Magnetite texture and trace-element geochemistry fingerprint of pulsed mineralization in the Xinqiao Cu–Fe–Au deposit, Eastern China

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The origin of stratabound deposits in the Middle-Lower Yangtze River Valley Metallogenic Belt (MLYRB), Eastern China, is the subject of considerable debate. The Xinqiao Cu–Fe–Au deposit in the Tongling ore district is a typical stratabound ore body characterized by multi-stage magnetite. A total of six generations of magnetite have been identified. Mt1 is commonly replaced by porous Mt2, and both are commonly trapped in the core of Mt3, which is characterized by both core-rim textures and oscillatory zoning. Porous Mt4 commonly truncates the oscillatory zoning of Mt3, and Mt5 is characterized by 120° triple junction texture. Mt1 to Mt5 are commonly replaced by pyrite that coexists with quartz, whereas Mt6, with a fine-grained foliated and needle-like texture, commonly cuts the early pyrite as veins and is replaced by pyrite that coexists with calcite. The geochemistry of the magnetite suggests that they are hydrothermal in origin. The microporosity of Mt2 and Mt4 magnetite, their sharp contacts with Mt1 and Mt3, and lower trace element contents (e.g., Si, Ca, Mg, and Ti) than Mt1 and Mt3 suggest that they formed via coupled dissolution and reprecipitation of the precursor Mt1 and Mt3 magnetite, respectively. This was likely caused by high-salinity fluids derived from intensive water-rock interaction between the magmatic-hydrothermal fluids associated with the Jitou stock and Late Permian metalliferous black shales. The 120° triple junction texture of Mt5 suggests it is the result of fluid-assisted recrystallization, whereas Mt6 formed by replacement of hematite as a result of fracturing. The geochemistry of the magnetite suggests that the temperature increased from Mt2 to Mt3, and implies that there were multiple pulses of fluids from a magmatic-hydrothermal system. Therefore, we propose that the Xinqiao stratiform mineralization was genetically associated with multiple influxes of magmatic hydrothermal fluids derived from the Early Cretaceous Jitou stock. This
study demonstrates that detailed texture examination and in-situ trace elements analysis under robust geological and petrographic frameworks can effectively constrain the mineralization processes and ore genesis.

Keywords: Magnetite; Stratabound mineralization; Xinqiao Cu–Fe–Au deposit; Middle–Lower Yangtze River Valley Metallogenic Belt.
INTRODUCTION

Magnetite is a ubiquitous mineral phase in different geological environments and represents a dominant metallic mineral phase in wide variety of hydrothermal ore systems (Nadoll et al. 2014, 2015). Octahedral and tetrahedral coordinated positions in the magnetite structure provide host sites for many trace elements (e.g., Al, Mn, Ti, V, Ni, Cr, Zn, Co, Sn, Ga, and Mg) via isovalent and coupled substitutions (Dupuis and Beaudoin 2011; Nadoll et al. 2012; Deditius et al. 2018). The trace-element compositions of hydrothermal magnetite are mainly governed by the composition of the hydrothermal fluids, temperature, oxygen fugacity ($f_{O_2}$), sulfur fugacity ($f_{S_2}$), co-crystallized mineral phases and fluid-rock interactions (McIntire 1963; Dare et al. 2012, 2014; Nadoll et al. 2014; Knipping et al. 2015; Huang et al. 2019a, b; Liu et al. 2019; Salazar et al. 2019; Sun et al. 2019). Therefore, a number of studies have focused on the trace-element geochemistry of magnetite to constrain mineralization type and ore genesis (Beaudoin et al. 2007; Dupuis and Beaudoin 2011; Dare et al. 2012, 2014; Nadoll et al. 2012, 2014, 2015), fingerprint the temporal and/or spatial evolution of the ore-forming hydrothermal fluids (e.g., Li et al. 2019; Liu et al. 2019), and reconstruct the mineralization processes (e.g., Li et al. 2019; Hu et al., 2020). More importantly, magnetite undergoes dissolution and reprecipitation (DRP), oxy-exsolution, and/or recrystallization to reach chemical and textural re-equilibration, and consequently detailed studies of internal textures are necessary before conducting trace-element analyses (Hu et al. 2014, 2015; Salazar et al. 2019).

The Middle-Lower Yangtze River Valley Metallogenic Belt (MLYRB), Eastern China, is one of the most important mining regions in China, and is characterized by abundant large stratabound deposits (e.g., the Dongguashan Cu–Au deposit and the Xinqiao Cu–Fe–Au deposit; Mao et al.
The origin of these stratabound deposits is still a matter of debate with a number of models proposed including Late Paleozoic submarine exhalative processes (SEDEX, e.g., Gu et al. 2000; Xu and Zhou 2001), Early Cretaceous magmatic-hydrothermal fluids (skarn-type, e.g., Pan and Done 1999; Mao et al. 2009, 2011; Zhang et al. 2017b, c, 2018; Li et al. 2017, 2018a, 2019), or a combination of the two (e.g., Tang et al. 1998; Zhou et al. 2010; Guo et al. 2011). The Xinqiao Cu–Fe–Au deposit in the Tongling ore district has a proven reserve of 0.5 Mt Cu @ 0.71%, 24.9 Mt Fe @ 46%, 11.2 t Au @ 4.7g/t and 248.4 t Ag @ 248.4 g/t (Xu and Zhou 2001), and is dominated by a large-scale stratiform orebody with extensive skarn alteration and unique colloform pyrite (Zhang et al. 2017a). The fact that colloform pyrite in the Xinqiao stratiform orebody is cut by magnetite veins is consistent with a syn-depositional origin of colloform pyrite (Xiao et al. 2016). However, in-situ Sensitive High Resolution Ion Microprobe (SHRIMP) sulfur isotope compositions ($\delta^{34}$S$_{CDT} = -0.6$ to 2.7‰, Avg. 0.58‰; Zhang et al. 2017a) and Co/Ni ratios (0.67 to 2.94, Avg.1.66; Zhang et al. 2017a) of the colloform pyrite, similar ages between colloform pyrite (Re–Os age: 136.7 ± 4.6 Ma; Li et al. 2018a) and the quartz diorite of the Jitou stock at Xinqiao (zircon U–Pb age: 139.6 ± 1.5 Ma; Zhang et al. 2017c), coupled with the fact that colloform pyrite cements massive magnetite (Zhang et al. 2017a) suggests a magmatic hydrothermal origin for the colloform pyrite and the occurrence of multi-stage magnetite in the Xinqiao stratiform orebody. Therefore, the complex magnetite at Xinqiao offers an excellent opportunity to examine the detailed paragenesis of the stratiform mineralization in MLYRB.

This paper reports data for a paragenetically well-constrained suite of magnetite-bearing samples from the Xinqiao deposit. Using back-scattered electron (BSE) imaging of internal textures combined with electron probe microanalyzer (EPMA) and laser ablation inductively
coupled plasma mass spectrometry (LA-ICP-MS) analysis of magnetite, the textures and
geochemistry of the multi-stage magnetite at Xinqiao have been documented. These results
provide new constraints on the origin of the Xinqiao stratiform mineralization, and the stratabound
deposits of the MLYRB.

GEOLOGICAL BACKGROUND

Regional geology

The Middle–Lower Yangtze River Valley Metallogenic Belt is located along the northern
margin of the Yangtze craton, which is separated from the North China craton to the north by the
Triassic Qinling-Dabieshan orogenic belt, and from the Cathaysian block to the south by a
Neoproterozoic suture (Fig. 1a; Li et al. 2014; Zhang et al. 2019). The belt hosts seven ore
districts, which are from west to east the Edong, Jiurui, Anqing-Guichi, Luzong, Tongling,
Ningwu and Ningzhen districts with more than 200 known polymetallic deposits (Fig. 1a; Ling et
al. 2009). The Tongling ore district, located in the central part of MLYRB (Fig. 1a), is the largest
Cu–Au–Fe–Mo ore district in the belt and hosts numerous skarn deposits (Tang et al. 1998; Pan
and Dong 1999; Lai and Chi 2007; Mao et al. 2011; Sun et al. 2019). More than 50 ore deposits
have been discovered in the Tongling district, clustered in five ore fields, namely Tongguanshan,
Shizishan, Xinqiao, Fenghuangshan and Shatanjiao, distributed from east to west (Wu et al. 2014;
Fig. 1b). The dominant lithologies in the Tongling district are marine and continental sedimentary
rocks. Marine sedimentary rocks, including clastic sedimentary rocks, carbonates and evaporites,
were deposited in the Silurian to Middle Triassic, with a break in the Early to Middle Devonian.
Continental rocks including clastic and volcanic-sedimentary rocks were deposited from the

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Middle Jurassic to Quaternary, with a break in the Middle-Late Devonian (Wang et al. 2015; Cao et al. 2017). These sedimentary rocks were deposited on a stable Precambrian basement and are the host rocks for later Cu, Au, Fe, and Mo mineralization (Chang et al. 1991; Zhai et al. 1992). The Lower Permian Qixia Formation and the Lower Triassic Nanlinghu Formation are dominated by limestone and are important ore-hosting strata for the widespread skarn mineralization in the district. The unconformity between the quartz sandstone of the Upper Devonian Wutong Formation and the dolomite and limestone of the Upper Carboniferous Huanglong Formation constrains the economically significant stratiform mineralization in this district, including the Xinqiao and Dongguashan deposits. Structurally, the region contains NE-trending folds and NNE- and NW-trending faults that have influenced the emplacement of the intrusions. Igneous rocks are widely distributed in the region and are dominated by Late Jurassic – Early Cretaceous (ca. 156 to 137 Ma) high-K calc-alkaline granitoids (e.g., granite porphyry, granodiorite porphyry and quartz monzodiorite; Fig. 1b; Mao et al. 2011; Wang et al. 2015; Cao et al. 2017). Many small plutons occur as composite stocks, dikes and sills (Du et al. 2015).

Ore deposit geology

The outcropping sedimentary rocks in the mining area range from the Middle-Upper Silurian sandstone and siltstone to the Lower Triassic Yinkeng Formation limestone, whereas the Lower Carboniferous unit is absent. The NE-trending Dachengshan anticline and the NNE-trending Shenchong syncline are the major structures at Xinqiao, and have influenced the emplacement of the magmatic rocks (Fig. 2a). The dominant igneous rock in the region is the Jitou stock, which occurs in the core of the Shenchong syncline as a multiphase intrusion with quartz diorite at the
center and diorite porphyry along the margins. The quartz diorite has yielded Early Cretaceous SHRIMP and LA-ICP-MS zircon U–Pb ages of 140.4 ± 2.2 Ma (Wang et al. 2004) and 139.6 ± 1.5 Ma (Zhang et al. 2017c), respectively.

There are two major mineralization types at Xinqiao, namely the economically significant stratiform mineralization (No. I Orebody, accounting for 90% of the Cu, S and Fe reserves of deposit) and the economically less important skarn mineralization (No. V Orebody). The stratiform mineralization is confined to the unconformity between the Upper Devonian Wutong Formation quartz sandstone and the Upper Carboniferous Huanglong Formation limestone, whereas the skarn-type mineralization is hosted along the intrusive contact between the Jitou stock and the Lower Permian Qixia Formation limestone (Fig. 2b).

The stratiform orebody is 2560 m long, 1810 m wide, averaging 21 m thick, striking NE and dipping to the NW, parallel to the Upper Devonian Wutong and the Upper Carboniferous Huanglong formations (Fig. 2b), with a quartz-pyrite stockwork in the Upper Devonian Wutong Formation quartz sandstone acting as the footwall to the stratiform orebody. The stratiform ores have replaced the limestones of the Middle and Upper Carboniferous Huanglong and Chuanshan formations, with the Lower Permian Qixia Formation limestone and chert forming the hanging wall (Fig. 2b). The ore minerals in the stratiform orebody include magnetite, chalcopyrite, pyrrhotite, hematite, native gold and electrum (Dai and Liu 1984), whereas gangue minerals include primarily garnet (two stages of garnet; Zhang et al. 2017b, 2018), diopside, epidote, chlorite, quartz and calcite. The metallic mineral assemblages in the stratiform orebody show proximal to distal zoning away from the Jitou stock: magnetite + pyrite → chalcopyrite + pyrite → pyrite (Zhang et al. 2017c). The wall rock alteration includes garnet, sericite, quartz, chlorite
and kaolinite, with silicic alteration mainly developed in the footwall of the orebody. The
paragenetic sequences of mineralization and alteration within Xinqiao was documented by Zhang
et al. (2017a, c). It can be divided into five stages, the early skarn (Stage I, garnet – diopside), late
skarn (Stage II, epidote – magnetite), metallic oxide (Stage III, hematite), colloform pyrite (Stage
IV) and quartz-sulfide (Stage V, quartz – chalcopyrite – pyrite).

Both the endoskarn and exoskarn ore-bodies are calcic skarn, and consist predominately of
garnet, wollastonite and subordinate pyroxene (Wang et al. 2011). Major metallic minerals include
massive / vein / disseminated magnetite, pyrite, chalcopyrite, pyrrhotite, sphalerite and galena.

SAMPLING AND ANALYTICAL METHODS

Sampling

A total of ten magnetite-bearing samples (XQ11-3, XQ17-1, XQ17-3, XQ22-2, XQ22-7,
XQ33-11, XQ47-6, D006-5, D006-7 and D006-10) were collected from the Xinqiao stratiform
orebody. Samples XQ11-3, XQ17-1 and XQ17-3 were collected from the southwest part of the 60
m level in the Xinqiao open pit. Samples XQ22-2 and XQ22-7 were collected underground in the
E24 stope at depths of −270 m. Sample D006-5 were collected in the W16 stope underground at
depths of −270 m. Sample XQ47-6 was collected in the No. 6 Tunnel at a depth of −300 m, and
samples XQ33-11, D006-7 and D006-10 were collected in the W105 stope at a depth of −300 m.
Detailed sample locations are shown in Figure 2.

Analytical methods

Prior to the EPMA and LA-ICP-MS in-situ major and trace elements analysis, BSE imaging
of the magnetite samples was carried out using a TESCAN MIRA3 field emission scanning electron microprobe (FE-SEM) at the Testing Center, Tuoyan Analytical Technology Co. Ltd. (Guangzhou, China). Working conditions of the BSE imaging include 20 kV accelerating voltage and 15nA beam current.

In-situ major element analysis using EPMA was carried out in the School of Geosciences and Info-Physics of the Central South University, using a 1720 EPMA (Shimadzu Corporation, Japan). Analytical parameters include 15kv (acc. voltage), $2.0\times10^{-8}$ A (probe current) and 1μm (spot size), with a detection limit of 0.01%. By using a spot size of 1μm it is possible to effectively avoid the influence of micro-inclusions trapped in magnetite. Elements analyzed include TiO$_2$, SiO$_2$, FeO, MnO, NiO, CoO, Cr$_2$O$_3$, CaO, V$_2$O$_3$, Al$_2$O$_3$, and MgO. The analyses were calibrated using natural and synthetic mineral standards as follows: spinel for Mg and Al, diopside for Si and Ca, ilmenite for Ti, chromite for Cr and Fe, manganese oxide for Mn, niccolite (NiAs) for Ni, cobalt metal for Co, and vanadium metal for V.

Magnetite LA-ICP-MS trace element analysis was carried out at the Key Laboratory of Marine Resources and Coastal Engineering, Sun Yat-sen University. The detailed method for in-situ trace-element analysis for magnetite is given in Sun et al. (2017). The analysis was performed using a pulsed 193 nm ArF Excimer laser (GeoLasPro), and ion-signal intensities were acquired using an Agilent 7700x ICP-MS. A 32 μm spot was used with an energy density of 8 J/cm$^2$ and a repetition rate of 5 Hz. The trace element compositions of magnetite were calibrated against the USGS synthetic basalt glass GSE-1G, using Fe determined by EPMA data as the internal standard. Each analysis consisted of a 20 s background measurement (laser-off) followed by 45 s of data acquisition. Data reduction was performed using the ICPMSDataCal software (Liu...
et al. 2010). Twenty-three elements were analyzed (Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Sn, W, Au, Pb, Bi, Th and U).

RESULTS

Petrogenesis, internal texture and paragenesis of magnetite

Based on mineral assemblages and textural relationships, six stages of magnetite were identified in the Xinqiao stratiform orebody. Magnetite in the first four stages can be identified in samples of XQ33-11, XQ47-6, D006-7, and D006-10. The fifth stage of magnetite (Mt5) is corresponding to samples of XQ22-2, XQ22-7, and D006-5, whereas the sixth stage of magnetite (Mt6) occurs in samples of XQ11-3, XQ17-1, and XQ17-3. These stages are described in greater detail as follows:

The first stage of magnetite (Mt1) commonly occurs as anhedral grains ranging from 5 to 10 μm, and is dark gray under BSE (Fig. 3a and b). It is often replaced by porous anhedral second stage magnetite (Mt2) which is light gray under BSE and 5 to 10μm in size (Fig. 3b). The boundary between Mt1 and Mt2 is irregular and sharp (Fig. 3b), consistent with replacement textures.

The third stage of magnetite (Mt3) commonly coexists with epidote as disseminated or massive forms and replaces the early garnet (Fig. 3c). It occurs as subhedral (Fig. 3c) or anhedral (Fig. 3d) grains ranging from 200 to 400 μm, and is commonly replaced by quartz, apatite, and pyrite (Fig. 3d). In BSE imaging, Mt3 are characterized by well-developed oscillatory zoning and core-rim textures (Fig. 3e–h). Importantly, Mt1 and Mt2 are only found in the cores of Mt3 grains (Fig. 3e and f). The cores (Mt3c; ca. 40–100 μm in size) of Mt3 are typically darker gray than the
rims (Mt3r; ca. 100–200 μm in size). Both Mt3c and Mt3r display chemical oscillatory zoning, parallel to the contact interface between Mt3c and Mt3r (Fig. 3f and h), which is consistent with growth zoning rather than replacement of multistage magnetite.

The local fourth stage of magnetite (Mt4) is porous and anhedral, and typically lighter gray than Mt3r in BSE imaging (Fig. 3g and h). It dominantly occurs as irregular veins (ca. 2–5μm in width) or patches (ca. 1–5μm in size) and truncates the oscillatory zoning of both Mt3c and Mt3r (Fig. 3g and h), indicating it formed later than Mt3.

Mt5 occurs close to the Jitou stock with massive textures (Fig. 3i). It is commonly cut by pyrite stockwork or replaced by disseminated pyrite (Fig. 3i). The magnetite primarily occurs as anhedral grains between 50 and 300 μm and is characterized by a well-defined 120° triple junction texture, an indication of textural equilibration and recrystallization of Mt1–Mt4 (Fig. 3j; Hu et al. 2015). The margins of the majority of magnetite grains are commonly oxidized into hematite (Fig. 3j). Mt5 shows homogeneous internal textures under BSE (Fig. 3k).

Mt6 commonly cuts the crystal (Fig. 3l) and colloform pyrite (Fig. 3m) as veins. The colloform pyrite in the reaction front with this magnetite vein has commonly recrystallized to crystal pyrite (Fig. 3m). Mt6 formed by replacement of hematite based on the metasomatic pseudomorph textures, particularly the fine-grained foliaceous (Fig. 3m) or needle-like (Fig. 3n and o) textures, generally 10–25μm across but up to ca. 60μm. Additionally, Mt6 is commonly replaced by later pyrite that coexists with calcite (Fig. 3n). Siderite occurs as anhedral grains among Mt6 grains in veins (Fig. 3m). Under BSE, Mt6 also shows homogeneous internal textures (Fig. 3p). Importantly, Mt1 to Mt5 are commonly replaced by pyrite coexisting with quartz, which is subsequently cut by Mt6 veins replaced by pyrite coexisting with calcite, indicating that Mt6 is...
the final magnetite stage at Xinqiao.

**Major element geochemistry**

A total of 130 EPMA spot analyses were completed on the six magnetite samples, with 16, 15, 15, 17, 20, 37 and 10 spots on Mt1, Mt2, Mt3c, Mt3r, Mt4, Mt5 and Mt6, respectively. The major element compositions of the six stages of magnetite at Xinqiao are listed in Appendix 1 and shown on Figure 4a. The contents of FeO, CoO and Al\(_2\)O\(_3\) were above detection limits in all samples. The contents of TiO\(_2\), SiO\(_2\), Cr\(_2\)O\(_3\), V\(_2\)O\(_3\) and MgO in most analysis are above the detection limits, whereas those of MnO, NiO and CaO were below detection limits. In general, Mt1 (86.25–90.02 wt. %; Avg. 88.37 wt. %) and Mt3c (87.80–89.28 wt. %; Avg. 88.49 wt. %) have lower FeO contents than Mt2 (91.65–93.16 wt. %; Avg. 92.35 wt. %), Mt3r (90.17–91.85 wt. %; Avg. 90.91 wt. %), Mt4 (89.38–93.28 wt. %; Avg. 92.34 wt. %), Mt5 (90.12–93.20 wt. %; Avg. 91.97 wt. %) and Mt6 (92.47–93.20 wt. %; Avg. 92.89 wt. %).

**Trace element geochemistry**

Mt1, Mt2 and Mt4 were too small for LA-ICP-MS analysis. Therefore, LA-ICP-MS spot analysis were conducted on six magnetite samples, with 18, 29, 38 and 13 spots on Mt3c, Mt3r, Mt5 and Mt6, respectively. All data was examined using time-resolved LA-ICP-MS signals, and only flat and stable signals of trace elements were selected to calculate their contents. Trace elements contents for the Xinqiao magnetite are listed in Appendix 2 and shown on Fig. 4b, with the corresponding detection limits listed in Appendix 3. Most of the data (> 60%) for Cu, As, Au and Bi are below detection limits. In general, Mt3, Mt5 and Mt6 have higher Mg, Al, Si, Ca and ...
Mn contents (generally higher than 100 ppm; Fig. 4) than the other stages of magnetite. Mt3 has higher Al (Avg. 8131 ppm), Si (Avg. 8266 ppm), Ti (Avg. 484 ppm) contents than Mt5 (Al: Avg. 482 ppm, Si: Avg. 2658 ppm, Ti: Avg. 1447 ppm, Si: Avg. 2398 ppm, Ti: Avg. 19.381 ppm), and Mt6 has the lowest contents of Al, Ti and Sn (Avg. 2.940 ppm), and the highest contents of Sc (Avg. 8.780 ppm), Ni (Avg. 1.565 ppm), Ge (Avg. 10.632 ppm), As (Avg. 51.331 ppm), W (Avg. 61.554 ppm), Pb (Avg. 4.781 ppm) and U (Avg. 1.790 ppm). Mt3c have higher Mg, Al, Si, Ca, Sc, Ti, Cu and Ga, and lower Cr, Mn, Co, Ni, Zn, As, Pb and Th contents than Mt3r. More importantly, Mt2 and Mt4 have lower trace-element concentrations (esp., Ti, Si, Ca and Mg; Fig. 4) than Mt1 and Mt3.

DISCUSSION

Origin of the Xinqiao magnetite

The trace-element geochemistry of magnetite can be used to investigate both the origin and paragenesis of the mineralized system (Dupuis and Beaudoin 2011; Nadoll et al. 2012, 2014, 2015). Therefore, it is essential to document the origin of the six-stages of the Xinqiao magnetite prior to discussing the ore-forming processes and the origin of the mineralization.

The FeO contents of Mt1, Mt3c, Mt2 and Mt4 are similar, but TiO$_2$, SiO$_2$, MnO, Cr$_2$O$_3$, CaO, Al$_2$O$_3$ and MgO vary between Mt1 and Mt3c, and SiO$_2$, MnO and CaO between Mt2 and Mt4 (Fig. 4a) reveal that Mt1 is not the residue of Mt3c after being replaced by Mt4, and that porous Mt2 is not equal to porous Mt4, supporting four distinct stages for the magnetite consistent with the internal textural differences between Mt3c with chemical oscillatory zoning and homogenous Mt1.

Dare et al. (2014) proposed a Ti versus Ni/Cr discriminant diagram to distinguish magnetite from...
igneous and hydrothermal origins based on the different behavior of Ni and Cr in magmatic and hydrothermal systems, but it is not very useful for hydrothermal magnetite formed in aqueous fluids at high temperature (T) or magmatic magnetite in absence of coprecipitating Fe sulfides (Knipping et al. 2015; Huang et al. 2019a). Some other diagrams, including Ti versus V (Nadoll et al. 2015) and V/Ti versus Fe (Wen et al. 2017), have also been proposed to discriminate between igneous and hydrothermal magnetite. At Xinqiao, most of the magnetite plots in the hydrothermal magnetite zone in both Ti versus V (Fig. 5a) and V/Ti versus Fe (Fig. 5b) diagrams. Furthermore, the Xinqiao magnetite contains low Ti (0.268–802 ppm) and V (0.483–625 ppm) (Appendices 1 and 2), distinct from igneous magnetite which is ubiquitously enriched in these lithophile elements when compared to hydrothermal magnetite (Dare et al. 2014; Nadoll et al. 2015).

Mt1 and Mt3 have been extensively replaced by light grey Mt2 (Fig. 3b) and Mt4 (Fig. 3g and h), respectively, preferentially along microfractures within or along grain margins. The well-developed microporosity in Mt2 and Mt4, their sharp contacts with Mt1 and Mt3, and the lower trace element contents (esp., Si, Ca, Mg, and Ti) from Mt1 to Mt2, and Mt3 to Mt4 (Appendix 1; Fig. 4a) suggest that they formed by coupled dissolution and reprecipitation (DRP) of the precursor Mt1 and Mt3 grains (Putnis 2009; Putnis and John 2010; Dare et al. 2015; Hu et al. 2015; Heidarian et al. 2016). The DRP is facilitated by a fluid-assisted process with dissolution of early magnetite and precipitation of a secondary variety near the reaction front, with Si, Ca, Mg, and Ti being removed from the early magnetite, and volume loss resulted in pervasive micro-porosities, that were conducive for fluid infiltration that contributed to further dissolution of magnetite (Hu et al. 2014, 2015).

Mt5 is characterized by 120° triple junction textures, which can form from either
high-temperature annealing in a closed system or fluid-assisted replacement in an open system (Nakamura and Watson 2001; Ciobanu and Cook 2004; Hu et al. 2015). Mt5 is characterised by distinct trace-element compositions compared to the other magnetite stages (esp., Mg, Al, Ca, V, Co, Ni and Cu; Fig. 4b), suggesting that Mt5 is most likely the result of fluid-assisted recrystallization processes rather than high-T annealing, and consistent with a hydrothermal origin.

Mt6 veins cut the euhedral and colloform pyrite which formed from magmatic hydrothermal fluids (Zhang et al. 2017a; Li et al. 2018a), and the colloform pyrite in the reaction front with Mt6 has recrystallized to euhedral pyrite (Fig. 3m). This suggest a hydrothermal origin for Mt6 and early hematite. The fact that hydrothermal magnetite and hematite formed later than the main sulfide mineralization stage is not common in either skarn-type or SEDEX deposits, and may reflect a distinct geological process. At Xinqiao, mineralization would have resulted in the conversion of carbonate to skarn that would release abundant CO\(_2\), and gradually increase the pressure within the mineralization system (Meinert et al. 2005). When the fluid pressure exceeds the lithostatic load, increasing shear stress creates extensive hydraulic fractures (Sibson et al. 1988), consistent with the magmatic hydrothermal origin of the broadly coeval quartz-pyrite stockwork mineralization in the Wutong Formation quartz sandstone (Rb–Sr isotope isochron age of quartz fluid inclusions from stockwork mineralization: 138.0 ± 2.3 Ma; zircon U–Pb dating of Jitou stock: 139.6 ± 1.5 Ma; Zhang et al. 2017c) and initial \(^{87}\text{Sr}/^{86}\text{Sr}\) values (quartz fluid inclusions from stockwork mineralization: 0.71138 ± 0.00014, Zhang et al. 2017c; Jitou stock: 0.7065, Yu et al. 1998) between stockwork mineralization and the Jitou stock. This fracturing caused a sudden drop in fluid pressure, which would result in a short-lived FeS\(_2\) supersaturation event, and promote
rapid growth of pyrite (Wu et al. 2018) probably causing the formation of colloform pyrite. It could also have resulted in phase separation and partitioning of reduced H₂S into the vapor phase to subsequently elevate the oxygen fugacity (fO₂) of the fluids (Ohmoto 1972; Drummond and Ohmoto 1985). This is consistent with the negative δ³⁴S_CDT values in the Xinqiao colloform pyrite (Zhang et al. 2017a) as fluid oxidation has been proposed to generate negative δ³⁴S values in sulfides (Drummond and Ohmoto 1985; Hodkiewicz et al. 2009; LaFlamme et al. 2018). The short-lived FeS₂ supersaturation and elevated fO₂ caused by the fracturing would create suitable conditions for hematite formation. The fine-grained, foliaceous and needle-like textures of Mt6 suggest the early hematite replaced by Mt6 formed rapidly in unstable conditions, consistent with the fracturing. Sealing of the fractures would allow fluid pressures to rebuild and the ore-forming system to revert back to lower oxygen fugacities, which, coupled with continuous release of CO₂, may explain the replacement of precursor hematite by Mt6 and the formation of siderite in the Mt6 veins. Therefore, Mt6 may have been genetically associated with fracturing.

Controlling factors for magnetite precipitation

Given that the trace-element composition of hydrothermal magnetite is determined by a number of factors, including the physicochemical conditions (esp., T and fO₂), fluid composition (intensity of fluid-rock interactions), and co-crystallizing minerals (e.g., Dare et al. 2012, 2014; Nadoll et al. 2014; Li et al. 2018b; Huang et al. 2019b), the trace element geochemistry can be used to constrain the precipitation conditions of the Xinqiao magnetite. Temperature is thought to significantly influence the incorporation of trace elements into magnetite (McIntire 1963; Nadoll et al. 2014; Knipping et al. 2015; Deditius et al. 2018). A
positive correlation between the formation temperature and Ti contents in magnetite has been
widely proven (Lindsley 1991; Rapp et al. 2010; Dare et al. 2012; Nadoll et al. 2012). At Xinqiao,
the decreasing TiO$_2$ from Mt3c (Avg. 0.11 wt.%) through Mt3r (Avg. 0.05 wt.%), Mt4 (Avg. 0.03
wt.%) and Mt5 (Avg. 0.01 wt.%) to Mt6 (below detection limit) (Appendix 1; Fig. 4a) is
consistent with gradual cooling from Mt3c to Mt6. However, the increasing Ti concentrations
from Mt1 (Avg. 0.05 wt.%) and Mt2 (Avg. 0.04 wt.%) to Mt3c suggest the temperature increased
during their formation. Plots of Al + Mn vs. Ti + V can also reflect the formation temperature of
magnetite (Nadoll et al. 2014; Deditius et al. 2018). The Xinqiao magnetite plots in Al + Mn vs. Ti
+ V diagram (Fig. 5c) consistent with the gradually decreasing temperatures from Mt3c to Mt6.
Although the dataset for Mt1 is small, there is evidence for increasing temperatures from Mt1 to
Mt3 (Fig. 5c).

Vanadium concentrations in hydrothermal magnetite can record the $f$O$_2$ evolution of
hydrothermal fluids as vanadium is incompatible at high oxygen fugacities (Toplis and Corgne
2002; Dupuis and Beaudoin 2011; Nadoll et al. 2014; Knipping et al. 2015; Papike et al. 2005).
EPMA V$_2$O$_3$ data in different types of magnetite are consistent within error (Fig. 4a), but
LA-ICP-MS V data of Mt3, Mt5, and Mt6 decrease from Mt3c (Avg. 72.392 ppm) and Mt3r (Avg.
76.842 ppm) to Mt5 (Avg. 21.263 ppm), and increase from Mt5 to Mt6 (Avg. 72.000 ppm), which
suggests that $f$O$_2$ during the formation of Mt5 was higher than during the formation of Mt3 and
Mt6. This is consistent with variations in the Sn content that increase from Mt3c (Avg. 33.417
ppm) and Mt3r (Avg. 36.648 ppm) to Mt5 (Avg. 75.100 ppm), and then decrease from Mt5 to Mt6
(Avg. 2.940 ppm) because Sn is redox sensitive in magnetite (Carew 2004; Huang et al. 2019b).
The similar contents of V and Sn in Mt3c and Mt3r suggest that $f$O$_2$ conditions were stable during
their formation.

Extensive fluid-rock interactions commonly result in hydrothermal magnetite being enriched in Mn, Mg, Al, and Si (Einaudi et al. 1981; Carew 2004; Meinert et al. 2005; Nadoll et al. 2014; Deditius et al. 2018), but temperature can also influence the Mn content in magnetite (Nadoll et al. 2014; Deditius et al. 2018), so Liu et al. (2019) used Mg + Al + Si contents to investigate the intensity of fluid-rock interactions. For the Xinqiao magnetite, Mt1 and Mt3c have the highest Mg + Al + Si contents (Fig. 5d), suggesting that they have undergone the strongest fluid-rock interactions during their formation. The lower Mg + Al + Si contents of Mt3c to Mt3r (Fig. 5d) suggests a gradual decrease in the intensity of fluid-rock interactions. Both Mt5 and Mt6 have lower Mg + Al + Si contents than Mt3c, suggesting they were affected by less intense fluid-rock interactions, consistent with Mt5 having formed from fluid-assisted recrystallization processes and Mt6 having grown rapidly under unstable conditions associated with fracturing. Moreover, Mt2 and Mt4 have the lowest Mg + Al + Si contents (Fig. 5d), consistent with them having formed by DRP of pre-existing Mt1 and Mt3, respectively.

Dissolution and reprecipitation processes can be driven by variations in the properties of the fluids, such as fluid compositions, T, pressure and \( f_{O_2} \) (Hemley and Hunt 1992; Putnis 2002; Putnis and Putnis 2007). Mixing of saline fluids with Fe-rich magmatic-hydrothermal solutions, an increase in T, and decreasing pressure and \( f_{O_2} \) are considered the most important causes for DRP of primary magnetite (Hu et al. 2015) because these would enhance the solubility and consequently the undersaturation of iron in the fluids (Hemley and Hunt 1992; Hu et al. 2014).

The lack of obvious increase in \( V_2O_3 \) and TiO\(_2\) contents from Mt1 to Mt2 (\( V_2O_3 \): Avg. 0.14 wt.% vs. 0.18 wt.%; TiO\(_2\): Avg. 0.05 wt.% vs. 0.04 wt.%), and Mt3r to Mt4 (\( V_2O_3 \): Avg. 0.02 wt.% vs. 0.08 wt.% vs.
0.03 wt.%; TiO$_2$: Avg. 0.05 wt.% vs. 0.03 wt.%), and the gradually increasing pressure before the formation of the colloform pyrite associated with hydraulic fractures suggests variations in T, $f$O$_2$ and pressure may not be the cause of DRP at Xinqiao. Previous multi-isotopic data (Re–Os, S and Pb) of pyrite has shown that the Xinqiao stratiform mineralization was predominantly formed by intensive water-rock interaction between the magmatic-hydrothermal fluids associated with the Jitou stock and the Late Permian metalliferous black shales (Li et al. 2017, 2018a), which is consistent with high Cl$^-$ concentrations in fluid inclusions (up to 3.346 μg/g; Zhang 2015) at Xinqiao. The saline fluids resulted from this water-rock interaction may be responsible for DRP of the Xinqiao magnetite.

Metallogenic implications

Several diagrams, such as Ca + Al + Mn vs. Ti + V, Ni/(Cr + Mn) vs. Ti + V (Dupuis and Beaudoin 2011) and Mn + Al vs. Ti + V (Nadoll et al. 2014) have been proposed to discriminate various deposit types. Given that Ca and Ni concentrations in some EPMA analyses are below the detection limits, the Mn + Al vs. Ti + V diagram (Fig. 6) was applied in this study, and Mt3, Mt4, Mt5 and Mt6 dominantly plot in the skarn zones, suggesting that these stages of magnetite are genetically associated with magmatic hydrothermal fluids, consistent with the hypothesis that the Xinqiao stratiform mineralization is genetically associated with the Early Cretaceous magmatic-hydrothermal fluids as a skarn deposit (e.g., Pan and Done 1999; Mao et al. 2009, 2011; Zhang et al. 2017b, c, 2018; Li et al. 2017, 2018a, 2019). A large variation in Ti + V and relatively stable Mn + Al in Figure 6 may be ascribed to the intensive fluid-rock interactions in the skarn system. Mt1 plots in the BIF and IOCG zones close to skarn zone (Fig. 6), but a BIF source can be
excluded by the absence of Precambrian banded iron formations in the Tongling district, and the
IOCG mineralization is not supported by the low Ni contents of Mt1 and the absence of Na-Ca
alteration at Xinqiao (Huang et al. 2019a). The dark Mt1 under BSE has relatively high contents
of Si, Al, Ca, and Mg, which might be related to a major contribution of magmatic-derived fluids
due to a large fluid-rock ratio (Nadoll et al. 2012, 2014; Dare et al. 2014). Therefore, the
formation of Mt1 was influenced by both sedimentary and skarn-type processes, namely intensive
fluid-rock interactions, coinciding with the high Mg + Al + Ca of Mt1 (Fig. 5d), and the Xinqiao
magnetite may have been genetically associated with skarn mineralization derived from magmatic
hydrothermal fluids.

If the Xinqiao deposit formed from a single hydrothermal event, the ore-forming temperature
would gradually decrease over time. Although the temperatures decrease from Mt3 to Mt6, the
increase from Mt2 to Mt3c implies that the Xinqiao stratiform mineralization may reflect at least
two hydrothermal events. The combination of close spatial and temporal relationship between the
Jitou stock (zircon U–Pb age of 139.6 ± 1.5 Ma; Zhang et al. 2017c) and the stratiform orebody
(quartz fluid inclusions Rb–Sr isotope isochron age of 138.0 ± 2.3 Ma (Zhang et al. 2017c) and
Re–Os isotope isochron ages of 136.7 ± 4.6 Ma, 143 ± 16 Ma, and 135.5 ± 4.0 Ma for colloform
pyrite, pyrite from garnet-bearing skarn ore, and euhedral pyrite cemented by calcite, respectively
(Li et al. 2018a)), the iron (δ^{57}Fe: −1.22‰ to 0.15‰; Wang et al. 2011, 2013), S isotope
compositions (δ^{34}S_{CDT} of −0.6 to 2.7‰, 1.8 to 2.5‰, and 1.9 to 4.4‰ for colloform pyrite,
fine-grained pyrite formed from recrystallization of colloform pyrite, and coarse-grained pyrite
coexisting with quartz and calcite, respectively; Zhang et al. 2017a) and Co/Ni ratios (0.67–2.94,
1.05–3.24, and 1.03–4.67 for colloform pyrite, fine-grained pyrite, and coarse-grained pyrite;
Zhang et al. (2017a) of pyrite in the stratiform orebody, and the H–O isotope data ($\delta D_{\text{SMOW}} = -48.02$–$-61.82\%_o$, $\delta^{18}O_{\text{SMOW}} = 12.56$–$22.74\%_o$; Liu, 2002) of ore-bearing quartz in the stratiform orebody suggests that the magmatic hydrothermal fluids associated with the Jitou stock are dominantly responsible for the stratiform mineralization. One diorite porphyry dyke has been found in the Xinqiao mining area, but it yielded a zircon U–Pb age of 130.6 ± 1.1 Ma (Li et al. 2017) and obviously cut through the stratiform orebody (Zhang 2015). Additionally, there is no evidence to support other concealed intrusions in the region. Therefore, we conclude that the increasing fluid temperatures from Mt2 to Mt3 likely resulted from episodic release of hydrothermal fluids derived from magma associated with the Early Cretaceous Jitou stock, given that the injection of multiple pulses of fluid is typical of magmatic-hydrothermal systems (Hedenquist and Lowenstern 1994). Moreover, multiple influxes of fluid are also consistent with the formation of multigenerational garnet at Xinqiao (Zhang et al. 2017b).

Here we propose a textural and trace-element geochemical evolution (Fig. 7) for the Xinqiao magnetite. The first Si + Fe-rich magmatic-derived hydrothermal fluids released from the deep magma chamber associated with the Jitou stock, entered the low-pressure unconformity between the Upper Devonian Wutong Formation quartz sandstone and the Upper Carboniferous Huanglong Formation limestone and interacted with limestone to form Mt1 enriched in Si, Al, Ca, and Mg. Meanwhile, some fluids evolved into high-salinity fluids after intensive interaction with the Late Permian metalliferous black shales, and mixed with the magmatic hydrothermal fluids to enhance the solubility of iron in the fluids resulting in the formation of porous Mt2 by DRP which is depleted in Ti, Si, Ca, V and Mg, that replaced Mt1. Subsequently, a second pulse of abundant Si + Fe-rich magmatic hydrothermal fluid was released. Fluctuating fluid compositions and
physicochemical conditions resulted in the formation of core-rim magnetite (Mt3) with oscillatory zoning. Similarly, high-salinity fluids derived from interaction between magmatic hydrothermal fluids and the metalliferous black shales induced the dissolution of Mt3 and precipitation of Mt4. During this process, Ti, Si, Ca, Al, and Mg were removed from Mt3, and the FeO content increased. During mineralization early magnetite (Mt1-Mt4) recrystallized to Mt5 under conditions of decreasing temperature and fluid-rock interactions intensity and increasing $fO_2$. Lastly, the gradual increase in ore-forming pressure due to the release of abundant CO$_2$ during the conversion of carbonate to skarn would have exceeded the lithostatic load to create extensive hydraulic fractures in the Wutong Formation quartz sandstone. This fracturing would have resulted in elevated $fO_2$ fluids that formed hematite with fine-grained foliaceous and needle-like textures. After sealing of the fractures, fluid pressures would increase and the ore-forming system revert back to low oxygen fugacity, with Mt6 l replacing the precursor hematite.

**IMPLICATIONS**

Primary magnetite easily undergoes dissolution and reprecipitation, oxy-exsolution, and/or recrystallization to reach chemical and textural reequilibration, and consequently texture examination is necessary before conducting trace-element analyses. At Xinqiao, the microporosity of Mt2 and Mt4 magnetite, and their sharp contacts with Mt1 and Mt3, suggest that they formed via coupled dissolution and reprecipitation of the precursor Mt1 and Mt3 magnetite, respectively. Based on the metasomatic pseudomorph textures, Mt6 formed by replacement of hematite as a result of fracturing. Moreover, this study also demonstrates that in-situ trace elements analysis based on detailed texture examination under robust geological and petrographic frameworks can
effectively constrain the mineralization processes and ore genesis. Increasing Ti content from Mt2 to Mt3 suggests the elevated temperature during their formation, which is ascribed into multiple pulses of magmatic-hydrothermal fluids, and reveals that the Xinqiao stratiform mineralization was genetically associated with multiple influxes of magmatic hydrothermal fluids derived from the Early Cretaceous Jitou stock.

ACKNOWLEDGEMENTS

Our especial thank goes to Dr. Minghong Zheng and Dr. Zhongfa Liu for their field assistance, and to Dr. Huajie Tan for assisting with the EPMA analysis. In particular, thanks are extended to Prof. Julie Roberge and two anonymous reviewers for constructive and insightful suggestions that greatly improved this manuscript.

FUNDING

This research was financially supported by the National Natural Science Foundation of China (41972081), the Open Fund for the Important Instruments of Central South University (CSUZC201902) and the Research Start-up Fund of Central South University (202045009).

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FIGURE CAPTIONS

FIGURE 1. (a) Location of the Tongling ore district in the Middle-Lower Yangtze River Valley metallogenic belt (after Mao et al. 2011). TLF: Tancheng–Lujiang fault; XGF: Xiangfan–Guangji fault; YCF: Yangxing–Changzhou fault. (b) Geological map of the Tongling district (modified from Chang et al. 1991).

FIGURE 2. (a) Geological map and (b) representative cross section of the Xinqiao Cu–Fe–Au deposit (after Tang et al. 1998 and Zang et al. 2004, respectively).

FIGURE 3. Photographs showing representative mineral assemblages and textural features of magnetite in the Xinqiao stratiform orebody. (a) Anhedral Mt1 grain replaced by porous Mt2 (BSE); (b) Irregular and abrupt contact boundary between Mt1 and Mt2, indicating replacement texture (BSE); (c) Subhedral Mt3 grain coexisting with epidote occurs among garnet grains (PPL); (d) Anhedral Mt3 grain coexisting with and replaced by quartz, apatite, and pyrite; (e) Mt1 and Mt2 only trapped in the core of Mt3 (BSE); (f) The same chemical oscillatory zoning occurrence of Mt3c and Mt3r, parallel to the contact interface between Mt3c and Mt3r (BSE); (g) Mt4 veins and patches replacing Mt3c and truncating the chemical oscillatory zoning of Mt3c (BSE); (h) Mt4 veins truncating the chemical oscillatory zoning of Mt3r (BSE); (i) Mt5 replaced by stockwork and disseminated pyrite; (j) Mt5 grains with 120° triple junction texture and locally replaced by hematite; (k) Homogeneous Mt5 replaced by pyrite and quartz (BSE); (l) Mt6 vein cutting through crystal pyrite; (m) Mt6 coexisting siderite cuts through colloform pyrite as vein; (n)
Mt6 replaced hematite in the form of metasomatic pseudomorph textures; (o) Needle-like Mt6 is
replaced by pyrite coexisting with calcite; (p) Homogeneous internal texture of Mt6.

**Abbreviations:** Ep = epidote, Cal = calcite, Grt = garnet, Qtz = quartz, Ap = apatite, Hem =
hematite, Py = crystal pyrite, Py$_c$ = colloform pyrite.

**FIGURE 4.** Box diagram of major (a) and trace (b) elements concentrations for the Xinqiao
magnetite.

**FIGURE 5.** Ti versus V (a), V/Ti versus Fe (b), (Al + Mn) vs. (Ti + V) (c; modified after Nadoll
et al. (2014) and Deditius et al. (2018)) and (Mg + Al + Si) vs. Ti (d) diagrams for the Xinqiao
magnetite.

**FIGURE 6.** Discrimination plot of Mn + Al vs. Ti + V for the Xinqiao magnetite mineralization
types (Nadoll et al. 2014).

**FIGURE 7.** Schematic diagram showing the textural and trace-element geochemical evolution for
the Xinqiao magnetite. See text for details.

**APPENDIX CAPTIONS**

**APPENDIX 1.** EPMA geochemical data (wt.%) of the Xinqiao magnetite. “b.d.l” means below
detection limit.
APPENDIX 2. LA-ICP-MS trace element data (ppm) of the Xinqiao magnetite. “b.d.l” means below detection limit.

APPENDIX 3. LA-ICP-MS trace element detection limits (ppm) of the Xinqiao magnetite.