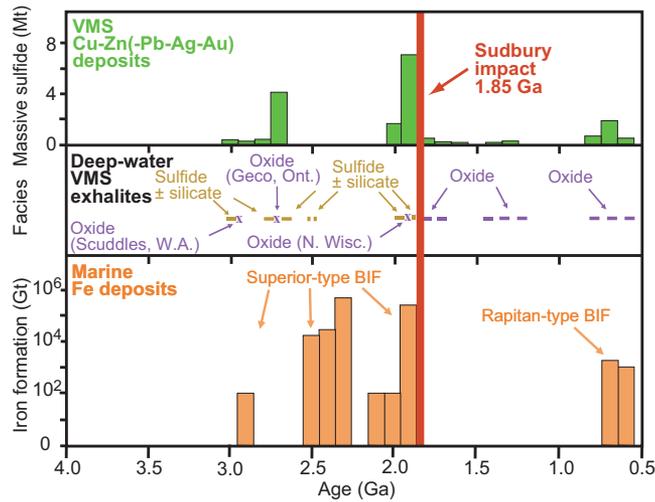
model by Slack et al. (2007), based on spatial associations of 1.79–1.24 Ga hydrothermal oxide-facies chemical sedimentary rocks with Cu-rich volcanogenic massive sulfide (VMS) deposits, suggests that the post-1.8 Ga deep ocean was suboxic (<5 μM O₂), periodically or locally, if not pervasively. A minority opinion (Ohmoto et al., 2006) holds that the deep oceans have been fully oxic since 3.8 Ga, and that BIF mineralization ceased at 1.8 Ga due to a decrease in the size and frequency of mantle plumes, which produced smaller and shorter-lived submarine-hydrothermal systems. In all of these models, the end of BIF deposition at ca. 1.8 Ga is attributed, explicitly or implicitly, to gradual processes in the evolution of the lithosphere, hydrosphere, or atmosphere.

The BIFs in the Lake Superior region are among the youngest deposited during the Paleoproterozoic Era (Fig. 1; Table DR1 in the GSA Data Repository¹). A new age constraint for the end of BIF deposition comes from the recent discovery and tracing of the Sudbury impact layer throughout the Lake Superior region (Cannon et al., 2010, and references therein), which provides a precise time line at 1850 ± 1 Ma, the age of the Sudbury impact event. The Sudbury impact layer, up to 40 m thick, contains ejecta produced by the Sudbury bolide impact and is documented at distances between 450 and 900 km from the impact point at Sudbury, Ontario. The ejecta-bearing breccia layer has been found in five of the seven major iron ranges and in two additional basins that contain low-grade iron formation and equivalent ferruginous calcareous chert. In three of the iron ranges and the two additional basins, the Sudbury impact layer lies directly on BIF or equivalent ferruginous chert and is overlain by fine-grained clastic rocks, most commonly black shale. In one iron range, the Sudbury impact layer transects a few tens of meters of stratigraphy and varies from lying directly on BIF to occurring a few tens of meters above. In the remaining range, BIF deposition ended significantly earlier, and the Sudbury impact layer is ~300 m above the top of the BIF (Cannon et al., 2010). Deposition of the Sudbury impact layer throughout the

¹GSA Data Repository item 2009255, Table DR1 (Precambrian Superior-type banded iron formations and Rapitan-type iron formations) and Table DR2 [exhalites associated with Precambrian deep-water (Cu-rich) volcanogenic massive sulfide deposits], is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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Figure 1. Secular distribution of Superior-type banded iron formation (BIF) and Rapitan-type iron formation during Precambrian Era plotted as amount of iron formation in billion metric tonnes (Gt), integrated over time intervals of 100 m.y. (data in Table DR1 [see text footnote 1]). Superior-type BIF includes granular iron formation. Also shown are size distributions in million metric tonnes (Mt) of massive sulfide in volcanogenic massive sulfide (VMS) deposits, similarly plotted for 100 m.y. intervals (data from Franklin et al., 2005), and facies variations of exhalative chemical sedimentary rocks (exhalites) associated with deep-water (Cu-rich) VMS deposits (data in Table DR2).



region appears to demarcate a large-scale termination of BIF deposition in a variety of sedimentary facies, from intertidal to deep water and in settings from shallow shelf to foreland basin (Cannon et al., 2010). This apparently synchronous end of BIF deposition over the entire region and in diverse depositional and tectonic environments is consistent with a cataclysmic event throughout the basin rather than a gradual change in local sedimentary conditions. Furthermore, the changes produced by the impact appear to have been irreversible; large-scale BIF deposition never returned, although hundreds to thousands of meters of marine sediments were deposited in the iron ranges following the Sudbury impact. The only known exceptions are two carbonate and silicate iron formations within anoxic strata (Cannon et al., 2010), but these have Algoma-type volcanic affinities.

The termination of BIF deposition in the Lake Superior region at 1.85 Ga may correlate with a worldwide end of BIF deposition during the late Paleoproterozoic. From ca. 1.88 Ga to ca. 1.84 Ga, vast amounts of BIF were deposited in the Sokoman Iron Formation in the Labrador Trough in Canada, the Frere Formation in the Earahedy Basin in Western Australia, and the Hutchison Group on the Gawler Craton in South Australia, together with lesser amounts in the Shoshong Formation of eastern Botswana (Table DR1). The age ranges of BIF mineralization in these regions are not precisely constrained; hence, it is uncertain whether their deposition ended synchronously with that in the Lake Superior region. However, the ages of 1.88–1.84 Ga estimated for these deposits are consistent with their termination at 1.85 Ga, based on stratigraphic locations of the dated units relative to the BIF deposits and on the likelihood of long durations for the BIF mineralization (cf. >28 m.y. in the Gunflint Forma-

tion; Cannon et al., 2010). Within the limits of available radiometric dating, therefore, major BIF mineralization apparently ceased globally at 1.85 Ga, coincident with the Sudbury impact. A global change in the oceanic Fe cycle at ca. 1.8 Ga is also suggested by iron isotope data for pyrite in Precambrian black shales (Rouxel et al., 2005). Renewed deposition of iron formation in Rapitan-type deposits during the Neoproterozoic (Fig. 1; Table DR1) probably resulted from depletion of seawater sulfate during snowball Earth episodes (Kump and Seyfried, 2005). The absence of BIF mineralization from ca. 2.4 to 2.2 Ga followed the GOE and assembly of a major supercontinent (Barley et al., 2005), and may reflect temporary sulfidic conditions produced by increased sulfate reduction in seawater following this event (Bjerrum and Canfield, 2002) or a major decrease in submarine magmatic activity during this time period (Condie et al., 2009).

DEEP-WATER EXHALITES

Deep-sea exhalative sedimentary rocks (“exhalites”) of hydrothermal origin provide independent evidence of a major change in ocean chemistry on a global scale relatively close in time to the Sudbury impact. Exhalite aprons at or along strike from Cu-rich VMS deposits formed from vent fluids and hydrothermal plumes in relatively deep water (≥ 850 m), based on solubility limitations for Cu imposed by hydrothermal temperatures ≥ 300 °C (needed to form abundant Cu sulfide minerals on or near the seafloor) and by sufficient hydrostatic pressures to prevent fluid boiling in the subsurface (Slack et al., 2007). A change in the typical oxidation state of these deposits occurred approximately at 1.85 Ga, the age of the Sudbury impact (Fig. 1). Prior to 1.85 Ga, deep-water VMS-related exhalites mainly consist of sulfide iron formation

or pyritic chert, or, less commonly, silicate or carbonate iron formation (Table DR2 [see footnote 1]). After 1.85 Ga, the exhalites dominantly consist of jasper (hematitic chert) and hematite or magnetite iron formation. The older sulfide-, silicate-, and carbonate-facies exhalites, which contain little if any Fe(III), probably were deposited in anoxic seawater, based on thermodynamic and geochemical arguments (Klein, 2005; Huston and Logan, 2004; Ohmoto et al., 2006), and thus their distribution is consistent with the presence of anoxic conditions at depths of ≥ 850 m prior to 1.85 Ga. Occurrence of the younger deposits of jasper and oxide iron formation, and their high Fe(III)/Fe(II) ratios, suggests at least minimal oxygen contents of the coeval deep ocean, assuming that no significant oxidation of iron occurred after lithification (Slack et al., 2007, 2009). Uncommon carbonate, silicate, and sulfide iron formations at or near Precambrian Cu-rich VMS deposits younger than 1.85 Ga likely reflect mineralization in local anoxic basins beneath a mildly oxygenated water column.

Several well-documented exceptions to this secular pattern involve spatial associations of oxide-facies iron formation or jasper with Cu-rich VMS deposits older than 1.85 Ga (Table DR2): the 2.96 Ga Scuddles deposit in Western Australia, the 2.72 Ga Geco and Willroy deposits in southern Ontario, and the ca. 1.87 Ga Eisenbrey and Bend deposits in northern Wisconsin. These and other Fe(III)-rich exhalites older than 1.85 Ga may reflect: (1) deposition from seawater having a very low ΣS content (Huston and Logan, 2004), (2) hydrothermal plumes that rose above the chemocline (Ohmoto et al., 2006), (3) phase separation in the seafloor-hydrothermal systems (Foustoukos and Bekker, 2008), (4) mineralization during a temporary oxygenation of deep seawater, or (5) formation in local oxygenated basins.

DISCUSSION

Our proposal of a cause-and-effect relationship between the Sudbury impact and apparently contemporaneous global changes in marine metallogeny requires an impactor of sufficient mass to severely alter surficial and oceanographic conditions. The Sudbury impact is widely recognized as one of the three largest preserved extraterrestrial impact structures on Earth, together with the 2.02 Ga Vredefort structure in South Africa and the 0.65 Ga Chixculub structure in Mexico (e.g., Grieve et al., 2008). The original size of the Sudbury crater, now deformed and partly eroded, is controversial. Estimates range from 150 km to 270 km in diameter (Grieve et al., 2008). Even the lower estimates put Sudbury at a similar size to the Chixculub impact (170 km crater), which produced profound changes on a global scale (e.g., Kring, 2007).

Increasing oxygenation of the atmosphere after the GOE formed a stratified ocean that consisted of a shallow oxic layer overlying a much more voluminous anoxic water column (e.g., Holland, 2006; Scott et al., 2008). We propose that bolide-generated impact effects overturned and mixed the previously stratified ocean worldwide. Computer modeling by Ward and Asphaug (2002) shows that a 10-km-diameter stony asteroid striking a 1-km-deep ocean, conditions at least roughly similar to those inferred for Sudbury (Grieve et al., 2008; Cannon et al., 2010), produces a tsunami with heights of ~1000 m at the impact site and ~100 m at a distance of 3000 km. Because wave amplitudes decrease geometrically with increasing distance, even giant tsunamis of this magnitude might not mix oxygenated shallow and anoxic deep seawater on a global scale. However, other processes initiated by the impact may have produced significant overturning and mixing of the ocean, including interaction of the vertical plume jet of vaporized seawater with the more oxygenated atmosphere (Gisler et al., 2003), cavitation of the ocean and scouring of the seafloor generated by multiple shock waves from the impact and their interaction with the seafloor (Ward and Asphaug, 2002; Gisler et al., 2003), and formation of large submarine debris flows produced by the collapse of continental margins such as occurred in the western North Atlantic following the Chicxulub impact (Norris et al., 2000). Continents and islands would have deflected even large tsunamis and submarine shock waves, but at ca. 1.9 Ga, all major land masses were likely joined to one supercontinent, Columbia (Zhao et al., 2004), hence interference by land on such submarine processes was probably minimal. In the paleogeographic reconstruction of Columbia by Zhao et al. (2004), the Lake Superior region was located on the southern margin (present coordinates) of this supercontinent, thus impact-generated submarine processes at Sudbury may have had a large expanse of open ocean to traverse.

Assuming thorough mixing of the shallow oxic layer with the anoxic deep global ocean, mass balance calculations using a box reservoir model (Fig. 2) indicate that the resulting deep ocean after 1.85 Ga was suboxic and had a dissolved O_2 concentration of $\sim 1 \mu M$. Such a low oxygen content in seawater greatly reduced Fe(II) solubility, based on analogy with the stratified water columns of the modern Cariaco Basin (De Baar et al., 1988). In the anoxic zone of this basin at a depth of 410 m, the dissolved Fe concentration ($[Fe]$) is $\sim 328 nM$, which abruptly decreases to $\sim 31 nM$ just above the chemocline at 290 m, where dissolved O_2 is $\sim 0.5 \mu M$. The Cariaco Basin thus shows a tenfold decrease of dissolved $[Fe]$ in suboxic seawater within the transition zone above the chemocline relative to anoxic seawater below.

In modern oceans, minimum distances between continental margins, where BIF typically formed in the past, and deep hydrothermal vents on mid-ocean ridges or in backarc basins, are generally ~ 200 km. The half-life of Fe(II) under modern suboxic conditions ranges from 0.16 to 0.65 d, depending on O_2 contents and assuming the presence of H_2O_2 (a major oxidant of Fe(II)) at very low concentrations of 0.5–2 nM (Hopkinson and Barbeau, 2007). Using an average mid-depth current velocity (estimated from Reid, 1981) of 3 cm/s (2.6 km/d), and ignoring shallow gyres and other fast currents, transport of dissolved Fe(II) for 200 km at such depths would require 77 d. These calculations indicate that under suboxic conditions, the Fe(II) in each fluid packet would be fully oxidized within 2 d, forming insoluble oxyhydroxide particles that settle to the seafloor, thus preventing transport of dissolved Fe(II) to continental margins for BIF deposition. Dissolved Fe concentrations in Precambrian anoxic deep oceans are unknown; a value of $30 \mu M$ was used by Konhauser et al. (2007). A comparison of this estimate to dissolved $[Fe]$ of $\sim 31 nM$ in the suboxic transition zone of the Cariaco Basin implies that dissolved $[Fe]$ in the pre-1.85 Ga anoxic ocean

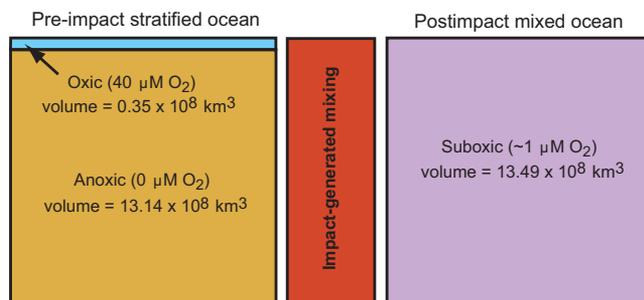
decreased by a factor of 10^3 following the Sudbury impact. In our model, this dramatic loss of Fe prevented the necessary flux of hydrothermal Fe from the deep ocean to continental-margin settings for BIF mineralization. This process predicts the deposition of ferruginous marine sediments in deep-water settings directly above the Sudbury impact horizon, which provides one test of our model.

Marine Mn deposition in the Paleoproterozoic also ended at ca. 1.8 Ga (e.g., Groves et al., 2005; Holland, 2006), probably because these deposits share a similar origin with BIF. Newly created suboxic conditions in the deep ocean at 1.85 Ga would have greatly decreased the solubility of dissolved Mn, as in the transition zone of the modern Cariaco Basin (De Baar et al., 1988). The termination of marine Mn deposition, and similarly of major phosphorite deposition, is consistent with the existence of a mildly oxygenated deep ocean during late Paleoproterozoic and Mesoproterozoic time (Holland, 2006). Our model also may relate to the secular distribution of sedimentary-exhalative (SEDEX) Zn-Pb deposits, which first appear in the geologic record at ca. 1.8 Ga (Groves et al., 2005).

Two interrelated processes would have produced an increase of dissolved O_2 to the deep ocean soon after the Sudbury impact: (1) removal of ferrous iron in seawater as an oxygen acceptor for anoxygenic phototrophs, resulting in increased oxygenic photosynthesis by cyanobacteria (Sleep and Bird, 2008), and (2) increased dissolved phosphate that formerly was adsorbed onto iron oxyhydroxide deposits (protoliths of BIF), which would have raised nutrient levels, increased productivity and photosynthesis, and increased burial rates of organic carbon (Bjerrum and Canfield, 2002). Occurrences of black organic-rich shale directly above the Sudbury impact layer (Cannon et al., 2010) may record such increased productivity and organic carbon burial. Over a longer time scale, the new suboxic state in the deep ocean beginning at 1.85 Ga may have been maintained by a greatly lowered flux of hydrothermally derived reductants such as H_2 and H_2S , consistent with a major decrease in VMS mineralization after 1.85 Ga (Fig. 1), and with feedbacks involving the nitrogen, carbon, and oxygen cycles (Fennel et al., 2005). After the Sudbury impact, renewed bacterial photosynthesis likely reestablished a stratified ocean, with a shallow oxic layer overlying a suboxic ocean.

Large bolides that struck Earth from 3.46 to 2.48 Ga produced impact ejecta/fallout units in the Pilbara craton of Western Australia and the Kaapvaal craton of South Africa, some of which are directly overlain by BIF (Glikson, 2008, and references therein). This stratigraphic relationship, which is opposite the pattern observed in

Figure 2. Box model showing redox changes from pre- to postimpact global ocean after mixing of shallow oxic layer with underlying anoxic water mass due to processes related to impact of Sudbury extraterrestrial bolide at 1.85 Ga. Seawater volumes are inferred to be similar to those of all modern oceans combined. For oxic shallow layer, a conservative thickness of 100 m is used, together with a value for dissolved oxygen of $40 \mu M$ based on assumption of equilibrium between ocean and atmosphere (Ohmoto et al., 2006) and an atmospheric oxygen level of 20% present atmospheric level (Holland and Beukes, 1990; Holland, 2006).



the Lake Superior region, may reflect impact-generated mafic volcanism or submarine-hydrothermal activity that increased the Fe(II) content of the coeval deep ocean (Glikson, 2008). Based on a variety of studies (e.g., Scott et al., 2008), there is no evidence that these impacts significantly changed the redox state of deep seawater, probably because they occurred prior to the GOE at ca. 2.4 Ga and prior to the formation of a stratified ocean. The Vredefort impact took place ~0.4 b.y. after the GOE when atmospheric oxygen contents were above 0.02 atm but far below the present level of 0.2 atm (Holland, 2006), and when seawater had a shallow oxygenated layer (Scott et al., 2008). Applying our model for the Sudbury impact, the Vredefort bolide might have similarly affected the redox state of deep seawater at 2.02 Ga. However, the Vredefort crater is deeply eroded (Grieve et al., 2008), and it is unknown whether this bolide hit the ocean. If not, the Sudbury impact at 1.85 Ga may have created the first megatsunami on Earth after the GOE and the first thorough mixing of the stratified global ocean. Other environmental consequences of the Sudbury impact, including possible effects on biological evolution, remain to be explored.

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