Ordovician ironstone of the Iberian margin: Coastal upwelling, ocean anoxia and Palaeozoic biodiversity

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Abstract

Middle to Upper Ordovician ironstone and associated sedimentary rocks of the West Asturian-Leonese and Cantabrian tectonostratigraphic zones, Spain, provide new information regarding the Palaeozoic Fe cycle and the palaeoceanography of the Rheic Ocean. Examination of drill cores and outcrops indicates the southeastern margin of this narrow seaway was a dynamic continental shelf where upwelling of ferrous seawater and storm currents controlled lithofacies character. Parasequence composition and stacking relationships suggest ironstone accumulated during marine transgression as accommodation increased from lowstand conditions. Proximal parasequences record aggradation from deep subtidal to shoreface environments. Hummocky cross-stratified sandstone and organic-rich siltstone grade upwards into swaley cross-stratified sandstone and granular Fe-silicate-rich ironstone capped by a flooding surface. Distal parasequences were deposited below storm wave base on the distal shelf and are composed of variably bioturbated organic-rich siltstone with thin Fe-chlorite and phosphorite layers. These differences in parasequence character define two different ironstone factories where Fe was concentrated and precipitated in sediment. Lithofacies associations support an emerging model for ironstone deposition where coastal upwelling delivered and stimulated the precipitation of Fe within shelf sediment. This notion provides further evidence for the development of intermittent anoxic water masses in an Ordovician ocean that was near the threshold of becoming fully ventilated. This style of Fe delivery probably represents a tipping point in the oxygenation history of the Phanerozoic oceans and is a throwback to the Precambrian when widespread anoxia allowed hydrothermal Fe to concentrate in the global ocean. New data suggest that minor extinction events punctuating the Great Ordovician Biodiversification Event may be traced to these anoxic waters, which in addition to Fe, were also enriched in biologically toxic, redox sensitive trace elements. Conversely, precipitation of upwelling-related ironstone may have helped sequester these trace elements, providing a negative feedback response that would aid post-extinction recovery.
INTRODUCTION

The Ordovician was characterized by a long-lasting greenhouse climate with the highest sea levels of the Palaeozoic flooding continental interiors to form expansive epeiric seas (Achab and Paris, 2007; Munnecke et al., 2010). New ocean currents developed as the Iapetus Ocean closed with convergence between Baltica and Laurentia and the Rheic Ocean opened with the separation of Avalonia from Gondwana (Díez Fernández et al., 2010; van Staal et al., 2012; Harper et al., 2014). Intervals of deep ocean anoxia were apparently common (Elrick et al., 2011; Saltzman et al., 2015; Kah et al., 2016), suggesting the ventilation of seawater that began in the Neoproterozoic (Och and Shields-Zhou, 2012) was more protracted than previously proposed. These anoxic intervals are marked by positive carbon isotope excursions preserved in carbonates that accumulated during the Great Ordovician Biodiversification Event (GOBE; ca 480–445 Ma), the most sustained increase of marine biodiversity in Earth history (Munnecke et al., 2010; Servais et al., 2010; Elrick et al., 2011; Harper et al., 2014; 2015; Saltzman et al., 2015; Edwards and Saltzman, 2016; Stigall et al., 2017). Also punctuating this interval are penecontemporaneous minor extinction events and episodes of ironstone deposition (Young and Taylor, 1989; Van Houten, 2000).

Ironstone is an enigmatic Phanerzoic biochemical sedimentary rock containing ≥15 wt% Fe. Ironstone is different from the Precambrian iron formation, which is less aluminous and generally forms much larger deposits with a more complex array of Fe minerals (Bekker et al., 2010; Pufahl, 2010). Unlike the earlier iron formation, Palaeozoic ironstone also commonly co-occurs with sedimentary phosphorite (Petránek, 1991; Todd et al., 2019), an upwelling-related biochemical sediment containing >18 wt% P₂O₅ (Glenn et al., 1991; Todd et al., 2019), an upwelling-related biochemical sediment containing >18 wt% P₂O₅ (Glenn et al., 1994; Pufahl and Groat, 2017). Precise causes remain unclear, but several studies imply that a greenhouse climate and related intensification of chemical weathering may have been important for increasing the delivery of Fe and P to the ocean (Van Houten and Bhattacharyya, 1982; Föllmi, 1996; Robb, 2005; Yilmaz et al., 2015; Pufahl and Groat, 2017). Thus, understanding the apparent relationship between climate, periods of ocean anoxia, biological evolution and episodes of ironstone accumulation may provide new insight into the unique conditions that permitted the Lazarus-like return of widespread Fe deposition that was so common in the Precambrian.

The purpose of this paper is to investigate Middle and Upper Ordovician (ca 470–444 Ma) ironstone from the Luarca Formation of the West Asturian-Leonese Zone (WALZ) in the Leonese Mountains, and the Castillejo and Fombuena formations in the southwestern continuation of the Cantabrian Zone (CZ) in the Eastern Iberian Chain, Spain (Figure 1). Collectively, these predominantly siliciclastic formations record storm-dominated deposition along the southeastern margin of the Rheic Ocean, which evolved through time to permit the accumulation of ironstone. A primary aim is to help clarify the connection between Fe deposition, oceanic anoxic events, regional extinctions and the GOBE by comparing results to recent research on ironstone from the northern Rheic margin (Todd et al., 2019).

Changes in palaeoenvironment that produced ironstone in the Castillejo, Fombuena and Luarca formations are interpreted herein by documenting the sedimentology and sequence stratigraphy. Relating variability in lithofacies character to fluctuations in relative sea level provides new information regarding the physical and chemical controls on ironstone deposition. Results demonstrate that ironstone is not simply a geologic curiosity but the consequence of geosphere-biosphere-hydrosphere feedback processes that regulated Earth system evolution during the GOBE.

GENERAL GEOLOGY AND STRATIGRAPHY

The WALZ and CZ are autochthonous tectono-stratigraphic zones of the Iberian Massif, which encompasses a large region of the European Variscan orogenic belt in northern Spain (Figures 1 and 2; Martínez Catalán, 1990; 2004; Quesada, 1991; Villas et al., 2011). The Gondwana affinity autochthonous units of the Iberian Massif are primarily composed of amalgamated Neoproterozoic terranes (Quesada, 1991; Shelley and Bossière, 2000; Martínez Catalán et al., 2004; Nance et al., 2010) that are unconformably overlain by Cambrian rift-related successions (ca 530–490 Ma; Sánchez-García et al., 2019 and references therein). The syn-rift successions are overlain by Tremadocian-Floian (ca 485–478 Ma) sedimentary rocks recording a rift-to-drift transition and subsidence (Pérez Estaún et al., 1990), which resulted in passive margin conditions on the northern margin of Gondwana that persisted until the onset of the Variscan orogeny in Early Devonian times (Gutiérrez-Marco et al., 2019). A Furongian (ca 497–485 Ma) break-up unconformity is interpreted to have formed as the Avalonia microcontinent separated from...
northern Gondwana during opening of the Rheic Ocean (Quesada, 1991; Shelley and Bossière, 2000; Martínez Catalán et al., 2004; von Raumer et al., 2006; Álvaro et al., 2018a).

With continued rifting and development of the Rheic Ocean (Figure 3), full separation of Avalonia probably occurred by the Floian or Dapingian (ca 478–467 Ma; Murphy et al., 2006; Nance et al., 2010; Torsvik and Cocks, 2013). The Rheic Ocean continued to widen until the Rhuddanian (ca 444–441 Ma) when the Iapetus Ocean began to close. The Early Silurian collision of Baltica and Avalonia was followed by collision of this amalgamated block with Laurentia to form Laurussia during the Early Devonian (Matte, 2001; Murphy et al., 2004; Nance et al., 2010; 2012; Torsvik and Cocks, 2013). Protracted closure of the Rheic Ocean started in the Early Devonian with subduction along the southern Baltic and northern Gondwana margins (Nance et al., 2010) followed by Eifelian to Givetian (ca 393–382 Ma) collision between promontories of Laurussia and Gondwana (Quesada, 1991; Kroner and Romer, 2013; Murphy et al., 2016). These events were followed by Mediterranean-style subduction of intervening ocean basins (Murphy et al., 2016) culminating in final closure of the Rheic Ocean and amalgamation of Pangea during the Late Carboniferous (Shelley and Bossière, 2000; Matte, 2001; Nance et al., 2010). The Variscan orogeny lasted until the Cisuralian (ca 290 Ma; Quesada, 1991) and subjected the WALZ to multiple episodes of deformation (Martínez Catalán et al., 2004; Nance et al., 2010).

Ordovician strata in the WALZ are exposed in the Leonese Mountains and consist of a ca 4,000 m thick, ironstone-bearing siliciclastic succession overlain by Katian carbonates (Figures 1, 2 and 4; Pérez Estaún et al., 1990; Villas et al., 2011; Cole et al., 2017). A southeastern continuation of the CZ also contains ironstone and occurs in the Eastern Iberian Chain (Villas et al., 2011; Álvaro et al., 2018a). Deposition occurred on the Iberian shelf where storm processes dominated to constantly rework sediment (Cole et al., 2017). Research reported herein focuses on the upper Los Cabos Group and Luarca Formation in the Leonese Mountains and the Armorican Quartzite, Castillejo Formation, and Fombuena Formation in the Eastern Iberian Chain (Figures 2 and 4). Collectively, these units record accumulation from the Floian to middle Katian (ca 478–449 Ma; Pérez Estaún et al., 1990; Gutierrez-Marco et al., 1999; Cole et al., 2017; Colmenar and Rasmussen, 2017). Detrital zircon provenance analysis suggests sediment was derived from both the West African and Saharan cratons, placing the Iberian shelf near northern Africa (Figure 3; Díez Fernández et al., 2010; Pastor-Galán et al., 2013; Shaw et al., 2014).

The Los Cabos Group and Luarca Formation (WALZ) are interpreted to have accumulated further outboard than the Armorican Quartzite, Castillejo Formation, and Fombuena Formation.
Formation (CZ: Pérez Estaún et al., 1990; Villas et al., 2011; Cole et al., 2017). The Los Cabos Group is composed of a Wuluan to early Darriwilian (ca 506–466 Ma) silty sandstone that is generally considered correlative to the coarse sandstone of the Armorican Quartzite (Marcos, 1973; Pérez Estaún et al., 1990; Gutiérrez-Marco et al., 1999). The overlying Luarca Formation is in conformable contact and consists of monotonous black shale with middle to late Darriwilian (ca 461 Ma) and Sandbian-Katian (ca 453 Ma) ironstone horizons (Figure 4; Lunar and Amorós, 1979; Pérez Estaún et al., 1990; Gutiérrez-Marco et al., 1999). Biostratigraphic ages of these units are based on occurrences of Cambrian and Ordovician trilobites, graptolites and molluscs (Gutiérrez-Marco et al., 1999; Pérez Estaún et al., 1990).
The Armorican Quartzite is composed primarily of cross-beded quartz arenite and interbedded quartz wacke (Carls, 1975). Shelly fossils are conspicuously absent and concentrated in rare layers containing asaphid trilobites, xyphosurids, connulariids, molluscs and lingulids (Babin and Hammann, 2001; Villas et al., 2001). However, a rich ichnofossil assemblage of *Skolithos*, *Cruziana* and *Daedalus* provides a poorly constrained Floian to early Darrwilian age (ca 478–470 Ma; Carls, 1975; Villas et al., 2011). Resting paraconformably above the Armorican Quartzite is the middle Darrwilian to early Sandbian (ca 463–456 Ma) Castillejo Formation, which is subdivided into the Marité, Alpartir and Sierra members (Figure 4; Cole et al., 2017). The Marité Member is composed of ironstone (Carls, 1975) and contains middle to late Darrwilian (ca 463–459 Ma) graptolites (Cole et al., 2017). The occurrence of *Didymograptus murchisoni* near its base suggests the stratigraphic gap between the Castillejo Formation and the Armorican Quartzite spans the lower Oretanian regional stage (Gutiérrez-Marco, 1986), which is equivalent to a middle Darrwilian age between ca 465 and 463 Ma. The overlying Alpartir and Sierra members define a coarsening upwards succession that grades from shale to quartz wacke (Cole et al., 2017). Trilobites, gastropods, bivalves, brachiopods and rare conodonts in the Sierra Member constrain the age of the upper Castillejo Formation to the Sandbian (ca 456 Ma; Carls, 1975; Kolb, 1978; Hammann et al., 1982; Hammann, 1983; Villas, 1985; Gutiérrez Marco, 1986; Cole et al., 2017). The overlying Fombuena Formation is divided into the Piedra del Tormo and Huerva members (Figure 4; Villas et al., 2011; Cole et al., 2017). The bottom of the Piedra del Tormo Member is a basal ironstone that grades upwards into a shale containing late Sandbian (ca 452 Ma) bryozoans, brachiopods, gastropods, graptolites, echinoderms and rare conodonts (Villas et al., 2011; Cole et al., 2017). The Huerva Member consists of cross-beded arenites and intercalated shales with early to middle Katian (ca 453–449 Ma) fossils (Carls, 1975; Villas et al., 2011; Cole et al., 2017).

**3 | METHODS**

In the Leonese Mountains, vertical and lateral facies changes characterizing the Los Cabos Group and Luarca Formation were described from well-exposed outcrops and four drill cores housed in the Instituto Geológico y Minero de España’s core repository in Peñarroya-Pueblonuevo. Lithofacies composing the Armorican Quartzite, Castillejo Formation and
Fombuena Formation in the Eastern Iberian Chain were logged in road-cuts and quarry walls (Figure 2). Emphasis was placed on understanding palaeoenvironments through time by identifying sequence stratigraphic bounding surfaces and interpreting regional lithofacies trends. The degree of bioturbation was recorded in the field using the Droser-Bottjer ichnofabric index of 1 (no bioturbation), 2 (up to 10% bedding bioturbated), 3 (11%–40% of bedding disturbed), 4 (41%–60% infaunal reworking), 5 (bedding nearly completely disturbed) and 6 (total homogenization; Droser and Bottjer, 1986). Such information provides constraints on the bottom and pore-water redox conditions that produced authigenic Fe minerals.

Unaltered and altered samples of all facies (n = 167) were collected to understand ironstone paragenesis. Percentages of ironstone and clastic grains were estimated from polished thin sections (n = 39) using a Nikon Optiphot-POL transmitted and reflected light microscope (Nippon Kogaku Inc.). Modal compositions were determined for all minerals using abundance indices of rare (<5%), uncommon (5%–24%), common (25%–49%) and abundant (≥50%). Textures were further investigated using a JEOL JSM-5900 LV scanning electron microscope (JEOL Ltd.) equipped with a Princeton Gamma-Tech IMIX-PC EDS detector (Princeton Gamma Instruments Inc.) in the Acadia Centre for Microstructural Analysis. Mineralogy was confirmed using X-ray diffraction analysis at Queen’s University where samples (n = 23) were analysed using an Xpert-Pro Philips powder diffractometer (PANalytical BV) with a Co X-ray target source across scattering angles from 5° to 70°. This information was integrated with sedimentologic and sequence stratigraphic data to develop an oceanographic model for ironstone deposition in the WALZ and CZ.

**FIGURE 4** Lithostratigraphy of Ordovician strata in the WALZ and its eastern extension in the Eastern Iberian Chain. Ironstone occurs in the Herrera Unit of Álvaro et al. (2018b). Pale red colour in stratigraphic column highlights approximate depositional age of ironstone (Gutiérrez-Marcos et al., 1999; Cole et al., 2017; Colmenar and Rasmussen, 2017). The base of ironstone in the Peña del Tormo and Marité members is locally erosive. Starred numbers correspond to drill core and outcrop location: 1—Oscos-5 drill core. 2—W-4-A drill core; 3—W-5-A/B drill core; 4—Peña del Tormo Road Cut; 5—Marité Quarry. Flo—Floian; Dp—Dapingian; Mar—Marité Member; PT—Piedra del Tormo Member
Eight distinct siliciclastic lithofacies are interpreted to record deposition in subaerial to offshore environments on a storm-dominated shelf (Table 1).

### Table 1 Lithofacies descriptions and interpretations

| Facies       | Description                                                                 | Interpretation                                                                 |
|--------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| F1           | Poorly sorted breccia: Poorly-sorted, matrix-supported, polymictic breccia. Abundant secondary botryoidal haematite cement with zoning of elongated crystallites | Subaerial exposure and development of palaeo-regolith. Reworked by fairweather waves during marine transgression |
| F2           | Trough and planar cross-stratified granular ironstone composed of spherical or elliptical coated grains. Nuclei consist of mudstone clasts, Fe-chlorite cortex fragments, granular ironstone intraclast, and polycrystalline quartz. Thick, discordant cortex mineralogy is primary haematite or chamosite/clinochlore with secondary haematite, goethite, and magnetite | Shoreface deposition near fairweather wave-base with frequent storm activity. Primary haematite mineralogy in most proximal stratigraphy, chamosite/clinochlore in marginally deeper marine environment within the proximal ironstone factory. (Bhattacharyya, 1989; Taylor and Macquaker, 2000a; Pufahl and Grimm, 2003; Pufahl, 2010) |
| F3           | Swaley cross-stratified quartz arenite: Thickly bedded, swaley cross-stratified quartz arenite. Commonly associated with F2. Very well sorted mature sediment contains abundant sub-angular quartz. Accessory minerals include muscovite, plagioclase, biotite, goethite and haematite | Lower shoreface deposition as a result of storm-induced combined-flow (Leckie and Walker, 1982; Duke, 1985; Allen and Underhill, 1989; Arnott, 1992; Dumas and Arnott, 2006) |
| F4           | Hummocky cross-stratified quartz wacke: Thinnly bedded hummocky cross-stratified quartz wacke. Moderately well sorted, sub-mature sediment containing sub-angular quartz in a muscovite-rich silty matrix. Accessory minerals include goethite, magnetite and haematite with rare pyrite | Shallow offshore deposition as a result of storm-induced combined-flow above storm wave-base (Hamblin et al., 1979; Dott and Bourgeois, 1982; Duke, 1985; Arnott, 1992) |
| F5           | Thinly laminated siltstone: Thinly laminated siltstone commonly interbedded with F4 with rare thin beds of phosphatic intraclasts. BI = 0–4 with common Planolites ichnofossils. Moderately sorted immature sediment contains biotite, and sub-rounded quartz in a muscovite-rich matrix. Accessory minerals include goethite, magnetite and haematite framboids | Suspension settling in the offshore during quiescence between storms (Ogston et al., 2000; Worden and Morad, 2003; Dunbar and Barrett, 2005; Ghadeer and Macquaker, 2011) |
| F6           | Bioturbated bryozoan-rich siltstone: Burrow-mottled, fossiliferous siltstone dominated by thinly branching bryozoa with common brachiopods, as well as rare crinoids and ostracod fragments. Well sorted muscovite-rich matrix contains sub-rounded quartz, plagioclase as well as secondary goethite and haematite framboids. Matrix supported fossils are commonly fill with block calcite and rarely exhibit mouldic porosity. Inferred BI = 6 | Suspension settling near storm wave-base (Fürsich and Hurst, 1974; Worden and Morad, 2003; Reid, 2010; Plotnick et al., 2013; Taylor and James, 2013; Colmenar et al., 2014) |
| F7           | Very thinly bedded ironstone: Very thinly bedded ironstone, composed of very fine detrital quartz grains and frambooidal pyrite cemented by clinochlore. Concentrically layered chamosite and clinochlore-rich coated grains common. Bedding overprinted by fabric destructive magnetite. BI = 0 | Low-oxygen distal offshore deposition within distal ironstone factory as a result of suspension settling (Madon, 1992; Ogston et al., 2000; Dunbar and Barrett, 2005) |
| F8           | Medium laminated ironstone: Planar laminated ironstone composed of silt-sized quartz grains cemented with intergrown chamosite and clinochlore. Primary layering overprinted by fabric destructive magnetite. BI = 0 | Anoxic, distal offshore deposition within furthest extent of distal ironstone factory (Madon, 1992; Pufahl, 2010) |

### 4 | Lithofacies and Palaeoenvironments

Eight distinct siliciclastic lithofacies are interpreted to record deposition in subaerial to offshore environments on a storm-dominated shelf (Table 1).

#### 4.1 | Poorly sorted breccia

Facies 1 is a poorly sorted, matrix-supported, polymictic breccia formed of clasts derived from underlying lithologies (Figure 5A). Beds have an erosive base and are 5–40 cm thick. Angular clasts are supported by a coarse...
quartz arenite matrix that is cemented with goethite. Larger pores are filled with complexly zoned botryoidal haematite (Figure 5B).

This facies is interpreted to record subaerial exposure and development of a palaeo-regolith that was later re-worked by fair-weather waves during marine transgression. Goethite and botryoidal haematite cements probably precipitated as Fe-rich diagenetic fluids penetrated the breccia beds. The complex zoning in botryoidal haematite likely reflects precipitation from multiple burial-related fluids.

4.2 | Trough and planar cross-stratified granular ironstone

Facies 2 is a classic granular ironstone facies composed of haematite and coated Fe-silicate grains in 50–120 cm thick trough and planar cross-stratified beds (Figure 5C). Trough cross-stratified beds have an erosive base with pebble-sized rip-ups of underlying grainstone concentrated at their base. Coated grains are spherical or elliptical with nuclei of detrital quartz, mudstone intraclasts and fragments of other coated grains. Grain cortices are either composed of haematite or
intercalated layers of chamosite and clinochlore that truncate each other (Figure 5D,E). In chloritic grains, the outermost layers have been altered to secondary haematite (Figure 5F). Grains are overprinted by fabric-destructive magnetite and are cemented with colloidal haematite and goethite.

Facies 2 is interpreted as a shoreface deposit (Clifton et al., 1971; Plint, 2010) that was continually reworked and winnowed by wave activity to remove the fine-grained matrix (Bhattacharyya, 1989; Taylor and Macquaker, 2000). The Fe-rich porewaters are interpreted to have promoted the heterogenous nucleation of authigenic Fe-(oxyhydr)oxide and Fe chlorites on abundant detrital clasts to form coated grains. Coated grains record the synsedimentary cycling of Fe at the Fe-redox boundary where the reductive dissolution of Fe-(oxyhydr)oxide below produces Fe$^{2+}$ that diffuses upwards to re-precipitate as Fe$^{3+}$ upon reaction with O$_2$ (Heggie et al., 1990). Such Fe-redox pumping concentrates Fe$^{2+}$ in pore water (Pufahl, 2010; Taylor and Konhauser, 2011; Taylor and Macquaker, 2011), resulting in either the reprecipitation of Fe-(oxyhydr)oxide that changes to haematite during burial, or formation of multi-valence authigenic chlorite minerals like chamosite (Pufahl and Grimm, 2003; Todd et al., 2019).

Discordances between laminae forming coated grains are interpreted to record multiple episodes of Fe precipitation beneath the seafloor, exhumation, erosion and reburial into the zone of precipitation near the Fe-redox boundary (unconformity-bounded grains sensu Pufahl and Grimm, 2003). Such stratigraphic condensation (cf. Föllmi, 2016) is a pre-requisite for coated grain formation because it stabilized the Fe-redox boundary in sediment (Pufahl and Grimm, 2003). Chamosite cortical layers may have originally been dominated by berthierine (Aagaard et al., 2000; Morad et al., 2000) and precipitated from Fe-rich pore water that also contained H$_2$SiO$_4$, Mg$^{2+}$ and Al$^{3+}$ (Harder, 1980; 1989). Clinochlore is the Mg-rich endmember of a solid solution series with chamosite (Mücke, 2006) and forms when porewater alkalinity increased (Bodine, 1983a; 1983b) and Fe concentration decreased (Todd et al., 2019).

Secondary haematite alteration of the outermost chloritic cortical layers is interpreted to record meteoric diagenesis during relative sea-level fall. Fabric destructive magnetite that overprints grains suggests the reductive transformation of haematite to magnetite during burial (Mel'nik, 1982; Till and Nowaczyk, 2018). Colloidal haematite and goethite cements are the last paragenetic phase and are interpreted to have formed through re-exposure to meteoric conditions.

### 4.3 | Swaley cross-stratified quartz arenite

Facies 3 is a thickly bedded, swaley cross-stratified (SCS) quartz arenite that is commonly associated with Facies 2. Beds are typically 40–60 cm thick, have erosive lower and upper contacts (Figure 6A), and are composed of abundant coarse-grained, sub-angular, monocrystalline quartz grains with annealed boundaries (Figure 6B). Some beds also contain detrital muscovite and plagioclase. Haematite-filled fractures are common and characterized by haematite cemented, goethite-replaced grains.

Swaley cross-stratification is interpreted to form through storm-induced combined flow on the lower shoreface (Leckie and Walker, 1982; Duke, 1985; Allen and Underhill, 1989; Arnott, 1992; Dumas and Arnott, 2006). The coarse-grained nature, lack of bioturbation and conspicuous absence of mudstone in Facies 3 support these interpreted high-energy conditions (Duke, 1985; Yagishita et al., 1992). Combined flow is produced when the oscillatory motion of storm waves and storm-generated geostrophic currents together influence the settling of suspended sediments (Hamblin et al., 1979; Dott and Bourgeois, 1982; Arnott, 1992; Dumas et al., 2005). The co-occurrence of decametre-scale swales and well-defined erosional surfaces is indicative of a strong unidirectional component of combined flow (Allen and Underhill, 1989; Yagishita et al., 1992).

### 4.4 | Hummocky cross-stratified quartz wacke

Facies 4 is a hummocky cross-stratified (HCS) quartz wacke (Figure 6C). Individual beds are 5–30 cm thick and composed of very fine-grained, subangular quartz grains with common muscovite. The thickest beds have erosive bases that scour underlying lithofacies. Secondary minerals include uncommon goethite, euhedral magnetite, and colloidal haematite lining pores. Quartz veinlets that cross-cut bedding contain euhedral pyrite.

This facies is interpreted to have accumulated between fair-weather and storm wave-bases through combined flow (Dott and Bourgeois, 1982; Duke, 1985; Arnott, 1992; Quin, 2011). The result is metre-scale, circular to elliptical hummocks and swales that are internally cross-stratified with low angle truncation surfaces and curved intersections.

### 4.5 | Thinly laminated siltstone

Facies 5 is a thinly laminated (0.1–0.3 mm thick), organic-rich siltstone (Figure 6D) that is intercalated with the HCS quartz wacke of Facies 4. Laminasets are 2–10 cm thick and have sharp, non-erosive basal contacts. Top contacts are also sharp but scoured by overlying HCS beds (Figure 6E). The ichnofabric index is highly variable, ranging between 1 and 4, and dominated by Planolites (Figure 6F). Mineralogically, siltstone laminae are composed of silt-sized sub-rounded quartz grains in a micaceous matrix. Some laminae also contain granule-sized carbonate fluorapatite intraclasts (Figure 6G).
**FIGURE 6** (A) Facies 3 and 4. SCS quartz arenite beds with erosive basal contacts are tan and dominate upper half of photograph. Interbedded HCS quartz wacke is dark grey. Scale bar is 10 cm in length. Peña del Tormo Road Cut. (B) Facies 3. Subangular quartz grains with annealed, sutured grain boundaries. Cross-polarized transmitted light. Core sample OS-5-128.30. (C) Facies 4. HCS bed with characteristic low angle truncation surfaces. Peña del Tormo Road Cut. (D) Facies 5. Thinly laminated silstone layers composed of subangular quartz grains and detrital muscovite that are separated by organic-rich partings (yellow arrow). Cross-polarized transmitted light. Core sample OS-5-152.60. (E) Facies 4 and 5. HCS beds (tan) scour underlying laminasets composed of thinly laminated silstone (dark grey). Peña del Tormo Road Cut. (F) Facies 5. Pervasive bioturbation in some laminasets by *Planolites* produces an ichnofabric index of 4. Peña del Tormo Road Cut. (G) Facies 5. Thin intraclastic beds of carbonate fluorapatite occur in some laminasets. Core sample W-5-B-252.50. (H) Facies 5. Pseudomorphic haematite replaced frambooidal pyrite (reddish specks) in more organic-rich layers composing laminasets. Goethite is the matrix material between framboinds and has brownish-red internal reflections. Cross-polarized reflected light. Core sample OS-5-63.20.
or haematite-replaced framoidal pyrite (Figure 6H). Secondary minerals include euhedral magnetite and uncom-
mon goethite laths.

Laminasets are interpreted to record fair-weather settling between storms (Ogston et al., 2000; Worden and Morad, 2003; Dunbar and Barrett, 2005; Ghadeer and Macquaker, 2011). The conspicuous presence of Planolites is characteristic of the Cruziana ichnofacies and reflects infaunal colonization by deposit-feeding annelids (Pemberton and Frey, 1984; Pemberton and MacEachern, 1997). The variably bioturbated nature of this ichnofacies probably records a combination of fluctuating benthic oxygen levels and differences in the length of time between storms (Duke, 1985; Nøttvedt and Kreisa, 1987; Savrda and Bottjer, 1991; Ghadeer and Macquaker, 2011).

Laminae containing carbonate fluorapatite intraclasts are the product of authigenic precipitation at, and subsequent reworking of, the seafloor. Carbonate fluorapatite forms in organic-rich facies through a combination of benthic microbial processes and Fe-redox pumping (Föllmi et al., 1994; Pufahl, 2010). Precipitation occurs when pore water becomes supersaturated with phosphate. Phosphate is liberated in sedi-
ment as sedimentary organic matter is degraded by heterotrophic bacteria and when Fe-(oxyhydr)oxide with adsorbed phosphate dissolves below the Fe-redox boundary. The gran-
ule-sized, carbonate fluorapatite peloids that precipitate are commonly reworked to form granular layers (Föllmi et al., 1991; Pufahl and Groat, 2017).

Bacterial sulphate reduction is especially efficient at facilitating phosphogenesis (Coleman et al., 1993; Arning et al., 2009) and produces H2S that combines with Fe2+ to produce framoidal pyrite (Taylor and Macquaker, 2000; Schieber, 2002). As in Facies 2, haematite and magnetite are interpreted to have precipitated during progressive burial and goethite formed during late stage meteoric diagenesis.

4.6 | Bioturbated bryozoan-rich siltstone

Facies 6 is a burrow mottled, bryozoan-rich siltstone contain-
ing abundant delicate branching trepostome bryozoans, common pseudopunctate brachiopods, and rare crinoid and ostracod fragments (Figure 7A). Brachiopods are identified as Rafinesquina pseudoloricata and Svobodaina armoricana (Villas, 1983; 1992; Colmenar, 2016). Hosting siltstone contains abundant muscovite, and silt-sized, quartz and plagi-
oclase grains. Fossils are filled with blocky, low Mg-calcite cement and, when dissolved, preserve a mouldic porosity (Figure 7B). With an ichnofabric index of 6, any original bedding has been completely homogenized making it impos-
able to identify individual trace fossil types.

This fossiliferous siltstone is interpreted to have ac-
cumulated through suspension rain near storm wave base (Worden and Morad, 2003). Svobodaina armoricana and R. pseudoloricata generally inhabited middle shelf environ-
ments (Fürsich and Hurst, 1974; Williams and Carlson, 2007; Plotnick et al., 2013). The lack of a pedicle in both species suggests a non-turbulent environment where the ability to attach to the substrate was not required. These recliners colo-

nized the seafloor by ‘floating’ like icebergs in the surface of soft muds (Leighton, 1998; Plotnick et al., 2013; Colmenar et al., 2014). Their co-occurrence with delicate branching bryozoans in such intensely bioturbated siltstone implies a low energy depositional environment (Reid, 2010; Taylor and James, 2013) with sufficient oxygen to support a robust in-
faunal community.

Blocky calcite is interpreted to have precipitated early, during meteoric diagenesis, because fossils filled with this cement are preferentially preserved. Those left open were dissolved during later burial diagenesis to form abundant moulds.

4.7 | Very thinly bedded ironstone

Facies 7 is a dark green to black, unbioturbated, thinly bedded ironstone (Figure 7C). Beds are ca 1 cm thick, ungraded, organic-rich, and composed of abundant, very fine detrital quartz grains and framoidal pyrite cemented with clinochlore. Coated grains are also common but, unlike those in Facies 2, chloropane and clinochlore cortical layers are concentric, lacking internal discordances, and nucleated on very fine-grained, chloropane peloids (Figure 7D). Fabric-destructive euhedral magnetite over-
prints bedding, and blocky low Mg calcite fills pores, completely enveloping some magnetite crystals and coated grains.

The conspicuous occurrence of coated grains in thin unbioturbated beds suggests Facies 7 is a condensed deposit that accumulated primarily through suspension rain in a low-oxygen, offshore environment below storm wave-base (Chamley, 1989; Savrda and Bottjer, 1991; Madon, 1992; Ogston et al., 2000; Dunbar and Barrett, 2005). The concentric nature of cortical layers forming coated grains is interpreted to reflect authigenic precipitation without exhumation and erosion of grains on the seafloor (redox-aggraded grains sensu Pufahl and Grimm, 2003). Cortex thickness is likely proportional to the residence time of grains in the zone of precipitation near the Fe-redox boundary. As in Facies 2, cortical layer mineralogy reflects variability in pore water alkalinity and re-
dox-driven changes in Fe concentration. Such changes were probably driven by fluctuations in surface ocean productivity and related deposition of sedimentary organic matter. A rise in primary productivity produces a concomitant increase in the rate of microbial degradation of organic matter, which in turn elevates alkalinity and lowers Eh of pore water (Pufahl
and Grimm, 2003; Mazzullo, 2004). Changing pore water redox potential in this way causes the Fe-redox boundary to oscillate vertically beneath the seafloor in step with organic matter productivity to produce coated grains (Pufahl and Grimm, 2003). Clinochlore is interpreted to have precipitated in alkaline, Fe depleted pore water above the Fe-redox boundary, whereas chamosite or berthierine formed near this interface. The presence of framboidal pyrite indicates bacterial sulphate reduction was a significant influence on pore water pH and Eh.

Fabric-destructive magnetite developed during burial diagenesis. Blocky calcite is also interpreted to have formed during burial and, based on textural relationships, was the last phase to precipitate.

4.8 | Medium laminated ironstone

Facies 8 is composed of organic-rich laminae with chamosite and clinochlore. Laminae are ca 0.5 cm thick, unbioturbated and contain uncommon, subrounded, silt-sized quartz grains cemented with intergrown chamosite and clinochlore. Fabric destructive magnetite and a strong cleavage overprint primary layering (Figure 7E,F).
Like Facies 7, laminae are interpreted to have formed through suspension rain of organic matter and detrital silt below storm wave-base on the anoxic distal shelf. The thinner, finer and more organic-rich nature of laminae suggest deposition occurred further outboard than the thinly bedded ironstone. However, the same productivity-driven authigenic processes are inferred to have produced chamosite and clinochlore. The conspicuous absence of coated grains probably reflects the lack of persistent seafloor reworking in a slightly deeper environment than Facies 7. Under such low energy conditions, the exhumation-reburial cycles that are a prerequisite for coated grain formation could not develop. Fabric-destructive magnetite and a cross-cutting cleavage indicate burial diagenesis followed by deformation and low-grade metamorphism.

5 | SEQUENCE STRATIGRAPHY AND PARASEQUENCES

Lithofacies stacking patterns from two partially preserved stratigraphic sequences record deposition through at least two relative sea-level cycles during flooding of the Iberian shelf. Higher-order oscillations preserved as metre-scale shallowing-upward cycles are interpreted as parasequences (Catuneanu et al., 2011; Catuneanu, 2019). Parasequences without ironstone characterize the lower sequence whereas the upper sequence is composed of stacked parasequences containing ironstone (Figure 8).

The lower sequence forms the base of the Luarca Formation in the WALZ (Figure 4). It records parasequence development and storm-dominated deposition under non-ferruginous conditions during the late Dapingian to early Darriwilian (ca 469–465 Ma; Gutiérrez-Marco et al., 1999). Superimposed subaerial exposure surfaces (Facies 1) overlying lower shoreface deposits (Facies 3; Figure 8) are a sequence boundary representing basinward migration of the shoreline during accumulation of the lowstand systems tract (LST). The transgressive surface is the sharp transition from SCS sandstone (Facies 3) to offshore laminated siltstone (Facies 5; Figure 8), which marks the landward migration of the shoreline and defines the early transgressive systems tract (TST).

The younger upper sequence occurs in the middle Luarca Formation and correlative Fe-rich sedimentary rocks of the Eastern Iberian Chain. This sequence contains two distinct ironstone horizons of middle Darriwilian (ca 463 Ma) and late Sandbian (ca 454 Ma) age that are important stratigraphic markers throughout the region (Figure 9; Gutiérrez-Marco et al., 1999; Bergström et al., 2009; Cole et al., 2017; Colmenar and Rasmussen, 2017). In the Eastern Iberian Chain, haematitic granular ironstone forming these horizons caps proximal parasequences (Facies 2; Figure 9), whereas in the Luarca Formation laminated ironstone composed of Fe and Mg-silicates characterizes the base of distal parasequences (Facies 7 and 8; Figure 9). A synsedimentary erosional contact with pebble-size rip-ups between granular ironstone of the upper horizon (Facies 2) and the overlying more distal bryozoan-rich siltstone (Facies 6) is interpreted as the transgressive surface defining the transition between the LST and TST.

Proximal and distal parasequences define two different ironstone factories where Fe was concentrated and precipitated in sediment. Proximal parasequences are 10–20 m thick and record the deposition of haematitic grainstone on a storm reworked lower shoreface. These aggradational cycles coarsen-upwards from HCS quartz wacke (Facies 4) through SCS quartz arenite (Facies 3) to trough cross-stratified ironstone (Facies 2; Figure 8). Distal parasequences are 10–30 m thick, enriched in sedimentary organic matter, and reflect the authigenic precipitation of chamosite and clinochlore below storm wave base. Cycles fine upwards from thinly bedded ironstone containing abundant coated grains (Facies 7) to thinly laminated chamositic ironstone (Facies 8) that, in turn, is overlain by phosphatic siltstone (Facies 5; Figure 9). The organic-rich nature of distal parasequences and occurrence of phosphatic siltstone containing abundant filter feeders suggest ironstone deposition was associated with elevated surface productivity stimulated by coastal upwelling (Glenn et al., 1994; Pufahl and Groat, 2017). Aggradation into shallower Fe-barren lithofacies (Facies 5) indicates upwelling cells migrated basinward as relative sea-level fell through the thickness of each distal parasequence.

6 | IRONSTONE DEPOSITION, SUPERPLUMES AND BIODIVERSITY

Ironstone-barren parasequences of the lower sequence record similar hydrodynamic conditions as those containing ironstone from the upper sequence, indicating that the delivery of Fe was the consequence of factors extrinsic to the Iberian shelf (Figure 10). These allogenic processes are interpreted to have supplied Fe to co-eval proximal and distal ironstone factories from distinctly different sources. The shallow nature of the proximal factory suggests Fe was derived from continental runoff (Figures 10 and 11). In the Middle Ordovician, a greenhouse climate accelerated the hydrologic cycle to intensify chemical weathering and increase surface runoff, supplying Fe as Fe-(oxyhydr) oxide to some coastal environments (Van Houten and Bhattacharyya, 1982; Young, 1989; Bhattacharyya and Crerar, 1993; Van Houten, 2000). Erosional scours and abundant coated haematite grains in shoreface deposits (Facies 2 and 3) suggest that constant wave reworking
**Figure 8** Parasequences and sequence stratigraphy of the lower sequence that is barren of ironstone. Direction of taper on triangles indicates fining. Drill core OS-5. SB—sequence boundary; TS—transgressive surface; LST—lowstand systems tract; TST—transgressive systems tract; cly—clay; slt—silt; Vf—very fine grained; F—fine-grained; M—medium grained; C—coarse grained; Vc—very coarse-grained; G—Granule; Pbl—pebble; Cbl—cobble. Legend is also applicable to stratigraphic sections depicted in Figure 9.
stabilized the Fe-redox boundary, providing sufficient time to dissolve freshly deposited Fe-(oxyhydr)oxide and concentrate Fe in porewater (Pufahl and Grimm, 2003; Todd et al., 2019). The lack of ironstone in middle shelf environments implies that the rapid authigenic precipitation of recycled Fe, together with the biological uptake of this micronutrient, restricted Fe precipitation to the nearshore (Young, 1989; Fung et al., 2000; Van Houten, 2000; Parekh et al., 2005; Taylor and Konhauser, 2011). In addition, sedimentologic evidence suggests that the offshore transport and suspension rain of fine-grained sediment, derived from constant reworking of the shallow seafloor, probably increased the rate of deposition on the mid shelf to prohibit stratigraphic condensation, a prerequisite for ironstone accumulation (Figure 11). The conspicuous absence of coated grains in middle shelf facies implies that traction currents were inefficient at moving coarser, denser grains across the energetic shoreface into deeper, muddier environments (cf. Keen and Slingerland, 1993).

In contrast to this traditional view of ironstone accumulation, which relies on a continental source of Fe (Van Houten and Bhattacharyya, 1982; Young, 1989; Bhattacharyya and Crerar, 1993; Van Houten, 2000; Robb, 2005; Yilmaz et al., 2015), lithofacies associations suggest that Fe was also supplied through coastal upwelling (Figures 10 and 11). The organic-rich nature and occurrence of synsedimentary Fe and Mg silicates, francolite and framboidal pyrite in offshore lithofacies (Facies 5–8) imply deposition near an upwelling front (Glenn et al., 1994; Pufahl and Groat, 2017) and development of a distal ironstone factory. Such characteristics are consistent with other Ordovician, upwelling-related ironstones from the northern margin of the Rheic Ocean (Dunn et al., 2019; Todd et al., 2019). These deposits also contain a variety of coated grain types and are organic-rich with phosphatic lags, signatures of stratigraphic condensation beneath the sites of active coastal upwelling. This emerging model for ironstone deposition relies on high surface ocean productivities and the microbial respiration of accumulating organic matter to fuel the synsedimentary precipitation of Fe and Mg silicates (Todd et al., 2019). As bacteria degrade accumulating organic matter, the alkalinity maximum that develops in pore water triggers the precipitation of chamosite and clinochlore (Bodine, 1983a; 1983b; Tosca et al., 2016), linking the occurrence of these silicates in offshore facies to coastal upwelling. Thus, the redox-sensitive mineralogies of cortical layers forming coated grains in the distal factory are the best record of productivity driven changes in biological oxygen demand (BOD) and pore water pH during authigenesis (Figure 11; Pufahl and Grimm, 2003).
The delivery of upwelling-related Fe requires tapping of deep ferruginous seawater that by the middle Darriwilian (ca 463 Ma) is interpreted to have impinged on the Iberian shelf. During the Cambro-Ordovician, such anoxic water masses are thought to have developed intermittently until the global ocean became fully oxygenated after the Devonian (Berry et al., 1990; Zhang et al., 2011; Thompson and Kah, 2012; Algeo et al., 2016; Kah et al., 2016; Todd et al., 2019). Recent palaeogeographic reconstructions suggest that upwelling along the Iberian shelf (Figure 3; Harper et al., 2014; Servais et al., 2014; Pohl et al., 2018) supplied nutrient-rich, ferruginous seawater for the production of distal ironstone. As the Rheic Ocean started to open in the Furongian (ca 497 Ma), rifting of Avalonia from Gondwana progressively created a narrow, restricted seaway with ferruginous bottom waters enriched in locally sourced hydrothermal Fe that was periodically tapped via upwelling (Todd et al., 2019). Evidence for such localized Fe input occurs in the Iberian Range where bryozoan-echinoderm mud mounds were replaced in the Katian by hydrothermal magnesite and siderite (Fernández-Nieto et al., 2003; Álvaro and Van Vliet-Lanoë, 2009).

This style of Fe delivery probably represents a tipping point in the oxygenation history of the Phanerozoic oceans and is a throwback to the Precambrian when widespread anoxia allowed hydrothermal Fe to concentrate in the global ocean (Klein, 2005; Bekker et al., 2010; Pufahl, 2010; Taylor and Konhauser, 2011). In the Neoproterozoic and Palaeoproterozoic, the combination of a sizeable Fe reservoir and upwelling produced continental margin iron formation, the largest Fe deposits on Earth (Trendall and Blockley, 2004; Pufahl, 2010; Pufahl et al., 2014). The ubiquity of Ordovician ironstone suggests that bottom water anoxia and input of hydrothermal Fe were common in many expanding seaways. This increase in Fe flux is coincident with a superplume event and period of major plate reorganization (Algeo, 1996; Tan et al., 2002; Shields et al., 2003; Barnes, 2004; Murphy et al., 2009; Torsvik et al., 2014; Algeo et al., 2016). Marine transgression, the formation of volcanogenic massive sulphide deposits, and emplacement of ophiolites during the Middle and Upper Ordovician are all consistent with the accelerated generation of juvenile oceanic crust (Eastoe and Gustin, 1996; Vaughan and Scarrow, 2003; Murphy et al., 2009). A steep decline in seawater $^{87}$Sr/$^{86}$Sr ratios in the Middle Ordovician (Qing et al., 1998; Shields and Veizer, 2004; Edwards et al., 2015) is interpreted to record the weathering of young continental volcanic rocks (Young et al., 2009; Saltzman et al., 2014; Swanson-Hysell and Macdonald, 2017) associated with the onset of this superplume event (Alego et al., 2016). Thus, geodynamic processes in the
mantle may have ultimately created the conditions that provided both an oceanic and continental source of Fe to feed proximal and distal ironstone factories.

In the WALZ and CZ of the Iberian Massif, the occurrence and age of two distinct stratigraphic horizons of ironstone (Figure 4) suggest upwelling intensified to access deeper, ferruginous waters during the middle Darriwilian (ca 463 Ma) and late Sandbian (ca 454 Ma). The timing of these upwelling events is coincident with the onset of two separate positive carbon isotope excursions and post-extinction recoveries (Elrick et al., 2011; Saltzman et al., 2015; Algeo et al., 2016; Edwards and Saltzman, 2016; Colmenar and Rasmussen, 2017). The Mid-Darriwilian Carbon Isotope Excursion (MDICE) and the Guttenberg Carbon Isotope Excursion have been linked to invigorated coastal upwelling and enhanced burial of sedimentary organic matter (Pope and Steffen, 2003; Algeo et al., 2016). Drawdown of atmospheric CO₂ resulting from increased organic C burial is interpreted to have decreased global temperatures in this otherwise greenhouse world (Gill et al., 2007; Young et al., 2010; Zhang et al., 2011; Pohl et al., 2018), which likely amplified the equator-to-pole temperature gradient and intensified upwelling cells (Patzkowsky and Holland, 1996; Pope and Steffen, 2003).

These positive carbon isotope excursions are also synchronous with periods of evolutionary crisis and extinction during the GOBE (Figure 12; Wang et al., 1993; Saltzman et al., 1995; 2015; Buggisch et al., 2003; Saltzman, 2005; Elrick et al., 2011; Kröger et al., 2019; Fan et al., 2020), implying a connection between changes in upwelling dynamics and biodiversity. The GOBE is characterized by major structural changes to marine ecosystems (Algeo et al., 2016). Diversification of phytoplankton and the evolution of diverse zooplankton drove the radiation of nektonic vertebrates and benthic filter feeders (Servais et al., 2010; Harper et al., 2015; Algeo et al., 2016). Beneath the sediment, an increase in infaunal burrowing accompanied these changes (Algeo et al., 2016). Evolution occurred in a series of pulses punctuated by minor extinction events (Harper et al., 2015; Ernst, 2017; Kröger et al., 2019), with the primary radiation in the Darriwilian (Harper et al., 2015; Algeo, 2016). Correlation of WALZ-CZ ironstone horizons with periods of post-extinction faunal recovery (Figure 12), suggests that these rebounds may have been connected at least in part to the accumulation of ironstone.

In the late Silurian, episodes of ironstone deposition and extinction have been attributed to the encroachment of metal-enriched, anoxic water masses onto oxygenated shelves (Vandenbroucke et al., 2015). Metal-induced malformations in fossil plankton communities highlight the effectiveness of this kill mechanism (Vandenbroucke et al., 2015). Evidence presented herein suggests the encroachment of these anoxic waters was likely driven by coastal upwelling. In addition to Fe, upwelling that tapped ferruginous intermediate and/or bottom water would have delivered a sustained supply of Cd, Cu, As, Zn, Co, Ni, Se, Cr, Ba, Ge, As, Pd, Te and REEs (Wilde et al., 1990), possibly triggering regional extinction events. Although many of these trace elements are micronutrients required for a myriad biological processes, high...
concentrations are toxic (Leary and Rampino, 1990; Wilde et al., 1990; Falasco et al., 2009; Delebroye et al., 2012; Vandenbroucke et al., 2015; Holan et al., 2019). The contemporaneous nature of WALZ-CZ ironstone horizons with periods of post-extinction faunal recovery (Figure 12) suggests that, with time, ironstone accumulation was also an important sink for lowering metal toxicity in seawater. The precipitation of authigenic Fe minerals directly controls the redox cycling and sequestration of many trace metals through scavenging and adsorption (Heggie et al., 1990; Bayon et al., 2004; Sheoran and Sheoron, 2006). The widespread occurrence of Ordovician ironstone suggests the ability of this style of upwelling to ‘kill and cure’ is a previously unrecognized negative feedback mechanism that may have been critical for the sustained increase in marine biodiversity through the GOBE.

7 | CONCLUSIONS

Five siliciclastic and three chemical sedimentary lithofacies define the Middle and Upper Ordovician stratigraphy of the WALZ and the southwestern continuation of the CZ in the Eastern Iberian Chain. Lithofacies associations are indicative of storm-dominated deposition on a passive continental margin with periodic coastal upwelling.

Lithofacies stacking patterns suggest clastic and chemical sediments accumulated during relative sea-level rise during the transition from LST to TST conditions, producing at least two stratigraphic sequences. Parasequences without ironstone characterize the lower sequence, whereas the upper sequence is composed of stacked parasequences containing ironstone. The lower sequence reflects deposition on the Iberian shelf under non-ferruginous conditions. The upper sequence records periods of iron delivery and the accumulation of ironstone.

Parasequences define two different ironstone factories where Fe was concentrated and precipitated in sediment. Proximal parasequences define a nearshore ironstone factory where haematitic grainstone precipitated on a storm reworked lower shoreface. Iron and nutrients were probably supplied via continental weathering. Distal parasequences reflect the authigenic precipitation of chamosite and clinochlore below storm wave base. Ironstone accumulation was driven by coastal upwelling and the delivery of nutrient-rich ferruginous bottom water. A principal control on Fe mineralogy in each factory was pore-water Eh, which was governed mainly by the intensity of primary production in the surface ocean and corresponding changes in the biological oxygen demand on the seafloor.

This depositional model is corroborated by ironstone from the northern Rheic margin, and challenges historical interpretations of Phanerozoic ironstones that rely solely on a continental source of Fe. The recognition of an upwelling-related distal ironstone factory requiring a sustained supply of
ferruginous bottom water implies anoxic water masses developed though the Ordovician. This style of Fe delivery probably represents a tipping point in the oxygenation history of the Phanerozoic oceans and is a threshold to the Precambrian when widespread anoxia allowed hydrothermal Fe to concentrate in the global ocean. Periods of deep ocean anoxia in the Ordovician suggest that the ventilation of seawater that began in the late Neoproterozoic was more protracted than previously surmised.

An Ordovician mantle superplume event is interpreted to have accelerated rifts to create semi-restricted seaways like the Rheic Ocean that were ideal depocentres for ironstone accumulation. In addition to generating narrow seaways with intermittently anoxic bottom waters, this episode of enhanced mantle activity also provided oceanic and continental sources of Fe to feed both proximal and distal ironstone factories. Intense hydrothermal input of mantle-derived Fe produced ferruginous water masses that were periodically tapped by coastal upwelling. Weathering of juvenile basalts from the mantle provided an indirect source of Fe to coastal environments.

WALCZ-CZ ironstone correlates to minor extinction events punctuating the GOBE. Although the upwelling of ferruginous seawater may have triggered these extinctions, precipitation of related Fe-rich authigenic minerals may have also helped sequester biologically toxic trace elements to aid in post-extinction recovery. The ability of this style of upwelling to ‘kill and cure’ may be a previously unrecognized negative feedback mechanism that was critical for the sustained increase in marine biodiversity through the GOBE.

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CONFLICT OF INTEREST
The authors have no conflict of interest to declare.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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