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

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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 XML 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) short-age 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 (Planavsky 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 Jingtleshan 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 (Fe₄py). Isotope values (δ⁵⁶Fe) from whole rock samples were determined and expressed as the δ⁵⁶Fe/δ⁵⁴Fe 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 were measured.

References

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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 iron formation defined as unit 5 of the Xiamaling Formation. Photos of laminar (e) and nodular (f–h) siderites from the core in 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 (<0.15), 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 lower 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 FePy/(Fe2++Fe3++FePy). Data of the FeT, total organic carbon (TOC), Eu/Eu*, carbon isotopes of carbonate (δ13Ccarb) and kerogen (δ13Corg) 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 δ13Ccarb panel represent the proportions of organic-sourced bicarbonate of measured samples, with an initial δ13Corg 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 Fe2+/Al ratios (Lyons and Severmann, 2006) and high Fe2+/Ti ratios (Dauphas et al., 2004), combined with high Fe2+/FeT ratios (>0.8) and extremely low Fe2+/FeT 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 where the Fe2+/Al and Fe2+/Ti ratios well exceeded the crustal average values (~0.5 and ~10, respectively, Rudnick and Gao, 2003). For the clastic rocks of the upper part, high Fe2+/Al ratios (0.5–2.7), high Fe2+/Ti ratios (10–30) and extremely low sulphurised Fe2+ ratios (Fe2+/FeT < 0.01) indicate ferruginous deposition conditions. For clastic rocks of the lower part, the Fe2+/Al and Fe2+/Ti ratios hover around the crustal average values, and the sulphurised Fe2+ 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 Fe2+ may have been the most important source of Fe2+ to the Precambrian ocean (Johnson et al., 2020). During the deposition of the XML IF, a hydrothermal Fe2+ 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 Fe2+ 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 Fe3+ 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 Fe2+ to Fe-oxyhydroxides (Fe(OH)3), likely at the chemocline of the ancient marine basin, 2) reduction of Fe(OH)3 to diagenetic Fe3+, in the water column and sediments, and 3) crystallisation of Fe2+ as siderite. Whole rock δ56Fe values would be affected by the initial δ56Fe of seawater Fe2+ and the net isotopic fractionation between products and reactants (Δδ56Feproduct-reactants) 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 Fe2+ generates δ56Fe-enriched Fe(OH)3 (Fe3+) compared to the Fe2+ source. With the subsequent reduction of this Fe3+, and generation of diagenetic Fe2+, both the Fe3+ product and the residual Fe3+ will be progressively δ56Fe-enriched. Due to the Δδ56Fe product-reactants of diagenetic Fe3+ and residual Fe3+, whole rock δ56Fe values in clastic rocks with residual Fe3+ are generally heavier than the Fe2+ in siderite alone. For the higher molar ratio of Fe2+ and bi-carbonate (HCO3−) as products during step 2 (4:1), than as reactants in step 3 (1:1), excessive diagenetic Fe3+ diffuse upwards and/or insufficient HCO3− diffuse downwards during step 3. Because of the different isotopic trends of diagenetic Fe2+ and HCO3−, the δ56Fe and δ13C 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 δ56Fe 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 δ56Fe 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 during all of the XML IF formation, the siderites from the lower part (Fig. 3). However, the elevated δ13C-values from the upper part (Fig. 3). Following this logic, if we assume that the patterns of water column precipitated closer to the water interface, consistent with heavier δ13C-values of 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 δ13C-values of the lower XML IF.

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 diagenetic siderite 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 δ13C-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 δ13C-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 δ13C-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 δ56Fe-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 δ56Fe-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 ‰. The hydrothermal fluids with elevated Fe2+ concentrations (German et al., 1990) generated higher Fe2+ concentrations and elevated δ56Fe values in the bottom waters of the Yanliao Basin. Higher Fe2+ concentrations would have resulted in siderite precipitation with lower HCO3− concentrations and closer to the sediment–water interface, consistent with heavier δ13C-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).

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
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.

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References


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Supplementary Information

The Supplementary Information includes:

- Geological Background
- Methods
- Table S-1
- Figures S-1 to S-4
- Supplementary Information References

Geological Background

The North China Craton

The North China Craton (NCC) is an old craton with a maximum age of well-preserved gneiss of ~3.8 Ga and an area of ~3 × 10^6 km². After the formation of a continental nucleus (>3.3 Ga) and the growth of a massive continental crust (2.9–2.7 Ga) (Jia et al., 2019), the western and eastern blocks of the NCC separately completed micro-block assembly and cratonisation at ca. 2.5 Ga. The western and eastern blocks amalgamated along the Trans-North China Orogen (TNCO) to constitute a unified basement at ca. 1.85 Ga, eventually forming the present tectonic framework of the NCC (Fig. S-1). The continental growth, assembly and breakup of the NCC from 2.5–1.3 Ga is considered an essential component of the assembly of the Columbia supercontinent (Li et al., 2020).

According to the global paleogeographic reconstruction model for the process of the assembly and breakup of the Columbia supercontinent (Pisarevsky et al., 2014), the NCC was considered to be adjacent to Australia during 1.77–1.41 Ga (Zhang et al., 2017). In addition, putative stratigraphic correlations also provide new evidence that the NCC, Siberia and North Australia might have been neighbours and formed a single large intracratonic basin in the Columbia supercontinent (Mitchell et al., 2021).

The Yanliao Basin

From 1.85–1.80 Ga, the tectonic properties of the NCC shifted from compressional to extensional, and remained so for almost one billion years (1.80–0.80 Ga) or perhaps longer (Zhao and Zhai, 2013). Several rift systems (basins) were
formed successively along the margins of the NCC, including the Xiong’er Basin at the southern margin, the Helan-Jinshan Basin at the southwestern margin, and the Zha’er-tai-Bayan Obo-Huade and Yanliao basins at the northern margin (Fig. S-4). The Yanliao Basin is a typical intracratonic rift basin that extends from the northeastern end to the interior of the NCC. Geometrically, it can be divided into two branches: one oriented in a nearly northeast-east direction in the north and the other oriented in a nearly north-south direction in the south (Lu et al., 2002; Deng et al., 2021). However, the basin structure might have undergone a major change at ca. 1.6 Ga, connecting with the open sea in the north direction (Zhang et al., 2021). The Xiamaling Formation (1.42–1.35Ga) was likely deposited in an offshore basin (Zhang et al., 2019; Lyu et al., 2021).

In the Yanliao Basin, the Paleo- and Mesoproterozoic sediments are found with a maximum thickness of up to 8000 m (Meng et al., 2011). From bottom to top, these sediments can be classified as the clastic rock-dominated Changchengian System (including the Changzougou, Chuanlinggou, Tuanshanzi, and Dahongyang formations), the carbonate rock-dominated Jixian System (including the Gaoyuzhuang, Yangzhuang, Wumishan, Hongshuizhuang, and Tieling formations), and the clastic-rock-dominated Xiamaling Formation (Fig. S-2). The duration and boundary ages of the Changchengian and Jixian systems, and the Xiamaling Formation have been well defined by using the U-Pb ages of zircons or baddeleyites from the ash layers, volcanic rocks and intrusive rocks (Fig. S-2).

The structural evolution and sedimentary sequences of the Yanliao Basin during 1.8–1.3 Ga are believed to be related to the breakup of the Columbia supercontinent (Deng et al., 2021; Zhang et al., 2021). Therefore, hydrothermal vents should have been active in a vicinity for an extended period of time. Evidence for hydrothermal contributions to basin geochemistry include the iron formation of the Chuanlinggou Formation (ca. 1640Ma) (Lin et al., 2019), the manganese deposit and polymetallic pyrite deposit of the Gaoyuzhuang Formation (ca. 1590 Ma) (Gao et al., 2021; Jin et al., 2022), the syndepositional chert bands and nodules of the Wumishan Formation (ca. 1490 Ma) (Shen et al., 2018), the black shale events of the Hongshuizhuang Formation (ca. 1460 Ma) (Ma et al., 2017), and the iron formation of the Xiamaling Formation (Canfield et al., 2018; Tang et al., 2018). However, there is no direct evidence for the position of hydrothermal vents during the deposition of the Xiamaling iron formation.

The Xiamaling Formation

The Xiamaling Formation is mainly composed of shale and siltstone, and deposited over the carbonate rocks of the Tieling Formation with a parallel unconformity. Two zircon U-Pb TIMS ages (1384.4 ± 1.4 Ma and 1392.0 ± 1.0 Ma; Zhang et al., 2015) and a zircon U-Pb LA-ICP-MS age (1418 ± 14 Ma; Lyu et al., 2021) have been obtained from the volcanic ash layers in the middle and bottom of the Xiamaling Formation, respectively (Fig. S-3). In addition, abundant baddeleyite U-Pb ages of ca. 1320 Ma, obtained from the intruded gabbro-diabase sills (Li et al., 2009; Liu et al., 2011; Zhang et al., 2017; Wang et al. 2020), are considered to be accompanied by pre-magmatic uplift that started at about 1350 Ma (Zhang et al., 2017), further constraining that the minimum age of the Xiamaling Formation should be older than 1350 Ma (Fig. S-2). Independent studies gave geological and paleographic evidence of an open system of the Yanliao Basin during the whole of the Xiamaling depositional period (Zhang et al., 2019; Gao et al., 2021; Wang et al., 2020; Lyu et al., 2021; Mitchell et al., 2021).

Based on lithological characteristics, the Xiamaling Formation has been traditionally divided into four stratigraphic members in ascending order (e.g., Tang et al., 2018; Fig. S-3). Comparing the outcrop and core from the Xiahuayuan section (N 40°28’13.41", E 115°15’52.9"), we have made a detailed geochemical and sedimentological investigation of the Xiamaling Formation (e.g., Zhang et al., 2015; Wang et al., 2017; Canfield et al., 2018; Zhang et al., 2019), and have suggested a stratigraphic division scheme of 6 lithologic units (Fig. S-3). More detailed petrological and mineralogical descriptions of the Xiamaling iron formation can be seen in Canfield et al. (2018) and Tang et al. (2018).
Methods

Sample collection

All samples for geochemical analysis were obtained from a fresh drill core, where drilling was conducted with fresh water as the drilling fluid to minimise contamination. Fresh core samples were collected and crushed to powders with a diameter of <75 μm by using a tungsten carbide grinding disc.

Elemental measurements

Major and trace elements were determined at the Analytical Laboratory of Beijing Research Institute of Uranium Geology, China National Nuclear Corporation, after the methods described in Zhang et al. (2015). Briefly, major elements were determined using a Philips PW2400 X-ray fluorescence spectrometer (XRF). The relative standard deviations (RSD) of Fe and Al were both lower than 1.0 %. Trace elements were obtained on an ELEMENT XR inductively coupled plasma mass spectrometer (ICP-MS) after rock powders were subjected to complete digestion following the procedures described in Zhang et al. (2015). The resulting RSD of each rare earth element concentration was <1.5 %. Accuracies were also tested with the shale standard (GBW 03014) that was measured along with the samples. The concentrations of the interest elements were within 10 % of their reported values.

TOC measurement

Samples for TOC measurement were de-carbonated and combusted in a LECO CS-230HC carbon/sulphur analyser at the Key Laboratory of Petroleum Geochemistry, China National Petroleum Corporation and following the procedures described in Canfield et al. (2018). The resulting RSD of each sample was lower than 2.0 %.

Diagenetic minerals measurement

Diagenetic minerals of samples were determined through X-ray diffraction (XRD) analysis with a Rigaku MiniFlex X-ray diffractometer using a 600 W Cu-ka source. The measurement were performed at the Key Laboratory of Petroleum Geochemistry, China National Petroleum Corporation and following procedures described in Canfield et al. (2018). The data were acquired through measurements of 10° per min over a range from 10° to 70° and analysed in the PDXL Software.

Carbon isotope measurement

Carbon isotopes of carbonate (δ13C_carb) and organic carbon (δ13C_org) of the samples were measured at the Key Laboratory of Petroleum Geochemistry, China National Petroleum Corporation and the University of Southern Denmark, after the methods described in Canfield et al. (2018). Briefly, pure kerogen was extracted from rocks through HCl and HF treatment as fully described in Zhang et al. (2016). The δ13C_org values were measured on the extracted kerogens by using a Flush EA 1112 HT O/H-N/C combined with a Delta V Advantage mass spectrometer. The δ13C_carb of each sample was determined by reacting with phosphoric acid in an online carbonate preparation device and analysis on a Finnigan Mat-252 mass spectrometer (Thermo Scientific). All δ13C values were reported relative to the Vienna Pee Dee Belemnite (VPDB), with standard deviation (SD) of each sample was lower than 0.2 % based on replicate analysis.

Extractable Fe2+ and Fe3+ analysis

We found that the standard iron speciation protocol (Poulton and Canfield, 2005) did not effectively extract the siderite in our samples due to their high contents. This was apparent as residues identifiable as siderite by XRD analysis were present after the “Fe carbonate” phase of the standard protocol. For this reason, we applied an HCl acid digestion procedure to these samples. This procedure involved reacting the samples overnight at 50 °C with 0.5 M HCl. This procedure was effective at removing both siderite and iron oxides from the sample. After extraction, samples were reacted with ferrozine to determine the Fe2+ contents.
Separate splits of each sample were also reacted with hydroxylamine to reduce Fe$^{3+}$ to Fe$^{2+}$. This solution was reacted with ferrozine to yield total extractable iron, and the difference between the total extractable iron and the iron extracted as Fe$^{2+}$ yielded the Fe$^{3+}$ contents. This procedure was effective at removing iron from siderite and iron oxide-rich samples in the IF, but it might have also removed some silicate-bound iron in the clastic-rich samples. Analyses were conducted at the University of Southern Denmark. Details of the protocol used in partitioning between Fe$^{2+}$ and Fe$^{3+}$ can be found in Viollier et al. (2000).

**Chromium reduction method**

Pyrite sulphur was extracted by Cr reduction, trapped as Ag$_2$S, with concentrations calculated gravimetrically (Canfield et al., 1986). Replicate extractions of PACS-2 and in-house standards indicated an analytical uncertainty of $<$5%. These extractions were conducted at the University of Southern Denmark.

**Iron isotope compositions analysis**

The iron isotope compositions were measured at the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences. The protocols used are briefly summarised here.

For iron isotope analyses, whole rock powers were digested with HF+HNO$_3$+HCl+HClO$_4$. After complete dissolution, the final solution was treated with concentrated HCl repeatedly to convert the cations to a chloride-form. The solution after HCl treatment was finally dissolved in 6 M HCl plus 0.001 % H$_2$O$_2$ for chemical purification of Fe$^{3+}$. The AG MP-1 anion exchange resin was used in the chromatographic separation procedure of Fe$^{3+}$. Samples were loaded and first washed with 6 M HCl plus 0.001% H$_2$O$_2$ to remove ions other than Fe$^{3+}$ and Zn$^{2+}$, then 2 M HCl plus 0.001% H$_2$O$_2$ was used to strip Fe$^{3+}$ from Zn$^{2+}$. Iron isotope ratios were determined in high mass resolution mode on a Nu Plasma high resolution multi-collector inductively coupled plasma mass spectrometer (HR MC-ICP-MS) using standard-sample bracketing (SSB) approach. Samples were introduced into the mass spectrometer in 0.1 M HNO$_3$ using a DSN 100 desolating nebulizer with 5 ppm Fe$^{3+}$. The $^{56}$Fe/$^{54}$Fe ratio of each sample was reformulated into $\delta^{56}$Fe-notation and expressed in units of per mille (‰), relative to the reference material of IRMM-014 as follows:

$$
\delta^{56}\text{Fe (‰)} = \left[\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{sample}}/\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{standard}} - 1\right] \times 1000
$$

(Eq. S-1)

The long-term external reproducibility at high-resolution mode is better than 0.05 ‰ at 2 SD. Figure S-4 illustrates the relationship of $\delta^{56}$Fe versus $\delta^{57}$Fe ratios obtained for all Xiamaling samples. All the data lie on the mass-dependent fractionation line within analytical uncertainty.

**Fe cycle and isotope systematics**

The sources of oceanic Fe$^{2+}$ include hydrothermal fluids, the benthic shuttle from continental margins, and terrestrial input through riverine sources and aerosol deposition. Based on the compilations and models of Condie (1993), the average Fe$_T$/Al ratios of the Precambrian crust is taken to be 0.46, and average Fe$_T$/Ti is taken to be 11.23. These compositions would reflect the average detrital input to the ocean, ignoring biogeochemical diagenetic effects. Although riverine and aeolian sources of Fe might be important in the modern and Precambrian oceans, these terrestrial Fe inputs bear no obvious isotopic fractionations ($\Delta^{56}$Fe$_{\text{ferrous ion-total iron}}$) and probably had a minimal effect on the Fe isotope compositions ($\delta^{56}$Fe) of the Mesoproterozoic ferruginous marine waters (Johnson et al., 2020). For hydrothermal and benthic Fe fluxes, atmospheric O$_2$ levels and marine sulfate-sulfide would have affected the Fe$^{2+}$ oxidation extents in the oceans, the relative control of sulfides and oxides on isotopic exchange/fractionation with Fe$^{2+}$, and the Fe mass balances in the oceans. All of which could be recorded in the Fe composition and isotope values of sedimentary rocks.

Based on the modeling of Kump and Seyfried (2005), Precambrian hydrothermal fluids would have had much higher Fe/S ratios, with lower sulfide contents, and much higher Fe$^{3+}$ contents. For the low O$_2$ and sulfate contents in the Mesoproterozoic ocean, especially in the deep ocean, the Fe$^{2+}$ would have undergone minimal oxidation. Therefore, the $^{56}$Fe of Fe$^{2+}$ derived from distal hydrothermal plumes should have been preserved in transit to
continental margin basins. In the low-oxygen conditions of the Mesoproterozoic ocean, benthic Fe fluxes controlled by escape of pore fluid Fe$^{2+}$ from marine sediments, might have been a very important source of Fe$^{2+}$ (Raiswell and Canfield, 2012). The benthic Fe flux is also a function of the contents of reactive Fe$^{3+}$, organic carbon (C$_{org}$), and bottom-water O$_2$. Sufficient delivery of reactive Fe$^{3+}$ and C$_{org}$ are needed to support dissimilatory iron reduction (DIR) and generate Fe$^{2+}$. Decreased Fe$^{2+}$ oxidation in a low oxygen environment and decreased Fe$^{2+}$ pyritisation in a low sulfide environment will increase the transport of diagenetic Fe$^{2+}$ to water column.

The extremely negative $\delta^{13}$C$_{carb}$ values (from $-27$ % to $-8$ %) of siderites from the XML IFs were suggested to have formed in 3 steps (Canfield et al., 2018), including: 1) oxidation of seawater Fe$^{2+}$ to Fe-oxo-hydroxides (Fe(OH)$_3$), likely at the chemocline of the ancient basin, 2) reduction of the Fe(OH)$_3$ to diagenetic Fe$^{2+}$ in the water column and sediments, and 3) crystallisation of Fe$^{2+}$ as siderite. The Fe(OH)$_3$ in step 1 can form either through the oxidation of seawater Fe$^{2+}$ with O$_2$ (Eq. 1) or from anoxygenic photosynthesis at the chemocline (Eq. 2). Step 1 generates $^{56}$Fe-enriched Fe-(oxy)hydroxides with an abiotic $\Delta^{56}$Fe$^{2+}$-ferrous ion of ca. +3.0 or biotic $\Delta^{56}$Fe$^{2+}$-ferrous ion from +1.5 % to +3.0 % (Johnson et al., 2020). Step 2 can occur both in the seawater and in the pore-waters, and generates $^{56}$Fe-depleted diagenetic Fe$^{2+}$ (Eq. 3) with a similar $\Delta^{56}$Fe$^{2+}$-ferrous ion in the abiotic system (Wiesli et al., 2004).

\[
\begin{align*}
4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{O}_2 & \rightarrow 4\text{Fe(OH)}_3 + 8\text{H}^+ \quad (1) \\
4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{HCO}_3^- & \rightarrow 4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 7\text{H}^+ \quad (2) \\
4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 7\text{H}^- & \rightarrow 4\text{Fe}^{2+} + \text{HCO}_3^- + 10\text{H}_2\text{O} \quad (3) \\
4\text{Fe}^{2+} + 4\text{HCO}_3^- & \rightarrow 4\text{FeCO}_3 + 4\text{H}^+ \quad (4)
\end{align*}
\]

### Calculation of the clastic and diagenetic siderite end-members using iron isotope mass balance

Whole rock $\delta^{56}$Fe reflect the net Fe isotopic composition of a mixture of different iron-bearing minerals, whose contents and isotopic compositions vary between samples. For the siderite-dominated Xiamaling Iron Formation, the contents of Fe-oxides and pyrite are much lower than siderite. So, clastic Fe and diagenetic siderite were assumed to be the two main endmembers that affect the whole rock $\delta^{56}$Fe. A simple mixing model was used to calculate the evolution of $\delta^{56}$Fe by mixing between clastic and diagenetic endmembers, whose $\delta^{56}$Fe were also refined in the modelling. In our model, the whole rock $\delta^{56}$Fe was defined to be:

\[
\delta^{56}\text{Fe}_{\text{wh}} = \frac{\text{Fe}_{\text{cl}} \times \delta^{56}\text{Fe}_{\text{cl}} + \text{Fe}_{\text{dia}} \times \delta^{56}\text{Fe}_{\text{dia}}}{\text{Fe}_{\text{cl}} + \text{Fe}_{\text{dia}}} \quad \text{(Eq. S-2)}
\]

Here, $\delta^{56}\text{Fe}_{\text{wh}}$, $\delta^{56}\text{Fe}_{\text{cl}}$ and $\delta^{56}\text{Fe}_{\text{dia}}$ are iron isotopic values of whole rock, clastic endmember and diagenetic endmember, respectively. Fe$_{\text{cl}}$ and Fe$_{\text{dia}}$ are the iron amounts in the clastic and diagenetic endmembers, respectively. The sum of Fe$_{\text{cl}}$ and Fe$_{\text{dia}}$ is total Fe (Fe$_{\text{T}}$).

\[
\text{Fe}_{\text{T}} = \text{Fe}_{\text{cl}} + \text{Fe}_{\text{dia}} \quad \text{(Eq. S-3)}
\]

Fe$_{\text{cl}}$ and Fe$_{\text{dia}}$ can be further defined as:

\[
\text{Fe}_{\text{cl}} = f_{\text{cl,Fe}} \times T_{\text{cl,Fe}} \quad \text{(Eq. S-4)}
\]

\[
\text{Fe}_{\text{dia}} = f_{\text{dia,Fe}} \times T_{\text{dia,Fe}} \quad \text{(Eq. S-5)}
\]

Here, $f_{\text{cl,Fe}}$ and $f_{\text{dia,Fe}}$ are the fractions of clastic endmember and diagenetic endmember, respectively. $T_{\text{cl,Fe}}$ and $T_{\text{dia,Fe}}$ are iron contents of the clastic endmember and diagenetic endmember, respectively. The sum of $f_{\text{cl,Fe}}$ and $f_{\text{dia,Fe}}$ is 1.

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Then, Equation S-2 can be transformed into:

\[
\delta^{56}\text{Fe}_{\text{wh}} = T_{\text{cla-Fe}} \times T_{\text{dia-Fe}} \times (\delta^{56}\text{Fe}_{\text{cla}} - \delta^{56}\text{Fe}_{\text{dia}})/(T_{\text{dia-Fe}} - T_{\text{cla-Fe}})/\text{Fe}_T + \\
(T_{\text{dia-Fe}} \times \delta^{56}\text{Fe}_{\text{dia}} - T_{\text{cla-Fe}} \times \delta^{56}\text{Fe}_{\text{cla}})/(T_{\text{dia-Fe}} - T_{\text{cla-Fe}})
\]  
(Eq. S-5)

So, we can use the formula \(Y = a/x + b\) to do the optimal fitting between \(\delta^{56}\text{Fe}_{\text{wh}}\) and \(\text{Fe}_T\), with

\[
a = T_{\text{cla-Fe}} \times T_{\text{dia-Fe}} \times (\delta^{56}\text{Fe}_{\text{cla}} - \delta^{56}\text{Fe}_{\text{dia}})/(T_{\text{dia-Fe}} - T_{\text{cla-Fe}}) \\
b = (T_{\text{dia-Fe}} \times \delta^{56}\text{Fe}_{\text{dia}} - T_{\text{cla-Fe}} \times \delta^{56}\text{Fe}_{\text{cla}})/(T_{\text{dia-Fe}} - T_{\text{cla-Fe}})
\]  
(Eq. S-6)(Eq. S-7)

With a \(T_{\text{cla-Fe}}\) of 3.6 % (upper crust value; Rudnick and Gao, 2003) and \(T_{\text{dia-Fe}}\) of 48 %, the \(\delta^{56}\text{Fe}_{\text{cla}}\) and \(\delta^{56}\text{Fe}_{\text{dia}}\) can be calculated with the optimised \(a\) and \(b\) values.

Supplementary Table

Table S-1  Geochemical data of the Xiamaling Iron Formation.

Table S-1 is available for download (Excel file) from the online version of the article at https://doi.org/10.7185/geochemlet.2208.
Supplementary Figures

Figure S-1  Distributions of the Proterozoic rift systems (basins) and sedimentary covers in the North China Craton. Modified from Deng et al. (2021).

Figure S-2  The Palaeo- and Mesoproterozoic stratigraphic framework and U-Pb ages of zircons or baddeleyites from the ash layers, volcanic rocks and intrusive rocks in the Yanliao Basin, North China Craton. Modified from Zhang et al. (2021).
Figure S-3  The stratigraphic column of the Xiamaling Formation in the Yanliao Basin, North China Craton, modified from Zhang et al. (2019). The age of 1418 ± 14 Ma is from Lyu et al. (2021).
Figure S-4  \( \delta^{56}\text{Fe} \) versus \( \delta^{57}\text{Fe} \) of the Xiamaling samples normalised by IRMM-014. The red line is the theoretical mass-dependent fractionation line (slope = 1.474) based on a simple harmonic oscillator approximation (Criss, 1999).

Supplementary Information References


Precambrian Research 326, 222–239. https://doi.org/10.1016/j.precamres.2017.11.013


