New observations of Ambient inclusion trails (AITs) and pyrite framboids in the Ediacaran Doushantuo Formation, South China

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Abstract: Ambient inclusion trails (AITs) are intriguing microtubular structures that commonly occur in association with pyrite in Precambrian organic-rich cherts and phosphorites. They are thought to be created by the migration of pyrite or other crystal grains through a lithified substrate driven by pressure solution from the in situ thermal decomposition of organic matter.
New phosphorite samples of the Ediacaran Doushantuo Formation (South China) contain abundant AITs exhibiting diverse morphotypes, which may be distinguished from filamentous microfossils and endolithic microborings with a suite of morphological criteria based on optical microscopy and scanning electron microscopy (SEM). Black shales of the Baizhu section contains abundant pyrite frambooids whose size distributions reveal significant temporal variations of redox conditions in shallow marine waters that probably promoted the formation of the Doushantuo phosphorites.

AITs in the phosphorites are categorized into three types and further into five subtypes (I-a, I-b, II-a, II-b, and III) based on their morphologies and observed or interpreted associations with various kinds of terminal pyrite crystals. Among these, subtype II-a, single striated microtubes 2-10 μm wide, are interpreted to have resulted from migration of intact pyrite frambooids. Those of subtype II-b, dense clusters of outward radiating microtubes with consistent widths and inward-facing cuspate ridges, likely have formed by explosive disintegration and propulsion of pyrite frambooids due to highly concentrated carbon dioxide gas during the oxidation of organic matter. During early diagenesis, formation of euhedral and framboidal pyrites involve a suite of biogeochemical and physical processes including non-biological oxidation of organic matter and reduction of sulfate in the presence of ferrous iron. Following the burial of pyrites, further oxidative degradation of organic matter produced abundant CO₂ gas, which drives the pyrites to move through the solid, but not yet fully lithified phosphatic gel composing granules. This model explains the formation of previously reported but unexplained star-burst type AITs and it may be tested by experimental studies.

Our new observations provide evidence for the widespread occurrence of AITs in the
Doushantuo phosphorites and urges careful petrographic examinations and differentiation between AITs and morphologically similar biogenic microstructures.

Keywords: Phosphorite; Microtubes; Non-biological sulfate reduction; Oxidation of organic matter; Paleoredox variations.

1. Introduction

Ambient Inclusion Trails (AITs) are a relatively rare but intriguing component of the rock record, first reported as “ambient pyrites” from the Gunflint chert in North America (Tyler and Barghoorn, 1963). They have been described in detail from a number of Precambrian successions, including the 1.9-2.0 Ga Gunflint and Biwabik Formations on the southwestern margin of the Superior Craton (Tyler and Barghoorn, 1963), the 3.5 Ga Warrawoona Group (Awramik et al., 1983), the c. 3.4 Ga Strelley Pool Formation (Wacey et al., 2008a) and the 2.7 Ga Fortescue Group (Knoll and Barghoorn, 1974; Lepot et al., 2009; Lepot et al., 2011) of Western Australia, and the Ediacaran Doushantuo Formation in South China (Zhang, 1984; Xiao and Knoll, 1999).

In thin section, AITs appear as void or infilled microtubes that terminate in a metal-rich grain (typically pyrite), which is of equivalent diameter to the tubular trail itself.

AITs have been studied for the genesis of their unique morphology. As the width of the microtubes systematically conforms to the diameter of the terminal pyrite crystals, it is apparent that the pyrites had moved through the precursor microcrystalline chert matrix, leaving mineral trails in their wakes (Wacey et al., 2008b). The driving mechanism of the pyrite, however, remains unclear. It is generally hypothesized that the heating decomposition of organic matter attached to the pyrites is necessary for the formation of AITs (Wacey et al., 2008b). Previous reports have been
mainly focused on siliceous rocks, so it is uncertain whether the proposed genetic mechanisms for
AITs in chert is applicable to AITs in other types of rock, such as phosphorites. A few studies have
reported AITs from phosphorites of the Doushantuo Formation (Xiao and Knoll, 1999; Liu and
Yin, 2006), but a thorough study of their mineral structure and a detailed petrographic
documentation has yet to be presented to explain their formation. In addition, relatively little
attention has been paid to the terminal grains of AITs in previous studies.

In this work, we observed abundant AITs and pyrite framboids from the Doushantuo
Formation in the Baizhu phosphorus mine near Baokang City, north Yangtze Block. For
comparison, samples from phosphorite mines in Taopinghe, ca. 60 km south of Baizhu, and
Weng'an, southwest Yangtze Block were also studied. Detailed petrography by optical microscopy,
scanning electron microscopy (SEM) and micro-Raman spectroscopy are presented here to discuss
the origin of AITs and their associated pyrites, which can help to understand non-biological
processes involved in the decomposition of biomass and to reconstruct the oceanic redox
conditions of the Doushantuo basins.

2. Geological setting and samples

The Doushantuo Formation is a carbonate-black shale-phosphorite sequence and now appears
as a lithostratigraphic zone distribution on the Yangtze Block (Jiang et al., 2011). It is underlain by
Cryogenian glacial and interglacial successions, and is overlain by carbonates of the Dengying
Formation. The depositional age of the Doushantuo Formation is constrained by many
geochronological studies. A zircon U-Pb age of 636.4 ± 4.9 Ma from the Cryogenian Nantuo
tillites constrains the maximum age of the Doushantuo Formation(Zhang et al., 2008). Zircon
U-Pb TIMS age data from ash beds have been published from the Yangtze Gorges area, including 635.26 ± 1.07 Ma, 632.48 ± 1.02 Ma and 651.09 ± 1.02 Ma ages from Members I, II and IV of the Doushantuo Formation (Condon et al., 2005). Liu et al (2009) also reported a 614 ± 7.6 Ma zircon U-Pb age from an ash bed in strata correlated to Member II. In addition, whole rock Re-Os isochron ages of 598 ± 16 Ma (Kendall et al., 2009) and 591.1 ± 5.3 Ma (Zhu et al., 2013) from member IV black shales have also been reported.

The Baizhu section is located in the north of the Yangtze Block (Fig. 1a). The samples studied herein were collected from outcrops in the Baizhu mining area (GPS coordinates: 31°40′52.9″N, 110°56′20.1″E) near Baokang City (Fig. 1a). The stratigraphy of this ~ 60 m thick studied section is somewhat similar to that of the Jiulongwan section although a one-to-one correlation of the classic four-member sequence is not evident (Fig. 1b). A ca. 2.5 m- thick basal cap dolostone is observed, with abundant, partly-filled sheet cracks. Phosphorus-bearing horizons are interbedded with dolostone and cherty shale (Fig. 1b). The main phosphorus-bearing horizon (horizon 12 in Fig. 1b) consists of dolostone-phosphorite cycles containing cherty phosphatic lenses, stromatolites, concretions and micro-oncoids. These rocks locally contain P$_2$O$_5$ up to 38 wt% (She et al., unpublished data) and are actively mined in the study area. The presence of stromatolites, micro-oncoids and abundant cyanobacterial fossils indicates that these phosphorites were formed within the photic zone, and Zhou et al. (2004) proposed that they were deposited in a shallow subtidal to intertidal, high energy environment, above the fair-weather wave base. Further up-section, the sequence is characterized by medium-thickly bedded dolostones and cherty black shales, which eventually grade upward into the thickly bedded dolostones of the Dengying Formation. According to an earlier paleogeographic reconstruction by Jiang et al. (2011), both the
Baizhu and Taopinghe sections were deposited on the proximal margin of an intra-shelf basin.

Two granular phosphorite samples (ZK511-30 and ZK511-32) were collected from a drill hole (GPS coordinates: 27°02'31"N, 107°24'15"E) in Weng'an phosphorus mine, southwest Yangtze Block, corresponding to the "black bituminous phosphorite" of unit 4A of the Doushantuo Formation described in Xiao et al. (2014). Location and geological settings of an additional granular phosphorite specimen (TP0901) from the Taopinghe phosphorus mine (GPS coordinates: 31°16'29.9"N, 111°16'30.8"E), ~65 km north of Yichang are described in She et al. (2013).

3. Methods

3.1. Optical microscopy

Petrographic studies were performed on polished thin sections with a Nikon LV100 POL or a Zeiss Axio Scope. Diameters of 1876 pyrite framboïds in nine thin sections were measured under reflected light along several parallel lines across each thin section until a size population of more than 190 framboïds was achieved.

3.2. Micro-Raman spectroscopy

Micro-Raman spectroscopic imaging was performed at the London Centre for Nanotechnology with a WITec alpha 300R system equipped with a 532 nm laser with output power maintained at ~5 mW. Raman hyperspectral scans were performed with a 100X objective (N.A. = 0.9) and a 50µm diameter optic fiber, and collected on a Peltier-cooled EMCCD detector for acquisition times between 0.4 and 0.6 seconds per spectrum. Spatial resolution was ~360 nm/pixel and
spectral resolution was \~4 \text{ cm}^{-1}. Raman hyperspectral analyses were performed \geq 1 \text{ micron below the thin section surface}, therefore ruling out potential artifacts induced by polishing or surface contamination. Raman spectral images of mineral associations were generated by mapping peak intensity for specific chemical bonds in minerals from each spectral scan using the WiTec Project software (Bernard et al., 2008; Papineau et al., 2010).

Spot analysis by micro-Raman spectroscopy was also conducted at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan), with a Thermo Scientific DXR dispersive Raman micro-spectrometer equipped with a petrographic microscope (Olympus BX51) and a 532 nm Nd-YVO4 laser. The output laser power was maintained at \~10 \text{ mW}. The use of a grating with 900 grooves per mm and a pinhole with 25 \mu m diameter produced Raman spectra from 3500 to 50 \text{ cm}^{-1} with a spectral resolution of \~3 \text{ cm}^{-1}. Raman spectra were collected in 10 accumulations of 5 s each.

All measurements were conducted under conditions of atmosphere pressure, room temperature (21±1°C) and humidity < 50%. Raman spectral characteristics of organic matter (OM) were obtained after processing the data with a cosmic ray reduction routine and background subtraction with a polynomial fit followed by peak deconvolution using a Lorentzian function.

3.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out at China University of Geosciences (Wuhan). Images were acquired with both secondary electrons (SEI) and backscattered electrons (BSE) with a FEG Quanta 200 environmental SEM or a Hitachi SU8010 field emission SEM, both equipped with an energy dispersive X-ray spectrometer (EDS). Accelerating voltage was 2.5 kV.
(FEG Quanta 200) or 15 kV (Hitachi SU8010) for SEI mode and 7.5 kV (FEG Quanta 200) or 15 kV (Hitachi SU8010) for BSE mode during imaging and analysis. Samples were coated with a thin layer of gold or platinum prior to SEM analyses and after Raman analyses.

4. Results

4.1. Petrography

Four main types of phosphorite can be recognized in the Baizhu section based on their sedimentary structures (Figs. 2a-d). Type 1 is banded phosphorite (Fig. 2a), which is characterized by alternating layers of phosphate, dolomite and chert (Figs. 2e and g). The phosphatic layers consist of organic-zoned granules (micro-oncoids, Fig. 2f) or generally ellipsoidal clots (Fig. 2h) or granules that often contain AITs (Fig. 2i). Type 2 includes stromatolite-like and lenticular phosphorites (Fig. 2b). Stromatolite-like structures can be non-branching columnar, or dome-shaped and wavy. They are characterized by discontinuous organic-rich laminae 30-40 μm in thickness (Fig. 2j). AITs occur in both the organic-rich laminae and the transparent groundmass, but they are locally enriched in the transparent apatite groundmass (Fig. 2k). Type 3 consists of concretionary phosphorite (Fig. 2c). Concretions are generally elliptical and variable in size, range between major axes of 3 to 6 cm, and minor axes of 2 to 5 cm. They are typically brownish and appear to be silicified and surrounded by a layer of dolomite. Type 4 is intraclastic phosphorite (Fig. 2d), composed of abundant, medium-sand sized angular to subangular grains of detrital quartz along with phosphatic and carbonate intraclasts and rhombs cemented by clear, isotropic apatite. By contrast, samples from Weng’an and Yichang granular phosphorite all display a
granular texture (Fig. 2i), similar to those described in She et al. (2013).

According to previously published powder X-ray diffraction, infrared spectral and geochemical data, the phosphate minerals in the Baizhu mining area are exclusively carbonate fluorapatite (Huang, 1989).

4.2. Petrographic characteristics of the AITs

AITs are present in all the four types of phosphorites in Baizhu, with those in organic-rich banded phosphorite and concretionary phosphorite displaying smaller diameters. In general, AITs appear to preferentially occur in light-colored portions in banded or intraclastic phosphorite (Table 1). In the Doushantuo phosphorite in Yichang and Weng'an, however, they are often observed from inside phosphatic granules (Figs. 2i and 3m-3u). Occasionally, extremely abundant AITs can be observed in the isotropic, phosphatic groundmass of a type 1 banded phosphorite (Fig. 2l).

4.2.1 Morphology, size and distribution of the AITs

AITs have diverse morphologies (Figs. 2i, 2k-2l, 3a-3f, and 3m-3s), varying from straight, to gently curved, to twisted and spiral forms. Occasionally, the path of a later AIT appears to have been changed by collision with earlier terminal minerals (Fig. 3j). In some cases, the occurrence of the Doushantuo AITs appears to be related to localized abundances of OM, despite the overall low organic content of the host rock. As is shown in Figs. 3k and 3m-3n, the AITs radiate outwards from an organic-rich central locus, similar to the star-burst type reported in Knoll and Barghoorn (1974). This association might be diminished by later alteration during diagenesis and oxidative weathering (Figs. 3d and 3e). In some specimens, pyrite crystals moved inward from the outermost layer of phosphatic granules (Figs. 3p-3u). Occasionally, AITs can follow the outer
zones of phosphatic granules (Fig. 2i). Wherever AITs occur, the substrate is systematically
cryptocrystalline and isotropic under crossed nicols (Figs. 2l, 3a and 3q-3r).

The width of the AITs is variable (Table 1). In light-colored phosphorites, AITs are relatively
abundant, with diverse morphologies and variable diameters ranging from 2 to 68 μm. They are
often present in the interstitial cement containing pyrite aggregates that were later oxidized (Figs.
3d and 3e). The cross sections of AITs can be nearly circular (Fig. 3e), square (Figs. 4a and 4e),
sub-hexagonal (Fig. 4g) or irregular. In organic-rich banded phosphorites, AITs are less abundant
and are generally smaller, with width varying from 1 to 10 μm (Table 1).

4.2.2 Infilling material in the microtubes

AITs can be vacant (Figs. 3e and 4c-4d), partly filled (Fig. 4f), or completely filled (Figs. 4a
and 4e). In some cases, well-preserved casts of microtubes can be observed (Fig. 4e). The most
common infilling material is carbonate with diagnostic high-order white interference color (Table
1, Figs. 2l, 3a and 3q-3r), which is confirmed by Raman hyperspectral imaging (Figs. 3o and 3u).

The infillings in AITs are identified to be calcite with a strong Raman peak at 1092 cm\(^{-1}\) (weak
peaks at 157 cm\(^{-1}\), 286 cm\(^{-1}\), and 705 cm\(^{-1}\)) and sometimes, apatite with a strong Raman peak at
970 cm\(^{-1}\) (Fig. 6). Observations of thin sections stained with alizarin red S reagent further
document that most microtubes are filled with calcite. Other microtubes are coated with orange
Fe-oxide minerals that suggest oxidative weathering of sulfide (Figs. 3d and 3e).

4.2.3 Longitudinal striae

Longitudinal striae created by migration of terminal pyrite crystals are frequently observed on
the walls of the AITs (Figs. 3c, 3l and 4a-4d). Striae in AITs are diagnostically parallel and never
intersect with each other. In Figs. 4b-4d, inward-facing cusparse longitudinal ridges (crude striae,
arrowed) are clearly visible, whereas in other AITs fine longitudinal striae with low relief are present (Fig. 3a). Interestingly, the longitudinal ridges on the AIT casts in Fig. 4e correspond well to the striae in Fig. 4a, although the crystal sizes of the casts are larger than the submicrometer sized phosphatic groundmass. The striae are usually regularly spaced, with distances ranging from 0.3 to 1.9 μm (Table 2). In Fig. 4c, for instance, the spacing of longitudinal striae in a twisted AIT measures around 0.7 μm.

4.2.4 Terminal grains

In some cases, terminal crystal grains can be observed at one end of the microtubes. These can be a single pyrite crystal, which can be anhedral (Figs. 3c, 3g, and 3p-3q) or euhedral (Figs. 3i, 3k), or a cluster of crystals (Fig. 3e). Some of the terminal pyrites retain their original crystal shape (Figs. 3f and 3l), whereas others appear to have been modified (Fig. 3c).

4.3. Pyrite frambooids and their possible association with AITs

In the Baizhu section, both individual euhedral to anhedral pyrite grains and pyrite frambooids are observed. Pyrite frambooids generally occur in discontinuous black shale layers (horizons 8, 13, 14, 17, 20 and 23) which are separated by dolostone layers without frambooids (horizons 9-12, 15-16, 18-19 and 21-22). Frambooids range in size from 1 to 11 μm (Table 3) and are composed of micro-crystals 0.4 to 1.5 μm across (Figs. 4h-4o, Table 2). The micro-crystals show cubic-octahedron (Figs. 4h and 4i), pentagonal dodecahedron (Figs. 4j and 4k) and subspherical (Fig. 4l) crystal forms. Frambooids are often coated with a thin layer of amorphous (carbonaceous?) material (Fig. 4m). In some cases, a thin (carbonaceous?) layer, or membrane covers each of the micro-crystals (Fig. 4i). Within the dark sedimentary laminae, pyrite frambooids are occasionally
aligned parallel (Fig. 4o). Pyrites hosted in dolostones and phosphorites can be oxidized during post-depositional processes, as is shown in Fig. 3f where goethite is present as a pseudomorph after pyrite. Pyrite aggregates with diameters between 35 and 80 μm can also be oxidized by post-depositional fluid circulation in more porous areas (Figs. 3d and 3e).

The size distribution of pyrite framoids is shown in Table 3. In horizons 14 and 20, the framoids are on average smaller and less variable, ranging in size between 2.9 and 3.3 μm (SD between 0.9 and 1.3). Here the maximum framoid diameter (MFD) varies between 6.6 and 7.7 μm, and no framoid is larger than 10 μm. In horizons 8, 13, 17 and 23, the observed range of mean framoid diameter is between 3.6 and 4.5 μm (SD between 1.0 and 1.7). Two populations from horizon 17 contain relatively high proportions (16% to 29%) of framoids larger than 5 μm, with a MFD of 10.7 μm.

In the Doushantuo phosphorites, however, pyrite framoid is relatively rare and has hindered direct comparisons between AITs and pyrite framoids. Examples of possible oxidized framoid (Figs. 3g and h) and unambiguous pyrite framoid (Fig. 3i) have been observed from a phosphorite sample in the Taopinghe section. The apparent diameter of the latter (5.8 μm) appears to be slightly greater than the mean diameters of framoids in black shales but falls into the range of the AIT widths.

Considering the rarity of well-preserved pyrite framoids in phosphorites, we tentatively compared the sizes of framoids in black shales and AITs in phosphorites, which often occur in adjacent layers at the scale of less than 1 cm. The SEM images of pyrite framoids show that most micro-crystals are of similar size (Figs. 4h-4m). Ratios of overall framoid diameter to micro-crystal diameter (Dfrm/dm) range from 3.7 to 10.2. Interestingly, measurements of pyrite
framboids and a group of smaller AITs yielded comparable results (Table 2). These AITs range in width from 1.6 to 9.7 μm, whereas the spacings of longitudinal striae are 0.3 to 1.8 μm wide, corresponding closely to the diameters of micro-crystals in the framboids (0.4 to 1.5 μm). The ratios of microtube diameter to longitudinal striation spacing (D_{AIT}/d_{AIT}) vary between 4.1 and 7.9 (Fig. 5), well within the range of dispersed D_{frm}/d_{frm} ratios.

4.4. Raman spectroscopic characteristics and organic crystallinity

Micro-Raman spectroscopy has revealed the presence of carbonate, apatite and disseminated OM in all the Doushantuo samples (Figs. 3o, 3u and 6). Major spectral peaks are systematically detected at wavenumbers of 970 cm\(^{-1}\), 1092 cm\(^{-1}\), 1101 cm\(^{-1}\), 1348 cm\(^{-1}\) and 1605 cm\(^{-1}\) (Fig. 6). Apatite is characterized by the prominent peak at 970 cm\(^{-1}\), whereas the other peaks (435 cm\(^{-1}\), 594 cm\(^{-1}\), 1059 cm\(^{-1}\) and 2790 cm\(^{-1}\)) are weak due to the low degree of crystallinity of the phosphate. The systematic presence of OM in the banded phosphorites is confirmed by the Raman D- (1348 cm\(^{-1}\)) and G- (1600 cm\(^{-1}\)) bands. Interstitial cement between phosphatic granules is dolomite with a strong peak at 1101 cm\(^{-1}\) (minor peaks at 181 cm\(^{-1}\) and 305 cm\(^{-1}\)). Although the spectra of calcite and dolomite are similar, the systematic difference in their strong and weak peak positions are resolvable (spectra 3-8 vs. 7 and 9 in Fig. 6).

The degree of graphitic order is indicated by Raman spectral parameters, which record peak metamorphic conditions and remain unaffected by retrogression (Beyssac et al., 2002). As shown in Fig. 6, the Raman spectra of OM in the Baizhu and Weng'an phosphorites are characterized by the co-existence of D-band (indicating disordered OM) and G-band (graphitic OM) in the first order region (1000 - 1800 cm\(^{-1}\)), which can be decomposed into five bands (G, D1, D2, D3, and...
D4; Table 4). For the Baizhu samples, the D1-bands are centered between 1342 and 1350 cm\(^{-1}\) (FWHM = 52 - 115 cm\(^{-1}\)) with a greater intensity, whereas the G-bands are centered at around 1600 cm\(^{-1}\) (FWHM = 41 - 45 cm\(^{-1}\)) and are of lower intensity (spectra 10 and 11 in Fig. 6, Table 4). In the Weng'an phosphorites, however, the G-band (1590 cm\(^{-1}\), FWHM = 59 cm\(^{-1}\)) is more prominent than the D1-band (1348 cm\(^{-1}\), FWHM = 142 cm\(^{-1}\)) (spectra 12 and 13 in Fig. 6, Table 4). Using the empirical equations proposed by Lahfid et al. (2010), we calculated maximum metamorphic temperatures of the OM in the Baizhu and Weng'an phosphorites to range between 290 and 360 °C except for sample BK10-8-2_02 (Table 4). This is similar to those estimated for the Doushantuo phosphorites in Yichang (She et al., 2013). Notably, when compared with the Baizhu samples, the Weng’an phosphorites appear to have formed under lower metamorphic temperatures as indicated by their broader and lower D-bands (Kouketsu et al., 2014), which is consistent with the lower calculated metamorphic temperature (sample ZK511-32_01 in Table 4). These indicate a generally low degree of thermal maturation of the OM in these samples, consistent with metamorphism at the prehnite-pumpellyte facies.

5. Discussion

5.1 Formation of pyrite framboids and their paleoredox implications

Pyrite formation involves complex processes that are controlled by the availability of decomposable OM, dissolved sulfate, and reactive iron minerals (Berner, 1985). Nucleation and growth of framboidal pyrites have been observed in euxinic conditions, such as the Black Sea (Wilkin et al., 1997), and in anoxic sediment pore waters underlying oxygenated bottom waters,
such as the Great Salt Marsh, USA (Wilkin et al., 1996). Syngenetic framboids formed in euxinic conditions are generally smaller and less variable in size than those formed diagenetically within sediments underlying oxygenated waters, because the former have shorter residence times near the oxic-anoxic boundary than the latter (Benning et al., 2000; Wilkin and Arthur, 2001). Both mean and maximum diameters (MFD) of pyrite framboids have been used to discriminate between euxinic and non-euxinic environments (Wilkin et al., 1996; Wilkin and Barnes, 1997; Wignall and Newton, 1998; Nielsen and Shen, 2004). Bond and Wignall (2010) have also shown that the mean size ranges of framboids forming in euxinic, anoxic and dysoxic environments are 3-5 µm, 4-6 µm and 6-10 µm, respectively. The common occurrence of well preserved pyrite framboids in the Doushantuo Formation attests to their potential as paleoredox indicators, although secondary overgrowths of primary pyrites during burial diagenesis may obscure primary textures (e.g., Wacey et al., 2015) and result in a decrease in the proportion of framboidal pyrite (Benning et al., 2000).

Pyrite framboid size distributions in the Baizhu section indicate the frequent occurrence of euxinic, shallow marine conditions (Fig. 7). In horizons 14 and 20, the small mean diameter of framboids (3.0 µm - 3.3 µm) and the absence of framboids larger than 10 µm suggest pyrite formation within a euxinic water column. In horizons 8, 13, 17 and 23, the mean diameters of framboids range between 3.6 and 4.0 µm. This, along with the abundance of small framboids with diameters <5 µm, also indicate a euxinic environment. Among these, one sample from horizon 17 (BK17-2) shows a larger standard deviation (1.4 µm) and MFD (10.8 µm), and another sample from horizon 17 (BK17-1) has a larger mean framboid diameter (4.5 µm) and standard deviation (1.7 µm), with those >5 µm in diameter accounting for 29% of the total framboids. These two
samples indicate that a slightly higher redox state, probably transient development of dysoxic condition, might have occurred in level 17.

Various proxies have been used previously to investigate the redox conditions of the Doushantuo basins. Based on Fe speciation and S isotope data, Li et al. (2010) suggested that the Ediacaran ocean was strongly stratified, with an oxic surface layer resting above a euxinic wedge that was sandwiched within ferruginous waters on the continental shelf. Analyses of pyrite framboids in the upper and lower slope sections of the Doushantuo Formation has revealed decameter-scale euxinic and non-euxinic alternations (Wang et al., 2012). Guan et al. (2014) has also shown the frequent redox fluctuations during the Ediacaran Period based on size distribution and $\delta^{34}$S of pyrite framboids, and redox sensitive element geochemistry of black shales in the Ediacaran Lantian Formation in South China. A recent paleoredox study of late Ediacaran shales in the Three Gorges area of South China has documented significant spatial redox heterogeneity for the Doushantuo basins, even at the kilometer-scale (Li et al., 2015). All these models posit oxygenated surface waters underlain by euxinic waters either below the chemocline or within the deep bottom waters. It is somewhat surprising, therefore, that framboids indicative of euxinic waters are observed in the shallow-water Baizhu section, which is considered to have been deposited well above the chemocline that is defined in the coeval Jiulongwan and Xiaofenghe sections (Li et al., 2010; Wang et al., 2012; Xiao et al., 2012; Cui et al., 2015). Moreover, it is generally believed that marine sedimentary phosphate accumulation occurs above the oxygen minimum zone (OMZ) and below the sediment water interface in both the Phanerozoic and modern oceans (Slansky, 1986; Knudsen and Gunter, 2002). If, as it seems from our data, framboidal pyrite in black shales from the Baizhu section records periods of water column euxinia,
it would appear that significant temporal redox fluctuations (Jiang et al., 2011; Wang et al., 2012) or spatial redox heterogeneity (Li et al., 2015) existed during the Doushantuo Period. Fluctuations of the chemocline led to the formation of the repeated cycles of black shale-phosphorite in the Doushantuo Formation (She et al., 2014), followed by diagenetic formation of abundant AITs. Although the cause of such redox variations remains unclear, euxinia might have developed locally in shallow waters like the Baizhu basin, modulated by cyanobacterial blooms fueled by continentally-derived nutrients (She et al., 2014) and increased sulfate availability following the meltdown of the Snowball Earth as manifested by the underlying Nantuo tillites.

5.2 Criteria for the identification of AITs

Tyler and Barghoorn (1963) presented an initial description of AITs (which they called, "ambient pyrites") from the Gunflint and Biwabik formations emphasizing that these inorganic "pseudofossils" were not genetically related to the morphologically distinct microfossils occurring in the same rocks. Knoll & Barghoorn (1974) proposed that AITs were formed by migration of pyrite grains in the matrix driven by gas pressure produced by degradation of OM. However, such structures have sometimes been alternatively interpreted as filamentous microfossils (Awramik et al., 1983; Awramik, 1992; Baturin et al., 2000) or endolithic microborings (Dong et al., 1984; Conway Morris and Bengtson, 1994; Zhang and Pratt, 2008) in subsequent publications. Xiao and Knoll (1999) discussed the three hypotheses and favored the Knoll and Barghoorn interpretation based upon the clearly visible longitudinal striae on the microtubes. Mcloughlin et al. (2007) also noted that longitudinal striae created by the facets of the propelled mineral grain would be absent from endolithic microborings and are perpendicular to any annulations that might reflect cell
septation. Wacey et al. (2008b) reviewed previously published examples of AITs and proposed nine criteria for the recognition of AITs by summarizing their morphological characteristics in petrographic thin section. These include: (1) presence of a terminal mineral grain which is of equivalent diameter to the microtubes; (2) presence of longitudinal striae along the wall of the microtubes; (3) the cross section of the microtubes mirroring the crystal geometry of the terminal grains; (4) unlike endolithic borings, AITs tend to occur both in the center and on the edge of a grain; (5) AITs may radiate away from clumps of organic material; (6) AITs may become twisted towards their ends; (7) they may display side branches showing a different diameter to the original microtube; (8) the presence of sharp angular turns of the microtubes; (9) they may cross cut each other and form tangled masses.

Here we propose two additional criteria for distinguishing AITs from filamentous microfossils. The first is variability of size. AITs tend to occur in the rock matrix, and their diameters vary in a single thin section from < 10 μm to > 50 μm (Figs. 2m and 3d). By contrast, filamentous microfossils of the same taxon tend to have similar diameters. If there are more than one species of filamentous microfossils, statistics of the size of filaments generally yield peaks with normal distribution (e.g., Strother and Tobin, 1987; She et al., 2013), whereas sizes of AITs are not likely to show similar distribution patterns. The second additional criterion concerns sharp outlines and distinct infilling materials. AITs generally have sharp outlines if the microtubes are filled or coated with minerals (e.g., calcite, Figs. 3a, 3d-3e, 3j, 3i, 3n-3p and 3r) that are different to the substrate in refractory index, whereas filamentous fossils often show fuzzy outlines because the organisms are embedded in cryptocrystalline silica or phosphate. Being one of the major products of the non-biological oxidation of OM that lead to the formation of AITs (discussed below in detail), the
calcite infillings thus might serve as a criterion for the recognition of AITs. In the search for AITs in phosphorites, as is shown in this study, examination of thin sections under crossed nicols is very helpful because the high-order white interference color of the carbonate infillings are in sharp contrast to the isotropic nature of the phosphatic groundmass.

With these criteria, it is possible to recognize many of these microtubular structures based on petrographic observations. However, uncertainty remains in distinguishing AITs from similar biological structures, especially endolithic microborings, and therefore further studies are needed.

5.3 Genesis of AITs

5.3.1 Terminal grains and other factors contributing to AIT formation

In the Baizhu, Taopinghe and Weng'an samples, terminal pyrite grains have been observed in many AITs, such as aggregates of pyrite micro-crystals or single pyrite crystals, which are sometimes oxidized or partly oxidized (Figs. 3c-f). In other cases, however, terminal grains were not observed (Figs. 3a and 3h), mainly due to the limited thickness of the thin sections (ca. 30 μm). These limitations hinder the establishment of the association of AITs and specific types of pyrites.

Another important feature of AITs is that longitudinal striae are often observed along the walls of the microtubes. This provides critical evidence for the propulsion and migration of ambient pyrite crystals (Knoll and Barghoorn, 1974; Xiao and Knoll, 1999; Wacey et al., 2008a; Lepot et al., 2011). Precisely how such striae are generated, however remains elusive. Wacey et al. (2008b) suggested that longitudinal striae are created by the facets of the propelled mineral crystal, but the authors did not provide direct evidence. Others believe that they correspond to angular faces.
formed in the wake of crystal movement (Lepot et al., 2011; Tiwari and Siddaiah, 2012). This interpretation, however, do not explain the fact that the spacings between striae are much smaller than the terminal pyrite crystals themselves in many of the observed AITs (Xiao and Knoll, 1999; Wacey et al., 2008b). As shown in Table 2 and Fig. 5, diameters of pyrite framboids ($D_{frm}$) in black shales are strikingly similar to those of the microtubes of AITs ($D_{AIT}$) in phosphorites. Moreover, the sizes of the micro-crystals of framboids ($d_{frm}$) are in the same range as the spacing of longitudinal striae ($d_{AIT}$), which yields similar $D_{frm}/d_{frm}$ and $D_{AIT}/d_{AIT}$ ratios. In addition, the inward facing cuspate ridges (crude longitudinal striae) on some of the AITs (Figs. 4b-d) appears to reflect the surface morphology of framboids (e.g., Fig. 4i), whereas fine longitudinal striae (Fig. 4a) probably correspond to facets of single pyrite crystal. These suggest that at least some of the AITs are probably caused by migration of pyrite framboids. The abundant occurrence of AITs in the Doushantuo phosphorites implies that physical and chemical environments during phosphatization probably facilitated the formation of pyrites and their subsequent propulsion and migration through the phosphatic matrix.

Previous studies have shown that both sulfur oxidising bacteria (Froelich et al., 1988; Schulz and Schulz, 2005; Bailey et al., 2007; Arning et al., 2009) and cyanobacteria (Papineau et al., 2013; She et al., 2013; She et al., 2014; Papineau et al., 2016) might have played active roles in the remineralization, recycling and precipitation of phosphorus. Extracellular polymeric substances (EPS) produced by cyanobacteria, in particular, might have contributed to the final precipitation of calcium phosphate (She et al., 2013). A close association between pyrite framboids and biofilms has also been documented, although substantial debate remains on the extent to which biology directly or indirectly contributes to framboid formation (Wacey et al., 2015).
Likewise, EPS may have also promoted the formation of AITs, in providing OM as a reactant for AIT formation.

The decomposition of OM is also an important factor for AITs formation (Wacey et al., 2008b).

As is shown in Figs. 3h and 3j-3k, AITs radiate outward from a center rich in OM, suggesting that the latter is necessary for the production of carbon dioxide, which leads to the propulsion of pyrite through the calcium-phosphate host gel. Occurrence of AITs in phosphatized crustacean body fossils in the Upper Cambrian of Northern Poland and Lower Devonian of Ukraine (Olempska and Wacey, 2016) might represent an analogue of this type of pyritization and migration from organic-rich centers. In other cases, pyrite crystals appear to migrate inward from an outer layer of phosphatic granules (Figs. 3m-3p), which suggest production of pyrites during organic degradation and sulfidization from sulfate reduction taking place in the intergranular pore spaces. Similar phenomena have been reported in Zhang and Pratt (2008), but the authors interpreted them as microborings produced by endolithic microorganisms. Although this possibility cannot be entirely ruled out, the common presence of a terminal pyrite crystal and longitudinal striae (Figs. 3a, 3c, 3i and 4a-4d) favors the interpretation that these microstructures are likely to be AITs, and can be more parsimoniously described as non-biological structures that require biological OM to form.

5.3.2 A genetic classification scheme for AITs

Based on previously published data and our new observations, we propose a new genetic classification scheme for AITs (Table 5). They are categorized into three types and further into five subtypes. Those of type I are associated with single terminal pyrite crystals, with (I-a, Figs. 3d and
Type II and type III AITs are interpreted to be produced by pyrite aggregates, including those related to framboidal (II-a and II-b) and non-framboidal (III) pyrites. Examples for type II-a AIT are relatively rare probably due to preservational effects or incomplete documentation. Olempska and Wacey (2016) reported microtubes with a diameter ranging from 4 to 7.7 μm, which terminated with framboidal rather than euhedral pyrite in the metacopine ostracod fossil from the Lower Devonian of Podolia, Ukraine. This discovery led us to consider similar scenarios in the Doushantuo phosphorites and other AIT-bearing successions. Possible AITs of this type include single microtubes 2-10 μm wide, with crude longitudinal striae that are often separated by inward-facing cuspate ridges (Figs. 4b-d; and Zhang and Pratt, 2008, Fig. 3F). The close correspondence between the spacings of longitudinal striae of AITs and the diameters of micro-crystals in the framboids (Table 3 and Fig. 5) suggest that many of the AITs in the Doushantuo phosphorites may be attributed to type II-a. Distinguishing type II-a AITs from type I-b ones could be difficult when terminal pyrite framboid is not observed, but the inward-facing cuspate ridges (Figs. 4b-d), which mirrors the gaps between adjacent micro-crystals in framboid, might serve as a diagnostic feature for the former. Type I-b AITs, by contrast, tend to display finer striae with lower relief (Fig. 4a).

Disintegration of framboidal and non-framboidal pyrite clusters and their subsequent migration might have produced dense clusters of AITs (types II-b and III) (Figs. 2i, 3a, 3d-3e and 3j-3k). Heavily clustered small microtubes of similar widths ranging from 0.4 to 1.5 μm, often radiating from a central locus, have been reported previously from a few localities (Knoll and Barghoorn, 1974, Fig. 2; Wacey et al., 2008b, Fig. 9d; Lepot et al., 2011, Fig. 5A; and Olempska
and Wacey, 2016, Figs. 5A and G-H) but their origin remains unexplained prior to the present study.

We propose that consistent microtube widths within the typical range of framboid micro-crystal (i.e., 0.4-1.5μm) in a star-burst AIT cluster may be used as a criteria to distinguish type II-b AITs (e.g., Figs 5A and G-H in Olempska and Wacey, 2016) from type III AITs (Fig. 3e in this study and Fig.3L in Schopf et al., 2010). Knoll and Barghoorn (1974) described AITs from the Gunflint Formation and Fortescue Group and noticed that one group of AIT clusters have consistent microtube width ranging between 0.5 and 0.8 μm, which are one order of magnitude smaller than the other AITs. These small AITs are here attributed to type II-b that are produced by propulsion of disintegrated pyrite framboids. Depending on the number of micro-crystals in a framboid, the number of microtubes in the resulting cluster of AITs can be variable (from dozens to thousands) but would be difficult to measure with limited exposure in a thin section or on a broken surface. The numerous AITs of variable sizes which radiate from the central organic-rich nucleus in Figs. 3 m-n, however, could be produced by disintegration of either multiple framboidal or non-framboidal aggregates.

5.3.3 A revised model for the genesis of AITs

Tyler and Barghoorn (1963) hypothesized that AITs were formed when pyrite grains were propelled through solid rock by the force of crystallization of either quartz or carbonate in the appendage. Knoll and Barghoorn (1974) later proposed that the propulsion force resulted from pressure solution, which led to the movement of terminal grains. Thermal degradation of OM attached to individual pyrite grains generates CO₂ and other gases, which in turn, would have built
up enough pressure to create compaction of the encompassing chert on the front face of the
moving pyrite grain. They noted however that cross-cutting relations of the trails to lithified
oncoids indicated that the matrix was lithified at the time the trails were formed. This model is
dependent upon the impermeability of the surrounding chert, which allowed pressure to build up
sufficiently to propel individual pyrite grains.

Wacey et al. (2008b) added some refinements to the Knoll and Barghoorn model by
suggesting that the (thermal) degassing of primary OM during early stages of diagenesis may have
been insufficient by itself to propel mineral grains, and that the biological activity of living
microbial communities may have assisted movement by locally increasing pH to promote silica
dissolution on the front face of the moving grains. This aspect of the model was based on a
reference to living experiments that claim to show silica dissolution by diatoms, heterotrophic
bacteria and cyanobacterial biofilms (Brehm et al., 2005). The ability of microorganisms to inhabit
the early diagenetic stage of deposition that produced AITs is not well-known however. Diatoms
did not evolve until the Mesozoic, so if their role in the microbial dissolution of silica in extant
settings is essential, support of this aspect of AIT formation would wane. As pointed out by Wacey
et al. (2008b) more experimental work will have to be done to ascertain the extent to which living
microbial communities were directly or indirectly essential for AIT formation.

The facts that AITs are filled with calcite whereas the cement between the apatite granules is
dolomite and that AITs never cut through the dolomitic cement (Figs. 3o, 3u and 4) suggest that
the formation and infilling of AITs took place before pervasive dolomite cementation during early
diagenesis. Considering the sub-micrometer size of apatite crystals and exceptional preservation of
microfossils in the Doushantuo phosphorites (e.g., Xiao et al., 1998; She et al., 2014), phosphate
crystallization must have been a rapid process during which diagenetic oxidation of OM could have produced CO$_2$ gas. It is well known that biogenic gas can be trapped within microbial mats and lead to gas domes during early diagenesis in modern environments (e.g., Gerdes et al., 1993). Similar microbial mats or EPS preserved in phosphatic granules probably facilitated trapping of gas during early diagenesis of the Doushantuo Formation. Moreover, the low permeability of nanoscopic phosphate could have allowed pressure to build up inside the granules which eventually led to propulsion of the pyrites. Therefore, we propose that propulsion of the pyrites probably took place sometime between the initiation of apatite crystallization and the final lithification of apatite granule.

The almost exclusive calcite infilling of AITs in the Doushantuo phosphorites is also notable. We hypothesize that calcium carbonate precipitation in the Doushantuo AITs was a natural product of organic decomposition during putrefaction of biomass, which is known to form gaseous CO$_2$ or HCO$_3^-$ in pore water solutions. Many microbial processes can be involved in putrefaction and these contribute to the production of CO$_2$, however some non-biological processes may also be involved in organic decomposition. During the post-glacial oxygenated world of the Doushantuo Formation, sulfate was more abundant than before and was trapped as phosphate associated sulfate in the apatite, such as in microfossiliferous granules of apatite in phosphorite from Yichang, as detected by as trace by NanoSIMS (She et al., 2013). The corrosive effects of sulfuric acid on biomass lead to the escape of CO$_2$ and hydrogen sulfide, which can conceivably form nano- to micrometric pyrite if Fe$^{2+}$ is present in solution. Since Ca$^{2+}$ and Mg$^{2+}$ were also present during diagenesis as inferred from the co-occurrence of micron-size calcite flakes in AIT, massive intergranular dolomite, and apatite in granules, we propose the following non-biological reaction
for the source of carbonate and hydrogen sulfide:

\[ CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + H_2S + 2H_2O \] (01)

In this reaction, the reactants include humic acid represented by CH$_3$COOH (acetic acid) and sulfuric acid, now preserved as kerogen and phosphate-associated sulfate, respectively. The reaction products of this reaction are thus proposed to underlie the non-biological formation of AITs from the products of the oxidation of biomass with sulfate reduction.

The H$_2$S then combines with dissolved ferrous iron to form colloidal FeS, which subsequently converts to Fe$_3$S$_4$ (greigite) that is thermodynamically unstable relative to pyrite (Berner, 1967). Fe$_3$S$_4$ aggregates into close-packed microcrystals, forming greigite frambooids (Taylor, 1982).

Pyritization of the greigite through Fe loss is represented by the following reaction (Furukawa and Barnes, 1995):

\[ Fe_3S_4 + 2H^+ \rightarrow 2FeS_2 + Fe^{2+} + H_2 \] (2)

This leads to the formation of discrete euhedral pyrite grains or frambooidal pyrites, depending on the rate of pyritization (Wilkin and Barnes, 1996). Following the burial of the pyrites with the phosphate containing OM, further oxidative degradation of the OM produces abundant CO$_2$ gas.

While the phosphatic gel was not fully lithified in order to allow plastic deformation, it was sufficiently sealed and viscous to prevent CO$_2$ escape, thereby creating a pressure on the pyrite and force it through the phosphate substrate. Propulsion of single pyrite crystals with smooth or striated surfaces might have produced types I-a and I-b AITs, respectively, whereas propulsion of intact pyrite frambooids probably led to the formation of type II-a AITs (Table 5 and Fig. 8a). In most cases, however, oxidation of OM inside pyrite frambooids might have created local high pressure environments in between microcrystals in the viscous gel, which could have led to the
eventual explosions of such framboids and produced type II-b AITs (Fig. 8b). Similar mechanism 
may also apply to type III AITs. This model explains the formation of dense clusters of the 
smallest AITs with similar diameters (equal to the diameter of the pyrite micro-crystals in 
framboids) (e.g., Knoll and Barghoorn, 1974, Fig. 2; Lepot et al., 2011, Fig. 5A; and Olempska 
and Wacey, 2016, Figs. 5A and G-H).

6. Conclusions

Abundant pyrite framboids and ambient inclusion trails have been documented from the 
Doushantuo Formation in the Baizhu, Yichang, and Weng'an sections, South China. Pyrite 
framboid size distributions in the black shale in Baizhu suggest that spatiotemporal redox 
variations in the shallow marine environments, probably with frequent occurrence of euxinic 
water columns stimulated by episodic cyanobacterial blooms, might have occurred during the 
Doushantuo period and promoted phosphogenesis. While pyrite framboids also occur in granular 
phosphorites of the Doushantuo Formation, they are more abundant in black shales, which do not 
contain AITs because of the less viscous nature of the siliciclastic matrix.

AITs presented in this study and previous works may be distinguished from filamentous 
microfossils and endolithic micro-borings with typical morphological features such as the 
presence of a terminal mineral grain or cluster and longitudinal striae. We also propose additional 
criteria for the recognition of AITs including the large variability of size, sharp outlines and 
distinct infilling materials. AITs are then categorized into three types and further into five subtypes 
(I-a, I-b, II-a, II-b, and III) based on their morphologies. Among these, types II AITs are 
interpreted to be associated with framboidal pyrites. During early diagenesis, pyrites formed
primarily through non-biological oxidation of OM and reduction of phosphate-associated sulfate in the presence of ferrous iron. Following the burial of pyrite frambooids, accumulation of CO$_2$ gas produced by oxidation of organic matter builds up the pressure and eventually drives the movement of pyrite frambooids, forming trails with striated walls in the viscous impermeable matrix of fluorapatite. While biological processes may have participated in AIT formation, their characteristics are more consistent with an indirect role by some microorganisms as well as a requirement for abundant organic matter and a viscous gelatinous matrix for their formation. Although it is unknown if AITs could form in similar context but only with non-biological organic matter, AITs should be considered an indirect morphological and mineral biosignature.

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Lepot, K., Benzerara, K. and Philippot, P., 2011. Biogenic versus metamorphic origins of diverse


Wignall, P.B. and Newton, R., 1998. Pyrite framboid diameter as a measure of oxygen deficiency in


Figure captions

Fig. 1 Geological map and stratigraphic column. (a), Simplified geological map of the study area during the early Ediacaran Period. Inset shows the geographic location of the Yangtze Block. Locations of the Baizhu and Taopinghe sections are indicated. (b), Measured stratigraphic column of the Doushantuo Formation in Baizhu showing sampled horizons. NT: Nantuo Formation; DY: Dengying Formation.

Fig. 2 Structures and microstructures of the Doushantuo phosphorites and the occurrences of AITs. (a-c), Outcrops of phosphorites: (a), Banded phosphorite; (b), Stromatolitic and lenticular phosphorite; (c), Concretionary phosphorite. (d), Intraclastic phosphorite containing detrital quartz (qtz) and carbonate (carb) and phosphatic (apa) intraclasts that are cemented by transparent phosphatic groundmass, transmitted light (TL). (e), Banded phosphorite showing intercalation of finely laminated organic-rich layers and silica-cemented granular layers, scanned image of a thin section. (f), Close-up view of the granular layer in (e) showing organically-zoned micro-oncoids (TL). (g), Banded phosphorite showing dark organic-rich phosphatic stripes (apa) and transparent dolomitic layers (dol), scanned image of a thin section. (h), Enlarged view of the marked area in (g) showing granular-clotted texture in the dark phosphatic stripe, (TL). (i), An AIT with an oxidized terminal pyrite crystal observed in a phosphatic granule; note that the trail appears to follow the margin of the granule. (j), Alternating light and dark laminae in a stromatolite-like structure. (k), Abundant AITs in massive cryptocrystalline apatite. (l), Numerous AITs in isotropic substrate in a banded phosphorite (d), the high-order white interference color indicating filling of the AITs with carbonate minerals, crossed nicols (XPL). All images are obtained from the Baizhu samples, except for (i) which is from a Taopinghe phosphorite.

Fig. 3 Photomicrographs and Raman hyperspectral images of AITs and associated pyrites in the Doushantuo phosphorites. (a), Curved and twisted AITs filled with carbonate. (b), Longitudinal section of a spiral AIT (center of the image) in a phosphatic granule; notice terminal pyrite grain which is of comparable size as the spiral AIT (arrow). (c), Longitudinal striae following angular pyrite crystals. (d), AITs cross-cutting phosphatic granules (arrows), limonite
coating clearly visible on the wall of the tubes. (e), AITs radiating from a central locus; note the hollow microtube of the AIT in the bottom right corner and the presence of an oxidized pyrite cluster (framboid?) at the terminus of the microtube near the bottom left corner (arrowed). (f), Oxidized hexagonal terminal pyrites (arrows) and associated microtubes. (g-h), possible partially oxidized pyrite framboids in interstitial quartz cement in a granular phosphorite. (i) a well preserved pyrite framboid (apparent diameter = 5.8 microns) in phosphatic granule. (j) Bend of an AIT caused by collision with another terminal pyrite (arrowed). (k), AITs radiating from an organic-rich center in different directions (arrows). (l), A cubic pyrite crystal followed by a striated trail (oblique section); inset is the reflected light image of the pyrite at the same scale. (m-o), "Starburst" type AITs: (m), numerous AITs radiating outward from an organic-rich mass in a phosphatic granule, arrow showing the moving direction of pyrites; (n), sketch of the clearest AITs in Fig. 3m and (o), Raman hyperspectral image of apatite (turquoise), organic matter (OM, red), interstitial dolomite cement (green), and calcite infillings (purple) in AITs for the marked area in (m). (p-u), Inward migrated AITs. (p), Abundant anhedral pyrites in a granule, some followed with trails of equal diameters; arrows indicate the direction of pyrite movements. (q-s), AITs filled with carbonate minerals which are clearly recognized by their high-order white interference colors. (s), Close-up of the marked area in (r) showing the inward migration (arrowed) of pyrite from outside or the outer envelope of a granule. (t), Corresponding reflected light image of the pyrites. (u), Raman hyperspectral image of apatite (turquoise), organic matter (OM, red), interstitial dolomite cement (green), and calcite infillings (purple) in AITs, same area as (r). In (o) and (u), pyrites were not detected because the laser energy was too low (1mW). Transmitted light, crossed nicols: (a) and (p-s); transmitted light, plane polarized: (b-g), (j-k), (m), (p) and (s); Reflected light: (h-i), (l) and (t). (a), (c) and (j): Baizhu samples; (b), (k) and (m-u): Weng'an samples; (d-i) and (l): Taopinghe sample.

Fig. 4 Secondary electron images of typical microstructures of AITs and pyrite framboids: (a), Part of a microtube showing fine longitudinal striae; note the nearly right angle of the walls of the microtube (arrowed). (b-d), Inward-facing cuspate longitudinal ridges (crude striae) on the wall of AITs, note the AIT in (c) exhibiting a spiral shape. (e), Casts of the microtubes of two AITs; notice
the longitudinal ridges that correspond to the striae in (a) and the square cross section of the upper cast (arrowed). (f) Porous calcite flakes filling a microtube. (g) Cross sections of AITs. (h-i) Pyrite framboid composed of cubic micro-crystals; notice that a thin membrane covers each of the micro-crystals in (i). (j-k) Pyrite micro-crystals showing dodecahedron habit. (l) Pyrite framboid composed of subhedral micro-crystals. (m) Framboid coated with a thin layer of amorphous material. (n) A cluster of euhedral pyrites with flat crystal surface. (o) Parallel aligned framboids in the dark laminae. All images were obtained with the secondary electron (SE) mode, except for (h), (j) and (o) which were taken using the backscattered electron (BSE) mode. (a) and (e) are from the Weng'an samples (granular phosphorites), others are from the Baizhu samples (b-d and f-g: phosphorites, h-o: black shales).

Fig. 5 Comparison of sizes of AITs and pyrite framboids. \( D_{frm} \) and \( d_{frm} \) refer to the diameters of framboid and micro-crystals, respectively. \( D_{AIT} \) and \( d_{AIT} \) refer to the diameters of the microtube and the spacing of longitudinal striae, respectively.

Fig. 6 Raman spectra of apatite, organic matter and carbonate minerals of various occurrences in the Doushantuo phosphorites.

Fig. 7 Stratigraphic distribution of pyrite morphology for the Baizhu section. Pyrite morphotypes: 0 — negligible pyrites; Py — only non-framboidal pyrites; Frm — both non-framboidal and framboidal pyrites. MFD, maximum framboid diameter.

Fig. 8 A new model for the formation of type II AITs.
Table 1 The occurrences and mineralogical context of AITs in the Baizhu phosphorites

<table>
<thead>
<tr>
<th>Host rock lithology</th>
<th>Distribution of AITs</th>
<th>Diameter of AITs</th>
<th>Terminal grains</th>
<th>Infilling mineral</th>
<th>Longitudinal striae</th>
<th>Organic matter</th>
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<tr>
<td>Organic-rich banded phosphorite</td>
<td>Light-colored phosphatic band</td>
<td>1-10 μm</td>
<td>Pyrite</td>
<td>Iron oxide, organic matter</td>
<td>Present</td>
<td>Abundant</td>
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<td>Intraclastic phosphorite</td>
<td>Light-colored interstitial cement</td>
<td>2-44 μm</td>
<td>Iron oxide</td>
<td>Calcite</td>
<td>Present</td>
<td>Rare</td>
<td>9,12</td>
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<tr>
<td>Concretionary phosphorite</td>
<td>Phosphatic laminae</td>
<td>5-12 μm</td>
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<td>Iron oxide, organic matter</td>
<td>Present</td>
<td>Abundant</td>
<td>11,12</td>
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<tr>
<td>Stromatolitic phosphorite</td>
<td>Phosphatic laminae</td>
<td>4-56 μm</td>
<td>Iron oxide</td>
<td>Calcite</td>
<td>Present</td>
<td>Common</td>
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Table 2 Sizes of pyrite framboids and micro-crystals and width of ATIs and spacings of their longitudinal striae

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<tr>
<th>Sample Number</th>
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</tbody>
</table>

Data marked with * was measured from Fig. 14 in Wacey et al., 2008b. D_{frm} and d_{frm} refer to the diameter of individual framboids and mean diameter (n=5) of micro-crystals in the respective framboid, respectively. D_{ART} and d_{ART} refer to the diameters of the microtube and the spacing of longitudinal striaions (mean value of 3 to 5 measurements), respectively.
Table 3 Size distributions of pyrite framboids in the Baizhu samples

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>H (m)</th>
<th>n</th>
<th>d_{MIN} (µm)</th>
<th>d_{MAX} (µm)</th>
<th>D_{MEAN} (µm)</th>
<th>S.D. (µm)</th>
<th>R_D</th>
<th>R_F</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK8-1</td>
<td>11.3</td>
<td>214</td>
<td>1.6</td>
<td>7.3</td>
<td>3.8</td>
<td>1.0</td>
<td>12%</td>
<td>45%</td>
</tr>
<tr>
<td>BK13-1</td>
<td>25.6</td>
<td>231</td>
<td>1.6</td>
<td>7.4</td>
<td>4.1</td>
<td>1.0</td>
<td>18%</td>
<td>80%</td>
</tr>
<tr>
<td>BK14-2</td>
<td>28.6</td>
<td>200</td>
<td>1.7</td>
<td>6.7</td>
<td>3.3</td>
<td>0.9</td>
<td>4%</td>
<td>20%</td>
</tr>
<tr>
<td>BK17-1</td>
<td>32.9</td>
<td>194</td>
<td>1.8</td>
<td>9.3</td>
<td>4.5</td>
<td>1.7</td>
<td>29%</td>
<td>30%</td>
</tr>
<tr>
<td>BK17-2</td>
<td>33.4</td>
<td>236</td>
<td>1.0</td>
<td>10.8</td>
<td>3.6</td>
<td>1.4</td>
<td>16%</td>
<td>70%</td>
</tr>
<tr>
<td>BK20-2</td>
<td>40.8</td>
<td>194</td>
<td>0.9</td>
<td>7.8</td>
<td>3.2</td>
<td>1.3</td>
<td>10%</td>
<td>30%</td>
</tr>
<tr>
<td>BK20-3</td>
<td>41.7</td>
<td>200</td>
<td>1.3</td>
<td>7.7</td>
<td>3.0</td>
<td>1.0</td>
<td>5%</td>
<td>25%</td>
</tr>
<tr>
<td>BK20-4</td>
<td>41.9</td>
<td>207</td>
<td>1.4</td>
<td>7.5</td>
<td>3.0</td>
<td>1.0</td>
<td>4%</td>
<td>40%</td>
</tr>
<tr>
<td>BK23-1</td>
<td>49.1</td>
<td>200</td>
<td>1.3</td>
<td>6.9</td>
<td>3.7</td>
<td>1.2</td>
<td>14%</td>
<td>50%</td>
</tr>
</tbody>
</table>

Abbreviations: H - the stratigraphic level of sampling locality from the base of the Doushantuo Formation. “n” - the number of framboidal pyrites analyzed. “d_{MIN}”, “d_{MAX}” and “d_{MEAN}” - minimum, maximum and mean diameter of framboidal pyrites, respectively. S.D. - standard deviation of framboid diameters. “R_D” - percentage of pyrite framboids with diameter ≥10 µm in the total pyrite framboids. “R_F” - the areal ratio of pyrite framboids to all pyrites.
Table 4 Raman spectral characteristics and estimated temperatures for the Doushantuo phosphorites in Baizhu

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>G Position FWHM Area</th>
<th>D1 Position FWHM Area</th>
<th>D2 Position FWHM Area</th>
<th>D3 Position Area</th>
<th>D4 Position Area</th>
<th>RA1 °C</th>
<th>RA2 °C</th>
<th>T1 °C</th>
<th>T2 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK10-14-2</td>
<td>1598.1 40.8 1237.9</td>
<td>1343.6 73.2 4032.5</td>
<td>1616.9 24.5 574.1</td>
<td>1533.6 1018.0</td>
<td>1219.7 1303.3</td>
<td>0.65</td>
<td>1.89</td>
<td>347</td>
<td>359</td>
</tr>
<tr>
<td>BK15-1_01</td>
<td>1599.3 41.8 761.6</td>
<td>1344.3 87.7 2644.1</td>
<td>1619.0 26.4 422.8</td>
<td>1530.9 633.7</td>
<td>1210.6 534.8</td>
<td>0.64</td>
<td>1.75</td>
<td>325</td>
<td>329</td>
</tr>
<tr>
<td>BK10-8-2_01</td>
<td>1601.8 44.4 17954.3</td>
<td>1349.8 55.9 38343.6</td>
<td>1625.3 20.8 4754.3</td>
<td>1520.9 13234.6</td>
<td>1285.4 23742.1</td>
<td>0.63</td>
<td>1.73</td>
<td>322</td>
<td>324</td>
</tr>
<tr>
<td>BK10-8-2_02</td>
<td>1601.7 44.0 17787.9</td>
<td>1349.8 52.1 34088.0</td>
<td>1625.2 21.0 4892.8</td>
<td>1530.0 9267.2</td>
<td>1315.0 33603.1</td>
<td>0.68</td>
<td>2.12</td>
<td>379</td>
<td>411</td>
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<tr>
<td>BK10-8-3_03</td>
<td>1600.2 44.9 2760.0</td>
<td>1342.1 114.8 9420.8</td>
<td>1619.4 27.3 1134.0</td>
<td>1535.0 2507.9</td>
<td>1203.2 1505.4</td>
<td>0.63</td>
<td>1.71</td>
<td>318</td>
<td>319</td>
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<tr>
<td>ZK511-32_01</td>
<td>1590.1 59.0 5227.7</td>
<td>1347.8 142.2 17593.8</td>
<td>1611.9 33.3 4123.6</td>
<td>1499.3 4054.3</td>
<td>1233.4 3247.3</td>
<td>0.61</td>
<td>1.55</td>
<td>291</td>
<td>285</td>
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</tbody>
</table>

Raman spectral parameters (RA1 and RA2) and respective temperatures (T1 and T2) were calculated using the equations proposed for low-grade metasediments by Lahfid et al. (2010).
Table 5 A genetic classification scheme of AITs based on morphological features and associated pyrites

<table>
<thead>
<tr>
<th>Types</th>
<th>AIT morphology</th>
<th>Associated pyrites (interpretation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-a</td>
<td>Non-striated single microtubes with variable widths</td>
<td>Smooth single crystals, euhedral to anhedral</td>
</tr>
<tr>
<td>I-b</td>
<td>Finely striated single microtubes with variable widths</td>
<td>Striated single crystals, euhedral to anhedral</td>
</tr>
<tr>
<td></td>
<td>Single microtubes 2-10 μm wide, with longitudinal</td>
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</tr>
<tr>
<td></td>
<td>striae often separated by inward-facing cusprate ridges</td>
<td></td>
</tr>
<tr>
<td>II-a</td>
<td>Star-burst type AITs with microtubes of comparable</td>
<td>Intact framboids generally 2-10 μm in diameter</td>
</tr>
<tr>
<td></td>
<td>widths (0.4-1.5 μm)</td>
<td></td>
</tr>
<tr>
<td>II-b</td>
<td>Micro-crystals from disintegrated framboids</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Cluster of microtubes with variable widths</td>
<td>Non-framboidal aggregates</td>
</tr>
</tbody>
</table>
Figure 1_2 columns_black-and-white
Figure 2_2 columns_black-and-white
Figure 3_continued_2 columns_black-and-white
Figure 4.2 columns_black-and-white
Figure 5_1 column_black-and-white

![Graph showing the relationship between Dfrm and DAIT (µm) and dfrm and dAIT (µm). The graph includes two linear regression lines: y = 0.1069x + 0.3419 (R² = 0.5145) for AITs and y = 0.1926x + 0.0231 (R² = 0.9238) for Pyrite framboids. The data points are represented by different symbols for AITs and Pyrite framboids.]
(1) Apatite groundmass stromatolitic phosphorite, Baizhu
(2) Apatite infillings in AIT intraclastic phosphorite, Baizhu
(3) Calcite infillings in AIT intraclastic phosphorite, Baizhu
(4) Calcite infillings in AIT banded phosphorite, Baizhu
(5) Calcite infillings in AIT banded phosphorite, Baizhu
(6) Calcite infillings in AIT banded phosphorite, Weng'an
(7) Dolomite cement granular phosphorite, Weng'an
(8) Calcite infillings in AIT granular phosphorite, Weng'an
(9) Dolomite cement granular phosphorite, Weng'an
(10) Organic-rich laminae banded phosphorite, Baizhu
(11) Disseminated OM banded phosphorite, Baizhu
(12) Disseminated OM in dolomite cement granular phosphorite, Weng'an
(13) OM particles in granule granular phosphorite, Weng'an

Raman Shift (cm$^{-1}$)
Figure 7.2 columns black-and-white

Pyrite Morphotype   Mean diameter (µm)   MFD (µm)
Figure 8.2 columns black-and-white

Initial state

(a) Oxidation of OM and formation of pyrite
\[ CH_2COOH + H_2SO_4 \rightarrow 2CO_2 + H_2S + 2H_2O \]
Residual OM
Phosphatic gel

(b) Oxidation of OM and formation of pyrite
Residual OM
Phosphatic gel

Final state

Type II-a
Propulsion
Microtubes filled with calcite
\[ Ca^{2+} + CO_2 + 2OH^{-} \rightarrow CaCO_3 + H_2O \]
Longitudinal striae
Unlithified apatite-substrate

Type II-b
Disintegration and propulsion
Microtubes filled with calcite
Unlithified apatite substrate