17.1 INTRODUCTION

The Banded iron formations (BIFs) are nonactualistic rocks deposited in the Archean, Paleoproterozoic, and Neoproterozoic. They are characterized by rhythmic alternations of iron-rich layers (“bands”) and chert layers. Based on their iron mineralogy, BIFs can be classified as oxide-, carbonate-, silicate-, or sulfide-facies (James, 1954) & among which, the oxide-facies is most important. Based on depositional and geotectonic setting, Gross (1980) & distinguished between Algoma- and Lake Superior-type BIFs. Accordingly, the Lake Superior-type BIFs were deposited on stable continental platforms, and Algoma-type BIFs are associated with volcanic rocks and were deposited in arc or rift settings. A third BIF type, exclusively Neoproterozoic in age, is the Rapitan type (i.e., Beukes and Klein, 1992) & characterized by a glacially influenced depositional environment.

Geochemistry has played a central role in unraveling the origin of BIFs, and many proxies such as rare earth element (REE) concentrations, have been widely used (e.g., Kato et al., 2006) &. However, chemostratigraphic studies are scarce, probably because traditional stable and radiogenic isotope studies such as $\delta^{13}$C, $\delta^{18}$O, $\delta^{34}$S and $^{87}$Sr/$^{86}$Sr are impossible to apply for the more widespread oxide-facies BIF. Isotope chemostratigraphy has played a significant role in the study of Neoproterozoic successions since the pioneer reports by Knoll et al. (1986) and Kaufman et al. (1991). The establishment of the “snowball Earth” hypothesis was based mainly on chemostratigraphic and paleomagnetic evidences (Hoffman et al., 1998). Curves of global secular variations of $\delta^{13}$C and $^{87}$Sr/$^{86}$Sr in the Neoproterozoic (e.g., Jacobsen and Kaufman, 1999; Melezhik et al., 2001; Halverson et al., 2010) & have been important tools for correlation and geochronology, mostly in combination with biostratigraphy and U–Pb radiochronology. The caveat of all these studies is that, for analytical reasons, they can only be applied to the carbonate successions or, more rarely, to the organic-rich shales (e.g., Johnston et al., 2010), but not to the oxide-facies Neoproterozoic iron formations.

The development of new techniques, such as Fe speciation, Cr and Fe isotopes ($\delta^{57}$Cr, $\delta^{56}$Fe), and Mo concentrations and isotopes ($\delta^{98}$Mo) opened new horizons and enabled thorough chemostratigraphic
studies of thick BIF successions (Canfield et al., 2008; Frei et al., 2009; Halverson et al., 2011; Baldwin et al., 2013). Hence, for the first time, the study of secular variations within the iron formations became possible, enabling insights into the basin evolution and changes in the redox conditions. Studies using REE concentrations changed from only reporting REE distributions for whole iron formations (e.g., Graf et al., 1994; Kato et al., 2006) to reporting stratigraphic variations of certain REE parameters, such as Ce and Eu anomalies (e.g., Stern et al., 2013). This development had added the time dimension to fundamental parameters such as the importance of hydrothermal processes, redox conditions and sources of iron, which need not be constant throughout deposition of individual iron formations.

The new techniques, coupled with a growing interest on the Neoproterozoic iron formations, show a more complex picture than previously thought. We review here the occurrence of Rapitan, Algoma, and Lake Superior BIF types in the Neoproterozoic, and present recent chemostratigraphic data that enable their characterization.

17.2 AGE OF NEOPROTEROZOIC BIFS

It has been recently proposed that all the Neoproterozoic iron formations were deposited during the middle Cryogenian (“Sturtian”) glaciation at c. 715 Ma (Macdonald et al., 2010a; Cox et al., 2013). This is certainly the case for BIF of the Rapitan Group (Sayunei Formation, Canada), which is constrained by an U–Pb age of a felsic tuff of 716.5 ± 0.24 Ma (Macdonald et al., 2010b). Similarly, glacially influenced BIF of the Fulu Formation and associated diamicrites (Jiangkou Group, South China) directly overlie a tuffaceous siltstone that yielded an U–Pb age of 725 ± 10 Ma. The Chuos Formation of the Otavi Group (NW-Namibia) includes BIF associated to glacial diamicrites (Jiangkou Group, South China) directly overlie a tuffaceous siltstone that yielded an U–Pb age of 725 ± 10 Ma. The Chuos Formation of the Otavi Group (NW-Namibia) includes BIF associated to glacial diamicrites, which rests atop a porphyry lava dated U–Pb at 746 ± 2 Ma (Hoffman et al., 1996). This, combined with the fact that there are more than 500 m of intervening carbonates between the BIF and the end-Cryogenian Ghaub Formation, dated at 636 ± 1 Ma (Hoffmann et al., 2004), makes an age around 715 Ma for the Chuos Formation unlikely, but it cannot be completely ruled out. The Holowilena Ironstone of the Flinders Ranges, South Australia, is an interesting example that illustrates the problems of global correlations of Neoproterozoic ice ages. Fanning and Link (2008) reported U–Pb SHRIMP zircon age of 660 ± 5 Ma for the volcaniclastic intercalations in the partially glaciogenic lower Willyerpa Formation, which is part of the Sturtian type section. The Holowilena Ironstone occurs some 250 m stratigraphically beneath the Willyerpa Formation (Le Heron et al., 2011). Thus, although the Holowilena Ironstone is undoubtedly Sturtian, because it occurs at the Sturtian type section in Australia, it is probably much younger than the Rapitan glacials.

BIF occurring at Wadi Karim, Wadi El Dabbah, and Um Anab in Egypt (Basta et al., 2011, Fig. 1) and the correlative Sawawin BIF in northwestern Saudi Arabia are constrained between underlying metavolcanics dated U–Pb at 759 ± 17 Ma and intrusive rocks yielding U–Pb age of 710 ± 5 Ma (Stern et al., 2013, and references therein). Therefore, these BIFs are distinctively older than the Rapitan iron formation, and they are not related to glacial processes (Basta et al., 2011). The 10-m-thick Erzin BIF in southern Tuva (Russian Federation) and northern Mongolia occurs within the Mugur Formation, and rests on the top of the metavolcanics of the same unit dated U–Pb at 767 ± 15 Ma (Ilyin, 2009). The Shilu Group in South China (Fig. 1) hosts 50 to 400-m-thick, high-grade iron formation deposited in the Tonian between 960 and 830 Ma, as shown, respectively, by U–Pb ages of detrital zircons and the age of metamorphic overprint (Xu
Several occurrences of Neoproterozoic BIFs are demonstrably younger than the middle Cryogenian glaciation, including the largest one, the >300-m-thick BIF and associated manganese formations of the Jacadigo Group (Brazil) and its correlative Boqui Group (Bolivia). The glacially influenced BIF (Figs 2(A)–(B) and 3(C)) yielded youngest U–Pb detrital zircon age from interbedded sandstones of 695 ± 17 Ma (Dossing et al., 2010). Ar–Ar dating on cryptomelane within the Mn ores reveals a minimum depositional age of 587 ± 7 Ma (Piacentini et al., 2013), which may be interpreted as the age of early diagenesis. Considering that the metamorphic braunite yielded Ar–Ar ages between 547 and 513 Ma (Piacentini et al., 2013), which matches with the age of the Pan African-Brasiliano orogeny (587 ± 7 Ma) in the region (McGee et al., 2012), it could well approximate the depositional age and is within the error of the

**FIGURE 1**

Lithostratigraphy and facies association of Neoproterozoic iron formations: (A) Iron formation at the boundary between the Suyunei and Shezal formations, Rapitan Group, Canada (From Baldwin et al. (2013)). (B) Wadi El Dabbah iron formation, Egypt (From Ali et al. (2009)). (C) Jucuruçu Formation, Seridó Belt, NE Brazil (From Van Schmus et al. (2003), Nascimento et al. (2007)). Eq. Fm.: Equador Formation. (D) Shilu Group, South China (From Xu et al. (2013b)). Indicated are maximum thicknesses observed. S. Fm.: Shihuiding Formation.
CHAPTER 17 CHEMOSTRATIGRAPHY OF NEOPROTEROZOIC BIF

FIGURE 2
Outcrop and polished slab photographs of Neoproterozoic banded iron formation (BIF). (A) Elongate gneiss dropstone with long axis at high angle to bedding in BIF of the Jacadigo Group (W Brazil). (B) Granite dropstone in pure BIF of the Jacadigo Group. Note the separation between the dropstone and the gritty layer below. (C) Basement dropstone in BIF of the Jakkalsberg Member, Numees Formation (Namibia). (D) BIF of the Yerbal Formation (Uruguay) as exposed in a shallow exploration trench. (E) Polished slab of magnetite + hematite BIF of the Yerbal Formation, showing thin chert bands (From Gaucher et al. (2004)). Field of view is 9 cm wide. (F) BIF of the Jucurutu Formation, Seridó Belt, at Riacho Fundo section (NE Brazil). (G) Same unit as previous (Bonito Mine section), but showing thicker and more frequent chert bands. Scale in B, F, and G is 8 cm long.
FIGURE 3

Chem o stratigraphy of Neoproterozoic iron formations from South America. (A) Algoma-type banded iron formation (BIF), Ju curutu Formation, Seridó Belt (NE Brazil; Sial et al., submitted). Note high Eu/Eu* and Cr concentrations, and δ53Cr entirely within the high-temperature field (colored area). (B) Lower Arroyo del Soldado Group, Uruguay (Frei et al., 2013). Shaded areas mark chemical sediments characterized by high δ53Cr, Eu/Eu*, and FeHR/FeTot, and low εNd. Dashed line in Fe speciation column marks boundary between oxic and anoxic conditions. (C) Jacadigo Group (W Brazil, Dissing et al., 2010). Note secular variations in δ53Cr within the iron formation.
Gaskiers Glaciation (582.4 ± 0.5 Ma; Bowring et al., 2003). Correlative glaciogenic diamictites interbedded with BIF of the Puga Formation in the southern Paraguay Belt (Brazil; Piacentini et al., 2007) yielded U–Pb age of detrital zircons as young as 709 ± 6 Ma (Babinski et al., 2013). They are conformably overlain by the cap carbonates of the Corumbá Group (Boggiani et al., 2003, 2010), above which, well-preserved Ediacaran acritarchs and metazoans (Cloudina, Corumbella) occur (Gaucher et al., 2003). All these data suggest that deposition of the Jacondi Group and the Puga Formation (southern Paraguay Belt) took place in the end-Cryogenian or, more probably, during the Gaskiers glaciation.

BIF also occurs in the Jacurutu Formation located in the Seridó Belt, Brazil (Sial et al., submitted; Fig. 1). Van Schmus et al. (2003) reported U–Pb age for the detrital zircons of the same unit at its type area as young as 634 ± 13 Ma. Therefore, deposition of the Jucurutu BIF took place in the lower Ediacaran, between 634 Ma and the peak of metamorphism in the Brasiliano orogeny in this region (c. 600–585 Ma; Hollanda et al., 2010).

Dropstone-bearing BIFs of the Jakkalsberg Member of the Numees Formation (Fig. 2(C)) in the Gariep Belt (Namibia) were assigned to the Ediacaran on the basis of Sr isotope ratios and Pb–Pb ages of its cap carbonate (Fölling and Frimmel, 2002) and organic-walled microfossils occurring below and above the unit (Gaucher et al., 2005). More recently, Macdonald et al. (2010b) dispute this age assignment and prefer a correlation with the Rapitan BIF, on the basis of new geological mapping and chemostatigraphy. More work, especially reliable U–Pb ages, is needed to solve this issue.

Arguably the youngest examples of Neoproterozoic BIFs were reported from the Yerbal and Cerro Espuelitas formations of the Arroyo del Soldado Group, Uruguay (Gaucher, 2000; Gaucher et al., 2004; Frei et al., 2013). BIF of the Yerbal Formation (Figs 2(D)–(E) and 3(B)) is devoid of any glacial features, occurs 800 m above the sandstones for which Blanco et al. (2009) reported U–Pb detrital zircon age as young as 664 ± 14 Ma. Equivalent, more proximal sandstones of the Barriga Negra Formation yielded youngest U–Pb detrital zircon age of 566 ± 8 Ma. The iron horizons are further interbedded with siltstones bearing Cloudina riemkeae, an index fossil for the late Ediacaran (Gaucher and Sprechmann, 1999; Gaucher et al., 2003; Gaucher and Poiré, 2009). The magnetite-bearing BIFs of the Cerro Espuelitas Formation (Gaucher, 2000) occur at stratigraphically two formations above the Yerbal Formation, and are thus of latest Ediacaran age.

In summary, the Neoproterozoic BIFs, pre- and postdate the middle Cryogenian, c. 715 Ma glaciation, and occur in the Tonian, Cryogenian, and Ediacaran. Interestingly, not all the Neoproterozoic BIFs were deposited in glacially influenced settings. In fact, as we demonstrate in the following sections, examples of the three BIF types have been described from the Neoproterozoic successions.

17.3 DEPOSITIONAL ENVIRONMENT OF NEOPROTEROZOIC BIFS

17.3.1 SEDIMENTOLOGY AND FACIES ASSOCIATION

17.3.1.1 Glacially Influenced Iron Formations

Several Neoproterozoic iron formations were deposited in glacially influenced environments, and they are assigned to the “Rapitan-type” (Beukes and Klein, 1992). Apart from well-documented glaciomarine BIF of the Rapitan Group (Baldwin et al., 2012) other analogues show clear indications of having been influenced by glaciomarine environment. Basement dropstones occur in BIF of the Jakkalsberg Member of the Numees Formation (Fig. 2(C)). southern Namibia (Frimmel, 2008). Similarly, the Chuos Formation in northern Namibia comprises glacial diamictite with predominantly basement clasts, including some striated, and associated thin horizons of BIF (Hoffman and Halverson, 2008;
Miller, 2008). A well-developed cap carbonate yielding negative $\delta^{13}C$ values (Rasth of Formation) rests on top of the Chuos Formation (Hoffman and Schrag, 2002). Thus, BIFs of the Chuos Formation were deposited in unambiguously glaciomarine environment and can be assigned to the Rapitan type.

BIFs of the Jacadigo Group (Banda Alta or Santa Cruz Formation) and Puga Formation bear convincing evidences of a glacial environment. The Puga Formation includes both associated diamictites and dropstones in the BIF (Piacentini et al., 2007). In the Jacadigo Group, both planar and elongate, outsized clasts occur (Fig. 2(A)–(B)). Planar clasts tend to lie parallel to bedding, but elongated clasts often show major axes perpendicular to bedding (i.e., bullet clast). A 6 m long granite bullet-clast was illustrated by Möller (2004) from the top of the Banda Alta Formation (Fig. 3(C)). Attempts to explain these outsized clasts as nonglacial in origin, for example as the result of downslope sliding and/or mass flows (e.g., Freitas et al., 2011) are not convincing. Downslope sliding cannot account for the orientation of bullet clasts. The thin, sandy layers occasionally accompanying outsized clasts (Freitas et al., 2011; Trompette et al., 1998) do not contradict a glacial origin for the latter, because they can also be derived from melting icebergs. Granite dropstones weighing more than 100 tons in chemical sediments such as BIF and MnF are possibly the most convincing evidences of glaciation so far reported from the Neoproterozoic deposits.

Thus, a glaciomarine setting is ascribable for a number of Neoproterozoic iron formations, including the thickest ones (e.g., Jacadigo Group, Rapitan Group). Interestingly, most of these occurrences were deposited in rift basins. This has led to the development of models that dispute the importance of glaciation and emphasize the role of rifting and hydrothermal activity (e.g., Young, 2002; Eyles and Januszczak, 2004; Freitas et al., 2011).

17.3.1.2 BIF Associated with Volcanic Rocks

Neoproterozoic iron formations in Egypt and their correlative units in northwestern Saudi Arabia, up to 90 m thick, are interbedded with wackes, tuffs, lapilli and subordinate volcanic flows (basalts, andesites, dacites; Basta et al., 2011; Stern et al., 2013. Fig. 1). The geochemical affinities of the volcanic rocks point to an arc or back arc setting (Ali et al., 2009). $\epsilon$Nd (750 Ma) of these rocks is invariably positive, and ranges between +5 and +9 (Ali et al., 2009), showing their juvenile nature.

The 30 m thick BIF (Figs 1(C) and 3(A)) of the Jucurutu Formation (Brazil), is also associated with mafic metavolcanics and metabasalts, but it is overlain by carbonates characterized by negative $\delta^{13}C$ values (Nascimento et al., 2007; Sial et al., submitted). However, these carbonates do not exhibit the typical features of cap carbonates (e.g., Hoffman and Schrag, 2002). Furthermore, the glacial features are absent in the thinly banded BIF (Sial et al., submitted; Fig. 2(F)–(G)). Diamictites with faceted clasts occur elsewhere in the Seridó Belt, but is not associated with the BIF (Legrand et al., 2008). Van Schmus et al. (2003) proposed, on the basis of detrital zircon ages, the nature of the basement and lithostratigraphy, that the Jucurutu Formation was deposited in a rift basin as the result of late Neoproterozoic extension of a pre-existing continental basement, with the development of small marine basins (Fig. 4). This may explain the differences, such as the occurrence of carbonates, compared to BIFs deposited in an arc environment, such as the Egyptian and Saudi Arabian BIF described above.

These examples serve to illustrate that Algoma-type BIFs occur in Neoproterozoic successions, and that they were both associated to compressional and extensional geotectonic settings, as also known for older BIFs (Gross, 1980). As we will discuss in the following sections, these Algoma-type Neoproterozoic BIFs bear distinct geochemical and chemostratigraphic features that allow a distinction from the glacially influenced iron formations.
Deositional models for the three types of Neoproterozoic iron formations discussed in this work. (A) Deposition of Rapitan type banded iron formation (BIF) during glacial retreat, exemplified by the type occurrence in the Rapitan Group (Modified from Baldwin et al. (2012)). BSR: bacterial sulfate reduction. (B) Depositional model for Algoma type BIF of the Jucurutu Formation (NE Brazil) according to Sial et al. (submitted). (C) Depositional environment of Lake Superior type BIF of the Yerbal Formation, Arroyo del Soldado Group (From Frei et al. (2013), and references therein.).
17.3 DEPOSITIONAL ENVIRONMENT OF NEOPROTEROZOIC BIFS

17.3.1.3 BIF Associated with Platform Deposits but without Glacial Features

These are possibly the most neglected Neoproterozoic iron formations, despite being remarkably thick and laterally persistent. They share three characteristics: (1) they do not show glacial features or associated glacial deposits, (2) they are not associated with volcanic rocks, and (3) they occur in passive margin successions characterized by thick carbonate and shale deposits.

A well-documented example is the Yerbal Formation of the Arroyo del Soldado Group (Uruguay; Fig. 3(B)). Up to 50-m-thick, oxide-facies BIF, composed of alternating magnetite + hematite and chert bands (Fig. 2(D)–(E)), occurs at the top of the unit, just beneath the contact with the overlying carbonates of the Polanco Formation (Gaucher et al., 2004; Frei et al., 2013, Fig. 3(B)). BIFs are interbedded with siltstones, cherts, and dolostones, all of which show considerable lateral continuity (Gaucher, 2000; Gaucher et al., 2004). No volcanic or pyroclastic rocks occur in the whole of the 5-km-thick Arroyo del Soldado Group. Detrital zircon ages of the Yerbal Formation are mostly Paleoproterozoic, with subordinate Archean and Mesoproterozoic populations (Gaucher et al., 2008; Blanco et al., 2009). Thus, both facies association and provenance show that the geotectonic setting of the Yerbal Formation was a stable platform developed at the margin of an old craton (Río de la Plata Craton, Gaucher et al., 2003, 2008). The same setting is inferred for the younger BIFs of the Cerro Espuelitas Formation (Gaucher et al., 1996; Gaucher, 2000). They are predominantly magnetitic and are associated with thick, gray and black shales and chert. A likely metamorphic (amphibolite facies) equivalent of the Arroyo del Soldado BIF is represented by the Marco de los Reyes Formation, which crops out at the eastern edge of the Río de la Plata Craton (Chiglino et al., 2010). This unit hosts 40-m thick oxide-facies (magnetite) BIF having a mean composition of 64% Fe₂O₃ and 33% SiO₂ (Bossi and Navarro, 1991). This BIF is associated with cherts, carbonates, and metapelites. ⁸⁷Sr/⁸⁶Sr values of the high-Sr limestones range between 0.7070 and 0.7080 and δ¹³C between −3‰ and 4.4‰ VPDB (Chiglino et al., 2010), matching corresponding values of the Polanco Formation (Gaucher et al., 2004; Frei et al., 2011).

A shelf setting has also been proposed for the Tonian BIF of the Shilu Group (Hainan Province, South China). Four BIF horizons are interbedded with dolostones, pelites, and quartz-arenites (Fig. 1(D)) and the whole package has been metamorphosed in the upper greenschist facies (Xu et al., 2013a,b). Thickness of the BIF and intervening strata ranges between 50 and 400 m. No evidence of contemporaneous glaciation or volcanism occurs in the Shilu District which, together with the facies association, favor an assignment to the Lake Superior type (Xu et al., 2013b). A similar depositional setting was proposed also for BIFs of the Neoproterozoic Jingtieshan Formation (Gansu Province, North China) on the basis of their facies association (Sun et al., 1998).

Thus, despite being much smaller than their older counterparts, Lake Superior-type BIFs do occur in the Tonian and Ediacaran. This clearly shows that BIF deposition was not dependent on glacial conditions, a fact that can already be inferred from the ferruginous nature of the Neoproterozoic ocean (Canfield et al., 2008).

17.3.2 GEOCHEMISTRY AND CHEMOSTRATIGRAPHY

17.3.2.1 Rapitan-Type Neoproterozoic BIF

Rare earth elements (REE) are used to infer paleo-redox conditions and to elucidate the primary source of iron in the BIFs (hydrothermal vs. weathering, e.g., Kato et al., 2006). REE + Y data reported by Klein (2005), Halverson et al. (2011) and Baldwin et al. (2012) for the glacially influenced Rapitan iron formation (Canada) display a typical, LREE-depleted pattern and the absence of Eu or Ce anomalies. For
the Jacadigo Group. Klein and Ladeira (2004) also report the absence of Eu or Ce anomalies. This suggests that the primary iron source in the glacially influenced BIFs may have been glacially sourced iron oxyhydroxide nanoparticles that were subsequently bacterially reduced under ferruginous conditions, supplemented with distal hydrothermal sources from the deep ocean (Baldwin et al., 2012). In the particular case of the Jacadigo Group, REE patterns, unlike the Rapitan BIFs, are LREE-enriched, resembling modern estuarine or coastal waters (Graf et al., 1994), maybe due to the influx of meltwater.

Other trace elements used in Rapitan-type BIF chemostratigraphy include Mo, U, and W. These elements, when normalized against the Mud from Queensland (Kamber et al., 2005) exhibit secular variations in the Rapitan BIF, with enrichments at the base and top of the unit and low values in most of the BIF interval (Baldwin et al., 2012). This stratigraphic distribution indicates reducing conditions throughout the unit, with sulfidic ( euxinic) conditions at the base and top of the iron formation, as indicated especially by Mo (Baldwin et al., 2012). These conclusions were corroborated more recently by Mo isotopes (δ⁰⁸Mo, Baldwin et al., 2013). Similar low values of U and Mo were found by Dissing et al. (2010) throughout the glacially influenced BIF of the Jacadigo Group (Fig. 3(C)), with significant U and Mo enrichment only at the base (Corrego das Pedras Formation) but not at the top. Thus, it becomes clear that conditions during the deposition of these examples were characterized by ferruginous bottom waters and low sulfate availability.

Iron isotopes are obvious candidates for BIF chemostratigraphy, but the interpretation of isotopic signals is often complex due to the involvement of many processes, biotic and abiotic, that fractionate iron. Halverson et al. (2011) reported an increasing trend of δ⁵⁷Fe, from −0.7‰ to 1.2‰ IRMM-14, for BIF of the Sayunei Formation (Rapitan Group), which they interpreted as the reflection of rising sea-level and an isotopic gradient across the chemocline. Halverson et al. (2007) reported a similar δ⁵⁷Fe curve for the glacially influenced Holowilena Ironstone, but with significantly larger amplitude (−0.8‰ to 3.1‰ IRMM-14).

Chromium isotopes have become a useful tool for the study of BIF, carbonates, and other chemogenic rocks, essentially reflecting: (1) the degree of oxidative weathering on the continents (and thus atmospheric oxygenation), and (2) the relative input of oxidized, land-derived, fractionated Cr (VI) versus hydrothermal, unfractonated Cr (III) from vents (Frei et al., 2009). Whereas, the older Archean BIFs show mostly unfractonated, negative δ⁵³Cr values around −0.15‰ SRM 979, the Neoarchean and Paleoproterozoic BIFs exhibit positive values up to +0.5‰ SRM 979, depicting the early atmospheric oxygenation (Frei et al., 2009). Cr-isotope data for Neoproterozoic units include the Rapitan BIF, which yielded positive values between 0.9‰ and 0.96‰ (Frei et al., 2009). In an attempt to study the secular variations of δ⁵³Cr, Dissing et al. (2010) applied this method to the Jacadigo Group. BIF of the Banda Alta/Santa Cruz Formation yielded positive δ⁵³Cr values rising from 0.1‰ at the base to a peak of 0.9‰ in the upper part (Fig. 3(C)), slightly decreasing to c. 0.6‰ at the top (Dissing et al., 2010). The Fe-rich glaciogenic diamictites and associated BIF of the correlative Puga Formation also yielded positive δ⁵³Cr values from +0.1‰ to +0.4‰. Interesting in this regard is the parallelism of δ⁵³Cr and δ¹³C found in the Neoproterozoic carbonates (Frei et al., 2011), which allow the use of δ⁵³Cr in BIF as a proxy of δ¹³C of contemporaneous seawater. The coupling of both isotope systems is probably through photosynthetic activity, that affected both carbon burial and oxygen production (Frei et al., 2013).

17.3.2.2 Algoma-Type Neoproterozoic BIF
REE+Y patterns were presented by Basta et al. (2011) and Stern et al. (2013) for Algoma-type BIFs of Egypt and Saudi Arabia. They are LREE-depleted (normalized to the Post-Archean Australian Shale, PAAS), exhibit positive Eu anomalies (Eu/Eu*) of up to 1.41 (mean 1.13), and true negative Ce


anomalies (Ce/Ce\textsuperscript{*}) down to 0.7 (mean 0.9). The latter characteristics are in strong contrast with Raptitan-type BIF that do not show Eu or Ce anomalies. When plotted against the stratigraphy, Eu/Eu\textsuperscript{*} and Ce/Ce\textsuperscript{*}, allow the identification of the intervals of elevated hydrothermal input (Stern et al., 2013). Significantly, these intervals are also marked by higher εNd(t) values, which reach +6 in the Sawawin BIF of Saudi Arabia (Stern et al., 2013). Similar, albeit more extreme, REE + Y patterns were found by Sial et al. (submitted) for Algoma-type BIFs of the Jucurutu Formation (São da Bacia, Brazil). They are LREE-depleted and characterized by strongly positive Eu/Eu\textsuperscript{*} anomalies (up to 3.1) and true positive Ce/Ce\textsuperscript{*} anomalies up to 1.3 (Fig. 3(A); Bau and Dulski, 1996). Strong hydrothermal input related to rifting might have promoted the anoxic (ferruginous) conditions, as shown by positive Ce anomalies.

The proximity to hydrothermal vents is also shown by very high Cr contents of the Jucurutu BIFs (85–300, eventually 400 ppm) and by their δ\textsuperscript{53}Cr values that vary mostly between −0.30‰ and −0.12‰ (Sial et al., submitted; Fig. 3(A)), and within the field of magmatic values (Schoenberg et al., 2008). A negligible detrital component is shown by the occurrences of low Sc and Zr concentrations in the BIF (average Sc = 2.2 ppm, average Zr = 1.2 ppm). Less negative δ\textsuperscript{53}Cr values tend to appear at the base of the iron formation, becoming more negative up section (Fig. 3(A)). Overlying carbonates are characterized by equally negative to slightly fractionated δ\textsuperscript{53}Cr (−0.19‰ to −0.05‰) and “normal” Cr concentrations between 1 and 10 ppm (Fig. 3(A)). Interestingly, corresponding δ\textsuperscript{34}S values are very negative, around −7‰ VPDB, in the lower 20 m of carbonates (sitting atop BIF), passing into positive values up to 10‰ VPDB in the up section (Sial et al., submitted).

An arc setting was proposed for Algoma-type BIFs in Egypt and Saudi Arabia on the basis of the type, geochemical affinities and Nd isotopes of the accompanying volcanic rocks (Ali et al., 2009, Fig. 1). On the other hand, the Jucurutu BIFs were probably deposited in a starved rift basin (Fig. 4(B)), as shown by their low terrigenous contents, geochemistry and association with overlying carbonates (Sial et al., submitted). In his original definition, Gross (1980) erected the Algoma type to include BIFs that were deposited “along volcanic arcs or rift zones”. Thus, both of these Algoma subtypes occur in the Neoproterozoic.

17.3.2.3 Lake Superior Type Neoproterozoic BIF
Frei et al. (2009, 2013) reported REE + Y data for BIF of the Arroyo del Soldado Group (Fig. 3(B)). BIFs of the Yerbal Formation are LREE-depleted and characterized by positive Eu/Eu\textsuperscript{*} anomalies (1.15–1.71) and negative Ce/Ce\textsuperscript{*} anomalies ranging from 0.63 to 0.79 (data from Frei et al., 2009). Fe speciation (Fe\textsubscript{Y}(Fe\textsubscript{Tot})) values range from 0.5 to 0.7 for the BIF and associated cherts (Fig. 3(B); Frei et al., 2013) and thus indicate anoxic, ferruginous conditions (Canfield et al., 2008). However, interbedded shales and carbonates yielded Fe\textsubscript{Y}(Fe\textsubscript{Tot}) values far below the threshold value of 0.38 (Canfield et al., 2008; Frei et al., 2013, Fig. 3(B)), showing that predominantly oxygenated conditions alternated with anoxic events, as do the negative Ce anomalies mentioned above.

The εNd(t) values of the entire Yerbal Formation range between −19 and −5 (Fig. 3(B)), with Tdm values between 2.4 and 2.0 Ga that match with the source rocks of the Río de la Plata Craton (Frei et al., 2013). Understandably, the lowest εNd(t) values (−5 to −12) correspond to the BIFs and cherts, because they are pure chemical precipitates with little siliciclastic input. These values confirm the inference of stable platform setting for the Arroyo del Soldado Group (Fig. 4(C)), deduced from the facies association and detrital zircon U–Pb ages (see above).

The δ\textsuperscript{34}S values for BIF of the Arroyo del Soldado Group are strongly fractionated (Fig. 3(B)), yielding values between 0.7‰ and 5.0‰ (Schoenberg et al., submitted) (Fig. 3(A); Ali et al., 2009, 2013). The latter are the most positive δ\textsuperscript{34}S values reported for BIFs up to date (Frei et al., 2009), which is logical considering the young age of these iron formations and the progressive oxygenation of the surface environments leading up to the
Ediacaran–Cambrian boundary. Moreover, in Rapitan type BIF, rapid denudation and cold climate in the hinterland allows for less intense chemical weathering and could explain the lower \( \delta^{53}\text{Cr} \) compared to the Neoproterozoic Lake Superior type (see Fig. 4), which were deposited on deeply weathered, old cratons.

The Lake Superior-type BIF of the Shilu Group (China) are also characterized by LREE-depletion (PAAS-normalized), and positive Eu/Eu\(^*\) (up to 11) and Ce/Ce\(^*\) (1.0–2.4) anomalies (Xu et al., 2013b). Corresponding \( \varepsilon\text{Nd}(t) \) values for the BIF range between \(-7\) and \(-5\) (average = \(-6\)) and Tdm 1.9 to 2.1 Ga (Xu et al., 2013b). Thus, the Shilu BIFs also require an old cratonic region as source area, and represent a marine shelf setting, in line with the facies association observed. The only difference with the BIF of the Arroyo del Soldado Group is the more anoxic setting for the Chinese occurrence, which is also significantly older (Tonian).

In summary, it could be stated that the REE geochemical characteristics (e.g., Eu and Ce anomalies) of the Chinese and Uruguayan Superior type Neoproterozoic BIFs are intermediate between the Rapitan type and the Algoma type Neoproterozoic BIF. On the other hand, they show the most positive \( \delta^{53}\text{Cr} \) values due to a more open marine setting of these iron formations (Fig. 4) and the younger age of the Yerbal Formation.

### 17.4 DISCUSSION

It becomes clear from the data reviewed in the preceding sections that glaciation was not a pre-requisite for deposition of BIFs in the Neoproterozoic, as initially thought (e.g., Beukes and Klein, 1992). Contrary to the recent assumptions (Macdonald et al., 2010a; Cox et al., 2013) the age distribution of Neoproterozoic iron formations actually span the whole Era, from the Tonian to the late Ediacaran, and are not restricted to the Sturtian glaciation or even the Cryogenian. While it is true that many Neoproterozoic BIFs, including some of the largest, were deposited in glacially influenced settings (e.g., Jacadigo Group, Rapitan Group; Fig. 4(A)), many examples bear no indications of a glacial environment (Gaucher et al., 2004; Frei et al., 2013; Stern et al., 2013; Xu et al., 2013b; Sial et al., submitted). Instead, the prevalence of rifting and hydrothermal activity were important for the development of both glacial and nonglacial BIFs (Fig. 4), possibly due to the protracted fragmentation of Rodinia and the associated mantle superplumes (Li et al., 2008; Isley and Abbott (1999) already postulated a link between superplume events and BIF deposition in the late Archean and Paleoproterozoic. Ferruginous conditions were likely fueled by enhanced mid-ocean ridge hydrothermal circulation (Canfield et al., 2008). Both the increased length of mid-ocean ridges and enhanced heat flux during Rodinia breakup might have promoted the elevated hydrothermal activity (e.g., Gaucher et al., 2009), as is shown by extremely low \(^{87}\text{Sr}/^{86}\text{Sr} \) seawater ratios in the Tonian and Cryogenian (Melezhik et al., 2001; Halverson et al., 2007). The re-emergence of BIF in the Neoproterozoic after nearly 1 Gyr of nondeposition has more to do with the return to ferruginous conditions in the oceans than with near-global glaciation. Primary productivity must also be taken into account (Fig. 4), because it was the source of the large amounts of oxygen required to precipitate Neoproterozoic BIFs (e.g., Gaucher et al., 2004; Frei et al., 2013). In a basin covered by thick ice, dissolved oxygen would be rapidly exhausted due to the inhibition of photosynthesis. Thus, in glacial settings, most models require deposition of BIFs after ice retreat (e.g., Baldwin et al., 2012, Fig. 4(A)). Even in glacially influenced iron formations, there were no continued ice cover, and sea ice-free conditions are recorded at some levels (Le Heron et al., 2011). Finally, the progressive oxygen buildup in surface environments determine evolving geochemical and isotopic signatures for the Neoproterozoic BIFs (e.g., Frei et al., 2009), which in the future may be used as a chemostratigraphic tool for correlation and geochronology.
17.5 CONCLUSIONS

Neoproterozoic BIFs occur in Tonian, Cryogenian, and Ediacaran successions, and are not restricted to the middle Cryogenian (c. 715 Ma) glaciation. Many Neoproterozoic BIFs (North and South America, southern Africa, and Australia) were deposited in glacially influenced settings, and are traditionally assigned to the Rapitan type. Other occurrences in South America, Africa, and Asia, however, bear no indications of glacial processes and can be assigned to the Algoma and Lake Superior types.

Chemostratigraphy is a powerful tool for unraveling the depositional setting of Neoproterozoic BIFs. Some of the most useful methods are REE distribution, especially the Eu and Ce normalized concentrations, iron speciation, Nd and Cr isotopes (δ⁵³Cr). Whereas Rapitan type BIFs exhibit no Eu or Ce anomalies, Algoma type Neoproterozoic BIF show both. Positive δ⁵³Cr values characterize glacially influenced BIFs, and differentiates them from nonfractionated, mantle-like δ⁵³Cr values of Algoma type BIFs. The latter are also characterized by high Cr concentrations. The most positive δ⁵³Cr values occur in the open-shelf, Lake Superior type BIFs, especially those of Ediacaran age. Given the consistent secular variations exhibited by δ⁵³Cr, it is envisaged that it may be used for correlation and geochronology once the available database grows sufficiently.

It is demonstrated clearly that glaciation was not the main mechanism responsible for deposition of BIFs in the Neoproterozoic. Hydrothermal activity related to the rifting of Rodinia probably played the key role in their reappearance after the Mesoproterozoic gap, and promoted a return to ferruginous conditions after the demise of Mesoproterozoic euxinic oceans.

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