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## Revision 1

### Evidence for abundant organic matter in a Neoproterozoic banded iron formation

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## ABSTRACT

Microbial Fe(II) oxidation has been proposed as a major source of Fe minerals during  
deposition of banded iron formations (BIFs) in the Archean and Proterozoic Eons. The conspicuous  
absence of organic matter (OM) or graphitic carbon from BIFs, however, has given rise to divergent  
views on the importance of such a biologically-mediated iron cycle. Here, we present mineral  
associations, major element concentrations, total carbon contents and carbon isotope compositions  
for a set of lower amphibolite-facies BIF samples from the Neoproterozoic Zhalingzhangzi BIF in the

Qinglonghe supracrustal sequence, Eastern Hebei, China. Graphite grains with crystallization temperatures (~470°C) that are comparable to that predicted for the regional metamorphic grade are widely distributed, despite highly variable iron (12.9 to 54.0wt%) and total organic carbon (0.19 to 1.10wt%) contents. The crystalline graphite is interpreted to represent the metamorphosed product of syngenetic biomass, based on its co-occurrence with apatite rosettes and negative bulk rock  $\delta^{13}\text{C}_{\text{organic}}$  values (-23.8 to -15.4‰). Moreover, the crystalline graphite is unevenly distributed between iron- and silica-rich bands. In the iron-rich bands, abundant graphite relicts are closely associated with magnetite and/or are preserved within carbonate minerals (i.e., siderite, ankerite and calcite) with highly negative bulk rock  $\delta^{13}\text{C}_{\text{carb}}$  values (-16.73 to -6.33‰), indicating incomplete reduction of primary ferric (oxyhydr)oxides by OM. By comparison, only minor graphite grains are observed in the silica-rich bands. Normally, these grains are preserved within quartz or silicate minerals and thus did not undergo oxidation by Fe(III). In addition, the close association of graphite with iron-bearing phases indicates that ferric (oxyhydr)oxides may have exerted a first order control on the abundance of OM. Combined, the biological oxidation of Fe(II) in the oceanic photic zone and subsequent burial of ferric (oxyhydr)oxides and biomass in sediments to form BIFs, suggests that a BIF-dependent carbon cycle was important in the Archean Eon. Although significant re-adsorption of phosphorus to ferric (oxyhydr)oxides and the formation of authigenic phosphate minerals at the sediment-water interface would be expected, oxidation of biomass in BIFs may have recycled at least a portion of the P (and other nutrients) released from reactions between OM and ferric (oxyhydr)oxides to the overlying water column, potentially promoting further primary productivity.

**Keywords:** Organic matter, Carbon isotopes, Apatite, Raman spectroscopy, Banded iron formation, Neoarchean.

## INTRODUCTION

Banded iron formations (BIFs) are layered, iron-rich and siliceous chemical sediments that formed predominantly through the precipitation of ferric iron [Fe(III) (oxyhydr)oxide] in Archean and Paleoproterozoic ferruginous oceans (e.g., Bekker et al., 2014; Konhauser et al., 2017; Mänd et al., 2021). Although it remains possible that photochemical Fe(II) oxidation may have contributed to BIF deposition (e.g., Konhauser et al., 2007; Pecoits et al., 2015; Nie et al., 2017), biologically

assisted Fe(II) oxidation, either directly through photoferrotrophy or indirectly through oxygenic photosynthesis, is generally favored (Cloud, 1973; Konhauser et al., 2002; Kappler and Newman, 2004; Planavsky et al., 2009; Czaja et al., 2013). If so, BIFs likely record the activity of Earth's early photosynthetic biosphere, and the oxidation of Fe(II) would thus be expected to produce biomass that settled to the seafloor together with the Fe(III) minerals (e.g., Posth et al., 2010; Konhauser et al., 2011).

Studies to date, paradoxically, reveal a low content of organic matter (OM), or graphitic carbon as its metamorphosed equivalent, in BIFs, with total organic carbon (TOC) contents typically lower than 0.5 wt% (e.g., Gole and Klein, 1981; Klein, 2005; Heimann et al., 2010; Tong et al., 2021). This means that OM may have been oxidized either by the combined metabolic processes of fermentation and chemoheterotrophy during diagenesis (Konhauser et al., 2005), or abiotically during subsequent metamorphism (Van Zuilen et al., 2002). Significantly, coupling the oxidation of OM to the reduction of part of the Fe(III) mineral pool not only provides an explanation for the low TOC content of BIFs, but may also explain the presence of Fe(II)-bearing minerals (magnetite, siderite and greenalite) (Li et al., 2013; Konhauser et al., 2017), highly negative  $\delta^{13}\text{C}$  values of Fe(II)-rich carbonates (Heimann et al., 2010; Craddock and Dauphas, 2011), and negative  $\delta^{56}\text{Fe}$  values for some magnetite and/or siderite (Johnson et al., 2008; Heimann et al., 2010) in BIFs. Alternatively, the conspicuous absence of photosynthetic biomass produced from biological Fe(II) oxidation during BIF formation could be the result of a combination of the physical separation of biomass from Fe(III) by-products during iron deposition, and the oxidation of limited OM by Fe(III) after burial. Experiments and modeling (Thompson et al., 2019) have revealed that in the presence of high silica ( $\geq 1$  mM; Jones et al., 2015), which would be expected for Precambrian seawater (Siever, 1992), pelagic photoferrotrophs are particularly capable of avoiding co-sedimentation with Fe(III), and thus remain buoyant with the potential for separation of biomass from Fe(III) at a large scale. As a result, the excess biomass would have instead deposited in shales, where it likely fueled methanogenesis once reactive Fe(III) minerals had been reduced. Ultimately, this would have resulted in a significant flux of methane to the atmosphere, while the small fraction of biomass that co-precipitated with Fe(III) would have fueled the diagenetic formation of reduced Fe(II) phases in BIFs (Thompson et al., 2019).

By contrast to the above high bio-productivity hypothesis, the low TOC content in BIFs has also been interpreted as the result of minimal biomass production during BIF deposition. Considering that

clay minerals have the capability to protect OM from being oxidized (e.g., Kennedy et al., 2014; McMahon et al., 2016; Playter et al., 2017), Dodd et al. (2019a) compared the OM-clay associations in BIFs and associated metapelites ranging in ages from 3.7 to 1.8 Ga. This reveals that clays in both BIFs and metapelites show little difference in their ability to bind OM, and that in the pelite samples around 80-95% of the observable OM occurs with or within phyllosilicates (e.g., muscovite, chamosite and biotite), yet in the BIFs no OM was found within phyllosilicates (including grunerite, actinolite, minnesotaite and stilpnomelane). Given such constraints, Dodd et al. (2019a) conclude that there may have been minimal biomass production at sites of BIF formation, implying that the deposition of OM in BIFs was much lower than previously thought. If the initial availability of OM that fueled Fe(III) mineral reduction was minimal as Dodd et al. (2019a) propose, then the deposition of BIF itself would in turn lead to a less productive water column, due to the ability of Fe(III) minerals to scavenge and sequester phosphorus and other nutrients from the seawater (e.g., Bjerrum and Canfield, 2002; Scott et al., 2013). Accordingly, this process would have caused a particularly pronounced nutrient limitation and hence a negative productivity feedback.

To investigate whether the low organic content of Precambrian BIFs is a result of near-complete oxidation of available initial biomass, or an intrinsic feature related to limited OM production during iron deposition, we document the mineral associations, major element concentrations, total carbon contents and carbon isotope compositions of a set of BIF samples with highly variable iron and TOC contents from the late Neoproterozoic Zhalingzhangzi BIF in the Qinglonghe supracrustal sequence, Eastern Hebei.

## GEOLOGIC SETTING

Eastern Hebei is situated in the northern part of the North China Craton (NCC) (Fig. 1). The exposed strata in this area consists predominantly of early Archean to Paleoproterozoic metamorphic basement rocks that are either partially overlain by Mesoproterozoic to Mesozoic platform cover sequences or are intruded by Cenozoic granites (e.g., Geng, 1998; Nutman et al., 2011) (Fig. 1). The early Archean basement in this region is exposed in the Caozhuang area and is represented by 3.28-2.94 Ga orthogneisses and fuchsite-bearing quartzites with detrital zircon ages of 3.89-3.13 Ga (Liu et al., 1992; Wilde et al., 2008; Nutman et al., 2011). By comparison, Neoproterozoic rocks that comprise of 2.6-2.5 Ga plutonic gneisses and minor 2.8-2.5 Ga supracrustal rocks are more abundant

(Geng et al., 2006; Nutman et al., 2011; Guo et al., 2013), covering almost 95% of the total NCC basement exposed in Eastern Hebei. Notably, the minor Neoproterozoic supracrustal rocks are either interlayered with the orthogneisses or occur as rafts or sheets of variable dimensions within the plutonic gneisses (Fig. 1). They can be further divided into different groups in terms of various areas, including the Zunhua, Qianxi, Luanxian, Dantazi, Shuangshanzi and Zhuzhangzi groups (e.g., Qian et al., 1985; Zhang et al., 1986), although a consensus with respect to their relatively stratigraphic sequence has not been achieved (e.g., Sun et al., 2010; Lv et al., 2012; Liu et al., 2014).

The Qinglonghe supracrustal sequence (QSS) is located in the eastern part of Eastern Hebei (Fig. 1), and comprises the Shuangshanzi and Zhuzhangzi groups (Shen et al., 2005). In contrast to most amphibolite- to granulite-facies metamorphosed Neoproterozoic terranes in Eastern Hebei (Kröner et al., 1998; Zhao et al., 1998), the QSS has only experienced greenschist- to lower amphibolite-facies metamorphism related to the regional emplacement of a granite porphyry at ca. 2.50 Ga (Shen et al., 2005; Lv et al., 2012). The exposed rocks in the Shuangshanzi Group are dominated by volcanic units, including meta-mafic and -felsic volcanic rocks, and minor metapelites (Shen et al., 2005; Lv et al., 2012). By comparison, the overlying Zhuzhangzi Group comprises metaconglomerates and metapelites, as well as minor metasandstones and BIFs (Shen et al., 2005).

Zhalanzhangzi BIF of this study is preserved within the upper section of the Zhuzhangzi Group (Wan et al., 2012; Chen et al., 2015). The BIF layers normally form repeated cycles of metapelites (two mica quartz schist), BIFs and metasandstones (biotite quartz schist) (Fig. 2), and are inferred to have been deposited in a rifted basin based on a previously documented intra-continental rift setting (Lv et al., 2012) for the QSS. Zircon U-Pb dating shows that magmatic zircons from the meta-felsic volcanic rocks in the Shuangshanzi Group were crystallized at  $2511 \pm 12$  Ma (Lv et al., 2012), representing the maximum depositional age of the BIF, while magmatic zircons from a granite-porphyry intrusion which intruded into the upper section of the Zhuzhangzi Group (i.e., the BIF-bearing sequence) have been dated at  $2498 \pm 8$  Ma (Shen et al., 2005), constraining the minimum depositional age of the BIF. The depositional age of the Zhalanzhangzi BIF thus can be constrained between  $2511 \pm 12$  and  $2498 \pm 8$  Ma. The BIF samples for this study were taken from two well preserved drill cores located in the central part of the ~3.5 km long BIF-bearing sequence (Fig. S1), with drill core Zk1103 probably documenting a slightly shallower water depth relative to Zk1104 (Fig. 2).

## METHODS

### Sample preparation

Centimeter-sized rock chips were extracted from the internal regions of BIF samples by sawing with sterile, deionized water. Prior to cutting, the saw was treated with 5% sodium hypochlorite and then rinsed with sterile, deionized water. Twenty-six thin sections were then prepared with a final polishing step using Al<sub>2</sub>O<sub>3</sub> 0.5 µm power in deionized water, for subsequent investigation using optical and Raman spectroscopy. To limit laboratory contamination, no organic material was introduced during the procedure, except for the epoxy used to fix thin sections. Samples were not sputter coated before Raman spectroscopy and scanning electron microscopy analyses in order to avoid any contamination from carbon. After this stage, selected samples (see Table S1 for details) were coated with carbon for electron probe micro-analysis. Deionized water and an ultrasonic bath were used to clean the thin sections before observations. A broken rock fragment with an unexposed, fresh surface was also prepared for sample 1104d. By comparing the result of this fragment with those of the polished thin sections, we could further confirm whether any artificial organic component was introduced. In addition, approximately five-gram rock chips of fifteen representative BIF samples were crushed to powder (~200 µm) using an agate pestle and mortar for the analysis of major elements, total carbon contents and carbon isotopes. The agate mill was cleaned with deionized water and alcohol throughout the procedure.

### Major elements analysis

Major element contents were determined at the ALS Chemex, Guangzhou, China, using an X-ray fluorescence spectrometer with an analytical error of less than 3%, as estimated through analyses of the GBW07105, GBW07111, and GBW07112 geostandards. Loss on ignition (LOI) was determined by heating powders at 1,000°C for 2 h and measuring the relative decrease in weight. Values for replicates (1103a-r and 1104a-r) and geological standards are provided in Table S2.

### Raman spectroscopy

Raman spectroscopy was conducted on both the thin sections and the rock fragment using a WiTec alpha 300R confocal Raman spectrometer equipped with a 532 nm excitation laser, at the Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences, Sanya (IDSSE). The

analysis was operated at a power less than 1 mW, to avoid graphitization of the organic matter, with integration times of 10 s. Raman spectra were collected using a 100× objective to provide a spatial resolution of around 1 μm. All Raman spectra were fitted using the Fast Fourier transform method after background subtraction with a polynomial function. Assignment of molecular vibrations is based on published data (Dodd et al., 2019a, b).

### **Scanning electron and energy dispersive X-ray spectroscopy analyses**

Scanning electron microscopy (SEM) and energy dispersive spectroscopic (EDS) analyses were used to characterize the morphology and composition of selected targets, using a ThermoScientific Apreo C SEM equipped with an energy-dispersive X-ray spectroscope and AZtec system provided by Oxford Instruments at the IDSSE. Standard operating conditions for SEM imaging was 2 and 15 kV accelerating voltage at a working distance of 10 mm. An accelerating voltage of 15 kV was used for the X-ray analysis to obtain adequate X-ray counts.

### **Electron probe micro-analysis**

Major element compositions of minerals were obtained using a JEOL JXA8100 electron probe microanalyzer (EPMA) at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing (IGGCAS). Analysis was carried out at an accelerating voltage of 15 kV, current of 20 nA, beam spot diameter of 5 μm and a 10-30 s counting time on peak. The results were calibrated against standards of natural silicates, oxides, and specpure metals, with the analytical precision for most elements estimated to be better than 1.5%. A program based on the ZAF produce was used for data correction.

### **Total inorganic and organic carbon analyses**

Total inorganic carbon (TIC) and organic carbon (TOC) contents were analyzed at the ALS Chemex, China. Abundances of TIC were measured with an Ethanolamine Color Coulomb Instrument after being treated with HClO<sub>4</sub>. The precision of the analyses (1σ) was better than 0.2%. For the TOC analyses, 200 mg rock powders were first treated with 20 vol% HCl at 50 °C for 24 h to remove carbonate, and then washed with DI water to remove residual HCl. After that, the samples were dried overnight at 50 °C and then analyzed using a LECO CS-400 analyzer. The precision of the analyses (1σ) was better than 0.1%.

## Scanning electron microscopy based automated mineralogy analysis

Representative samples with relatively low (1104b with  $C_{\text{organic}}$  of 0.19 wt%), intermediate (1103b with  $C_{\text{organic}}$  of 0.63 wt%), and high (1104d with  $C_{\text{organic}}$  of 1.10 wt%) TOC contents were further selected for scanning electron microscopy-based automated mineralogy (SEM-AM) analysis at the IGGCAS. The SEM-AM is a combined analytical method designed for the characterisation of ores and mineral processing products. Measurements began with the collection of backscattered electron (BSE) images with a ZEISS Merlin field emission scanning electron microscope (FE-SEM) on thin sections of the above samples. The spatial resolution of the FE-SEM is 0.8 nm at 15 kV. Subsequently, energy dispersive X-ray spectra (EDS) analysis was performed on each sample over an approximate  $8000 \times 900 \mu\text{m}$  area, using a Bruker QUANTAX EDS according to the BSE image adjustments. Mineral identification and analyses were automatically carried out by classification of the sample EDS spectra against a list of approved reference EDS spectra, using an equipped advanced mineral identification and characterization system software package with the particle analysis pattern.

## Carbon isotope analysis

Carbon and oxygen isotope analyses of carbonate minerals were performed using the method described in Chen et al. (2005). Isotopic ratios were determined using a Finnigan MAT 253 mass spectrometer at the IGGCAS. Given that our samples contain siderite and ankerite, which normally require an extended time (e.g., 96 h at 25°C) to be fully digested with phosphoric acid relative to calcite (60 min at 72°C), an off-line method was employed instead of the continuous flow mode. Thus, it was possible to keep a vacuum condition during the whole analysis procedure. Carbon and oxygen isotope data were calibrated to the Vienna Pee Dee Belemnite (VPDB) and the standard mean ocean water (SMOW) scales, respectively. Analytical reproducibilities were better than 0.15‰ and 0.20‰ for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively, based on multiple analyses of the standards IAEA-603 ( $\delta^{13}\text{C} = 2.46\text{‰}$ ,  $\delta^{18}\text{O} = -2.37\text{‰}$ ) and IAEA-CO-8 ( $\delta^{13}\text{C} = -5.76\text{‰}$ ,  $\delta^{18}\text{O} = -22.7\text{‰}$ ). Analyses of organic matter in bulk rock powder were also conducted at the IGGCAS with a Finnigan MAT 253 mass spectrometer. Sample preparation and analytical details follow a previously devised protocol (Tong et al., 2021). The results were calibrated to the VPDB scale. Two standard materials, GBW04407 ( $\delta^{13}\text{C} = -22.4\text{‰}$ ) and IAEA-600 ( $\delta^{13}\text{C} = -27.5\text{‰}$ ), were analyzed for 5 numbers of

unknowns within each run to ensure a reproducibility of better than 0.06‰ (Table S2).

## RESULTS

### Mineral composition and distribution of OM in the BIF samples

The BIFs are grayish-white in color in hand sample and are finely banded with iron-rich bands ranging in thickness from 2 mm to a maximum thickness of about 1 cm. These iron-rich bands alternate with silica-rich bands of more variable thickness (Fig. 2). Generally, the contacts between these two types of bands are gradational, although minor deformation may be present locally (Fig. 3a). Given that the cummingtonite (see below), which is proposed to be metamorphic in origin in BIFs (Klein, 2005), is oriented and distributed along the lineation of the deformation, this deformation may have been formed during metamorphism. Dominant minerals in the iron-rich bands include magnetite, grunerite and siderite, as well as minor cummingtonite, ankerite, pyrite and brunsvigite (Table S1), while coarser (0.2-0.4 mm) almandine grains and/or calcite aggregates are also observed in places in some samples (Fig. 3b and Table S1), indicating a lower amphibolite facies metamorphic grade for these samples. The magnetite grain size is most commonly about 0.1 mm in diameter (Fig. 3a), although some iron-rich bands show recrystallized aggregates of up to 0.3 mm (Fig. 3b). The grunerite is subhedral to euhedral in shape (0.1-0.2 mm) (Fig. 3b), and normally intergrows with magnetite and siderite (Fig. 3a), although sometimes networks of grunerite crystals are developed alongside the magnetite and quartz interface (Fig. 3b). Similar to the grunerite, the fine-grained siderite (< 0.2 mm) occasionally occurs as independent siderite-rich networks which contain minor magnetite, grunerite and/or brunsvigite (Fig. 3a and c). By comparison, the silica-rich bands mainly consist of fine-grained quartz (0.05 to 0.1mm), although minor dusty magnetite, as well as fine-grained siderite, grunerite and pyrite (Fig. 3a and f) are also preserved in the matrix of quartz in places.

Abundant graphite is disseminated as microscopic particles (< 10 µm) in siderite (Fig. 3d), calcite (Fig. 3g) and grunerite (Fig. 3e, h, and i) grains, within both the iron- and silica-rich bands. Within single crystals of grunerite, minor magnetite particles (≤ 5 µm) were always observed within or around the grunerite grains (Fig. 3e). Moreover, a relatively high abundance of graphite also occurs outside the magnetite grains (Fig. 3e). By comparison, while graphite also occurs within the magnetite grains, it is present at a considerably lower abundance (Fig. 3j). In addition, minor

microscopic graphite grains ( $< 10 \mu\text{m}$ ) are also found to be closely related to the widely distributed pyrite grains of variable size (10 to  $30\mu\text{m}$ ) in both the iron- (Fig. 3d) and silica-rich (Fig. 3f) bands.

The mineral components, distributions and weight percent based on the SEM-AM analysis of three representative BIFs samples are shown in Fig. 4. In general, sample 1104d has the highest grunerite and magnetite contents of 53.76 wt% and 27.36 wt%, respectively, with the lowest quartz content of 8.58 wt% and graphite content of 0.39 wt% among the analyzed samples. By comparison, sample 1103b has an intermediate abundance of quartz (54.35 wt%) as well as the highest siderite (14.24 wt%) and feldspar (10.32 wt%) and the lowest magnetite (2.25 wt%) contents, while sample 1104b is distinguished by the highest abundances of quartz (72.85 wt%) and graphite (3.80 wt%).

To further quantify the association of graphite with other minerals, the SEM-AM analysis results were computed by software to obtain the mineral association data (Table 1). These data describe the direct contact of graphite in relation to its associated minerals. The values are expressed as % association. Based on the results of mineral association parameters in Table 1, it can be seen that the greatest amount of graphite in these samples is associated with silicates. For example, in sample 1104d graphite has a 59.9% association with grunerite, while in sample 1104b graphite has a 50.8% association with grunerite. However, for the full sample set, mineral associations can vary, and relate to the relative abundance of each mineral. For instance, the graphite in sample 1104d exists in contact with calcite (14.6%), whereas in samples 1103b and 1104b, which have low calcite contents (1.38 wt% and 2.54 wt%, respectively), the association of graphite and calcite are insignificant (3.3% and 0.6%, respectively). Moreover, graphite in both 1103b and 1104b is also closely associated with quartz (54.2% and 28.4%, respectively).

### Major element geochemistry

Results of whole-rock major element analyses are listed in Table 2. The contents of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  (representing total iron as  $\text{Fe}_2\text{O}_3$ ) for fifteen BIF samples range from 30.2 to 82.6wt% and from 12.9 to 54.0wt%, respectively. The  $\text{Al}_2\text{O}_3$  contents are normally low for most samples, varying from 0.19 to 1.19wt%, indicating the incorporation of a minor clastic component during deposition. By comparison, high  $\text{Al}_2\text{O}_3$  concentrations for samples 1103b (4.42 wt%) and 1103c (3.68 wt%) suggest that a terrigenous detrital source was an important component. The contents of MgO and CaO are highly variable for all samples, ranging from 0.90 to 4.31 wt% and from 0.74 to 4.87 wt%,

respectively. The former may be related to the different silicate mineral contents in these samples, while the latter likely relates to the variable abundance of calcite (Table S1). Other oxides, such as MnO, Na<sub>2</sub>O, K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> are consistently low (<1.0 wt%) in all samples. In addition, variable contents of SO<sub>3</sub> (0.17 to 1.80 wt%) were also obtained for these samples, in line with the presence of pyrite observed microscopically.

### **Bulk carbon contents and isotope geochemistry**

The TIC and TOC contents, as well as carbon isotope ratios, for the carbonate and organic carbon, are presented in Table 2. The studied BIF samples have a relatively large range in TIC, between 0.37 and 1.92wt%, which is comparable to other carbonate-bearing BIFs (e.g., Tong et al., 2021; 0.92 to 3.36wt%), and consistent with the highly variable LOI values (Table 2). The TOC abundances are also highly variable, ranging from 0.19 to 1.10wt% (0.55 wt% on average, n = 15), with some samples having much higher TOC contents than most Precambrian BIFs (< 0.5 wt%; Klein, 2005). Similarly, bulk rock inorganic carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ) and organic carbon ( $\delta^{13}\text{C}_{\text{organic}}$ ) isotopic ratios for our BIF samples are variable, between -16.73 and -6.33‰ (average of -11.1‰) and between -23.81 and -15.36‰ (average of -19.94‰), respectively (n = 15). It is also noted that positive correlations exist between Fe<sub>2</sub>O<sub>3</sub> and TOC (r = 0.46) and between TIC concentrations and  $\delta^{13}\text{C}_{\text{organic}}$  ratios (r = -0.67), while a moderate negative correlation exists between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{carb}}$  (r = 0.64) (Fig. S2).

## **DISCUSSION**

### **Source and origin of OM in BIF samples**

Although there is persuasive evidence that life emerged early in Earth's history and has persisted for well over 3.5 billion years (e.g., Hofmann et al., 1999; Allwood et al., 2006; Planavsky et al., 2021), caution is required when studying early traces of life (e.g., OM, or <sup>13</sup>C-depleted graphite as the metamorphic equivalent) in Earth's rock record. Contamination of geological samples can be particularly problematic, due to both incorporation of non-indigenous compounds into the rocks after burial, and/or addition of anthropogenic organic contamination from drilling, storage, or sample preparation (e.g., Brocks et al., 2008; Rasmussen et al., 2008). For this study, ultraclean analysis (see *Sample preparation*) was conducted to ensure that all organic matter was originally part of the BIF. Moreover, direct SEM and Raman analyses on the unexposed, fresh surface of a rock

fragment from sample 1104d reveal the presence of a graphite grain (Fig. 5) that is morphologically indistinguishable from those of the polished thin sections (Fig. 3g-j). Significantly, when observed at higher resolution it is common to see the intergrowth of fine-grained graphite and apatite (Fig. 5b), which further excludes any possible organic contamination. In addition, random Raman analysis was conducted on the epoxy used to fix our samples at variable powers (0.1 to 1.0 mW), which reveals that the epoxy has significantly different spectra from graphite grains in the studied BIF (Fig. 6a). Collectively, these observations indicate that the OM was not introduced during the polishing and analysis procedures and is a primary feature of the original samples.

It is also noteworthy that the Raman spectra of graphite grains in various BIF samples yield a narrow range of crystallization temperatures (Table S3), varying from 414 to 555 °C, with the most probable temperature of ~470°C (Fig. 6b). This temperature is compatible with the greenschist to lower amphibolite metamorphic grade (450-550 °C) documented for the ca. 2.50 Ga regional metamorphism (Shen et al., 2005; Lv et al., 2012) and the lower amphibolite-facies metamorphism indicated by the mineral association (almandine + grunerite + cummingtonite) of our BIF samples. Furthermore, it has been documented that apatite in BIFs is commonly diagenetic (Dodd et al., 2019a, b) or primary (Rasmussen et al., 2021) in origin. Thus, the close association of graphite with apatite (Fig. 7a-b and d), when combined with the above measured crystallization temperatures, further implies that the observed graphitic carbon is a syngenetic and prograde phase, rather than a non-indigenous product incorporated into the samples after burial. Moreover, since Al-rich minerals in BIFs are typically detrital in origin and sourced from weathered continental rocks (Klein, 2005), the presence of chlorite (Fig. 7b) and feldspar (Fig. 7c) in close association with graphite in some samples indicates that the OM may have been partially sourced from the detritally enriched, shallow-marine environment (e.g., Dodd et al., 2019a). Nevertheless, it is also noted that there is a stronger correlation between TOC and Fe ( $r = 0.46$ ) than for TOC and Al ( $r = 0.16$ ) (Fig. S2), indicating that OM in the Zhalingzhangzi BIF was mainly derived from areas of ferric iron production, or was preferentially co-precipitated with ferric minerals (e.g., Lalonde et al., 2012).

The generation of ferric iron minerals in BIF depositional settings is normally ascribed to the metabolic activity of planktonic bacteria in the oceanic photic zone (e.g., Konhauser et al., 2017; Mänd et al., 2021; also see Rasmussen et al., 2014; Tosca et al., 2016 for alternative models). This means that the deposition of Precambrian BIFs would have occurred in regions of high biological

productivity, regardless of whether aqueous Fe(II) was oxidized by oxygen sourced from cyanobacteria or their predecessors (e.g., Cloud 1973), or by anoxygenic photoautotrophic Fe(II)-oxidising bacteria (i.e., photoferrotrophs, Hartman 1984; Konhauser et al., 2002). Moreover, it has been documented that most bacteria have negatively charged surfaces at neutral pH (Fein et al, 1997), while ferric (oxyhydr)oxides have a positive surface charge at the same pH (Sverjensky and Sahai, 1996). In this regard, it is reasonable to propose that some of the biomass (or OM) may have been captured by Fe(III) minerals and then preserved in BIFs, since their opposite surface charge at neutral pH favored the formation of ferric (oxyhydr)oxides (e.g., Konhauser et al., 2017; Thompson et al., 2019).

Notably, thermal disproportionation of Fe-carbonates (siderite) can also yield graphite and magnetite, and has been suggested as a possible mechanism for graphite formation in amphibolite facies rocks (Perry Jr and Ahmad, 1977; Van Zuilen et al., 2002). Even though graphite-associated siderite is found in some of our BIF samples (Fig. 3d), this is not the first-order control on the spatial distribution of graphitic carbon, as evidenced by the absence of siderite in sample 1104d (Fig. 4) and the consistently low association between siderite and graphite in samples 1103b and 1104b (9.7% and 2.5%, respectively; Table 1). Furthermore, the above process is also incompatible with the fact that there is a high siderite content (14.24 wt%) but very low abundance of graphite (0.5 wt%) in sample 1103b (Fig. 4). In addition, magnetite is a common effective catalyst in Fischer-Tropsch-type reactions, during which CO<sub>2</sub> and H<sub>2</sub> are converted into a wide spectrum of abiogenic hydrocarbons (e.g., McCollom, 2013; Nan et al., 2021). However, this process requires a H<sub>2</sub>-rich condition that can be produced by hydrothermal alteration of ultramafic rocks (McDermott et al., 2015). The absence of ultramafic rocks (or mafic volcanics) along with the studied BIF indicates that Fischer-Tropsch-type reactions were likely insignificant. It is also noteworthy that the negative  $\delta^{13}\text{C}_{\text{organic}}$  values, ranging from -23.81 to -15.36‰, for graphitic carbon in the Zhilanzhangzi BIF are consistent with biological kerogen, rather than an abiogenic origin from carbonate reduction (with a  $\delta^{13}\text{C}$  signature between -12 and -10‰; Van Zuilen et al., 2002; Ohtomo et al., 2014). Meanwhile, the negative values largely overlap with isotope compositions of carbon produced by cyanobacteria and photosynthetic bacteria (-40 to -10‰) found in nature (e.g., Mojzsis et al., 1996), implying that the observed graphite grains are the metamorphic product of early biogenic organics.

Furthermore, considering that the formation of apatite [Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F, Cl, OH)] requires

phosphorus, which could be partially derived from the decomposition of phosphorus-bearing biomass during early diagenesis (e.g., Dodd et al., 2019b), the association of  $^{13}\text{C}$ -depleted organic carbon and apatite is accepted as a typical feature of sediments incorporating biomass (She et al., 2014; Papineau et al., 2016). On this basis, the presence of isotopically-light graphitic carbon associated with apatite in Precambrian BIFs has been used as evidence to argue for early life in oceans (e.g., Nutman, 2007; Papineau et al., 2016; Dodd et al., 2017). As mentioned before, the intergrowth of apatite rosettes with graphite grains, which have an average  $\delta^{13}\text{C}_{\text{organic}}$  value of -19.94‰ (Table 2), is observed in our samples (Fig. 5b). This supports a biological origin for the graphite. In addition, the presence of graphite inclusions in apatite in our samples (Fig. 7d and Fig. S3) is consistent with those observed in Neoproterozoic to Paleoproterozoic BIFs subjected to low-grade metamorphism (Dodd et al., 2019b), implying this phenomenon is unrelated to metamorphic grade. Thus, consistent with previous studies (e.g., Dodd et al., 2019b), the apatite with graphite inclusions likely represents the remineralization of biogenic organics.

Nevertheless, a fluid-depositional pathway, rather than a biological origin, for graphite associated with apatite in metamorphosed BIF has also been proposed (e.g., Lepland et al., 2011; Papineau et al., 2011). Moreover, Dodd et al. (2019b) highlighted the widespread occurrence of two types of graphite (i.e., crystalline graphite representing the metamorphosed product of syngenetic organic carbon deposited in BIF, and poorly crystalline graphite precipitated from fluids sourced from syngenetic carbon), through a detailed examination of ten variably metamorphosed BIFs ranging in ages from >3.8 to 1.8 Ga. As shown in Fig. 6b, all the studied graphite grains in our samples have a consistent crystallization temperature (~470°C, see Table S3) that matches that predicted for the regional metamorphic grade (450-550 °C). In addition, retrograde minerals such as greenalite and minnesotaite that replace grunerite, and secondary veins containing poorly crystalline carbon of fluid-depositional origin (e.g., Dodd et al., 2019b), are absent from our samples. Taken together, the  $^{13}\text{C}$ -depleted graphite in the Zhalingzhangzi BIF is likely biological in origin, representing the remineralization and metamorphism of syngenetic biomass.

### **Carbon isotope evidence for OM oxidation during BIF formation**

It is generally agreed that the observed minerals in BIFs are not primary in origin but reflect the products of multiple post-depositional alteration processes that occurred under both diagenetic and

metamorphic conditions (e.g., Bekker et al., 2014; Konhauser et al., 2017). The initial water column precipitate of BIF has been proposed to be ferric (oxyhydr)oxides formed in the photic zone (Holland, 1973; Morris, 1993) or to be green rust, a ferrous-ferric hydroxy salt, generated when there was abundant Fe(II) (e.g., Zegeye et al., 2012; Halevy et al., 2017). The ferric (oxyhydr)oxides would subsequently transform to Fe(III)-Si gel during deposition (Percak-Dennett et al., 2011) in the presence of high dissolved silica (~2.2 mM) in Precambrian seawater (Jones et al., 2015), and would be preserved as magnetite or iron carbonates in sediments when the remineralization of buried OM was coupled to Fe(III) reduction (Konhauser et al., 2005; Johnson et al., 2008; Mänd et al., 2021). Alternatively, green rust would age directly to magnetite within the water column and sediments (Halevy et al., 2017; Li et al., 2017). It is important to note that although greenalite has also been suggested as a primary precipitate that formed in the water column (Rasmussen et al., 2015, 2016, 2017), the large iron isotope ratios documented for Archean BIFs (e.g., Johnson et al., 2008) are inconsistent with small iron isotopic effects induced by direct seawater precipitation of greenalite (Mänd et al., 2021).

Estimates of the initial amount of OM precipitated in BIFs based on C isotope and magnetite mass balance suggests relatively high TOC contents of ~4.7 wt% in Precambrian BIFs. These concentrations are comparable with those measured in coeval black shales (e.g., Konhauser et al., 2017), supporting the interpretation that large amounts of OM may have been respired via microbial dissimilatory iron reduction (DIR) during diagenesis or thermal decomposition during metamorphism. Calculations of the minimum total primary OM content (see Tong et al., 2021 for the calculation method) precipitated in the Zhalingzhangzi BIF (0.74 to 1.82 wt%, 1.15 wt% on average; Table S4) support the above suggestion that part of the OM may have been respired via DIR. Significantly, although this value is lower than the estimation by Konhauser et al. (2017), it is much higher than the actual measured TOC content of our samples (average of 0.55 wt%), and indicates that more than 50% of the primary OM has likely been consumed (Table S4).

Nevertheless, the generally extremely low TOC contents (<0.1 wt%, e.g., Beukes et al., 1990; Beukes and Klein, 1990; Kaufman, 1996; Klein, 2005), when combined with the absence of OM (or graphite) in clays within some Precambrian BIFs (Dodd et al., 2019a), has been argued as evidence for minimal OM production during BIF deposition. Despite the relatively high TOC content measured in the Zhalingzhangzi BIF, the carbonate phases (i.e., siderite, ankerite and calcite) in this

BIF also have highly negative  $\delta^{13}\text{C}_{\text{carb}}$  values (-11.1‰ on average,  $n = 15$ ). Given that carbon isotope fractionation between calcite and siderite at near-equilibrium with the water mass is about -0.5‰ (at 25 °C; Jiménez-López et al., 2001; Jiménez-López and Romanek, 2004), estimated  $\delta^{13}\text{C}$  values for siderite formed in equilibrium with Archean seawater with  $\delta^{13}\text{C}$  value of ~0‰ should range from -1.5 to -0.5‰ (Tong et al., 2021). In this regard, the highly negative  $\delta^{13}\text{C}_{\text{carb}}$  values, ranging from -16.73 to -6.33‰, in the Zhilanzhangzi BIF are unlikely to be of seawater origin. This is the case even if the water column which precipitated the BIF was overprinted by hydrothermal fluids bearing mantle-derived dissolved inorganic carbon with a  $\delta^{13}\text{C}$  value around -6.5‰ (Shanks III, 2001). Moreover, the relatively uniform  $\delta^{13}\text{C}$  values of iron-poor carbonates deposited synchronously in the late Archean, across a wide range of water column depths from continental shelf to deep basin, argues against vertical stratification with respect to carbon isotopes in dissolved inorganic carbon (DIC) at that time (Fischer et al., 2009). This further precludes the possibility that the negative  $\delta^{13}\text{C}_{\text{carb}}$  values in the Zhilanzhangzi BIF are related to direct carbonate precipitation from seawater that was stratified with respect to  $\delta^{13}\text{C}$ .

Isotopically light  $\delta^{13}\text{C}$  in carbonate minerals may also implicate metamorphism, which can be parsed when paired with oxygen isotopes (e.g., Kaufman et al., 1990; Carrigan and Cameron, 1991; Li et al., 2013), as carbonates from metamorphosed BIFs typically have extremely low  $\delta^{18}\text{O}$  (Yang et al., 2015). However, such alteration would produce lighter  $\delta^{18}\text{O}$  without altering  $\delta^{13}\text{C}_{\text{carb}}$ , assuming a rock-buffered diagenetic environment comparable to that of BIFs (Jaffrés et al., 2007; Knauth and Kennedy, 2009). Despite this, hydrothermal alteration has been suggested to have influenced  $\delta^{13}\text{C}$  values in carbonates, producing negative  $\delta^{13}\text{C}$  and positive  $\delta^{18}\text{O}$  (Shanks III et al., 1995). At first glance, the moderate negative correlation between  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  values for our samples (Fig. S2) may appear compatible with the above situation, but we preclude this interpretation due to the absence of petrographic evidence (e.g., alterations and veinlets) and geochemical characteristics (e.g., variations in bulk rock trace element composition, not shown) that normally accompany hydrothermal alteration.

In addition, it has been proposed that because manganese oxides are significantly enriched in  $^{18}\text{O}$  compared to seawater (e.g., Mandernack et al., 1995), there would be a negative correlation between  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  values during diagenetic Mn oxide reduction and subsequent Mn carbonate precipitation (e.g., Neumann et al., 2002; Dong et al., 2022). Considering that Fe has

similar chemical properties to Mn (Armstrong, 2008), we suggest that in agreement with current models for BIF formation (e.g., Beukes and Gutzmer, 2008), the observed negative correlation between  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  values in our BIF samples may also have been formed during diagenetic Fe(III) reduction. This conclusion is supported by our SEM and Raman analyses, which reveal the reduction of Fe(III) minerals by OM during diagenesis or metamorphism (see the following sections). Furthermore, variations in  $\delta^{13}\text{C}_{\text{carb}}$  values for the carbonates are likely related to the relative contributions of different carbon sources during the diagenetic formation of carbonates. However, considering the positive correlation between  $\delta^{13}\text{C}_{\text{carb}}$  values and TIC contents ( $r = 0.67$ ; Fig. S2), seawater DIC appears to have been the dominant carbon source for the carbonate minerals.

### **The fate of OM in iron- and silica-rich BIF bands**

Detailed observations on the Zhilanzhangzi BIF samples indicate that OM (i.e., graphite) tends to be unevenly distributed in the iron- and silica-rich bands (Fig. 8a). In iron-rich bands, abundant fine-grained graphite grains ( $< 10\mu\text{m}$ ) are always closely associated with magnetite, siderite, pyrite and calcite (Fig. 8b). Significantly, if we accept that ferric (oxyhydr)oxides were the primary mineral forming the Zhilanzhangzi BIF, then formation of the magnetite, siderite and pyrite would need Fe(II) that could have been (or at least partially) sourced from DIR (e.g., Klein, 2005; Johnson et al., 2008; Li et al., 2013). At higher resolution, it is common to observe the presence of fine-grained ( $< 10\mu\text{m}$ ) magnetite (Fig. 8c), siderite (Fig. 8d) and pyrite (Fig. 8e) preserved within or in close association with graphite grains. Notably, all graphite grains in the above cases have consistent crystallization temperatures (Fig. 6b) that are comparable to the prograde crystallization temperature of the Zhilanzhangzi BIF, indicating that they should be relicts of primary OM that has been subjected to oxidation and metamorphism. In addition, carbonate minerals, such as siderite, ankerite and calcite, which are documented to be by-products of the DIR process (e.g., Konhauser et al., 2005, 2017), are widely distributed in the iron-rich bands (Fig. 4), and are closely associated with graphite (Fig. 8d-e). The above associations are readily explained by reactions between ferric (oxyhydr)oxides and OM, during which the Fe(II) produced is expected to react with additional ferric (oxyhydr)oxides to form magnetite, or with  $\text{HCO}_3^-$  and  $\text{S}^{2-}$  (or  $\text{HS}^-$ ) to generate siderite and pyrite, respectively, within the sediment porewater. Among all  $^{13}\text{C}$ -depleted carbonate minerals ( $\delta^{13}\text{C}_{\text{carb}} = -11.1\text{‰}$  on average,  $n = 15$ ), siderite in this BIF is likely to be an early product formed within the sediment porewater,

whereas ankerite and calcite likely represent diagenetic and metamorphic alteration of early siderite, respectively (e.g., Klein, 2005; Pecoits et al., 2009). The suggestion that the origin of calcite is from prograde metamorphism is supported by the replacement of siderite by coarse-grained calcite and the existence of siderite relict edges in coarser calcite grains (Fig. 8f). It is also noteworthy that although OM in iron-rich bands of the Zhalaizhangzi BIF show typical features of oxidation coupled to ferric iron reduction, the slightly positive correlation between TOC and Fe ( $r = 0.46$ , Fig. S2), in combination with the close associations of OM with iron-bearing phases, indicates that ferric (oxyhydr)oxides likely exerted a first order control on the abundance of OM.

By comparison, graphite is a minor component in the silica-rich bands (Fig. 8a), although in places a considerable amount of graphite was observed alongside the siderite and chlorite rims (Fig. 8g). Normally, the graphite exhibits anhedral to sub-spherical morphologies, and is sealed in quartz grains (Fig. 8g). This is in contrast to those observed in the iron-rich bands, where graphite always shows mineralogical signs of oxidation coupled to ferric iron reduction (e.g., the presence of graphite in association with Fe(II)-bearing minerals and/or carbonates). Nonetheless, the existence of graphite grains in silica-rich bands may indicate that the amorphous silica, which deposited during intervals of iron deposition (Posth et al., 2008) or was coprecipitated with primary ferric (oxyhydr)oxides (Ewers, 1983; Fischer and Knoll, 2009), was also able to capture and preserve OM. The primary amorphous silica is inferred to transform to quartz (e.g., Trendall, 1983; Klein, 2005) during the lower amphibolite-facies metamorphism identified for the Zhalaizhangzi BIF. Given that silicate minerals have the ability to protect OM from bacterial degradation (e.g., Keil et al., 1994; McMahon et al., 2016), OM bound to amorphous silica is thus expected to persist through recrystallisation. This assumption is in line with the observation that graphite in our BIF samples is closely associated with quartz grains, among which the SEM-AM analysis reveals an association up to 54.2% for these minerals in sample 1103b (Table 1). In addition, in contrast to previous studies that argued there is generally an absence of OM bounded to silicate minerals in Precambrian BIFs (Dodd et al., 2019a), we identify the existence of graphite within grunerite grains in our samples (Fig. 3h and 7c). The SEM-AM analyses (Table 1) on samples 1104b and 1104d also show relatively high associations for graphite with grunerite (59.9%) and for graphite with chlorite (50.8%), indicating that silicate minerals in BIF can also capture and preserve OM (e.g., Haugaard et al., 2017), irrespective of whether the silicates were primary water column precipitates (e.g., Rasmussen et al., 2017) or

formed during late-diagenesis (Klein, 2005). These observations, when combined with the close association of graphite with quartz discussed above, may help to explain why more than 40% of OM in the Zhalaizhangzi BIF (Table S4) was devoid of oxidation and subsequently transferred to graphite during the greenschist to lower amphibolite facies regional metamorphism (Shen et al., 2005; Lv et al., 2012).

### **Implications for BIF-dependent Archean carbon cycling**

Carbon is an element that undergoes important biogeochemical oxidation-reduction reactions at the Earth's surface (Berner, 1989), among which mineralization of OM can result in accumulation of greenhouse gasses like methane, while its burial can be a net source of oxidants (e.g., oxygen) and a net sink of CO<sub>2</sub> (Berner, 2003; Crowe et al., 2008; Keil, 2011). Therefore, biogeochemical cycles of carbon over geological time exert major long-term controls on atmospheric chemistry (Berner, 2003; Lalonde et al., 2012; Friese et al., 2021). Nevertheless, carbon cycles in modern and Archean marine sediments may have been different, depending on the species of oxidants presented. In oxygenated and sulfate-rich modern marine sediments, OM is mainly consumed by aerobic respiration and sulfate reduction (e.g., Jørgensen, 1982; Froelich et al., 1979). By comparison, in the absence of oxidants such as oxygen, sulfate and nitrate in Archean marine sediments (Strauss, 2003; Anbar et al., 2007; Godfrey and Falkowski, 2009), the carbon cycle is expected to have been more closely coupled to Fe cycling, in BIFs in particular, because the ferric minerals in BIFs would have been the most accessible electron acceptor for OM oxidation (e.g., Walker, 1987; Nealson and Myers, 1990; Konhauser et al., 2005).

The very low  $\delta^{13}\text{C}_{\text{carb}}$  values for carbonate minerals (Table 2) and the presence of OM-bearing apatite associated with magnetite (Fig. S3) in our BIF samples all point to OM oxidation by Fe(III), supporting the assumption that carbon cycling linked to Fe would have been an important process in Archean BIFs. However, if BIFs were deposited from an OM-starved water column (Dodd et al., 2019a), the significance of BIF-dependent carbon cycling would have been negligible. As discussed above, ferric (oxyhydr)oxides likely controlled the abundance of OM in the Zhalaizhangzi BIF. This is similar to the situation for the Transvaal BIF, which also shows a positive correlation between TOC and Fe ( $r = 0.74$ ; Klein and Beukes, 1989). In this respect, if we accept the “upwelling model”, in which dissolved Fe(II) is biologically oxidized in the photic zone to form the ferric

(oxyhydr)oxides (e.g., Bekker et al., 2014; Konhauser et al., 2017; Tong et al., 2021), the above observations indicate that the deposition of Precambrian BIFs largely occurred in regions of high biological productivity. This conclusion is supported by the “upside-down” biosphere proposed for the Archean Eon (Walker, 1987), during which regions of high biological productivity would have been underlain by Fe(III)-rich sediments produced by photosynthesis (Cloud, 1973).

Low OM contents in BIFs have also been attributed to the physical properties of iron oxides and the high silica concentrations of Archean seawater. For the first point, because oxidized iron is denser than cell material and organic compounds, it would have settled more rapidly than particulate OM, producing sediments rich in oxidized iron and deficient in OM (Walker, 1987). However, the opposite surface charges for bacterial cells and ferric (oxyhydr)oxides (Sverjensky and Sahai, 1996; Fein et al., 1997) would lead to a strong attraction between these two components, manifest as encrustation of bacterial cells and formation of cell and ferric (oxyhydr)oxide aggregates (Konhauser, 1998; Kappler and Newman, 2004). For the second point, although some laboratory experiments with photosynthetic bacteria have revealed that the photoferrotroph cell surfaces would repel iron (oxyhydr)oxides in the presence of silica (Thompson et al., 2019), observations on Chocolate Pots hot springs indicated that even at silica concentrations higher than that estimated for the Precambrian oceans, ~80% of the silica-rich hydrous ferric oxides would co-precipitate with, and be reduced by, the microbial communities (e.g., Percak-Dennett et al., 2011; Fortney et al., 2016). Moreover, high silica contents have been documented to be able to hinder the transformation of poorly crystalline ferric (oxyhydr)oxides into more crystalline minerals (Friese et al., 2021), and therefore would have facilitated the reaction between OM and iron (oxyhydr)oxides in Precambrian oceans. It is also noted that the OM co-precipitated with iron, as estimated by Trendall (2002), is comparable to the ratio of ferrihydrite to carbon substrate left at the end of DIR incubations in culturing experiments (Roh et al., 2003; Roden, 2003). Thus, we suggest that labile OM would have been co-precipitated with ferric (oxyhydr)oxides in Archean oceans and was subsequently oxidized by Fe(III), in the absence of other oxidants, to produce Fe(II) in the sediments.

Collectively, photosynthesis in Archean oceans would have led to the fixation of CO<sub>2</sub> and the production of precursor ferric (oxyhydr)oxides in BIFs (e.g., Konhauser et al., 2017). Following its generation, the ferric (oxyhydr)oxide would have adsorbed OM produced by photosynthesis, and this OM was significantly consumed to form the Fe(II)-bearing phases in BIFs. Significantly, the

rem mineralization of OM coupled to iron reduction would release phosphorus and other nutrients from both the biomass and from the ferric (oxyhydr)oxides (e.g., Ingall et al., 1993; Rutt enberg and Berner, 1993; Van Cappellen and Ingall, 1994; Bjerrum and Canfield, 2002). Although a proportion of the P released to pore waters may subsequently switch to authigenic phases such as carbonate fluorapatite (Rutt enberg and Berner, 1993) or vivianite (e.g., Dijkstra et al., 2014; Xiong et al., 2019), as well as being reabsorbed to ferric (oxyhydr)oxides at the sediment-water interface (e.g., Slomp and Van Raaphorst, 1993; Slomp et al., 1996), some of the P released may have been recycled back to the water column (Alcott et al., 2022). Given that the Archean biosphere is thought to have been predominantly P-limited (e.g., Kipp and Stüeken, 2017; Reinhard et al., 2017; Guilbaud et al., 2020), this BIF-dependent carbon cycling may have been an important source of P and other nutrients to the water column, helping to sustain a degree of productivity.

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## Figure Captions

**FIGURE 1.** Simplified geological map of Eastern Hebei indicating the study area (after Nutman et al., 2011). Insert shows the subdivisions of the North China Craton (NCC) and the location of Eastern Hebei (after Zhao et al., 2005). Stars represent typical BIFs in this area.

**FIGURE 2.** Simplified stratigraphic column of the Zhalanzhangzi BIF logged from drill cores Zk1103 and Zk1104. Sample locations (shown as arrows) and pictures of representative BIF samples are also provided.

**FIGURE 3.** Petrographic images showing mineral compositions and the distribution of graphite in the Zhalanzhangzi BIF samples. (a) Transmitted light image of the BIF, showing the contrast between the iron- and silica-rich bands. (b) Cross-polar image of the iron-rich band of BIF, with networks of grunerite crystals distributing alongside the magnetite and quartz interface. (c) Transmitted light image of a siderite-rich network in an iron-rich band of the BIF. (d) Reflected light image of the boxed area in (c), showing the presence of graphite within siderite, as well as associated with magnetite and pyrite. (e) Reflected light image of an iron-rich band, with the co-occurrence of magnetite, grunerite, and graphite. (f) Reflected light image of a silica-rich band, showing the presence of graphite in association with pyrite and calcite. (g–j) Scanning electron (left) and energy dispersive X-ray (right) spectroscopy images showing the presence of graphite within and/or associated with different mineral phases in the BIF samples. Abbreviations: Sid = siderite, Bru = brunsvigite, Qz = quartz, Gru = grunerite, Cal = calcite, Alm = almandine, Mag = magnetite, Cum = cummingtonite, Gr = graphite.

**FIGURE 4.** Images showing the mineral components, distributions and weight percent according to scanning electron microscopy based automated mineralogy analysis on three representative BIF samples with different total organic carbon contents.

**FIGURE 5.** (a) Scanning electron (first) and energy dispersive X-ray spectroscopy images of the unexposed, fresh surface of a rock fragment from sample 1104d, showing the intergrowth of fine-grained graphite and apatite. (b) Scanning electron spectroscopy image of the boxed area in (a), showing the co-occurrence of graphite with an

apatite rosette. (c) Representative Raman spectra for the graphite and apatite in this figure. Abbreviations: Gru = grunerite, Mag = magnetite, Py = pyrite, Gr = graphite.

**FIGURE 6.** (a) Representative Raman spectra for the random analyses on graphite grains from the BIF samples and the epoxy (at variable power levels) used to fix the BIFs. (b) Binned frequency histogram showing crystallization temperatures computed according to the Raman analyses on the crystalline graphite from the BIF samples.

**FIGURE 7.** (a) Scanning electron spectroscopy image showing the close association of graphite with apatite in the iron-rich band. (b) Scanning electron (left) and energy dispersive X-ray (right) spectroscopy images showing the co-occurrence of graphite and chlorite in the silica-rich band. (c) Representative Raman spectra for the interested area (left, reflected light), revealing the presence of graphite within grunerite and feldspar grains. (d) Reflected light (left) and Raman spectra (right) images showing the presence of graphite inclusions in apatite grain. Abbreviations: Qz = quartz, Ap = apatite, Mt = magnetite, Gr = graphite, Ank = ankerite, Py = pyrite, Chl = chlorite, Gru = grunerite, Fsp = feldspar.

**FIGURE 8.** (a) Scanning electron spectroscopy image showing that graphite is unevenly distributed in the iron- and silica-rich bands. (b) Scanning electron spectroscopy image of the boxed area in (a), showing the distribution of graphite in iron-rich bands. (c–e) Reflected light images showing the close associations of graphite with magnetite, siderite and pyrite. (f) Scanning electron spectroscopy image showing the replacement of siderite by coarse-grained calcite and existence of siderite relict edges in coarser calcite grains. (g) Scanning electron (upper) and energy dispersive X-ray (lower) images showing that anhedral to sub-spherical graphite grains were sealed in coarse-grained quartz. (h) Representative Raman spectra for this figure. Abbreviations: Qz = quartz, Sid = siderite, Py = pyrite, Mt = magnetite, Gr = graphite, Gru = grunerite, Cal = calcite, Chl = chlorite, Ap = apatite.

## Table Captions

**TABLE 1.** Mineral association (expressed as % association) of graphite with other minerals in the Zhalanzhangzi BIF, computed by SEM-AM analysis.

**TABLE 2.** Major oxides, total inorganic and organic carbon contents, and carbon isotope values for the Zhalanzhangzi BIF.

## Supplemental Material

**FIGURE S1.** Simplified geological map of the Zhalanzhangzi BIF showing the geologic context of the study area and locations of the two drill cores.

**FIGURE S2.** Cross-plot for selected data in the Zhalanzhangzi BIF. The inset shows the correlation between TOC and Al<sub>2</sub>O<sub>3</sub> excluding the two samples with high Al<sub>2</sub>O<sub>3</sub> contents.

**FIGURE S3.** (a) Scanning electron (left) and energy dispersive X-ray (right) spectroscopy images showing the close

1052 association of magnetite with the co-occurrence of apatite and graphite. **(b)** Scanning electron (first) and energy  
1053 dispersive X-ray spectroscopy images of the boxed area in **(a)**, showing the presence of fine-grained graphite  
1054 inclusions within apatite. Abbreviations: Gru = grunerite, Qz = quartz, Mag = magnetite, Gr = graphite, Ap =  
1055 apatite.

1056

1057 **TABLE S1.** Electron probe microanalysis of minerals in the Zhalanzhangzi BIF.

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1059 **TABLE S2.** Geological reference materials used in this study with recommended and measured values.

1060

1061 **TABLE S3.** Raman spectral parameters and crystallization temperature estimates (Beyssac et al., 2003) for graphitic  
1062 carbon in the Zhalanzhangzi BIF.

1063

1064 **TABLE S4.** Calculation of primary organic carbon.

**TABLE 1.** Mineral association (expressed as % association) of graphite with other minerals in the Zhalanzhangzi BIF, computed by SEM-AM analysis.

| Sample 1103b  |          |        |         |          |        |           |          |           |            |         |          |          |               |      |
|---------------|----------|--------|---------|----------|--------|-----------|----------|-----------|------------|---------|----------|----------|---------------|------|
| Minerals      | Graphite | Quartz | Calcite | Ankerite | Pyrite | Magnetite | Siderite | Grunerite | Actinolite | Apatite | Feldspar | Chlorite | Cummingtonite | Else |
| Graphite      | 0.0      | 54.2   | 3.3     | 3.1      | 2.5    | 4.2       | 9.7      | 3.8       | 1.0        | 0.8     | 6.4      | 7.7      | 0.1           | 3.1  |
| Quartz        | 3.0      | 0.0    | 4.8     | 1.6      | 2.7    | 1.6       | 21.0     | 13.8      | 6.6        | 1.4     | 22.4     | 14.9     | 0.5           | 3.5  |
| Calcite       | 2.2      | 57.1   | 0.0     | 9.3      | 0.2    | 0.6       | 8.9      | 6.2       | 0.2        | 0.1     | 1.2      | 4.4      | 0.0           | 8.7  |
| Ankerite      | 3.1      | 28.1   | 14.3    | 0.0      | 1.1    | 0.7       | 21.2     | 9.9       | 0.3        | 0.8     | 3.8      | 9.2      | 0.0           | 5.8  |
| Pyrite        | 2.5      | 47.8   | 0.3     | 1.1      | 0.0    | 2.8       | 21.9     | 2.7       | 0.1        | 0.3     | 2.6      | 4.6      | 0.0           | 12.8 |
| Magnetite     | 4.4      | 29.4   | 0.9     | 0.7      | 2.9    | 0.0       | 36.0     | 15.6      | 0.1        | 0.4     | 0.8      | 3.5      | 0.0           | 4.2  |
| Siderite      | 0.8      | 30.5   | 1.1     | 1.7      | 1.8    | 2.8       | 0.0      | 23.6      | 0.5        | 1.7     | 5.4      | 28.1     | 0.2           | 1.3  |
| Grunerite     | 0.5      | 31.3   | 1.2     | 1.2      | 0.3    | 1.9       | 36.7     | 0.0       | 0.6        | 0.8     | 3.7      | 20.4     | 0.1           | 1.0  |
| Actinolite    | 0.3      | 39.1   | 0.1     | 0.1      | 0.0    | 0.0       | 2.0      | 1.7       | 0.0        | 2.6     | 27.9     | 21.3     | 2.4           | 2.1  |
| Apatite       | 0.9      | 27.9   | 0.1     | 0.9      | 0.4    | 0.4       | 22.2     | 6.7       | 8.6        | 0.0     | 9.9      | 15.3     | 0.0           | 6.3  |
| Feldspar      | 0.7      | 45.0   | 0.2     | 0.4      | 0.3    | 0.1       | 7.4      | 3.3       | 9.5        | 1.0     | 0.0      | 28.0     | 1.8           | 1.4  |
| Chlorite      | 0.7      | 23.0   | 0.6     | 0.8      | 0.4    | 0.3       | 29.8     | 13.9      | 5.5        | 1.2     | 21.5     | 0.0      | 0.8           | 1.3  |
| Cummingtonite | 0.1      | 19.5   | 0.1     | 0.0      | 0.0    | 0.0       | 5.1      | 1.4       | 16.0       | 0.1     | 35.6     | 19.8     | 0.0           | 2.1  |
| Else          | 1.9      | 37.9   | 7.8     | 3.4      | 7.6    | 2.4       | 9.8      | 4.9       | 3.8        | 3.5     | 7.4      | 8.9      | 0.6           | 0.0  |
| Sample 1104b  |          |        |         |          |        |           |          |           |            |         |          |          |               |      |
| Graphite      | 0.0      | 28.4   | 0.6     |          | 0.4    | 1.7       | 2.5      | 3.3       | 0.8        | 1.6     |          | 50.8     |               | 9.5  |
| Quartz        | 16.4     | 0.0    | 6.2     |          | 4.3    | 9.0       | 7.3      | 19.0      | 0.2        | 0.8     |          | 17.4     |               | 11.7 |
| Calcite       | 2.2      | 37.3   | 0.0     |          | 0.3    | 1.5       | 5.3      | 19.4      | 0.1        | 0.3     |          | 14.9     |               | 17.5 |
| Ankerite      |          |        |         |          |        |           |          |           |            |         |          |          |               |      |
| Pyrite        | 3.1      | 54.0   | 0.6     |          | 0.0    | 1.1       | 2.0      | 3.8       | 0.3        | 0.0     |          | 4.9      |               | 29.7 |
| Magnetite     | 3.7      | 35.0   | 1.0     |          | 0.4    | 0.0       | 5.8      | 25.8      | 0.0        | 3.0     |          | 12.6     |               | 10.9 |
| Siderite      | 5.5      | 27.3   | 3.3     |          | 0.6    | 5.7       | 0.0      | 29.2      | 0.0        | 0.1     |          | 23.1     |               | 4.6  |
| Grunerite     | 3.2      | 32.0   | 5.5     |          | 0.5    | 11.2      | 13.1     | 0.0       | 0.0        | 1.5     |          | 26.2     |               | 6.7  |
| Actinolite    | 42.4     | 15.2   | 1.6     |          | 2.0    | 0.3       | 0.1      | 1.1       | 0.0        | 0.6     |          | 25.9     |               | 10.7 |
| Apatite       | 11.0     | 9.6    | 0.6     |          | 0.0    | 9.4       | 0.2      | 10.7      | 0.1        | 0.0     |          | 19.8     |               | 38.5 |
| Feldspar      |          |        |         |          |        |           |          |           |            |         |          |          |               |      |
| Chlorite      | 35.2     | 20.8   | 3.0     |          | 0.5    | 3.9       | 7.4      | 18.7      | 0.3        | 2.0     |          | 0.0      |               | 7.9  |
| Cummingtonite |          |        |         |          |        |           |          |           |            |         |          |          |               |      |
| Else          | 13.6     | 28.9   | 7.2     |          | 5.9    | 7.0       | 3.1      | 9.8       | 0.3        | 7.9     |          | 16.3     |               | 0.0  |

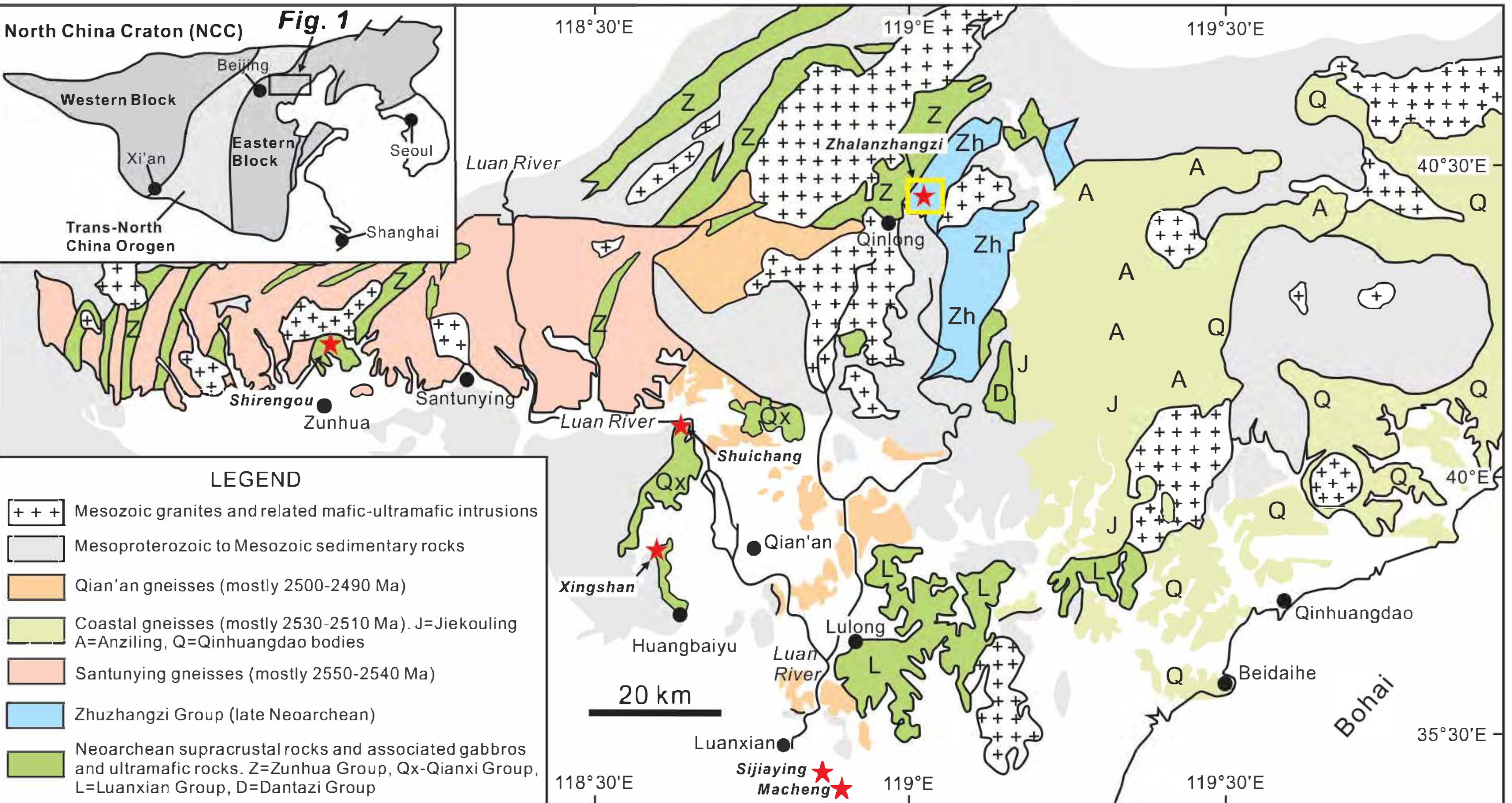
| Sample 1104d  |     |      |      |     |      |      |      |     |     |      |
|---------------|-----|------|------|-----|------|------|------|-----|-----|------|
| Graphite      | 0.0 | 1.6  | 14.6 | 0.1 | 8.7  | 59.9 | 1.5  | 2.9 | 1.0 | 9.7  |
| Quartz        | 0.8 | 0.0  | 3.7  | 0.0 | 14.1 | 67.4 | 0.4  | 0.2 | 2.0 | 9.8  |
| Calcite       | 6.3 | 3.4  | 0.0  | 0.0 | 10.0 | 35.4 | 16.3 | 1.0 | 0.5 | 25.6 |
| Ankerite      |     |      |      |     |      |      |      |     |     |      |
| Pyrite        | 2.0 | 1.6  | 1.8  | 0.0 | 44.8 | 23.3 | 0.5  | 0.0 | 0.8 | 22.3 |
| Magnetite     | 1.5 | 5.3  | 4.0  | 0.3 | 0.0  | 52.5 | 0.6  | 1.0 | 1.3 | 32.5 |
| Grunerite     | 6.7 | 16.4 | 9.2  | 0.1 | 34.0 | 0.0  | 6.5  | 2.2 | 5.0 | 17.8 |
| Actinolite    | 1.3 | 0.8  | 32.3 | 0.0 | 2.9  | 49.9 | 0.0  | 1.9 | 1.2 | 9.7  |
| Apatite       | 7.0 | 1.2  | 5.6  | 0.0 | 13.8 | 47.5 | 5.3  | 0.0 | 0.1 | 19.2 |
| Feldspar      |     |      |      |     |      |      |      |     |     |      |
| Chlorite      |     |      |      |     |      |      |      |     |     |      |
| Cummingtonite | 1.5 | 6.5  | 1.6  | 0.0 | 11.4 | 66.5 | 2.1  | 0.1 | 0.0 | 7.9  |
| Else          | 2.1 | 4.6  | 12.8 | 0.2 | 40.5 | 34.4 | 2.5  | 1.7 | 1.1 | 0.0  |

*Note:* The colour gradients of the table highlight the most prominent association of graphite with other minerals, while the blanks show the minerals that were not detected. EPMA analysis indicates the composition of chlorite is brunsvigite, see Table S1 for details.

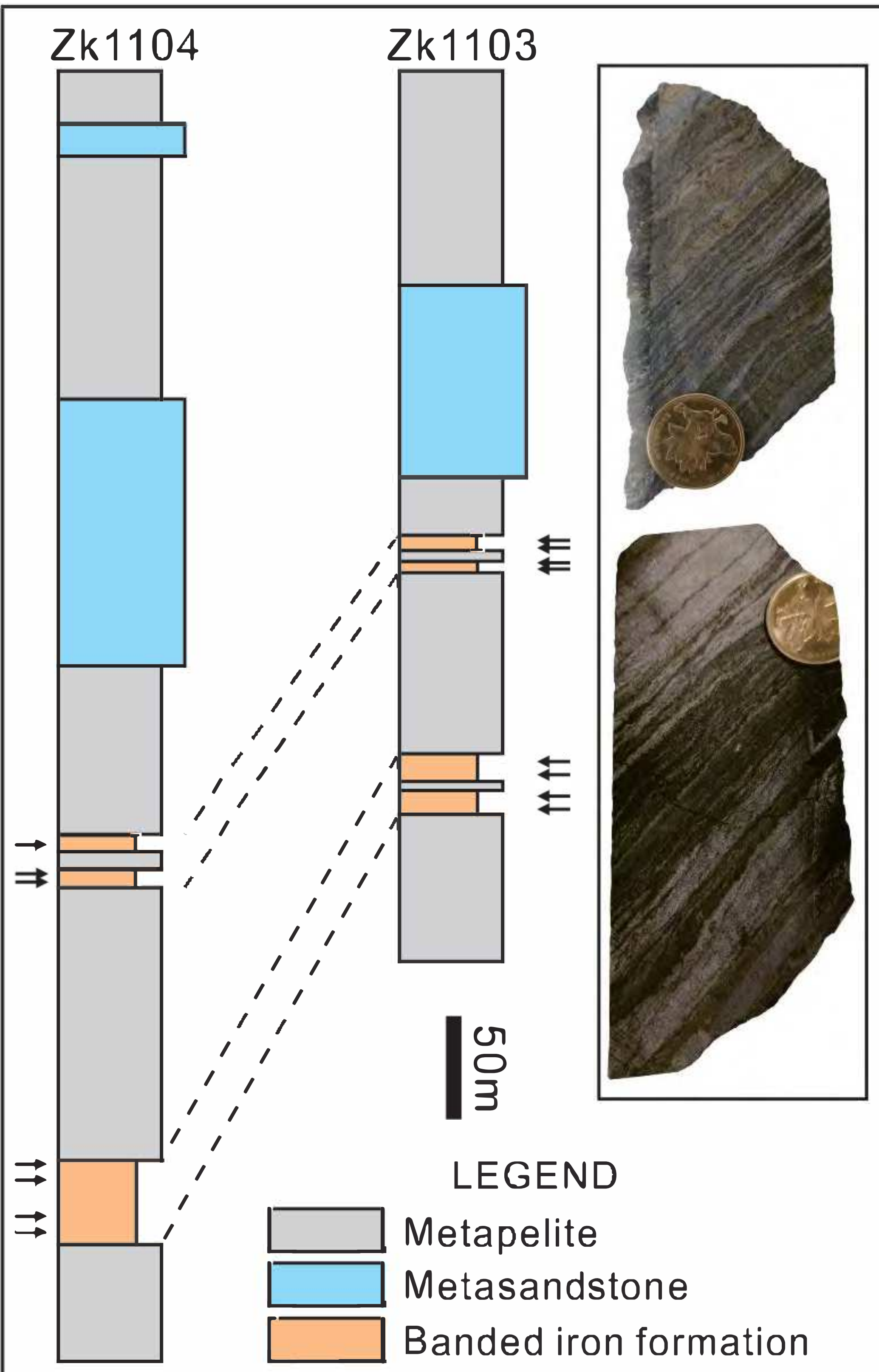
**TABLE 2.** Major oxides, total inorganic and organic carbon contents, and carbon isotope values for the Zhalaizhangzi BIF.

| Sample                               | 1103a  | 1103b  | 1103c  | 1103d  | 1103e  | 1103f  | 1103g  | 1103h  | 1104a  | 1104b  | 1104c  | 1104d  | 1104f  | 1104g  | 1104h  |
|--------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| wt%                                  |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| SiO <sub>2</sub>                     | 58.4   | 82.6   | 58.2   | 72.4   | 53.6   | 52.0   | 55.7   | 58.2   | 38.3   | 67.4   | 44.0   | 42.5   | 30.2   | 44.3   | 64.2   |
| TiO <sub>2</sub>                     | 0.02   | 0.01   | 0.09   | 0.01   | 0.02   | 0.10   | 0.03   | 0.02   | 0.03   | 0.02   | 0.02   | 0.01   | 0.02   | 0.03   | 0.01   |
| Al <sub>2</sub> O <sub>3</sub>       | 0.58   | 0.06   | 4.42   | 0.40   | 0.86   | 3.68   | 0.66   | 0.74   | 1.17   | 1.03   | 0.87   | 0.56   | 0.88   | 1.19   | 0.19   |
| Fe <sub>2</sub> O <sub>3</sub>       | 32.7   | 12.9   | 24.2   | 20.2   | 38.1   | 34.2   | 36.8   | 34.8   | 50.0   | 18.2   | 45.2   | 47.6   | 54.0   | 43.4   | 31.7   |
| MnO                                  | 0.15   | 0.10   | 0.33   | 0.13   | 0.22   | 0.39   | 0.24   | 0.14   | 0.16   | 0.26   | 0.12   | 0.15   | 0.23   | 0.16   | 0.12   |
| MgO                                  | 2.03   | 0.90   | 1.53   | 1.43   | 2.96   | 2.39   | 2.61   | 2.51   | 2.65   | 1.33   | 2.37   | 2.68   | 4.31   | 2.71   | 1.43   |
| CaO                                  | 3.63   | 1.24   | 2.29   | 2.35   | 2.22   | 2.52   | 2.37   | 1.02   | 4.32   | 4.00   | 4.13   | 3.33   | 4.87   | 4.69   | 0.74   |
| Na <sub>2</sub> O                    | 0.01   | 0.01   | 0.01   | 0.01   | 0.03   | 0.03   | 0.01   | 0.03   | 0.01   | 0.01   | 0.07   | 0.03   | 0.03   | 0.09   | 0.00   |
| K <sub>2</sub> O                     | 0.02   | 0.01   | 0.86   | 0.07   | 0.05   | 0.82   | 0.01   | 0.03   | 0.01   | 0.01   | 0.06   | 0.01   | 0.06   | 0.03   | 0.01   |
| P <sub>2</sub> O <sub>5</sub>        | 0.10   | 0.01   | 0.14   | 0.09   | 0.16   | 0.14   | 0.17   | 0.17   | 0.23   | 0.12   | 0.17   | 0.20   | 0.13   | 0.14   | 0.03   |
| SO <sub>3</sub>                      | 0.77   | 1.03   | 1.64   | 0.64   | 0.17   | 1.80   | 0.52   | 0.73   | 1.16   | 0.82   | 0.73   | 0.35   | 1.65   | 0.93   | 0.71   |
| LOI                                  | 1.57   | 0.77   | 6.16   | 2.19   | 1.09   | 1.82   | 0.70   | 0.82   | 1.57   | 6.20   | 1.71   | 2.07   | 3.36   | 2.05   | 0.80   |
| Total                                | 100.0  | 99.6   | 99.9   | 99.9   | 99.4   | 99.9   | 99.8   | 99.2   | 99.5   | 99.3   | 99.5   | 99.4   | 99.7   | 99.7   | 100.0  |
| TIC                                  | 1.32   | 1.26   | 1.66   | 0.89   | 0.47   | 0.48   | 0.37   | 1.31   | 0.81   | 1.92   | 0.83   | 0.73   | 0.81   | 0.96   | 1.05   |
| TOC                                  | 0.37   | 0.49   | 0.63   | 0.51   | 0.58   | 0.73   | 0.41   | 0.41   | 0.51   | 0.19   | 0.38   | 1.10   | 0.96   | 0.40   | 0.57   |
| ‰, VPDB                              |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| δ <sup>18</sup> O                    | 16.24  | 17.36  | 15.15  | 16.18  | 19.51  | 15.81  | 16.52  | 15.87  | 16.92  | 14.12  | 17.33  | 17.53  | 19.99  | 17.69  | 16.98  |
| δ <sup>13</sup> C <sub>carb</sub>    | -7.65  | -9.51  | -6.57  | -8.27  | -12.52 | -11.10 | -12.13 | -8.70  | -14.53 | -6.33  | -16.73 | -13.74 | -13.35 | -16.13 | -9.27  |
| δ <sup>13</sup> C <sub>organic</sub> | -16.15 | -15.36 | -17.87 | -17.80 | -17.64 | -18.86 | -20.11 | -19.92 | -20.27 | -21.38 | -23.61 | -20.68 | -23.81 | -23.21 | -22.42 |

# Figure 1



# Figure 2



## Figure 3

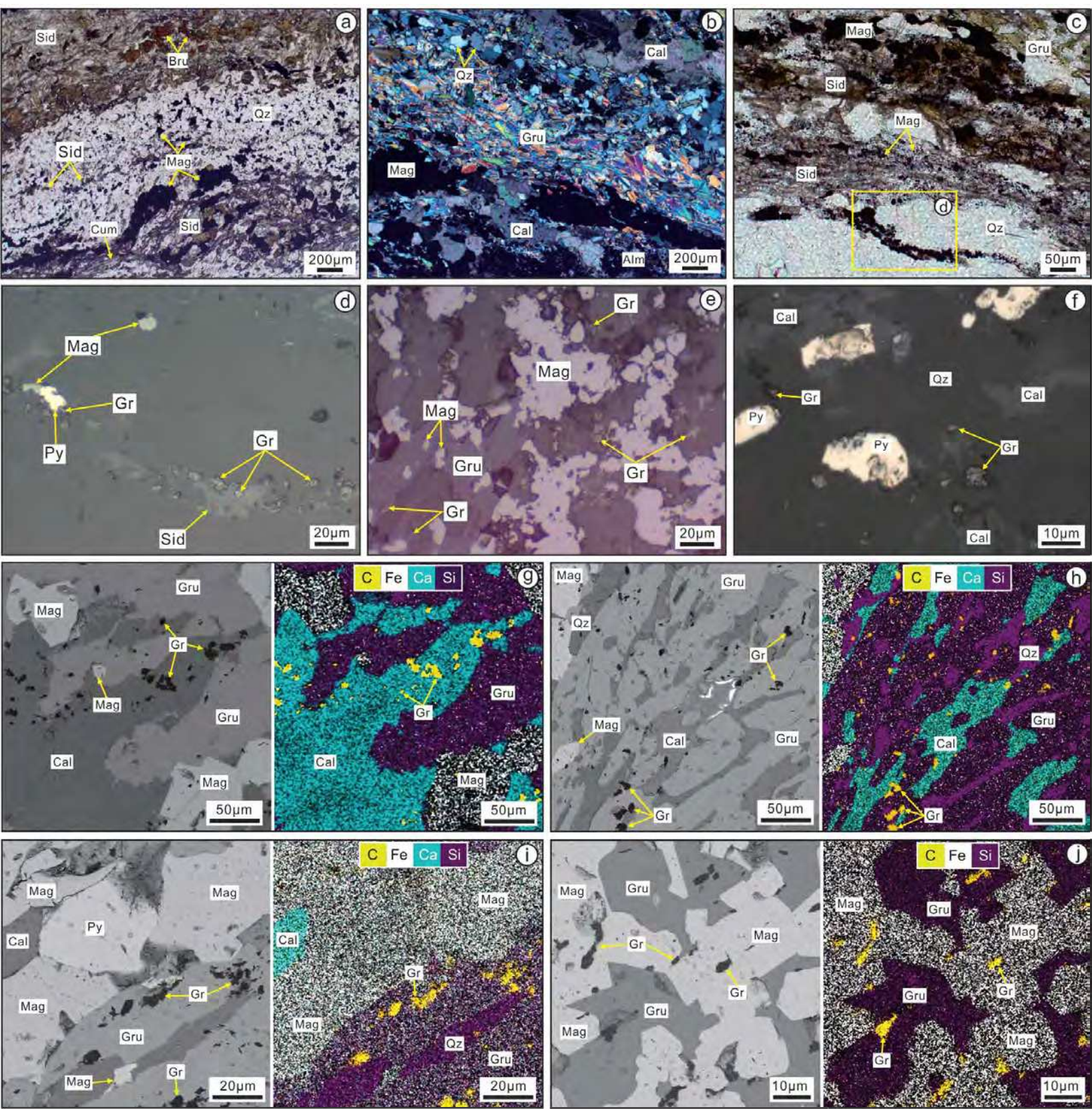
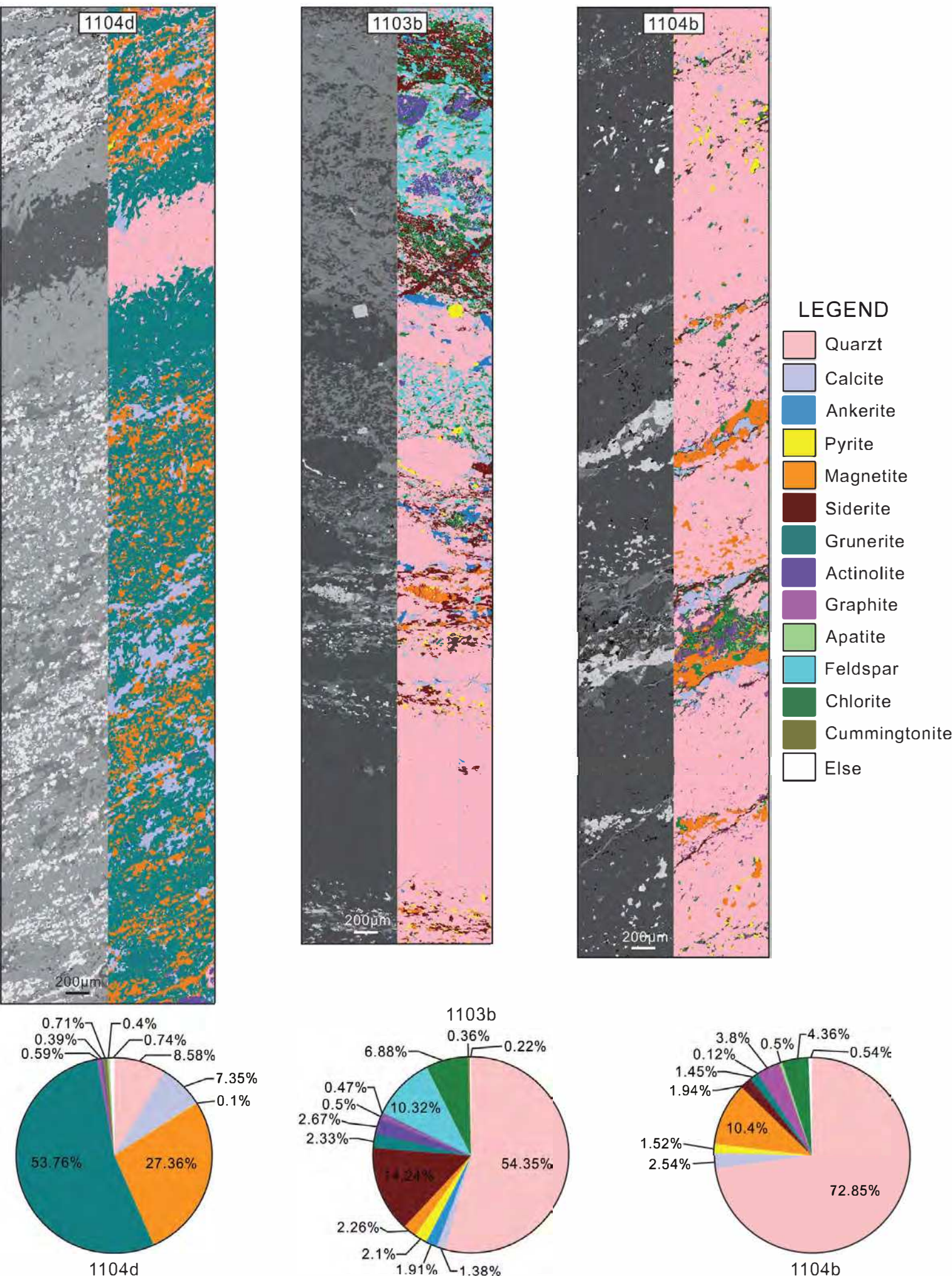
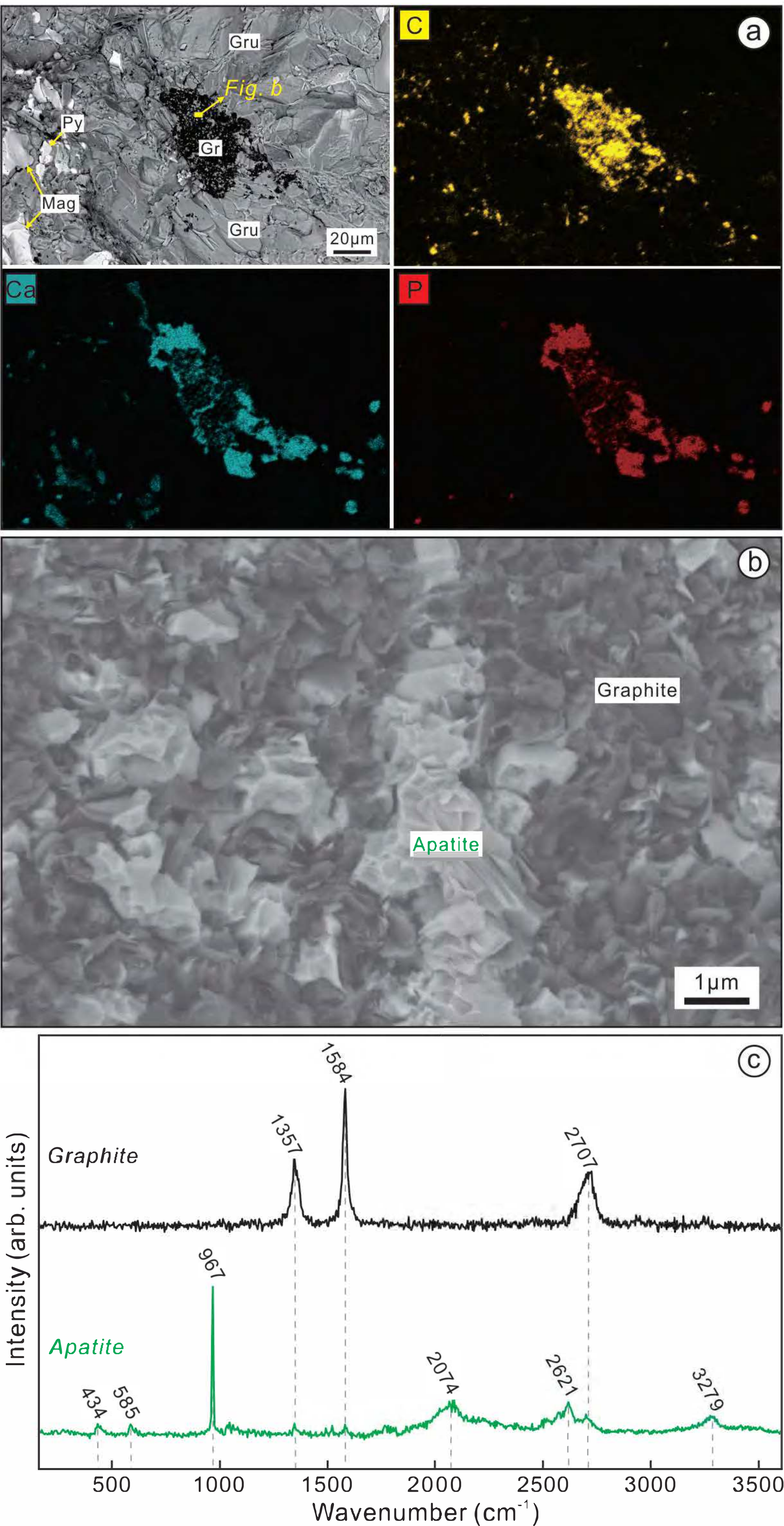


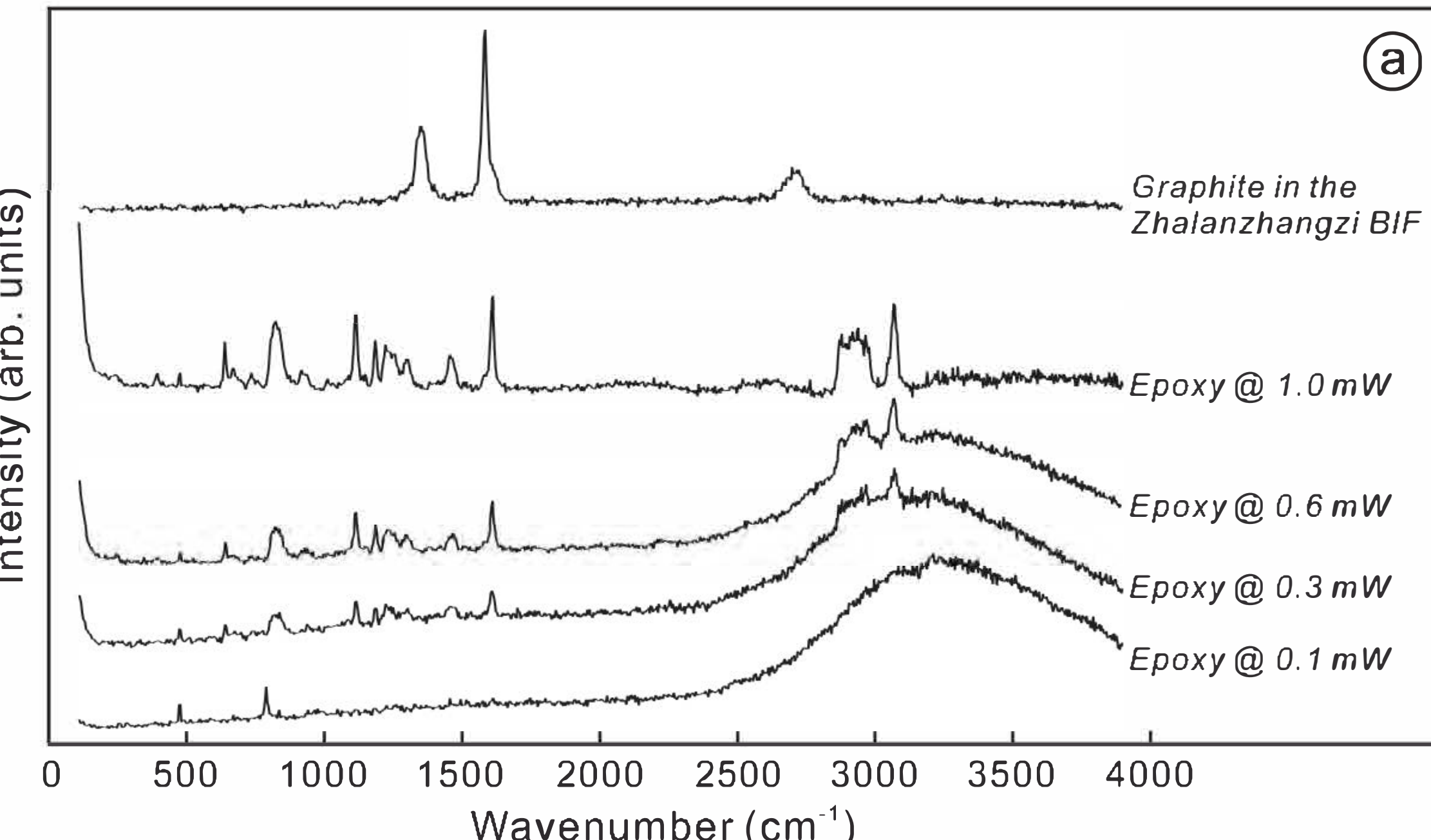
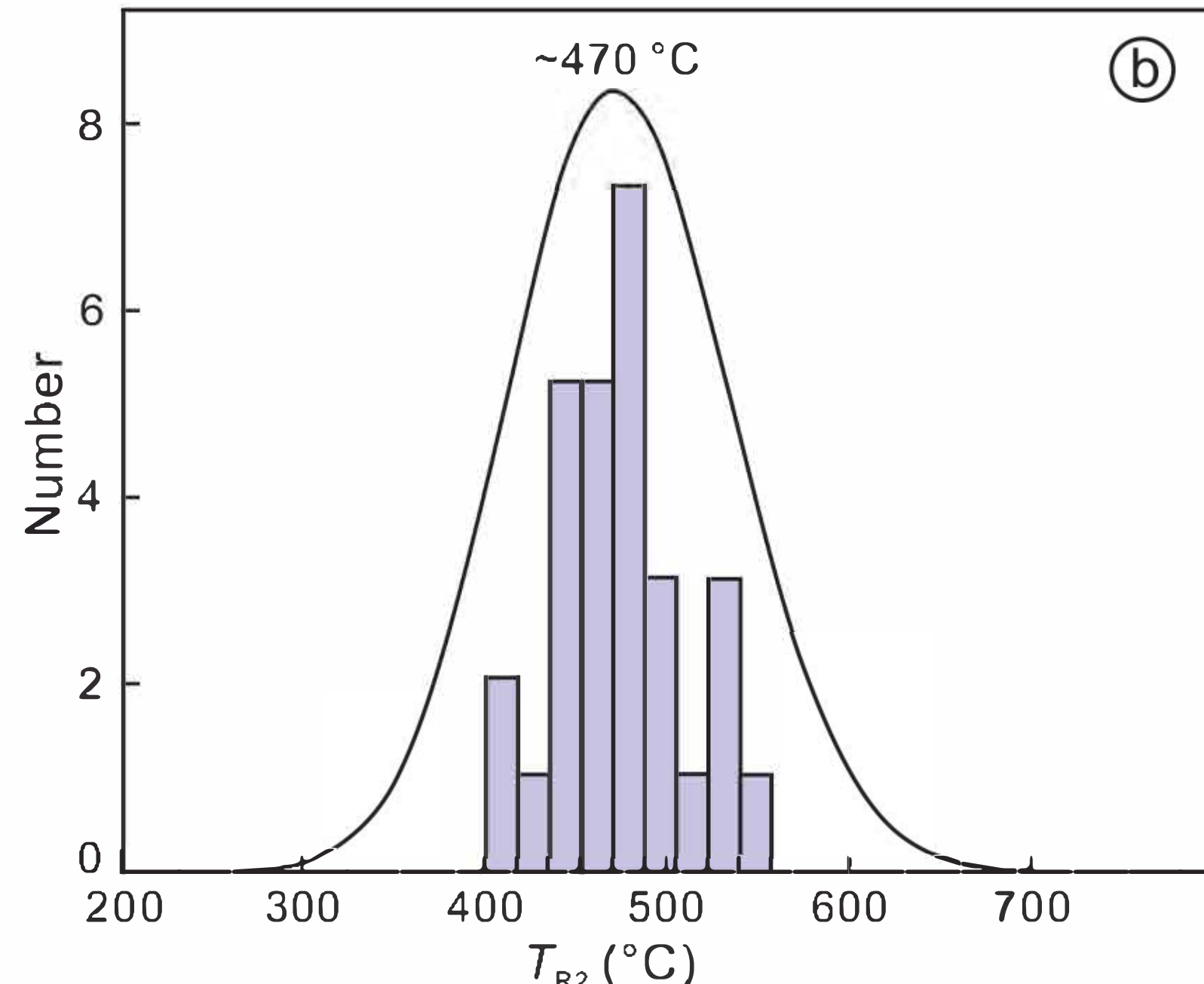
Figure 4



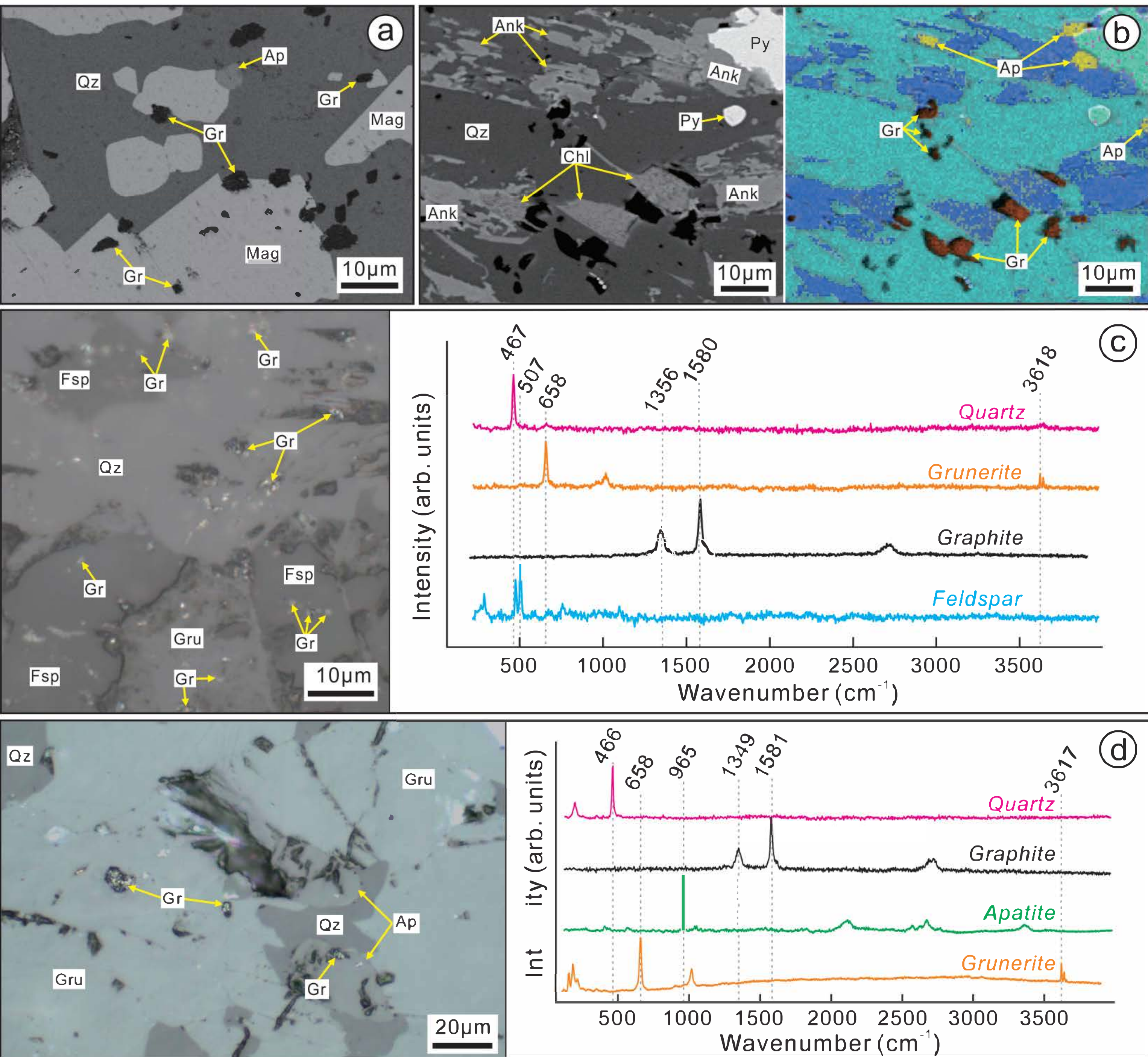
# Figure 5



# Figure 6



# Figure 7



# Figure 8

