Isotope evidence for the coupled iron and carbon cycles 1.4 billion years ago

H.J. Wang¹, Y.T. Ye¹⁻², Y. Deng¹⁻², X.M. Wang¹, E.U. Hammarlund³⁻⁴, H.F. Fan⁵, D.E. Canfield¹⁻³*, S.C. Zhang¹*

Abstract

Although ferruginous waters were widespread in the deep ocean until 0.58 Ga, massive Fe deposits were rare during the interval from 1.8−0.8 Ga. Here, we report the contents and isotopic compositions of Fe and C from the ~1.4 Ga Xiamaling (XML) siderite deposits, North China. A genetic model is introduced to interpret the dynamic and coupled Fe and C cycles in Mesoproterozoic oceans and sediments. Although the positive Eu anomalies of XM siderites are relatively low in the XML deposits, an enhanced input of hydrothermal Fe²⁺ is recognised from the isotopic compositions of Fe and C. Hydrothermal fluid is suggested as a key controlling factor during the XML siderite deposition.

Introduction

Most marine massive Fe deposits formed 3.0−1.8 Ga, with a billion-year hiatus until a brief return around 0.8 Ga (Konhauser et al., 2017). During this gap period, the iron formation (IF) shortage was thought to be a result of significantly decreased Fe²⁺ concentrations in the ocean, which was either substantially oxidised (Holland, 1990) or sulfurised (Canfield, 1998). Recent studies provide increasing evidence that ferruginous water was still widespread in the deep ocean until 0.58 Ga (Canfield et al., 2008). Although atmospheric oxygen levels are still controversial in the time window of 1.8−0.8 Ga (Planaovsky et al., 2014; Zhang et al., 2016, 2021; Canfield et al., 2021), it is believed that oxygen was deficient compared to the last 0.7 Ga.

Thus, although IF deposition is limited from 1.8−0.8 Ga, there are recent reports of significant ferrous carbonate deposition generating siderite-dominated IFs, such as the ~1.40 Ga Xiamaling (XML) IF in North China (Canfield et al., 2018; Tang et al., 2018) and the ~1.33 Ga Jingtieshan IF in Qilian (Yang et al., 2018). Siderite deposits are also found in the ~1.45 Ga Sherwin ironstone in Australia (Planavsky et al., 2014). To further explore the mechanisms of siderite-dominated IF deposition and the associated marine Fe and C cycles, we analysed the contents and isotopic compositions of Fe and C of the XML IF. Combined with the reported data in Canfield et al. (2018), our results show evidence for hydrothermal Fe²⁺ input during the deposition of XML IF, where the Fe and C cycles were tightly coupled.

Geological Background and Samples

Samples were obtained from a core in the Xiahuayuan region located in the Yanliao Basin, which was an offshore basin in North China during the breakup of the Columbia supercontinent (Fig. 1a–c). The XML IF is found over 45 m of stratigraphic thickness and is defined as unit 5, which can be further divided into the lower part with greyish-black mudstone and the upper part with green sandy mudstone (Fig. 1d). Centimetre- to decimetre-sized laminar and nodular siderites are embedded in the clastic rocks (Fig. 1e–h), indicating a pore-water diagenetic environment. Detailed information of the geological background is in the Supplementary Information (SI).

Methods and Results

As the normal Fe extraction protocol in Poulton and Canfield (2005) proved ineffective at removing siderite from our IF samples, an acid extraction method was used. We used ferrozine to determine the contents of acid-soluble Fe²⁺, and used ferrozine with the addition of hydroxylamine to determine the sum of Fe²⁺ and Fe³⁺. On separate samples, the Cr-reduction method was used to quantify the Fe bound in pyrite (Fepy). Iron isotope values (δ⁵⁶Fe) from whole rock samples were determined and expressed as the ⁵⁶Fe/⁵⁴Fe ratio relative to IRMM-014. Contents of total organic carbon (TOC), elements and main diagenetic minerals of whole rock samples were also determined. The isotopic composition of carbonate (δ¹³C_carb) of the IF samples and the isotopic composition of organic carbon (δ¹³C_org) of the clastic samples...
Figure 1. Location of the (a) 1.4 Ga and (b) present North China Craton, modified from Zhang et al. (2021). (c) Paleogeography of the Yanliao Basin 1.4 Ga, modified from Lyu et al. (2021). (d) Stratigraphy of the Xiamaling Formation, Photos of laminar siderites from the Xiahuayuan region.
were determined and expressed relative to VPDB. Detailed methods are in the SI.

Geochemical data of the IF samples (defined as samples with total Fe (FeT) > 15 %) and the interbedded clastic rocks are illustrated in Figure 2 and Table S-1. As has been observed in the upper part (discussed in Canfield et al., 2018), siderite is the dominant diagenetic mineral of the lower IF samples (Table S-1). The lower IF samples have extremely high FeT/Al ratios (mostly >15) and FeT/Ti ratios (mostly >200), high Fe2+/FeT ratios (>0.8), low Fe3+/FeT ratios (<0.01), and negative δ56Fe values (from −0.53‰ to −0.34‰). In contrast, the interbedded clastic rocks of the lower IF have low FeT/Al ratios (mostly from 3 to 15) and FeT/Ti ratios (mostly from 30 to 200), high Fe2+/FeT ratios (>0.8), low Fe3+/FeT ratios (<0.15), extremely low Fepy/FeT ratios (<0.01), and more negative δ56Fe values (from −1.20‰ to −0.32‰) than those of the lower IF samples. The interbedded clastic rocks of the upper IF have medium FeT/Al ratios (from 0.5 to 2.7) and FeT/Ti ratios (mostly from 10 to 30), medium Fe2+/FeT ratios (from 0.46 to 0.83), low Fe3+/FeT ratios (<0.15), extremely low Fepy/FeT ratios (<0.01), and fluctuating δ56Fe values (from −0.71‰ to +0.38‰). The sedimentary rocks of the lower part (including the IF samples) have higher TOC values (mostly from 0.3 % to 1.0 %) than those of the upper part (mostly <0.3 %). The δ13Corg values of most samples were between −33‰ and −32‰, while the δ13Ccarb values of the IF samples fluctuated from −27‰ to −8‰.

Figure 2 Geochemical profiles of the unit 5 of the Xiamaling Formation. Degree of pyritisation (DOP) was calculated by Fe_py/(Fe2++Fe3++Fepy). Data of the FeT, total organic carbon (TOC), Eu/Eu*, carbon isotopes of carbonate (δ13C_carb) and kerogen (δ13C_org) with a depth range of 390−350 m were from Canfield et al. (2018). Note the abscissas breaks of FeT/Al, FeT/Ti, Fepy/FeT are at 3, 30 and 0.01, respectively. Cycle and solid points represent IF (FeT > 15 %) and clastic (FeT < 15 %) samples, respectively. Dashed lines in the δ13C_carb panel represent the proportions of organic-sourced bicarbonate of measured samples, with an initial δ13C_carb of −32‰ and an initial δ13C of bicarbonate in water column of 0‰.
**Depositional Redox Environments**

We could not use standard Fe speciation protocols on the siderite-rich samples, but high Fe/Al ratios (Lyons and Severmann, 2006) and high Fe/Ti ratios (Dauphas et al., 2004), combined with high Fe<sup>3+</sup>/Fe<sub>T</sub> ratios (>0.8) and extremely low Fe<sub>T</sub>/Fe<sup>2+</sup> ratios (<0.01) confirmed ferruginous conditions during the deposition, consistent with the previous redox-sensitive element proxies from Canfield et al. (2018) and Tang et al. (2018). As we did not use the standard Fe speciation protocol, water column redox conditions in the clastic rocks could only be evaluated did not use the standard Fe speciation protocol, water column redox conditions in the clastic rocks could only be evaluated. However, we could use standard Fe speciation protocols on the siderite-rich samples, but high Fe/Ti ratios (Lyons and Severmann, 2004), so the XML IF may be rather distal from the supercontinent Columbia (Tang et al., 2018). For the clastic rocks of the upper part, high Fe/Al ratios (0.5–2.7), high Fe/Ti ratios (10–30) and extremely low sulphurised Fe ratios (Fe<sub>S</sub>/Fe<sub>T</sub> < 0.01) indicate ferruginous deposition conditions. For clastic rocks of the lower part, the Fe/Al and Fe/Ti ratios hover around the crustal average values, and the sulphurised Fe ratios range from 0.01 to 0.3, so the redox conditions during deposition are still uncertain. However, a euxinic depositional environment can be excluded, as it needs a degree of iron pyritisation (DOP) of at least 0.4 (Raiswell and Canfield, 2012).

**Sources of the Iron**

Positive Eu anomalies (Eu/Eu* ratios 1.0–1.4) for all IF samples (Fig. 2) indicate a hydrothermal impact on the water chemistry during the IF formation, and hydrothermal Fe<sup>2+</sup> may have been the most important source of Fe<sup>2+</sup> to the Precambrian ocean (Johnson et al., 2020). During the deposition of the XML IF, a hydrothermal Fe<sup>2+</sup> source may be associated with the breakup of the supercontinent Columbia (Tang et al., 2018). However, the positive Eu anomalies of the XML IF are rather muted when compared with the ~1.3 Ga Jingtieshan IF (Eu/Eu* ratios 4.4–6.5) (Yang et al., 2018), so the XML IF may be rather distal from the hydrothermal source.

Another source of Fe<sup>2+</sup> to seawater is released from clastic particulates depositing in anoxic waters on the shelf (Raiswell and Canfield, 2012). Indeed, a benthic clastic source of dissolved Fe<sup>3+</sup> likely supplies most Fe that accumulates as reactive Fe in anoxic depositional environments today, as revealed through sequential sediment extractions (Raiswell and Canfield, 2012).

**Iron Isotope Fractionation Models**

Formation of the XML IF has been suggested to result from three steps (Canfield et al., 2018), including: 1) oxidation of seawater Fe<sup>3+</sup> to Fe-oxyhydroxides (Fe(OH)<sub>3</sub>), likely at the chemo-line of the ancient marine basin, 2) reduction of Fe(OH)<sub>3</sub> to diagenetic Fe<sup>3+</sup> in the water column and sediments, and 3) crystallisation of Fe<sup>2+</sup> as siderite. Whole rock δ<sup>56</sup>Fe values would be affected by the initial δ<sup>56</sup>Fe of seawater Fe<sup>2+</sup> and the net isotopic fractionation between products and reactants (Δδ<sup>56</sup>Fe<sub>product-reactant</sub>) in the above steps. These steps are presented in Figure 3 and are reviewed in more detail in Johnson et al. (2020) as well as the SI.

To briefly summarise, the oxidation of Fe<sup>2+</sup> generates δ<sup>56</sup>Fe-enriched Fe(OH)<sub>3</sub> (Fe<sup>3+</sup>) compared to the Fe<sup>2+</sup> source. With the subsequent reduction of this Fe<sup>3+</sup>, and generation of diagenetic Fe<sup>2+</sup>, both the Fe<sup>2+</sup> product and the residual Fe<sup>3+</sup> will be progressively δ<sup>56</sup>Fe-enriched. Due to the Δδ<sup>56</sup>Fe<sub>(Fe(II)-Fe(III))</sub> of diagenetic Fe<sup>3+</sup> and residual Fe<sup>3+</sup>, whole rock δ<sup>56</sup>Fe values in clastic rocks with residual Fe<sup>3+</sup> are generally heavier than the Fe<sup>2+</sup> in siderite alone. For the higher molar ratio of Fe<sup>2+</sup> and bicarbonate (HCO<sub>3</sub>–) as products during step 2 (4:1) than as reactants in step 3 (1:1), excessive diagenetic Fe<sup>2+</sup> diffuse upwards and/or insufficient HCO<sub>3</sub>– diffuse downwards during step 3. Because of the different isotopic trends of diagenetic Fe<sup>2+</sup> and HCO<sub>3</sub>–, the δ<sup>56</sup>Fe and δ<sup>13</sup>C<sub>carb</sub> of siderite depend on the position of its precipitation. The genetic model shown in Figure 3 is illustrative only, not quantitative, but the trends in δ<sup>56</sup>Fe are similar to those reproduced in the open system diffusion/reaction model (Johnson et al., 2020).

**Dynamic Iron Cycle in the 1.4 Ga Marine Environment**

The δ<sup>56</sup>Fe values of both lower and upper IF samples are significantly reduced compared to those of the clastic rocks in the same intervals (Fig. 2). With an average Fe content in the upper crust of...
δmal − seawater HCO₃⁻ part should be more ⁵⁶Fe-depleted than those from the upper part during all of the XML IF formation, the siderites from the lower part (Fig. 3). However, the elevated values from the upper part (Fig. 2). This difference in siderite precipitation with lower HCO₃⁻ concentrations and closer to the sediment–water interface, consistent with heavier ⁸¹³Ccarb values of siderites from the lower part. Higher Fe²⁺ concentrations could have also elevated the rates of Fe-associated primary production, leading to higher values of TOC (Fig. 2).

Generally, the positive Eu anomalies of the XML IF can be taken to indicate hydrothermal contributions. We also note that the positive Eu anomalies are relatively small and of the same magnitude in both the upper and lower IFs. Overall, the positive Eu anomalies in the IFs (Fig. 4b) do support a hydrothermal source of Fe²⁺ to the Yanliao Basin. This conclusion is consistent with the enhanced hydrothermal Fe²⁺ supply that we argue impacted both the δ⁵⁶Fe and δ¹³Ccarb values of the lower XML IF.

**Implications on Marine Iron and Carbon Cycles**

The XML IF was formed within a ferruginous marine basin with an active iron cycle that was intimately coupled to the C cycle. However, there are differences in the dynamics of the Fe and C cycles in the upper and lower parts of the sedimentary sequence where the IFs are formed. In particular, an enhanced hydrothermal Fe²⁺ contribution elevated the concentrations of Fe²⁺ in the water column and the rates of Fe associated with the C cycle in the lower IF, and should be a key controlling factor in regulating the rates of Fe associated with marine primary production during the siderite-dominated XML IF formation.

**Acknowledgements**

We thank Zhihong Li, Heidi Jensen and Iben Rosendahl for the experimental analysis. The research is financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA14010101), National Key Research Program of China (XDA14010201), and the Youth Innovation Promotion Association of the Chinese Academy of Sciences (20150004) to ZH.

3.6 % (Rudnick and Gao, 2003), and for siderite of 48 %, rocks in the lower part are consistent with the mixing of a clastic end-member with a δ⁵⁶Fe value of +0.6 % and a diagenetic siderite end member with a δ⁵⁶Fe value of −0.4 % (R² = 0.895, Fig. 4a), which is close to the measured δ⁵⁶Fe values (from −0.53 % to −0.34 %) of IF samples. However, for the upper part, the optimal δ⁵⁶Fe value of the diagenetic siderite was −1.1 %, with a δ⁵⁶Fe value of the clastic end member also set to +0.6 % (Fig. 4a).

Thus, the circumstances of IF formation in the lower and upper parts were clearly different. Details of the calculation method are in the SI.

Moreover, the δ¹³Ccarb values of IF samples are much more ¹³C-depleted than the Mesoproterozoic seawater HCO₃⁻ (~0 %, Saltzman and Thomas, 2012), supporting the idea that the siderites most likely precipitated in diagenetic sediment environments with varied and limited exchange with the overlying waters. The δ¹³Ccarb values of siderites from the lower part are from −15 % to −12 %, and thus more ¹³C-enriched than most samples from the upper part (Fig. 2). This difference in δ¹³Ccarb values would suggest that the siderite from the lower part precipitated closer to the water–sediment interface, with a greater seawater HCO₃⁻ contribution, when compared to the siderites from the upper part (Fig. 3). Following this logic, if we assume that the patterns of water column δ⁵⁶Fe values remained similar during all of the XML IF formation, the siderites from the lower part should be more ⁵⁶Fe-depleted than those from the upper part (Fig. 3). However, the elevated δ⁵⁶Fe values (from −1.1 % to −0.4 %) contradict this hypothesis and indicate more ⁵⁶Fe-enriched water in the Yanliao Basin during the IF formation in the lower part.

We propose that the lower part of the XML IF received an enhanced input of hydrothermal fluids with δ⁵⁶Fe values of 0 %.

**Figure 4** Correlation diagrams of δ⁵⁶Fe with (a) Fe²⁺ and (b) Eu/Eu*. The correlation diagrams (a) are the optimal mixing lines of the lower and upper parts, respectively, with a clastic end member and a diagenetic end member. Grey areas mean the Fe cycle and δ⁵⁶Fe values were influenced by the hydrothermal fluids.
and Development Program of China (2017YFC0603101), National Natural Science Foundation of China (41872125, 42102146) and Villum Foundation (16518).

Editor: Claudine Stirling

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2208.

© 2022 The Authors. This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at https://www.geochemicalperspectivesletters.org/copyright-and-permissions.


References


Geochem. Persp. Let. (2022) 21, 1–6 | https://doi.org/10.7185/geochemlet.2208