Multisourced metals enriched by magmatic-hydrothermal fluids in stratabound deposits of the Middle–Lower Yangtze River metallogenic belt, China

Yang Li1,2,3*, David Selby1,4, Xian-Hua Li2, and Chris J. Ottley1
1Department of Earth Sciences, Durham University, DH1 3LE Durham, UK
2State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, 10029 Beijing, China
3Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06511, USA
4State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Resources, China University of Geosciences, Wuhan, 430074 Hubei, China

ABSTRACT
Stratabound deposits within late Carboniferous carbonate units in the Middle–Lower Yangtze River metallogenic belt are important copper producers in China. Hitherto, the genesis of these deposits has been debated, due to poor constraints regarding the timing and source of the mineralization. Proposed models include a late Carboniferous seafloor exhalative formation (SEDEX), or an Early Cretaceous magmatic-hydrothermal origin. These models imply different metal sources (basinal vs. magmatic fluid, respectively) and would require different exploration strategies. New pyrite Re-Os and trace-element results from the representative Xinqiao Cu-S-Fe-Au deposit favor a Cretaceous (ca. 138 Ma) magmatic-hydrothermal origin over a SEDEX origin. The distinct initial 187Os/188Os compositions (Osi) of different pyrite types (colloform Osi = 1.35 and euhedral grains Osi = 0.79), coupled with the pyrite trace-element abundance, indicate that the Os, and by inference other metals (e.g., Cu, Ag, Au), was sourced from a Cretaceous magmatic-hydrothermal system (Osi = 0.74) and Late Permian metalliferous black shales (Osi = 7.56 ± 3.76). In addition, the genesis of Au-bearing stockwork pyrite veins hosted by the Carboniferous sandstone is best explained by the leaching of existing mineralization (e.g., porphyry Au-Mo) by Early Cretaceous magmatic-hydrothermal fluids. This is implied by the lack of common Os, high Re abundances (0.1–3.7 ppm), and highly variable Re-Os model ages (379 and 173 Ma), which are positively correlated with Re and total abundances of Co, Ni, Ag, Au, Ti, and Ba. This study highlights the importance of recycling of multisourced metals (sedimentary and existing mineralization) in the formation of intrusion-related stratabound deposits. Furthermore, it demonstrates the importance of integrating information regarding the source and timing of mineralization within a well-defined geological framework, which can yield information about the ore-forming processes and help to guide mineral exploration.

INTRODUCTION
Intrusion-related stratabound deposits are an important end member of porphyry copper systems that contribute significantly to the world’s supply of copper (Cu), gold (Au), and other metals (Sillitoe, 2010). Nonmagmatic fluids in porphyry copper systems, i.e., meteoric fluids, have been ubiquitously documented (D’Errico et al., 2012; Fekete et al., 2016; Li et al., 2017a), but the current consensus is that the metals are derived from magmatic-hydrothermal systems. However, the close spatial association between metalliferous sedimentary rocks and many intrusion-related stratabound deposits raises the possibility that, in addition to magmatic-hydrothermal systems, metal-bearing strata could be a complementary origin of metals.

The expansive distribution of intrusion-related stratabound deposits in the Middle–Lower Yangtze River metallogenic belt, China (Fig. 1A), offers an excellent opportunity to examine the sources of these metals. These deposits predominantly consist of massive ores of chalcopyrite and pyrite, with gold-bearing pyrite-quartz stockworks. A unique feature of these stratabound deposits is the ubiquitous presence of colloform pyrite (Gu et al., 2007), and their close spatial association with Early Cretaceous magmatic-porphyry-skarn systems (Fig. 1). Although extensively studied, the genesis of these deposits remains ambiguous, with two principal genetic models having been proposed: (1) linkage to Early Cretaceous porphyry-skarn systems (Pan and Dong, 1999; Mao et al., 2011; Pirajno and Zhou, 2015); and (2) initial formation as a late Carboniferous seafloor exhalative formation (SEDEX) system, which was then enriched/overprinted by an Early Cretaceous magmatic-hydrothermal event (Zeng et al., 2002; Gu et al., 2007). The contrasting genetic models imply different metal enrichment mechanisms and different mineral exploration programs. For example, an Early Cretaceous magmatic-hydrothermal origin suggests that these deposits are similar to manto-type deposits (Mao et al., 2011; Li et al., 2017b; Zhang et al., 2017) in Mexico and Chile (Meinert, 1982; Sato, 1984). Therefore, a magmatic origin of metals is most likely, with stratabound deposits being expected to center around Cretaceous granites. On the other hand, a Carboniferous SEDEX origin (Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2007; Guo et al., 2011; Xie et al., 2014) would suggest that the metals were sourced from the underlying strata by a migrating basinal fluid, and therefore the stratabound mineralization could be more laterally extensive within the late Carboniferous limestone.

Uncertainty regarding ore genesis in the Middle–Lower Yangtze River metallogenic belt is primarily due to the lack of robust constraint on the timing of mineralization and a poor understanding of the source of the metals, which is a typical challenge for hydrothermal deposit studies. Here, based on a robust geological framework, the representative Xinqiao deposit of the Middle–Lower Yangtze River metallogenic belt was selected for a pyrite Re-Os and trace-element study, in order to provide an improved genetic understanding and yield implications for mineral exploration.

STRAFABBOUND DEPOSITS OF THE MIDDLE–LOWER YANGTZE RIVER METALLOGENIC BELT
As represented by the Xinqiao Cu-S-Fe-Au deposit (eastern China), stratabound ore bodies in the Middle–Lower Yangtze River metallogenic belt are hosted primarily by limestone...

*E-mail: yang.li@yale.edu; cugliyang@126.com
and dolomite units within the late–middle Carboniferous Chuanshan–Huanglong Formations. These units lie above the early Carboniferous Gaolishan Formation sandstone (Figs. 1B and 1C). Minor massive pyritic ores are also present in overlying Permian and Triassic carbonate units. The deposits exhibit a close spatial association with Early Cretaceous (ca. 145–135 Ma) granitoids (Zhou et al., 2008; Li et al., 2010), which are hosted by Carboniferous–Permian carbonate units. Many of the granitoids are associated with porphyry and skarn mineralization (Mao et al., 2011; Pirajno and Zhou, 2015). The stratabound ore bodies predominantly consist of Cu-bearing pyrite and pyrrhotite (Li et al., 2017b). A feature unique to these deposits is pyrite exhibiting a colloform texture (Xie et al., 2014). Locally, veins bearing colloform pyrite are observed to crosscut the Permian limestone (Fig. DR3 in the GSA Data Repository1). Vertical to subvertical Au-bearing pyrite stockworks occur beneath the stratabound ore bodies and are hosted by the early Carboniferous Gaolishan Formation sandstone (Guo et al., 2011).

PYRITE Re-Os AND TRACE-ELEMENT RESULTS
Four styles of pyritic mineralization (Figs. 1 and 2) from Xinqiao were examined for Re-Os and trace-element analysis. Euhedral pyrite grains (py1) from the stratabound ore body have Re and 180Os concentrations of 1.5–3.6 ppb and 1.7–4.0 ppt, respectively, and yield a Re-Os isochron age of 135.5 ± 4.0 Ma (Os i = 0.79 ± 0.11; n = 5; mean squared weighted deviation [MSWD] = 2.2; Fig. 2E). Colloform pyrite (py2) from the stratabound ore body possesses 1.2–9.3 ppb Re and 2.0–43.4 ppt 180Os and yields a Re-Os isochron age of 136.6 ± 4.6 Ma (Os i = 0.74 ± 0.24; n = 11; MSWD = 4.9; Fig. 2E). Euhedral garnet-skarn pyrite (py3) contains 1.4–1.6 ppb Re and 1.4–2.1 ppt 180Os. For py3, two analyses yielded a date of 143 ± 16 Ma and an Os i value of 0.63 ± 0.04 (Fig. 2E). The sandstone-hosted pyrites (py4) possess 57–3692 ppb Re, 1.3–43.1 ppt 180Os, and negligible common Os (<0.45%; see Table DR1 in the Data Repository). The model Os i values of these pyrite grains range from 173.2 ± 1.7 Ma to 378 ± 1.6 Ma (Fig. 2F). Overall, py1 and py3 are characterized by low trace-element abundance, but they contain moderate Mn, Cu, Pb, Zn, W, and Ag contents (Table DR2). Py2 has higher abundances of Mn, Pb, Cu, Zn, and Ag; py3 is enriched in Au, Ba, Co, Ni, and Ti (Fig. 3A). For py4, a positive correlation is observed between the total abundances of Co, Ni, Ag, Au, Ti, Ba, Re, and Re-Os model ages (Fig. 3B).

DISCUSSION AND IMPLICATIONS
Magmatic and Sedimentary Sourced Metals for Stratabound Ore
The Re-Os ages of py1 and py2 (135.5 ± 4.0 Ma and 136.7 ± 4.6 Ma, respectively; Fig. 2E) suggest that the two types of mineralization (euhedral and colloform pyrite) were formed broadly contemporaneously and are indistinguishable from the emplacement age of the Jitou Stock (138.5 ± 1.0 Ma; Li et al., 2017b) at Xinqiao. In addition, these ages overlap with the Re-Os age of the skarn pyrite (py3, 143 ± 16 Ma; Fig. 2E). Thus, a temporal link exists between the Early Cretaceous magmatic-skarn system associated with the Jitou Stock and the stratabound mineralization. This is inconsistent with a Carboniferous SEDEX origin (Xu and Zhou, 2001; Zeng et al., 2002; Xie et al., 2014).

At the time of emplacement of the Jitou Stock, the skarn pyrite (py3) had an Os i of 0.74 ± 0.24 (Table DR1). Taking this as the maximum estimate of the magmatic Os i, a crust-derived origin with limited mantle input (Os i = 0.13) is inferred for the Jitou Stock. This is consistent with Jitou Stock zircon depleted Hf isotope composition (εHf = ~11; Zhang et al., 2017). The similar Os i values (0.79 ± 0.11 vs. 0.74 ± 0.24) for py1 and py3, respectively, imply that the Os, and by inference the associated metals, was predominantly sourced from the Early Cretaceous magmatic-hydrothermal system.

It has been previously proposed that the colloform pyrite was initially formed in the Carboniferous (Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2007; Xie et al., 2014) and recrystallized to euhedral pyrite during the Early Cretaceous magmatic-hydrothermal event. This scenario is not supported by the sharp contact relationship between the euhedral and colloform pyrites (Fig. DR2A), nor by the crosscutting relationship between the colloform pyrite and Permian limestones at Dongguashan and Wushan (Fig. DR3). In addition, the Os i (Fig. 2E) and trace-element abundances (Figs. 3A and 3B) of py2 are distinct from py1; hence, a recrystallization origin of py1 from py2 is unlikely. Further, the colloform pyrite is composed of fine-grained (80 nm to 1.5 μm) cubic crystals and not frambooids, which is inconsistent with a sedimentary origin (Sweeney and Kaplan, 1973).

The highly radiogenic Os i value (1.35 ± 0.06) of the colloform pyrite indicates that the Os, and by inference the other metals, was not solely magmatically derived. In the Xinqiao area, the most likely source to provide a radiogenic 187Os/188Os composition is the Late Permian metalliferous black shales. These shales are enriched in Re (403–1002 ppb) and Os (0.3–1 ppb) and yield an Early Cretaceous 187Os/188Os composition of 7.6 ± 3.8 (Yang et al., 2004). Therefore, the most geological plausible scenario is that the colloform pyrite was formed through intensive water-rock interaction.
Au-Bearing Pyrite Stockworks

(Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2017) with py4 (up to 597 °C and 63.7% NaCl equiv.; Li et al., 2017b). In contrast, the fluid conduits in porphyry-skarn systems, the basinal fluid must interact with the Late Permian metalliferous black shales; this is further supported by the trace element data (Fig. 3A).

Reprocessing Existing Mineralization for the Au-Bearing Pyrite Stockworks

The Au-bearing pyrite (py4) veins hosted by the sandstone underlying the stratabound ore body are dated at 138 ± 2.3 Ma (quartz fluid inclusion Rb-Sr; Zhang et al., 2017), suggesting a temporal and genetic association with the Jitou Stock, which is further supported by fluid inclusion and δ18O data from quartz coprecipitated with py4 (up to 597 °C and 63.7% NaCl equiv.; 6.81‰ ± 2.76‰, Wang and Ni, 2009; Li et al., 2017b). In contrast, a 319 ± 13 Ma Re-Os date (n = 9; MSWD = 13; Guo et al., 2011) for py4 seems consistent with the hypothesis that these pyrite veins were the fluid conduit (stockwork feeder) for a Carboniferous SEDEX system (Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2007). However, a SEDEX scenario is not supported by the following observations. First, py4 Re-Os data from both this study and Guo et al. (2011) share similar characteristics (enriched in Re and limited to no common Os) and yield highly variable model ages (Fig. 2F; 379–173 Ma). Therefore, the py4 Re-Os data do not meet the necessary criteria for isochron dating. Second, py4 does not contain common Os, but in SEDEX systems, the basinal fluid must interact with the basement rocks, and hence should inherit common Os with a radiogenic Os value (Hatayshin et al., 2015). Third, the pyrite veins beneath the stratabound ore body are structurally controlled and only possess silicified and sericite-bearing selvages (Wang and Ni, 2009; Guo et al., 2011; Li et al., 2017b). In contrast, the fluid conduits in SEDEX systems are developed in syndepositional faults and are characterized by tourmaline- and albite-bearing alteration assemblages (Leach et al., 2005). As such, in accordance with the 138 ± 2.3 Ma Rb-Sr age (Zhang et al., 2017), we suggest that the sandstone-hosted mineralization was temporally associated with the Early Cretaceous magmatic-hydrothermal system.

For py4, in order to yield geologically reasonable ages (ca. 138 Ma), each sample had to be corrected using widely different and geologically implausible Os values (e.g., −223 to 59; Table DR1). Given the fact that these samples possess very high abundances of Re and radiogenic Os with negligible common Os, it is unlikely that the observed ages were caused by disturbance of the Re-Os systematics. In this regard, the most plausible genesis for py4 is the leaching of rocks enriched in Re and radiogenic Os by the Early Cretaceous magmatic-hydrothermal fluid. A higher degree of water-rock interaction resulted in the inheritance of more Re, 187Os, and trace elements, consistent with the positive correlations between model ages of py4 and their Re and trace-element concentrations (Figs. 2F and 3). Rhenium and Os concentrations are typically very low in crustal rocks (0.20 and 0.03 ppb, respectively), but they are known to be high in molybdenite (e.g., hundreds to thousands of ppm for Re, and up to ppm levels for 187Os) and to a lesser extent in other sulfides (Selby et al., 2009; Stein, 2014). As such, the most likely source for the elevated Co+W+Pb+Zn (ppm)

Figure 2. Representative pyrite mineralization at Xinqiao (eastern China) and Re-Os ages. A: Euhedral pyrite grains (py1) cemented by calcite from stratabound ore body. B: Colloform pyrite (py2) from stratabound ore body, which is composed of fine-grained (80 nm to 1.5 μm) cubic pyrite grains, with local distribution of calcite grains. No framboidal pyrite grains were observed in this study. C: Pyrite samples (py3) from garnet-bearing skarn ore. D: Pyrite samples (py4) hosted by sandstone beneath stratabound ore body. E: Re-Os isochrons of py1, py2, and py3. F: Model ages of py4 and their correlation with Re abundances. Also shown are data from Guo et al. (2011). Resin refers to materials used for making mounts. Py—pyrite, cal—calcite, qtz—quartz, gar—garnet, MSWD—mean squared weighted deviation. All uncertainties are at 2σ level.

Figure 3. Trace-element compositions of the studied pyrite samples. A: Py2 is characterized by high total abundances of Co, Ni, Ag, Au, Ti, and Ba; py4 is enriched in Cu, W, Pb, and Zn. In contrast, py1 and py3 are depleted in these trace elements. B: Model ages of py4 are positively correlated with total abundances of Co, Ni, Ag, Au, Ti, and Ba. Uncertainties are smaller than symbol size.

Implications for Ore Genesis and Origin of the Metals

In the Middle–Lower Yangtze River metallogenic belt, stratabound deposits are all spatially associated with the Early Cretaceous magmatic-porphyry-skarn systems (Fig. 1A), and the ore-forming fluids and alteration assemblages have a close magmatic affinity, but they show few characteristics of typical SEDEX systems (Pan