

Article

# Iron and Carbon Isotope Constraints on the Formation Pathway of Iron-Rich Carbonates within the Dagushan Iron Formation, North China Craton

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**Abstract:** Banded iron formations (BIFs) are enigmatic chemical sedimentary rocks that chronicle the geochemical and microbial cycling of iron and carbon in the Precambrian. However, the formation pathways of Fe carbonate, namely siderite, remain disputed. Here, we provide photomicrographs, Fe, C and O isotope of siderite, and organic C isotope of the whole rock from the ~2.52 Ga Dagushan BIF in the Anshan area, China, to discuss the origin of siderite. There are small magnetite grains that occur as inclusions within siderite, suggesting a diagenetic origin of the siderite. Moreover, the siderites have a wide range of iron isotope compositions ( $\delta^{56}\text{Fe}_{\text{sd}}$ ) from  $-0.180\text{‰}$  to  $+0.463\text{‰}$ , and a relatively negative C isotope composition ( $\delta^{13}\text{C}_{\text{sd}} = -6.20\text{‰}$  to  $-1.57\text{‰}$ ). These results are compatible with the reduction of an Fe(III)-oxyhydroxide precursor to dissolved Fe(II) through microbial dissimilatory iron reduction (DIR) during early diagenesis. Partial reduction of the precursor and possible mixing with seawater Fe(II) could explain the presence of siderite with negative  $\delta^{56}\text{Fe}$ , while sustained reaction of residual Fe(III)-oxyhydroxide could have produced siderite with positive  $\delta^{56}\text{Fe}$  values. Bicarbonate derived from both DIR and seawater may have provided a C source for siderite formation. Our results suggest that microbial respiration played an important role in the formation of siderite in the late Archean Dagushan BIF.

**Keywords:** banded iron formation; siderite; dissimilatory iron reduction (DIR); iron isotopes; carbon isotopes; North China Craton

## 1. Introduction

Banded iron formations (BIFs) are chemical sedimentary rocks composed of iron-rich (total iron >15 wt.%) and silica-rich bands [1–3] that were commonly precipitated during the Archean and Paleoproterozoic. BIFs reflect not only the massive extent of iron (Fe) cycling and deposition during the Precambrian, but they also record critical information about ancient seawater geochemistry and the different (bio)chemical pathways through which the atmosphere–biosphere–hydrosphere systems have been linked throughout Earth's history [4–7]. Four mineralogical end-member facies of BIF have been described

based on the characteristic Fe-bearing mineral assemblages, including (i) oxides (hematite, magnetite), (ii) carbonates (siderite, ankerite), (iii) silicates (e.g., greenalite, cummingtonite, grunerite), and (iv) sulfides (pyrite). Sulfide facies is not generally used to study sedimentary environments, as it is composed mainly of pyritic carbonaceous shale or slate and does not represent a chemical precipitate [2,3,8]. The abundance and distribution of these facies have been used to infer environmental conditions during deposition and subsequent sedimentary–diagenetic–metamorphic evolutionary processes [1–3,8].

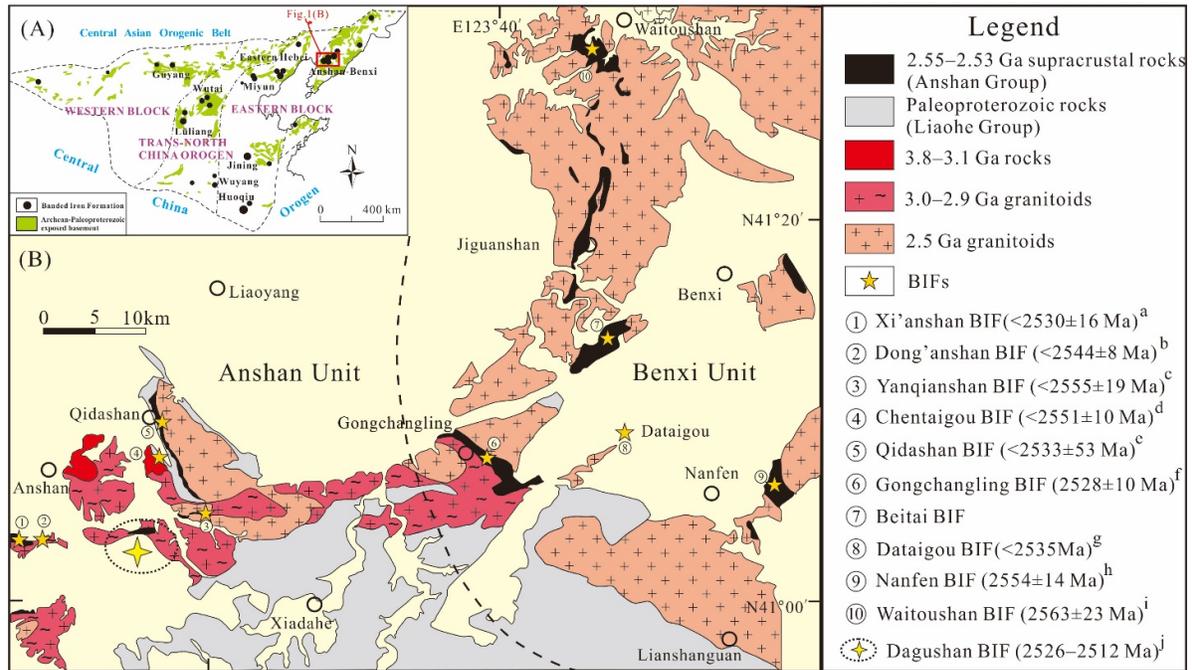
Amongst these four facies, the carbonate facies provide the most valuable insights on the origin and coupled cycling of Fe and carbon (C) in BIFs [9]. Siderite is the major Fe-rich component in the carbonate facies of BIFs and its formation requires anoxic, ferruginous conditions, high alkalinity, and low sulfate concentrations [10–12]. Despite significant scientific interest and research, there is still no consensus on the origin of siderite, and two main formation pathways are proposed [13–19]. First, in Archean oceans where Fe(II) and  $\text{HCO}_3^-$  concentrations would have been high and the prevailing redox conditions were reducing [20–23], the direct precipitation of siderite from seawater may have been feasible [13,22,24,25]; however, Jiang and Tosca [26] have suggested that seawater siderite precipitation may have been kinetically unfavorable. Seawater-like carbon isotopes ( $\delta^{13}\text{C} \sim 0\text{‰}$ ) of siderite in some BIFs have been taken as evidence to support this direct precipitation pathway [25,27]. Second, microbial dissimilatory iron reduction (DIR) during early diagenesis has been shown to be a viable formation pathway for siderite formation based primarily on the relatively negative  $\delta^{13}\text{C}$  and highly variable  $\delta^{56}\text{Fe}$  values of many siderites, as well as experimental simulations [16,28–33]. In particular, siderites in the ~2.5 Ga Brockman Iron Formation in Hamersley, Australia [30] and in the BIFs of the ~3.8 Ga Isua Supracrustal Belt, Greenland [31] are proposed to have been precipitated through DIR. Moreover, siderites have also been suggested to form through the ageing and transformation of green rust [34] and through the reaction of Fe(III) minerals and organic carbon ( $\text{C}_{\text{org}}$ ) at elevated burial temperatures and pressures (e.g.,  $\geq 170\text{ °C}$  and  $\geq 1.2\text{ kbar}$ ) [17,19,35].

Interestingly, siderites are generally more common in Superior-type than Algoma-type BIFs, which may reflect the commonly lower metamorphic grade in Superior-type BIFs. An exception to this is the Dagushan BIF (~2.53–2.51 Ga) in the Anshan area, North China Craton (NCC), where siderites are widely distributed. The Dagushan BIF is the first Algoma-type BIF to be reported that has retained a series of relatively integrated depositional facies, including carbonate, oxide, and silicate facies [36]. The relatively mild metamorphic grade (greenschist- to lower amphibolite-facies) compared to typical Archean rocks (typically amphibolite-facies) also makes the Dagushan BIF a good target for examining the sources of C and Fe and the mechanisms that transformed them to siderite. Here, we report an integrated petrographic and C and Fe isotopic study on the siderites of the Dagushan BIF in order to constrain the formation pathway. We compare our results to other siderite-forming pathways proposed for different geological periods in order to provide new constraints on C and Fe cycling through time.

## 2. Geological Setting

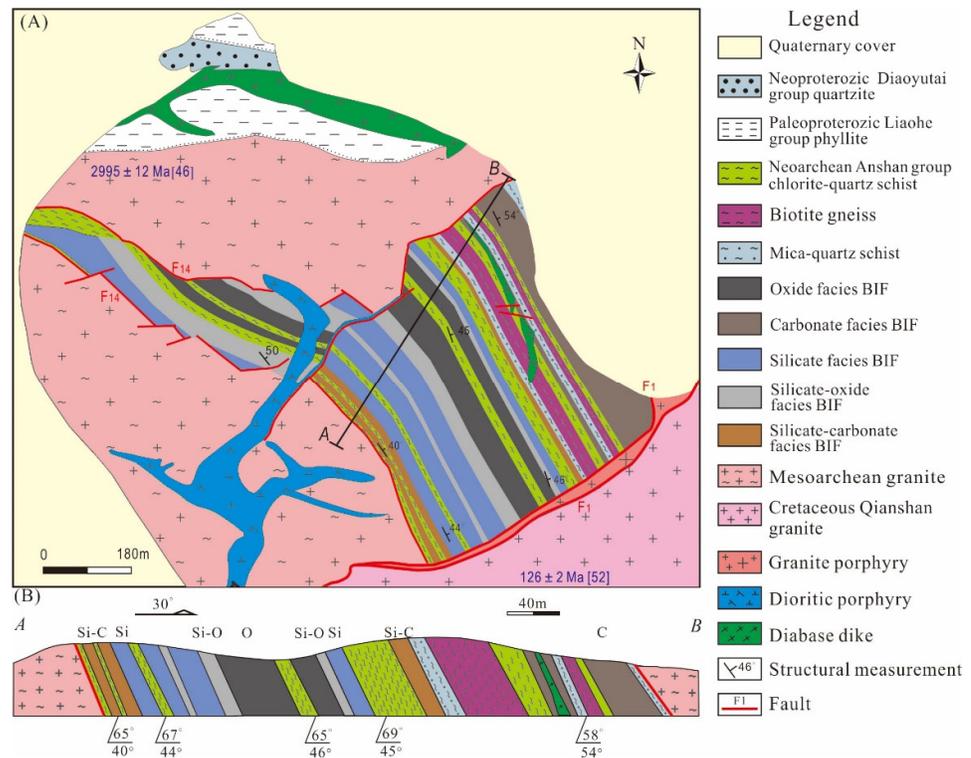
The Dagushan BIF is situated in the Anshan area of the Eastern Block of the NCC (Figure 1). The Anshan Group (~2.56–2.53 Ga) can be divided into two distinct units; the (1) Anshan and (2) Benxi units (Figure 1b) [37–43]. The Anshan unit has an upper greenschist- to lower amphibolite-facies metamorphic grade, and is dominated by ~2530 Ma BIFs (e.g., the Dagushan, Dong'anshan, and Qidashan BIFs), siliciclastic meta-sedimentary rocks, and minor metavolcanic rocks [44]. These meta-sedimentary rocks are composed of chlorite-quartz schist, biotite gneiss, mica-quartz schist, and phyllite [43,44]. By contrast, the Benxi unit is of a relatively higher metamorphic grade (amphibolite-facies), and mostly consists of ca. 2563 to 2530 Ma BIFs (e.g., Gongchangling, Beitai, Wai-toushan, and Nanfen BIFs), as well as basic to felsic volcanic rocks with lesser volcanoclastic and siliciclastic sedimentary rocks [42,44].

Located in the Anshan unit, the Dagushan BIF is an Algoma-type BIF that was deposited in a back-arc basin [43,44]. Age constraints on the Dagushan BIF are provided by weighted mean U-Pb ages from the youngest group of detrital zircons from the intercalated meta-greywacke, coupled with the maximum metamorphic age of ~2.51 Ga in the Anshan-Benxi area. It is suggested that the Dagushan BIF was deposited between 2.53 and 2.51 Ga [43], in accordance with the ages of other BIFs in the Anshan unit [42,45].



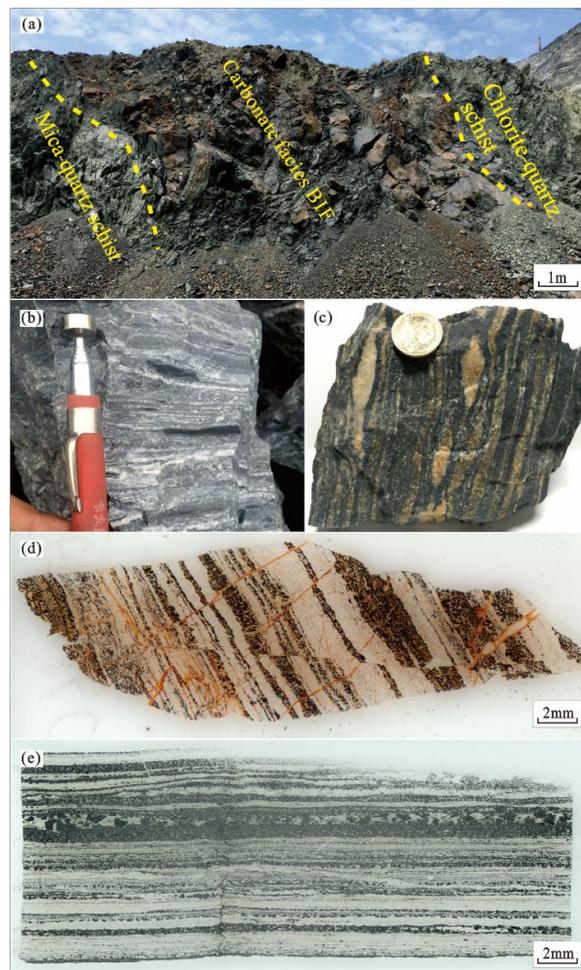
**Figure 1.** (A) Subdivisions of the North China Craton (NCC) showing the location of the Anshan-Benxi area and distribution of major Banded Iron Formations (BIFs) (modified from [46,47]); (B) geological sketch map of the Anshan-Benxi area indicating the study area (modified from [40]). Numbers show previous U-Pb zircon ages of supracrustal rocks associated with the BIFs. Age data sources: a—[45]; b—[48]; c—[49]; d—[39]; e—[42]; f—[38]; g—[50]; h—[41]; i—[51]; j—[43].

Three distinctive sedimentary facies are recognized in the Dagushan BIF: (1) an oxide facies, mainly composed of magnetite; (2) a silicate facies, composed of cummingtonite, stilpnomelane, and chlorite (silicate > 20%); (3) a carbonate facies, with siderite as the dominant Fe-bearing phase. As the major constituent (~50% vol.%) of the Dagushan BIF, the silicate facies BIF is distributed mainly in the south of the formation (Figure 2), and the oxide-facies BIF occurs primarily in the middle of the formation, making up to ca. 30 vol.% of the total BIF. The carbonate facies accounts for the remaining 20 vol.% of the Dagushan BIF and is spread predominantly over the northern region.



**Figure 2.** (A) Geological map of the Dagushan iron deposit (modified after [36]) including the main three depositional facies: O—oxide; Si—silicate; C—carbonate. (B) A cross-section of the Dagushan deposit, indicating the general stratigraphy of the Dagushan BIF and associated rocks. Transitional facies exist between the principal ones due to gradual facies transitions: silicate-oxide facies (Si-O) and silicate-carbonate facies (Si-C). For the purposes of this study, Si-O facies is merged into the silicate facies and Si-C into the carbonate facies.

The Dagushan BIF is associated with well-bedded chlorite-quartz schist, biotite gneiss, and minor mica-quartz schist (Figure 2) [43]. The beds strike north-west and dip 40–70° to north-east, and some of these supracrustal rocks are cross-cut by quartz and calcite veins that indicate later-stage hydrothermal alteration. Igneous rocks extend widely in the study area, consisting predominantly of Mesoarchean granite, Cretaceous granite, granite porphyry, diorite porphyrite, and diabase dikes (Figure 3a). The ~3.0 Ga Mesoarchean granite (Donganshan granite, [51]), is on the footwall of the Neoproterozoic supracrustal rocks (Figures 2 and 3b). All field observations indicate a fault contact between it and the BIF. The Cretaceous granite (Qianshan granite, [52]), as well as granite porphyry, shows evident unconformable contact relationships with the Dagushan supracrustal rocks.



**Figure 3.** (a) Field relationships of carbonate facies BIF and its associated rocks in the Dagushan iron deposit. Yellow dashed lines represent lithologic boundaries. (b) Fresh hand specimen of carbonate facies BIF with black and buff-white micro bands. (c) Weathered hand specimen of carbonate facies BIF, showing rotational porphyroclasts with right shearing characteristics. (d) Iron- and carbonate-rich bands with brown to yellow fractures. (e) Alternating buff-white and black microbands with gradational contacts, comprising siderite, quartz, and magnetite in varying proportions.

### 3. Analytical Methods

Samples were obtained from open pit outcrops in the northern part of the Dagushan iron mine (41°03'10" N, 123°03'27" E). Detailed petrographic examinations using transmitted and reflected light were carried out to determine the mineralogy and paragenetic history of all BIF samples. Scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS) was used to examine small-scale relationships between textures and measure elemental abundances at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing (IGGCAS). Major element compositions of siderite were determined by wavelength dispersive spectrometry using a JEOL JXA8100 electron probe microanalyzer (EPMA) at the IGGCAS, Beijing. The analyses were carried out at an accelerating voltage of 15 kV and a beam spot diameter of 5  $\mu\text{m}$  with a 20 nA beam current and a 10–30 s counting time on peak. The analytical precision for most elements is estimated to be better than 1.5%.

Ten representative carbonate facies samples were chipped with a hammer to remove weathered surfaces and cleaned with ultrapure water (1.82 M $\Omega$  cm). Pure siderite mineral

separates were obtained using standard density and magnetic techniques, and then powdered to ~200 µm fineness in an agate mill in order to avoid any metal contact before further geochemical analysis. The agate mill was cleaned with deionized water and alcohol between each sample.

Iron isotope analyses for siderite were conducted at the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences. A detailed description of the sample dissolution, chemical separation, and Fe isotope analysis is given in [53]. The procedure for chromatographic separation of Fe using an AG MP-1 anion exchange resin (100–200 mesh) followed that previously used by [54]. Following chromatographic separation, Fe isotope ratios were measured in high mass resolution mode on a Nu Plasma HR MC-ICP-MS using a standard-sample bracketing (SSB) approach. The Fe isotope results are expressed as deviations of the sample Fe isotope ratio from that of the reference material IRMM-14 in per mil:

$$\delta^{56}\text{Fe}_{\text{IRMM-014}} (\text{‰}) = [({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}}/({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}} - 1] \times 1000$$

$$\delta^{57}\text{Fe}_{\text{IRMM-014}} (\text{‰}) = [({}^{57}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}}/({}^{57}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}} - 1] \times 1000$$

The long-term external reproducibility is estimated to be better than 0.05‰ for  $\delta^{56}\text{Fe}$  at the SD level, based on repeated measurements of in-house CAGS Fe solutions and national basaltic standard reference material CAGSR-1 (GBW-07105) against IRMM-014 [53].

Total inorganic carbon (TIC), total organic carbon (TOC), and the isotopic composition of organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) were measured on 10 selected samples at ALS Chemex, China. Abundances of TIC were analyzed with an Ethanolamine Color Coulomb Instrument after being treated with  $\text{HClO}_4$ . The precision of the analyses ( $1\sigma$ ) was better than 0.2%. Aliquots (200 mg) for TOC analysis were first treated with 10 vol.% HCl at 60 °C to remove carbonate [9], and then washed with distilled water to remove HCl. Afterward, the samples were dried overnight (50 °C) and then analyzed using an LECO CS-400 analyzer. Sample splits (300 mg to 1.5 g) for  $\delta^{13}\text{C}_{\text{org}}$  analysis were acidified with 6 N HCl in a centrifuge beaker to remove any carbonates. The decalcified samples (30–100 mg) + CuO wire (1 g) were added to quartz tubes, and combusted at 500 °C for 1 h and at 850 °C for another 3 h. Isotopic ratios were analyzed using cryogenically purified  $\text{CO}_2$  on a Finnigan MAT-253 mass spectrometer and are reported in standard  $\delta$ -notation relative to the Vienna Pee Dee Belemnite (VPDB) standard:

$$\delta^{13}\text{C}_{\text{VPDB}} (\text{‰}) = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{VPDB}} - 1] \times 1000$$

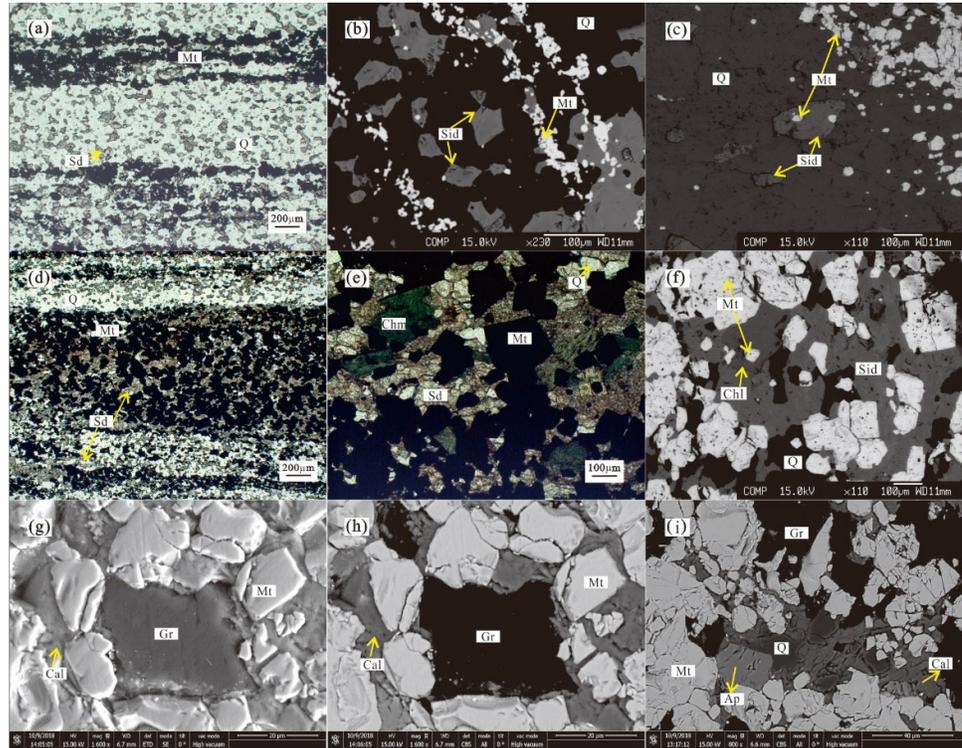
Analytical precision for the values is better than  $\pm 0.06\text{‰}$  ( $1\sigma$ ) based on measurements of geostandards GBW04407 (−22.43‰) and IAEA-600 (−27.5‰).

## 4. Results

### 4.1. Occurrence and Microscopic Features of Siderite

The carbonate facies, which is mainly interbedded with mica-quartz schist and chlorite-quartz schist (Figure 3a), appears brown to yellow in exposed surfaces due to strong weathering (Figure 3d). There are many rotational porphyroblasts (Figure 3c) and fractures (Figure 3d). Fresh samples from deeper in the outcrop show alternating buff-white and black microbands with gradational contacts (Figure 3b,e), comprising siderite, quartz, and magnetite in varying proportions. The buff-white siderite-rich microbands (Figure 4a) are mainly composed of fine-grained siderite (10–60 µm), quartz (30–100 µm), and microcrystalline magnetite (10–30 µm), accounting for 30, 50, and 20 vol.%, respectively. As shown in BSE images, siderite grains are subhedral to anhedral, with some being replaced by magnetite at the edge (Figure 4b). In the center of siderite grains, micrometer-scale magnetite is also commonly observed as inclusions (Figure 4c). The black microbands contain mainly subhedral-anhedral magnetite grains (10–100 µm, ~60 vol.%) and siderite aggregations (30–100 µm, ~20 vol.%), along with some tabular Fe-rich chamosite (50–150 µm) and quartz (Figure 4d). The siderite aggregations appear to be khaki and dirty, by which they can be distinguished from quartz that appears clear (Figure 4e). Clay

minerals surrounding siderite grains are mainly chamosite in the form of green platy crystals (Figure 4e). Magnetite inclusions are also observed in some chamosite grains (Figure 4f). It is noted that fine-grained graphite (20–80  $\mu\text{m}$ ) is observed in the carbonate facies (Figure 4g,h), which is intergrown with the magnetite, calcite (10–50  $\mu\text{m}$ ), and apatite (10–20  $\mu\text{m}$ ) in some places (Figure 4i).

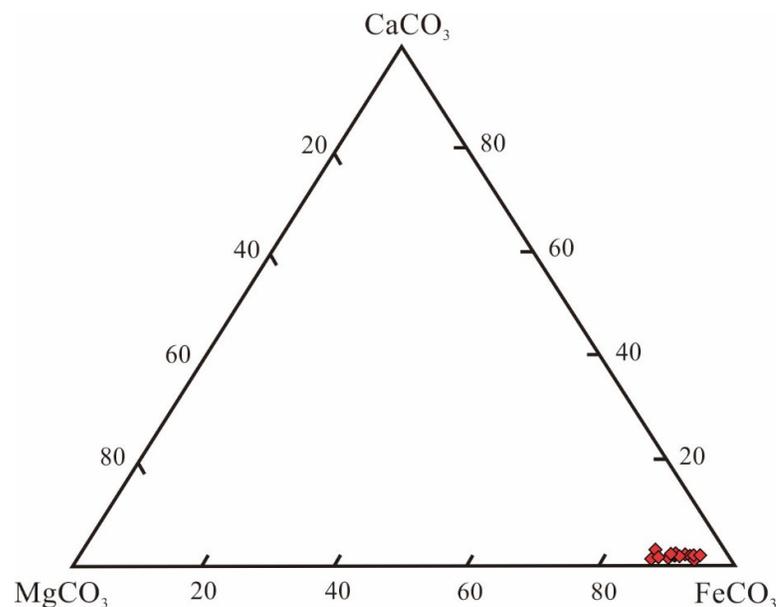


**Figure 4.** Photomicrographs showing representative textures of siderite in the carbonate facies BIF. (a) The buff-white microbands are composed mainly of fine-grained siderite (Sd) and quartz (plain-polarized light) (Q). (b) Siderite is subhedral to anhedral and replaced by magnetite (Mt) in part (scanning electron microscope image, SEM). (c) Micronmeter-sized granulous magnetites are found in the center of some siderite grains (SEM). (d) The black bands, comprising mainly subhedral-anhedral magnetite with some siderite aggregations (plain-polarized light). (e) The siderite aggregations appear to be khaki and dirty distinguishing them from quartz. There are also some green platy crystals of chamosite (Chm) (plain-polarized light). (f) The chamosite often encloses fine-grained magnetite (SEM). (g,h) Platy graphite (Gr,  $\sim 20\mu\text{m}$ ) in the carbonate facies (secondary electron image (SE) and back-scattered electron image (BSE) SEM, respectively). (i) Fine-grained graphite sometimes appears intergrown with the magnetite, calcite (Cal), and apatite (Ap) (SEM).

The major element compositions of Fe-rich carbonates are presented in Table 1 and plotted in Figure 5. Subhedral to anhedral siderite grains in the carbonate facies contain 47.48–55.31 wt.% FeO and 2.36–5.22 wt.% MgO with little CaO (<1 wt.%), corresponding to 87–93 mol.% and 6–12 mol.% of  $\text{FeCO}_3$  and  $\text{MgCO}_3$ , respectively. The content of MnO is relatively low, ranging from 0.27 to 1.55 wt.%.

**Table 1.** EPMA data of iron-rich carbonate from the Dagushan BIF.

| Composition                    | Unit | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    | 14    |
|--------------------------------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Na <sub>2</sub> O              | wt.% | 0.06  | 0.07  | 0.00  | 0.10  | 0.09  | 0.05  | 0.08  | 0.04  | 0.01  | 0.03  | 0.10  | 0.07  | 0.02  | 0.06  |
| MgO                            | wt.% | 3.59  | 2.70  | 3.69  | 4.78  | 2.36  | 5.22  | 3.43  | 3.24  | 2.58  | 4.19  | 3.66  | 2.65  | 4.13  | 3.77  |
| Al <sub>2</sub> O <sub>3</sub> | wt.% | 0.04  | 0.00  | 0.00  | 0.01  | 0.02  | 0.00  | 0.00  | 0.03  | 0.01  | 0.05  | 0.02  | 0.00  | 0.01  | 0.00  |
| K <sub>2</sub> O               | wt.% | 0.00  | 0.00  | 0.00  | 0.02  | 0.01  | 0.00  | 0.00  | 0.00  | 0.02  | 0.04  | 0.00  | 0.00  | 0.01  | 0.00  |
| CaO                            | wt.% | 0.66  | 0.64  | 0.69  | 0.49  | 0.29  | 0.32  | 0.85  | 0.56  | 0.72  | 0.42  | 0.77  | 0.61  | 0.11  | 0.20  |
| FeO                            | wt.% | 49.78 | 51.88 | 50.18 | 48.99 | 50.13 | 47.67 | 49.15 | 48.54 | 55.31 | 50.10 | 47.48 | 52.85 | 53.57 | 49.02 |
| MnO                            | wt.% | 1.19  | 1.08  | 1.35  | 1.14  | 0.81  | 1.26  | 1.27  | 1.55  | 0.92  | 1.42  | 1.67  | 1.22  | 0.54  | 0.27  |
| TiO <sub>2</sub>               | wt.% | 0.00  | 0.01  | 0.03  | 0.00  | 0.02  | 0.00  | 0.03  | 0.00  | 0.01  | 0.04  | 0.02  | 0.00  | 0.01  | 0.00  |
| SiO <sub>2</sub>               | wt.% | 0.01  | 0.05  | 0.06  | 0.00  | 0.03  | 0.02  | 0.00  | 0.06  | 0.01  | 0.03  | 0.02  | 0.05  | 0.01  | 0.01  |
| Cr <sub>2</sub> O <sub>3</sub> | wt.% | 0.02  | 0.03  | 0.00  | 0.01  | 0.00  | 0.01  | 0.00  | 0.02  | 0.00  | 0.00  | 0.01  | 0.02  | 0.00  | 0.00  |
| NiO                            | wt.% | 0.01  | 0.04  | 0.02  | 0.00  | 0.01  | 0.00  | 0.00  | 0.01  | 0.00  | 0.01  | 0.02  | 0.01  | 0.01  | 0.00  |
| FeCO <sub>3</sub>              | %    | 90.19 | 92.47 | 90.01 | 87.85 | 93.65 | 86.94 | 90.08 | 90.93 | 93.00 | 89.42 | 89.41 | 92.75 | 90.68 | 90.52 |
| CaCO <sub>3</sub>              | %    | 1.33  | 1.26  | 1.38  | 0.97  | 0.60  | 0.65  | 1.73  | 1.16  | 1.34  | 0.83  | 1.61  | 1.19  | 0.21  | 0.41  |
| MgCO <sub>3</sub>              | %    | 8.48  | 6.27  | 8.62  | 11.17 | 5.75  | 12.41 | 8.19  | 7.91  | 5.65  | 9.75  | 8.98  | 6.06  | 9.11  | 9.07  |



**Figure 5.** Major mineral end-member compositions of individual siderite in the Dagushan carbonate facies BIF based on the modal proportion of carbonate minerals. Three end-members are siderite, calcite, and dolomite, respectively. Data was obtained by electron microprobe analysis.

#### 4.2. Bulk Carbon Content and Isotopes and Siderite Iron Isotopes

The TOC and TIC of the BIF samples, and carbon isotope ratios of C<sub>org</sub>, are presented along with previously published siderite C isotope data ( $\delta^{13}\text{C}_{\text{sid}}$ ) in Table 2. The TOC contents in BIF samples are less than 0.11 wt.%, consistent with the minor amount of C<sub>org</sub> (graphite) observed microscopically, while the TIC contents of the samples are higher and range widely from 0.92 to 3.36 wt.%. Carbon isotope ratios of  $\delta^{13}\text{C}_{\text{org}}$  are relatively consistent, varying from  $-26.8\text{‰}$  to  $-23.2\text{‰}$ , with an average of  $-25.4\text{‰}$ . There is no obvious correlation between TOC and  $\delta^{13}\text{C}_{\text{org}}$  in the dataset. Neither is any obvious correlation observed between  $\delta^{13}\text{C}_{\text{sid}}$  and  $\delta^{18}\text{O}_{\text{sid}}$  values (Figure S1), suggesting that samples have only undergone low-grade alteration [55]. In addition, the contents of primary organic carbon precipitated on the seafloor are relatively low, varying from 0.73 to 1.25 wt.%, and the calculation process is shown in Table 3.

**Table 2.** Carbonate and organic carbon geochemical data of the Dagushan BIF.

| Sample  | TOC   | TIC   | $\delta^{13}\text{C}_{\text{org}}$ | $\delta^{13}\text{C}_{\text{carb}}^1$ | $\delta^{18}\text{O}_{\text{carb}}^1$ | DIC <sub>org</sub> | %DIC <sub>org</sub> /TIC |
|---------|-------|-------|------------------------------------|---------------------------------------|---------------------------------------|--------------------|--------------------------|
| Unit    | wt. % | wt. % | ‰, VPDB                            | ‰, VPDB                               | ‰, SMOW                               | wt. %              | %                        |
| D-3-1   | 0.08  | 2.98  | -26.50                             | -3.53                                 | 12.41                                 | 0.40               | 13.32                    |
| D-3-2   | 0.05  | 2.57  | -26.80                             | -4.64                                 | 13.87                                 | 0.44               | 17.31                    |
| D-3-3   | 0.06  | 0.92  | -24.80                             | -3.85                                 | 11.02                                 | 0.14               | 15.52                    |
| D-3-4   | 0.05  | 1.81  | -24.44                             | -4.12                                 | 12.94                                 | 0.31               | 16.86                    |
| D-3-5   | 0.06  | 2.19  | -25.32                             | -4.89                                 | 13.63                                 | 0.42               | 19.31                    |
| D-4-1   | 0.04  | 1.48  | -24.90                             | -6.20                                 | 11.93                                 | 0.37               | 24.90                    |
| D-4-2   | 0.11  | 2.41  | -23.15                             | -1.57                                 | 13.31                                 | 0.16               | 6.78                     |
| D-4-3   | 0.07  | 2.54  | -26.33                             | -5.34                                 | 12.71                                 | 0.52               | 20.28                    |
| D-4-4   | 0.09  | 1.85  | -26.74                             | -2.90                                 | 12.18                                 | 0.20               | 10.85                    |
| D-4-5   | 0.08  | 3.36  | -25.01                             | -3.68                                 | 13.92                                 | 0.49               | 14.71                    |
| average | 0.07  | 2.21  | -25.40                             | -4.07                                 | 12.79                                 | 0.35               | 15.98                    |

<sup>1</sup>The  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  data are from [56]. TOC = the content of total organic carbon in samples; TIC = the content of total inorganic carbon;  $\delta^{13}\text{C}_{\text{org}}$  = carbon isotope of organic carbon; [DIC]<sub>org</sub> = inorganic carbon derived from remineralized organic carbon; % [DIC]<sub>org</sub>/TIC = percentage of remineralized organic carbon in total inorganic carbon (with TIC = [DIC]<sub>org</sub> + [DIC]<sub>sw</sub>).

**Table 3.** Calculation of the organic carbon.

| Sam-<br>ple | m <sub>c</sub> | m <sub>Fe</sub> | M <sub>Sid</sub> | Total<br>Fe <sub>2</sub> O <sub>3</sub> <sup>1</sup> | TFe   | M <sub>Mt</sub> | M <sub>Fe(II)-<br/>Mt</sub> | M <sub>TFe(II)</sub> | m <sub>Fe(II)</sub> | M <sub>oc</sub> | TOC* | Consumed<br>TOC (%) |
|-------------|----------------|-----------------|------------------|--|-------|-----------------|-----------------------------|----------------------|---------------------|-----------------|------|---------------------|
| D-3-1       | 0.25           | 0.25            | 13.91            | 48.79  | 34.15 | 20.25           | 6.75                        | 20.66                | 0.37                | 1.11            | 1.19 | 93.26               |
| D-3-2       | 0.21           | 0.21            | 11.99            | 50.86  | 35.60 | 23.61           | 7.87                        | 19.86                | 0.35                | 1.06            | 1.11 | 95.51               |
| D-3-3       | 0.08           | 0.08            | 4.29             | 41.04  | 28.73 | 24.43           | 8.14                        | 12.44                | 0.22                | 0.67            | 0.73 | 91.74               |
| D-3-4       | 0.15           | 0.15            | 8.45             | 53.80  | 37.66 | 29.21           | 9.74                        | 18.18                | 0.32                | 0.97            | 1.02 | 95.12               |
| D-3-5       | 0.18           | 0.18            | 10.22            | 50.74  | 35.52 | 25.30           | 8.43                        | 18.65                | 0.33                | 1.00            | 1.06 | 94.34               |
| D-4-1       | 0.12           | 0.12            | 6.91             | 47.46  | 33.22 | 26.32           | 8.77                        | 15.68                | 0.28                | 0.84            | 0.88 | 95.45               |
| D-4-2       | 0.20           | 0.20            | 11.25            | 58.79  | 41.15 | 29.91           | 9.97                        | 21.22                | 0.38                | 1.14            | 1.25 | 91.18               |
| D-4-3       | 0.21           | 0.21            | 11.85            | 59.60  | 41.72 | 29.87           | 9.96                        | 21.81                | 0.39                | 1.17            | 1.24 | 94.35               |
| D-4-4       | 0.15           | 0.15            | 8.63             | 35.23  | 24.66 | 16.03           | 5.34                        | 13.98                | 0.25                | 0.75            | 0.84 | 89.27               |
| D-4-5       | 0.28           | 0.28            | 15.68            | 46.88  | 32.82 | 17.14           | 5.71                        | 21.39                | 0.38                | 1.15            | 1.23 | 93.47               |

<sup>1</sup>Total Fe<sub>2</sub>O<sub>3</sub> data are from [56]. m<sub>c</sub> = molar abundance of carbon (m<sub>c</sub> = TIC/12 g/mol); m<sub>Fe</sub> = molar abundance of iron (m<sub>Fe</sub> = m<sub>c</sub>); M<sub>Sid</sub> = mass fraction of Fe in siderite (M<sub>Sid</sub> = m<sub>Fe</sub> \* 56 g/mol = TIC/12 g/mol \* 56 g/mol); TFe = Total Fe content of the samples; M<sub>Mt</sub> = Total Fe content in magnetite (M<sub>Mt</sub> = TFe - M<sub>Sid</sub>); M<sub>Fe(II)-Mt</sub> = Fe(II) content in magnetite (M<sub>Fe(II)-Mt</sub> = M<sub>Mt</sub>/3); M<sub>TFe(II)</sub> = Total Fe(II) content in samples (M<sub>TFe(II)</sub> = M<sub>Fe(II)-Mt</sub> + M<sub>Sid</sub>); m<sub>Fe(II)</sub> = molar abundance of total Fe(II) (m<sub>Fe(II)</sub> = (M<sub>Fe(II)-Mt</sub> + M<sub>Sid</sub>)/56 g/mol); M<sub>oc</sub> = mass fraction of required organic carbon content (M<sub>oc</sub> = m<sub>TFe(II)</sub>/4 \* 12 g/mol); TOC\* = minimum total organic carbon that precipitated on the seafloor (TOC\* = M<sub>oc</sub> + TOC).

The iron isotope compositions ( $\delta^{56}\text{Fe}$ ) of siderite from the Dagushan BIF are predominantly positive and range from  $-0.180$  to  $+0.463$ ‰, with a mean value of  $+0.187$ ‰, and show an entirely mass-dependent relationship with  $\delta^{57}\text{Fe}$  ( $R^2 = 0.99$ ) (Table 4, Figure S2). Only three samples have slightly negative  $\delta^{56}\text{Fe}$  values between  $-0.18$  and  $-0.06$ ‰. Analytical error on the sample measurements (1 standard deviation) varies from 0.011 to 0.052.

**Table 4.** Iron isotope data of siderite from the Dagushan BIF.

| Sample  | $\delta^{57/54}\text{Fe}$ | SD    | $\delta^{56/54}\text{Fe}$ | SD    |
|---------|---------------------------|-------|---------------------------|-------|
| D-3-1   | 0.618                     | 0.019 | 0.390                     | 0.040 |
| D-3-2   | −0.119                    | 0.049 | −0.063                    | 0.042 |
| D-3-3   | 0.446                     | 0.030 | 0.316                     | 0.013 |
| D-3-4   | 0.284                     | 0.006 | 0.181                     | 0.015 |
| D-3-5   | −0.260                    | 0.024 | −0.180                    | 0.022 |
| D-4-1   | −0.205                    | 0.043 | −0.129                    | 0.033 |
| D-4-2   | 0.636                     | 0.031 | 0.463                     | 0.043 |
| D-4-3   | 0.149                     | 0.052 | 0.091                     | 0.011 |
| D-4-4   | 0.680                     | 0.014 | 0.438                     | 0.052 |
| D-4-5   | 0.545                     | 0.058 | 0.367                     | 0.049 |
| Average | 0.277                     | 0.032 | 0.187                     | 0.032 |

## 5. Discussion

### 5.1. Mineral Paragenesis

Siderite, typically occurring as microcrystalline, single rhomb-shaped crystals or massive layers, is the most common carbonate mineral in BIFs, and it may form penecontemporaneously with early ferric oxyhydroxide precipitates or during later diagenesis [13,16,17,57,58]. Siderite and magnetite are the main Fe-bearing minerals in the Dagushan carbonate facies BIF.

Fine-grained subhedral siderite crystallites (<50  $\mu\text{m}$ ) and fine-grained magnetite (<50  $\mu\text{m}$ ) are evenly distributed amongst the quartz (Figure 4a). These are likely to have formed relatively rapidly during the early stage of diagenesis due to their small sizes. Moreover, fine-grained magnetite occurs as inclusions within some medium to large-grained subhedral-euhedral siderites (50–150  $\mu\text{m}$ ) (Figure 4c), whereas siderite is not found within magnetite grains, suggesting that large-grained siderite post-dates the fine-grained magnetite and probably formed later during diagenesis. Additionally, the irregular siderite aggregates in the iron-rich microbands, intergrown with green platy chamosite (Figure 4e) and medium to large coarse-grained magnetite (50–150  $\mu\text{m}$ ), are formed from preferentially concentrated siderite grains where several Fe oxide layers coalesce due to burial compaction, and may distort the primary microlamination (Figures 3c and 4d), providing further evidence for siderite formation during later diagenesis. In addition, medium to large-grained siderite grains are occasionally replaced by magnetite on the edges (Figure 4b), likely through metamorphic alteration and oxidation.

In sum, fine-grained magnetite and siderite are likely to have formed during the early diagenesis, while medium to large-grained magnetite, siderite aggregates possibly formed during later diagenesis. Finally, siderite may have been oxidized to magnetite during subsequent metamorphism.

### 5.2. Formation Pathways of Siderite

#### 5.2.1. Direct Precipitation from Seawater

Siderite is typically formed in anoxic and Fe-rich (but S-poor) conditions under high alkalinity [10–12,59]. Accordingly, some previous publications have argued that, similar to other marine carbonates, ancient siderite in BIF formed through the combination of dissolved Fe(II) with dissolved carbon dioxide, in the form of  $\text{HCO}_3^-$ , and directly precipitated from seawater via the following reaction [13,20–22,24,25,60]:



Although it has recently been argued that the kinetics of Fe(II)-carbonate precipitation in Precambrian seawater would have limited its direct precipitation [26]. When considering the direct precipitation from seawater, the  $\delta^{13}\text{C}_{\text{sid}}$  composition can be used to

evaluate whether siderite precipitated directly in equilibrium with seawater. The dissolved inorganic carbon (DIC) pool in Precambrian seawater is expected to have had  $\delta^{13}\text{C}$  values close to 0‰, except for some anomalous periods in the early Paleoproterozoic and the late Neoproterozoic [61]. Thus, carbonate minerals comprising limestones and dolomite precipitated directly from the seawater, and typically have  $\delta^{13}\text{C}_{\text{carb}}$  values of  $\sim 0\%$  [61,62]. For example, Ca-Mg carbonates associated with the 2.52 Ga Gamoha Formation BIFs [63–66] and stratigraphically equivalent Campbellrand platform rocks [67] have  $\delta^{13}\text{C}_{\text{carb}}$  values from  $-1.0$  to  $0\%$ . Given that C isotope fractionation between calcite and siderite in equilibrium with the same fluid at  $25\text{ }^\circ\text{C}$  is about  $-0.5\%$  [68], estimated values of  $\delta^{13}\text{C}_{\text{sid}}$  formed in equilibrium with Archean seawater should range from  $-1.5$  to  $-0.5\%$ . However, the distinctly negative  $\delta^{13}\text{C}_{\text{sid}}$  values, ranging from  $-6.20$  to  $-1.57\%$ , in the Dagushan BIF (Table 2) fall below the expected values for seawater-derived siderite, suggesting that the more negative  $\delta^{13}\text{C}_{\text{sid}}$  values indicate that an additional negative C isotope reservoir, such as organic matter, must have contributed to siderite formation (see next section).

The Fe isotopic signatures in Dagushan siderites corroborate the C isotopes. The main Fe(II) source of the Archean ocean are hydrothermal fluids [4] which are expected to have a  $\delta^{56}\text{Fe}$  composition of around  $-0.2\%$  or less [29,31]. In addition, the equilibrium Fe(II)aq-siderite fractionation factor is estimated to be  $-0.5 \pm 0.2\%$  from experimental observations [69], or  $-2.1$  to  $-1.6\%$  based on theoretical calculations [70–72]. Accordingly, siderites precipitated in equilibrium with seawater are predicted to have negative Fe isotopic ratios from  $-2$  to  $-0.5\%$ . Similar light  $\delta^{56}\text{Fe}$  values are observed in Fe-poor carbonates from the Wittenoom Dolomite in the Hamersley basin [31]. By contrast, siderites in the Dagushan BIF have  $\delta^{56}\text{Fe}$  values that range from  $-0.180$  to  $+0.463\%$ , uniformly higher than values predicted for seawater-precipitated siderite. In sum, siderites from our study area do not carry typical isotopic signatures reflective of formation in equilibrium with seawater. Therefore, we posit that siderite in the Dagushan BIF could not have precipitated directly in the water column.

### 5.2.2. Authigenic Precipitation from Porewater by DIR

Another proposed formation pathway for siderite in BIFs is authigenic precipitation from sediment porewater, facilitated by dissimilatory iron reduction (DIR). DIR is a widespread microbial metabolic pathway through which Fe(III)-reducing bacteria oxidize organic carbon for energy and tie electron transport to the reduction of an Fe(III)-oxyhydroxide, such as ferrihydrite ( $\text{Fe}(\text{OH})_3$ ). This anaerobic metabolism produces dissolved Fe(II), depending on the porewater composition, can facilitate the precipitation secondary Fe(II)-bearing minerals such as siderite (R.2). This biologically induced form of biomineralization has been demonstrated to be a viable pathway capable of accounting for siderite in both modern sediments [73,74] and the rock record [28,29,32,33,75,76].



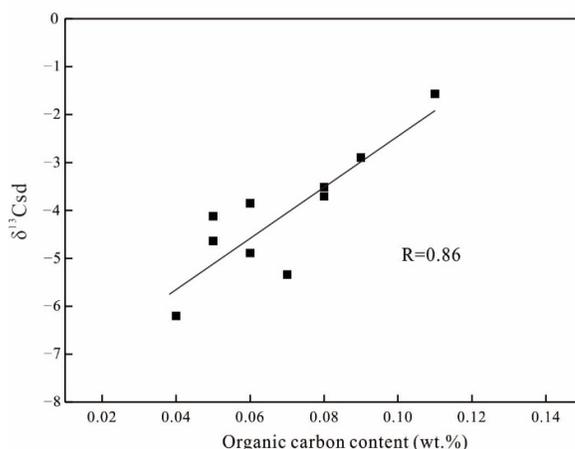
A flux of reactive ferrihydrite and  $\text{C}_{\text{org}}$  to the seafloor in Neoproterozoic oceans, where dissimilatory sulfate reduction was suppressed by low sulfate levels, would support high levels of DIR [29]. Such a pathway could have converted ferrihydrite to siderite in the Dagushan BIF, as is supported by several lines of evidence including petrographic observations, negative  $\delta^{13}\text{C}_{\text{sid}}$  values, and varying  $\delta^{56}\text{Fe}$  values in siderites, while the presence of graphite supports the previous presence of organic biomass that could have acted as the electron donor to facilitate DIR. In this regard, the fine-grained graphite ( $\sim 20\text{ }\mu\text{m}$ , Figure 4g,h) is likely to be the final product of remnant organic carbon after being metamorphosed.

From a petrographic perspective, there is no siderite found in magnetite grains, whereas small magnetite grains occur as inclusions within siderite (Figure 4c). This is important because not only does it confirm a diagenetic pathway rather than precipitation from seawater, but it also implies that magnetite formed even earlier. Furthermore, some

siderite and quartz grains appear as irregular aggregates that have distorted the primary microlamination and several Fe-rich microbands (Figure 3c), suggesting that these were preferentially concentrated during burial compaction.

The negative  $\delta^{13}\text{C}_{\text{Sid}}$  values,  $\sim -6.20$  to  $-1.57\text{‰}$ , of the Dagushan BIFs, which are significantly lower than those expected via precipitation from seawater, require a source of C with a lighter isotopic composition. The best candidate for this is the organic matter present in the Dagushan BIFs which displays a narrow range of very low  $\delta^{13}\text{C}_{\text{Org}}$  between  $-26.8$  and  $-23.2\text{‰}$ . The oxidation of  $\text{C}_{\text{Org}}$  delivers isotopically light dissolved inorganic carbon (DIC) to porewaters, where it mixes with seawater-derived DIC with  $\delta^{13}\text{C}$  around  $0\text{‰}$  ( $[\text{DIC}]_{\text{sw}}$ ). Theoretically, siderites with  $\delta^{13}\text{C}$  ratios nearing  $-25\text{‰}$  could be formed entirely from a pool of carbonate derived through DIR, while siderites possessing  $\delta^{13}\text{C}$  ratios around  $0\text{‰}$  could have formed entirely from an inorganic reservoir derived from seawater. Accordingly, the wide range of negative  $\delta^{13}\text{C}_{\text{Sid}}$  values in the Dagushan BIF may reflect varying proportions of both end member sources (i.e., seawater/diagenetic  $\text{HCO}_3^-$  anions) during siderite formation within sediments.

Mixing of bicarbonate pools is further implied by a positive correlation ( $R = 0.86$ , Figure 6) between TOC and  $\delta^{13}\text{C}_{\text{Sid}}$ . If the TOC contents of primary sediments were initially similar, this positive correlation would indicate that in samples where the residual organic matter content is lower, a relatively larger fraction of the organic matter was oxidized through DIR and a higher proportion of DIR-derived C participated in the forming of siderite, leading to a lower carbon isotope value.



**Figure 6.** Correlation diagram for organic carbon content (TOC, wt.%) of the bulk rock and carbon isotope composition of the siderite ( $\delta^{13}\text{C}_{\text{Sid}}$ , ‰).

Through a simple mass-balance model (R.3) presented in [3], the proportions of  $\text{HCO}_3^-$  ( $\delta^{13}\text{C}_{\text{sw}} = 0\text{‰}$ ) from seawater and organic carbon ( $\delta^{13}\text{C}_{\text{org}} = -25\text{‰}$ ) may be calculated as follows:

$$[\text{DIC}]_{\text{Sid}} \delta^{13}\text{C}_{\text{Sid}} = [\text{DIC}]_{\text{org}} \delta^{13}\text{C}_{\text{org}} + [\text{DIC}]_{\text{sw}} \delta^{13}\text{C}_{\text{sw}} \quad (3)$$

where  $[\text{DIC}]_{\text{Sid}}$  and  $[\text{DIC}]_{\text{sw}}$  are the mass fractions of inorganic C in siderite and seawater, respectively, while  $[\text{DIC}]_{\text{org}}$  represents inorganic carbon content that is derived from organic carbon through DIR. The  $\delta^{13}\text{C}_{\text{Sid}}$ ,  $\delta^{13}\text{C}_{\text{org}}$ , and  $\delta^{13}\text{C}_{\text{sw}}$  are the carbon isotope compositions of siderite ( $\sim -6.20$  to  $-1.57\text{‰}$ ), organic carbon ( $\sim -26.80$  to  $-23.2\text{‰}$ ), and seawater ( $\sim 0\text{‰}$ ), respectively. Accordingly, the proportion of the organic carbon that contributed to siderite formation ( $[\text{DIC}]_{\text{org}}/[\text{DIC}]_{\text{Sid}}$ ) depends on the value of  $\delta^{13}\text{C}_{\text{org}}/\delta^{13}\text{C}_{\text{Sid}}$ , and corresponds to about 6.78–24.90% of DIR-derived C in Dagushan BIF siderites (Table 2).

In addition to C isotopes, the Fe isotope composition of Fe-rich carbonates can be used to probe their formation processes. As mentioned above, siderites in the Dagushan BIF have  $\delta^{56}\text{Fe}$  values from  $-0.180$  to  $+0.463\text{‰}$ , which is best explained through inheritance



means that the Fe(II) content in magnetite ( $M_{\text{Fe(II)-Mt}}$ ) can be calculated as:  $M_{\text{Fe(II)-Mt}} = M_{\text{Mt}}/3$ . Consequently, total Fe(II) content  $M_{\text{TFe(II)}}$  is the sum of  $M_{\text{Fe(II)-Mt}}$  and  $M_{\text{Sid}}$ , and mole number is  $= (M_{\text{Fe(II)-Mt}} + M_{\text{Sid}})/56$  g/mol. During Fe(III) reduction, a ratio of 1C:4Fe(III) ratio is required if organic carbon serves as the reductant for chemoheterotrophic metabolism [R.4] [28], and thus, the required organic carbon content is:  $M_{\text{oc}} = m_{\text{TFe(II)}}/4 * 12$  g/mol.



Therefore, the minimum total organic carbon that precipitated on the seafloor during BIF deposition may be estimated by combining  $M_{\text{oc}}$  and tested residual TOC in samples. It is noted here that graphite is sparsely distributed within our samples, and that overall the TOC preserved in our samples remains low (down to 0.04 wt.%). This is much lower than those of other BIFs such as the Mozaan Group, South Africa, which have TOC contents ranging from 0.4 to 2.5 wt.% [83].

Constant organic material inputs to oceans are usually in the form of allochthonous and/or autochthonous particulates that sink from the surface down onto the seafloor. The water depth and the distance from the shore are the predominant factors that govern the flux of organic material to the seafloor [84]. According to Chester [85], less than 0.1% of organic material makes its way through deeper waters without being remineralized and ends up buried into pelagic sediments, compared to 5% in nearshore sediments. This relationship may help to explain the relatively low  $C_{\text{org}}$  abundance in the study materials, as the Dagushan BIFs were likely deposited in bathyal-abysmal basin.

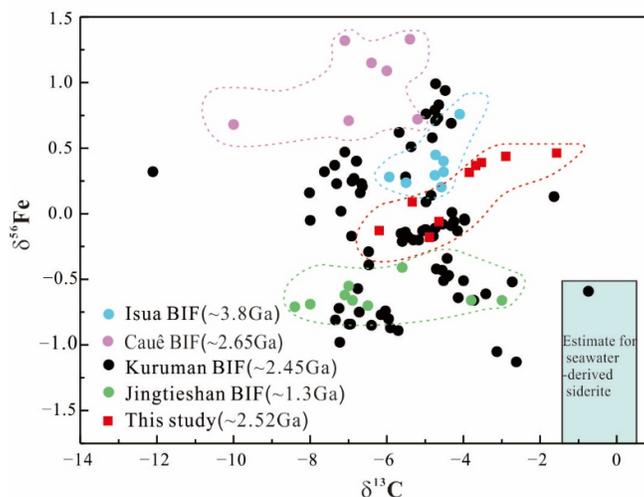
#### 5.4. Comparison with Siderites in Other BIFs through Time

Iron and C isotope data of siderite samples from a selection of BIFs of different ages (from 3.8 to 1.3 Ga) are summarized in Table 5 and plotted in Figure 8. These include the ~3.8 Ga Isua BIFs, West Greenland [31,86], the ~2.65 Ga Cauê BIF, Brazil [76], the ~2.45 Ga Kuruman BIFs, South Africa [16], the ~1.3 Ga Jingtieshan BIF, China [87], and the ~2.52 Ga Dagushan BIF, China (this study).

**Table 5.** Statistical data of the iron and carbon isotopes of siderites through different time periods.

| BIF Name                | Loction                        | Formation Age (Ga) | Type <sup>1</sup> | <sup>13</sup> C (‰) | <sup>56</sup> Fe(‰) | Origin               | References |
|-------------------------|--------------------------------|--------------------|-------------------|---------------------|---------------------|----------------------|------------|
| Isua BIF                | Greenland                      | ~3.8               | A                 | -4.52~-5.94         | +0.24~+0.76         | DIR                  | [31,86]    |
| Helen IF                | Wawa, Ontario                  | ~2.75              | A                 | ~0‰                 | -                   | Direct precipitation | [25]       |
| Brockman IF             | Hamersley, Australia           | ~2.5               | S                 | -12.59~-7.45        | -1.08~+1.21         | DIR                  | [31,87]    |
| Brockman IF             | Hamersley, Australia           | ~2.5               | S                 | -6.92~-11.00        | -                   | Direct precipitation | [21]       |
| Brockman IF             | Hamersley, Australia           | ~2.5               | S                 | -                   | -2.06~+1.00         | DIR                  | [29]       |
| Kuruman, Gamohaans BIFs | Transvaal, South Africa        | ~2.5               | S                 | -2.6~-12            | -0.32~+0.99         | DIR                  | [16]       |
| Cauê IF                 | Quadrilátero Ferrífero, Brazil | ~2.45              | S                 | -                   | -2.0~+1.33          | DIR                  | [76]       |
| Xiamaling Formation     | Hebei, China                   | ~1.40-1.35         | -                 | -24.44~-12.35       | -                   | DIR                  | [59]       |
| Jingtieshan BIF         | Gansu, China                   | ~1.3               | -                 | -8.4~-3.0           | -0.42~-0.71         | Direct precipitation | [88]       |

<sup>1</sup> Type "A" and "S" represent "Algoma" and "Superior", respectively.



**Figure 8.** Iron ( $\delta^{56}\text{Fe}$ ) and carbon ( $\delta^{13}\text{C}$ ) isotope data for siderites from typical BIFs of different ages, including the ~3.8 Ga Isua BIFs (blue circles, [31,86]), ~2.45 Ga Kuruman BIFs (black circles, [16]), ~2.65 Ga Cauê BIF (pink circles, [76]), ~1.3 Ga Jingtieshan BIFs (green circles, [88]), and ~2.52 Ga Dagushan BIF (red squares) in this study. The blue box is the predicted range of isotopic compositions for iron-rich carbonates precipitated directly from and in isotopic equilibrium with Archean seawater based on experimental [68,69] and theoretical estimates [70–72] of equilibrium isotope fractionation between  $\text{Fe(II)}_{\text{aq}}$ -siderite and  $\text{HCO}_3^-$ -siderite.

Most of the siderite samples summarized here range between  $-8$  to  $-3\text{‰}$  in  $\delta^{13}\text{C}$  and  $-0.75$  to  $+0.75\text{‰}$  in  $\delta^{56}\text{Fe}$ . Only a few samples are close to the estimated value of Archean seawater-derived siderite (Figure 8), which implies that siderites in BIF are generally not formed in equilibrium with seawater, but instead are products of early diagenetic mineral formation in the soft sediment prior to lithification [16,76]. One exception is the Jingtieshan BIF, which has a narrower Fe isotope range between  $-0.71\text{‰}$  and  $-0.41\text{‰}$  (apart from a single sample with  $\delta^{56}\text{Fe} = -1.62\text{‰}$ ), suggesting the possibility of isotope equilibrium with submarine hydrothermal fluids and seawater [81]; however, even there the  $\delta^{13}\text{C}$  values imply a significant contribution from remineralized  $\text{C}_{\text{org}}$ . The  $\delta^{56}\text{Fe}$  and  $\delta^{13}\text{C}$  signatures of siderite in the ~3.8 Ga Isua and 2.65 Ga Cauê BIFs—similarly an Algoma-type BIF—are the most similar to those of the Dagushan BIF. The most significant difference is that all  $\delta^{56}\text{Fe}$  values of siderite in the Isua BIF samples are positive, which have been interpreted as a result of complete DIR [31]. Thus, despite the large age difference between different siderites at different locations, microbial DIR seems to have persisted as a dominant influence on sediment geochemistry from ~3.8 to ~2.45 Ga in BIF depositional settings [31,39,76].

## 6. Conclusions

Based on the Fe and C isotopic analyses presented here, the formation pathways for siderite in the carbonate facies of the ~2.52 Ga Dagushan BIF (Anshan area, China) are well constrained. The relatively negative  $\delta^{13}\text{C}$  and highly variable  $\delta^{56}\text{Fe}$  values are inconsistent with the siderites forming in equilibrium with Archean seawater and negate the potential for the direct precipitation from the water column in our study area. Thus, our siderite samples cannot be used as a direct proxy of paleomarine conditions, but instead they represent a valuable record of early diagenetic processes.

The significant pathway for siderite formation was likely DIR, where organic matter was oxidized with ferrihydrite acting as the terminal electron acceptor, and siderite being produced as a passive by-product. The positive and negative  $\delta^{56}\text{Fe}$  values of siderites measured in this study may be explained, respectively, by partial to quantitative reduction of the precursor ferrihydrite, which was originally the product of partial oxidation

which generated the positive  $\delta^{56}\text{Fe}$  values. However, quantitative reduction would require that all ferrihydrite was reduced by DIR and all ferrihydrite was transformed to siderite. This is contradicted by abundant magnetite grains within the samples studied here. Consequently, a multiple-stage DIR process may offer the best explanation for siderite formation in the study area. Here, Fe(II) produced by partial reduction of the precursor ferrihydrite through DIR could have mixed with seawater-sourced Fe(II) in sediment porewater to produce a range of  $\delta^{56}\text{Fe}$  values. By contrast, sustained reaction of residual ferrihydrite would have produced positive  $\delta^{56}\text{Fe}$  values up to +1.5‰. The  $\delta^{56}\text{Fe}$  of the precursor ferrihydrite, the degree of DIR, and the proportion of DIR-derived and seawater-sourced Fe(II) that contributed to siderite formation are the most significant factors influencing the  $\delta^{56}\text{Fe}$  of siderites. In addition, the negative  $\delta^{13}\text{C}$  values in the Dagushan BIF require both DIR-derived and seawater-sourced  $\text{HCO}_3^-$ , with less than 25% being derived through DIR, consistent with the overall low  $\text{C}_{\text{org}}$  content of the Dagushan BIF. Similarities in the C and Fe isotope systematics between the Dagushan BIF and a series of other Archean-Paleoproterozoic are a testament to the pervasive nature of DIR in Precambrian marine sediments.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2075-163X/11/1/94/s1](http://www.mdpi.com/2075-163X/11/1/94/s1), Figure S1: Correlation diagram of  $\delta^{13}\text{C}_{\text{sid}}$  and  $\delta^{18}\text{O}_{\text{sid}}$  values, Figure S2: A plot of  $\delta^{57}\text{Fe}$ - $\delta^{56}\text{Fe}$  values showing an entirely mass-dependent ( $R^2 = 0.99$ ).

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