- 1 Multisourced metals enriched by magmatic-hydrothermal
- 2 fluids in stratabound deposits of the Middle–Lower
- 3 Yangtze River metallogenic belt, China
- 4

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14 ABSTRACT

15 Stratabound deposits within Late Carboniferous carbonate units in the Middle-

16 Lower Yangtze River metallogenic melt are important Cu producers in China. Hitherto,

- 17 the genesis of these deposits has been debated, due to poor constraints regarding the
- 18 timing and source of the mineralization. Proposed models include a Late Carboniferous
- 19 seafloor exhalative formation (SEDEX), or an Early Cretaceous magmatic-hydrothermal
- 20 origin. These models imply different metal sources (basinal vs magmatic fluid,
- 21 respectively) and would require different exploration strategies. New pyrite Re-Os and

22	trace element results from the representative Xinqiao deposit favor a Cretaceous
23	magmatic-hydrothermal genesis over a SEDEX origin. The distinct initial ¹⁸⁷ Os/ ¹⁸⁸ Os
24	compositions (Osi) of different pyrite types (colloform $Osi = 1.4$ and euhedral grains Osi
25	= 0.7), coupled with the pyrite trace element abundance, indicate that the Os, and by
26	inference other metals (e.g., Cu, Ag, Au), are sourced from a Cretaceous magmatic-
27	hydrothermal system ($Osi = 0.7$) and Late Permian metalliferous black shales ($Osi = 7.6$
28	\pm 3.8). In addition, the genesis of Au-bearing stockwork pyrite veins hosted by the
29	Carboniferous sandstone is best explained by the leaching of existing mineralization (e.g.,
30	porphyry Au-Mo) by Early Cretaceous magmatic-hydrothermal fluids. This is implied by
31	the lack of common Os, high Re abundances (0.6–3.7 ppm), and highly variable Re–Os
32	model ages (379 and 173 Ma), which are positively correlated with Re and total
33	abundances of Co, Ni, Ag, Au, Tl and Ba. This study highlights the importance of
34	recycling multi-sourced metals (sedimentary and existing mineralization) in the
35	formation of intrusion-related stratabound deposits. Furthermore, it demonstrates the
36	importance of integrating information regarding the source and timing of deposit
37	formation within a well-defined geological framework, which can yield information
38	about the ore-forming process and help to guide mineral exploration.
39	
40	INTRODUCTION

Intrusion-related stratabound deposits, together with porphyry, skarn, and
epithermal deposits, are important end-members of porphyry copper systems that
contribute significantly to the world's supply of Cu, Mo Au, and other metals (Sillitoe,
2010). The presence of non-magmatic fluids in porphyry copper systems, i.e., meteoric

45	and metamorphic fluids, has been ubiquitously documented (D'Errico et al., 2012; Fekete
46	et al., 2016; Li et al., 2017a), but the current consensus is that the metals are derived from
47	magmatic-hydrothermal systems. However, the close spatial association between
48	metalliferous sedimentary rocks and many intrusion-related stratabound deposits raises
49	the possibility that, in addition to magmatic-hydrothermal systems, metal-bearing strata
50	could be a complementary origin of metals.
51	The expansive distribution of intrusion-related stratabound deposits in the
52	Middle-Lower Yangtze River metallogenic belt (Fig. 1A) offers an excellent opportunity
53	to examine the sources of their metals. These deposits comprise predominantly massive
54	ores of chalcopyrite and pyrite, with quartz-Au-bearing pyrite vein stockworks. A unique
55	feature of these stratabound deposits is the ubiquitous presence of colloform pyrite (Gu et
56	al., 2007), and their close spatial association with Early Cretaceous magmatic-porphyry-
57	skarn systems (Fig. 1). Although extensively studied, the genesis of these stratabound
58	deposits remains ambiguous, with two principal genetic models having been proposed: 1)
59	linkage to Early Cretaceous porphyry-skarn systems (Pan and Dong, 1999; Mao et al.,
60	2011; Pirajno and Zhou, 2015); and 2) initial formation as a Late Carboniferous SEDEX
61	system, which was then enriched/overprinted by an Early Cretaceous magmatic-
62	hydrothermal event (Zeng et al., 2002; Gu et al., 2007). The contrasting genetic models
63	imply different metal enrichment mechanisms and alternate mineral exploration
64	programs. For example, an Early Cretaceous magmatic-hydrothermal origin suggests that
65	these deposits are similar to manto-type deposits (Mao et al., 2011; Li et al., 2017b;
66	Zhang et al., 2017) in Mexico and Chile (Meinert, 1982; Sato, 1984). Therefore, a
67	magmatic origin of metals is most likely, with stratabound deposits being expected to

68	center around Cretaceous granites. On the other hand, a Carboniferous SEDEX origin
69	(Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2007; Guo et al., 2011; Xie et al., 2014)
70	would suggest that the metals were sourced from the underlying strata by a migrating
71	basinal fluid, and therefore the stratabound mineralization could be more laterally
72	extensive within the Late Carboniferous limestone.
73	Uncertainty regarding ore genesis in the Middle-Lower Yangtze River
74	metallogenic belt is primarily due to the lack of constraint on the timing of mineralization
75	and a poor understanding of the source of the metals, which is a typical challenge for
76	hydrothermal deposit studies. Here, based on a robust geological framework, the
77	representative Xinqiao deposit of the Middle-Lower Yangtze River metallogenic belt is
78	selected for a pyrite Re-Os and trace element study, in order to provide an improved
79	genetic understanding and yield implications for mineral exploration.
80	STRATABOUND DEPOSITS OF THE MIDDLE-LOWER YANGTZE RIVER
81	METALLOGENIC BELT
82	As represented by Xinqiao, stratabound ore bodies in the MiddleLower
83	Yangtze River metallogenic belt are hosted primarily by limestone and dolomite units
84	within the Late-Middle Carboniferous Chuanshan-Huanglong formations. These units lie
85	above the Early Carboniferous Gaolishan Formation sandstone (Figs. 1B and 1C). Minor
86	massive pyritic ores are also present in overlying Permian and Triassic carbonate units.
87	The deposits exhibit a close spatial association with Early Cretaceous (ca. 135-145 Ma)
88	granitoids (Zhou et al., 2008; Li et al., 2010), which are hosted by Carboniferous-
89	Permian carbonate units. Many of the granitoids are associated with porphyry and skarn
90	mineralization (Mao et al., 2011; Pirajno and Zhou, 2015). The stratabound ore bodies

91	predominantly comprise Cu-bearing pyrite and pyrrhotite (Li et al., 2017b). Unique to
92	these deposits is pyrite exhibiting a colloform texture (Xie et al., 2014). In most cases, no
93	direct contact relationship is observed between the colloform ore and sedimentary rocks,
94	but veins bearing colloform pyrite are observed to locally cross-cut the Permian
95	limestone (Fig. DR3). Vertical to sub-vertical Au-bearing pyrite stockworks occur
96	beneath the stratabound ore bodies hosted by the Early Carboniferous Gaolishan
97	Formation sandstone (Guo et al., 2011; Zhang et al., 2017).
98	PYRITE RE-OS AND TRACE ELEMENT RESULTS
99	Four styles of pyritic mineralization (Figs. 1 and 2) from Xinqiao were examined
100	for Re–Os and trace element analysis. Deposit geology, sample details, analytical
101	methods, and pyrite Re-Os and trace element data are presented in the GSA data
102	repository. Euhedral pyrite grains (py1) from the stratabound ore body have Re and ¹⁹² Os
103	concentrations of 1.5–3.6 ppb and 1.7–4.0 ppt, respectively, and yield a Re–Os isochron
104	age of 135.5 ± 4.0 Ma (initial ¹⁸⁷ Os/ ¹⁸⁸ Os composition (Os <i>i</i>) = 0.79 ± 0.11 ; n = 5; MSWD
105	= 2.2; Fig. 2E). Colloform pyrite (py2) from the stratabound ore body possesses $1.2-9.3$
106	ppb Re and 2.0–43.4 ppt ¹⁹² Os, and yields a Re–Os isochron age of 136.6 ± 4.6 Ma (Osi
107	= 1.35 ± 0.06 ; n = 11; MSWD = 5.4; Fig. 2E). Euhedral garnet-skarn pyrite (py3)
108	contains 1.4–1.6 ppb Re and 1.4–2.1 ppt ¹⁹² Os. For py3, although only two samples
109	(XQ15-5-3 and XQ15-5-4) were analyzed, which is not sufficient to yield a statistically
110	valid isochron, the Re–Os data yield an errorchron with a date of 143 ± 16 Ma and an Os <i>i</i>
111	of 0.63 ± 0.44 (Fig. 2E). The sandstone-hosted pyrites (py4) possess 57–3692 ppb Re,
112	1.3–43.1 ppt 192 Os, and negligible common Os (< 0.45%, Table DR1). The model 187 Re–
113	¹⁸⁷ Os ages of these pyrite grains range from $173.2 \pm 1.7 - 359.0 \pm 1.8$ Ma (Fig. 2F).

- 114 Overall, Py1 and Py3 are characterized by low trace element abundance, but contain
- 115 moderate Mn, Cu, Pb, Zn, W, and Ag (Table DR2). Py2 has higher abundances of Mn,
- 116 Sb, Cu, Pb, Zn and Ag; py4 enriched in Au, Ba, Co, Ni and Tl (Fig. 3A). For py4, a
- 117 positive correlation is observed between the total abundances of Co, Ni, Ag, Au, Tl, Ba,
- 118 Re and Re–Os model ages (Fig. 3B).

119 DISCUSSION AND IMPLICATIONS

120 Magmatic and Sedimentary Sourced Metals for Stratabound Ore

- 121 The Re–Os ages of py1 and py2 (135.5 ± 4.0 and 136.7 ± 4.6 Ma; Fig. 2E)
- 122 suggest that the two types of mineralization (euhedral and colloform pyrite) were formed
- 123 broadly contemporaneously, and are indistinguishable from the emplacement age of the
- 124 Jitou Stock (138.5 \pm 1.0 Ma; Li et al., 2017b) at Xinqiao. In addition, these ages overlap
- 125 with the Re–Os age of the skarn pyrite, py3 (143 ± 16 Ma; Fig. 2E). Thus, a temporal link
- 126 exists between the Early Cretaceous magmatic-skarn system associated with the Jitou
- 127 Stock and the stratabound mineralization. This is inconsistent with a Carboniferous
- 128 SEDEX origin (Xu and Zhou, 2001; Zeng et al., 2002; Xie et al., 2014).
- 129 At the time of emplacement of the Jitou Stock (138.5 ± 1.0 Ma), the skarn pyrite
- 130 (py3) had an Osi of 0.74 ± 0.24 . Taking this value as the maximum estimate of the
- 131 magmatic Osi, a crust-derived origin with limited mantle input (Osi = 0.13) is inferred for
- 132 the Jitou Stock. This is consistent with Jitou Stock zircon depleted Hf isotope
- 133 composition ($\varepsilon_{\text{Hf}} = \sim -11$; Zhang et al., 2017). The similar Osi values (0.79 ± 0.11 vs 0.74
- ± 0.24) for py1 and py3 imply that the Os, and by inference the associated metals, were
- 135 predominantly sourced from the Early Cretaceous magmatic-hydrothermal system.

136	It has been previously proposed that the colloform pyrite was initially formed in
137	the Carboniferous (Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2007; Xie et al.,
138	2014), and then recrystallized to euhedral pyrite during the Early Cretaceous magmatic-
139	hydrothermal event. This scenario is not supported by the sharp contact relationship
140	between the euhedral and colloform pyrites (Fig. DR2A), nor by the cross-cutting
141	relationship between the colloform pyrite and Permian limestones at Dongguashan and
142	Wushan (Fig. DR3). In addition, the Osi (Fig. 2E) and trace element abundances (Figs.
143	3A and 3B) of py2 are distinct from py1, hence a recrystallization origin of py1 from py2
144	is unlikely. Further, the colloform pyrite is composed of fine-grained (80 nm–1.5 μ m)
145	cubic crystals and not framboids, which is inconsistent with a sedimentary origin
146	(Sweeney and Kaplan, 1973). Moreover, <i>in-situ</i> sulfur isotope data for the four types of
147	pyrite studied here have indistinguishable δ^{34} S values (0–4 ‰). All of these data support
148	a magmatic-hydrothermal origin rather than a SEDEX genesis (Zhang et al., 2017).
149	The highly radiogenic Osi (1.35 ± 0.06) of the colloform pyrite indicates that the
150	Os and by inference the metals are not solely magmatically derived. In the Xinqiao area,
151	the most likely source to provide a radiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os composition is the Late
152	Permian metalliferous black shales. These shales are enriched in Re $(403 - 1002 \text{ ppb})$ and
153	Os (0.3 – 1 ppb) and yield an Early Cretaceous 187 Os/ 188 Os composition of 7.6 ± 3.8
154	(Yang et al., 2004). Therefore, the most geological plausible scenario is that the
155	colloform pyrite was formed through intensive water-rock interaction between the Early
156	Cretaceous magmatic-hydrothermal fluids and the Late Permian metalliferous black
157	shales.

158 Cycling Existing Mineralization for the Au-Bearing Pyrite Stockworks

159	The Au-bearing pyrite (py4) veins hosted by the sandstone underlying the
160	stratabound ore body are dated at 138 ± 2.3 Ma (quartz fluid inclusion Rb–Sr; initial
161	87 Sr/ 86 Sr = 0.71138 ± 0.00014; Zhang et al., 2017), suggesting a temporal and genetic
162	association with the Jitou Stock, which is further supported by fluid inclusion and $\delta^{18}O$
163	data from quartz co-precipitated with py4 (up to 597 °C and 63.7 % NaCl equiv.; 6.81 \pm
164	2.76 ‰; Wang and Ni, 2009; Li et al., 2017b). In contrast, a 319 ± 13 Ma Re–Os age (n =
165	9; MSWD = 13; Guo et al., 2011) for py4 seems consistent with the hypothesis that these
166	pyrite veins were the fluid conduit (stockwork feeder) for a Carboniferous SEDEX
167	system (Xu and Zhou, 2001; Zeng et al., 2002; Gu et al., 2007). However, a SEDEX
168	scenario is not supported by the following observations. First, py4 Re–Os data from both
169	this study and Guo et al. (2011) share similar characteristics (enriched in Re and limited
170	to no common Os) and yield highly variable model ages (173-379 Ma). Therefore, the
171	py4 Re–Os data do not meet the necessary criterial for isochron dating. Second, py4 does
172	not contain common Os, but in SEDEX systems, the basinal fluid must interact with the
173	basement rocks, and hence should inherit common Os with a radiogenic Osi (Hnatyshin
174	et al., 2015). Third, the pyrite veins beneath the stratabound ore body are structurally
175	controlled and only possess silicified and sericite-bearing selvages (Wang and Ni, 2009;
176	Guo et al., 2011; Li et al., 2017b). In contrast, the fluid conduits in SEDEX systems are
177	developed in syn-sedimentary faults and are characterized by tourmaline- and albite-
178	bearing alteration assemblages (Leach et al., 2005). As such, in accordance with the 138
179	\pm 2.3 Ma Rb–Sr age (Zhang et al., 2017), we suggest that the sandstone-hosted
180	mineralization was temporally associated with the Early Cretaceous magmatic-
181	hydrothermal system.

182	For py4, in order to yield geologically reasonable ages (ca 138 Ma), each sample
183	has to be corrected using widely different and geologically implausible Osi (e.g., -223-
184	59; Table DR1). Given the fact that these samples possess very high abundances of Re
185	and radiogenic Os with negligible common Os, it is unlikely that the observed ages are
186	caused by disturbance of the Re-Os systematics. In this regard, the most plausible
187	genesis for py4 is the leaching of rocks enriched in Re and radiogenic Os by the Early
188	Cretaceous magmatic-hydrothermal fluid. A higher degree of water-rock interaction
189	resulted in the inheritance of more Re, ¹⁸⁷ Os and trace elements, which is consistent with
190	the positive correlations between model ages of py4 and their Re and trace element
191	concentrations (Figs. 2F, 3A and 3B). Rhenium and Os concentrations are typically very
192	low in crustal rocks (0.20 and 0.03 ppb, respectively), but are known to be high in
193	molybdenite (e.g., hundreds to thousands ppm for Re and ppm level for ¹⁸⁷ Os) and to a
194	lesser extent in other sulfides, such as chalcocite, chalcopyrite, bornite, and pyrite (Selby
195	et al., 2009; Stein, 2014). As such, the most likely source for the elevated Re (ppm level),
196	radiogenic Os (¹⁸⁷ Os, ppb level), and negligible common Os in py4 is porphyry-style Au-
197	Mo mineralization.

198 Implications for Ore Genesis and Metals Origin

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 barely show characteristics of typical SEDEX systems (Pan and Dong, 1999;
Mao et al., 2011). As such, an Early Cretaceous intrusion-related carbonate replacement
origin is suggested, with the stratabound orebodies being spatially controlled by the

205	unconformity between the Early Carboniferous sandstone and Late Carboniferous
206	carbonate units, and the Au-bearing stockworks being a product of recycled pre-existing
207	porphyry-style mineralization by the Early Cretaceous magmatic-hydrothermal fluid (Fig.
208	4).
209	This study highlights that coupling absolute timing and source constraints for
210	mineralization with a detailed geological framework can significantly advance our
211	understanding of the ore-forming process of intrusion-related stratabound deposits, and
212	underpin exploration models. Further, the recycling of metals from metalliferous
213	sedimentary rocks (i.e., black shales) and pre-existing mineralization by magmatic-
214	hydrothermal fluids could be an important mechanism for the formation of ore deposits.
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316	
317	FIGURE CAPTIONS
318	
319	Figure 1. A), Distribution of porphyry-skarn and stratabound deposits in the Middle-
320	Lower Yangtze River metallogenic belt and their spatial association with Early
321	Cretaceous granites. Modified after Pan and Dong (1999) and Mao et al. (2011). B),
322	Geological map of the Xinqiao stratabound ore deposit. C), Cross section of the Xinqiao
323	deposit and relevant chronological data. 1, Li et al. (2017b); 2, Yang et al. (2004); 3, this
324	study; 4, Guo et al. (2011); 5, Zhang et al. (2017).
325	
326	Figure 2. Representative pyrite mineralization at Xinqiao and their Re-Os ages. A),
327	Euhedral pyrite grains (py1) cemented by calcite from the stratabound ore body. B),
328	Colloform pyrite (py2) from the stratabound ore body, which is composed of fine-grained
329	(80 nm–1.5 μ m) cubic pyrite grains, with local distribution of calcite grains. No
330	framboidal pyrite grains are observed in this study. C), Pyrite samples (py3) from the
331	garnet-bearing skarn ore. D), Pyrite samples (py4) hosted by sandstone beneath the
332	stratabound ore body. E), Re–Os isochrons of py1, py2 and py3. F), Model ages of py4
333	and their correlation with Re abundances. Also shown are data from Guo et al. (2011). Py
334	= pyrite, cal = calcite, qtz = quartz, gar = garnet. Resin refers to the materials used for

335	DOI:10.1130/G39995.1 making mounts. MSWD = Mean Squared Weighted Deviation. All uncertainties are at
336	the 2-sigma level.
337	
338	Figure 3. Trace element compositions of the studied pyrite samples. A), Py2 is
339	characterized by high total abundances of Co, Ni, Ag, Au, Tl, Ba; py4 is enriched in Cu,
340	W, Pb, Zn. In contrast, py1 and py3 are depleted in these trace elements. B), The model
341	ages of py4 are positively correlated with their total abundances of Co, Ni, Ag, Au, Tl
342	and Ba. Uncertainties are smaller than the symbol size.
343	
344	Figure 4. Sketch illustrating the genesis of intrusion-related stratabound deposits in the
345	Middle-Lower Yangtze metallogenic belt, which is temporally and spatially associated
346	with Early Cretaceous granites, porphyry and skarn deposits. The model highlights the
347	importance of recycling metals from metalliferous sedimentary rocks and pre-existing
348	mineralization in the formation of intrusion-related stratabound deposits.
349	
350	1GSA Data Repository item 2018xxx, Deposit geology, samples, analytical methods,
351	Pyrite Re-Os and trace elements data, is available online at
352	http://www.geosociety.org/datarepository/2018/ or on request from
353	editing@geosociety.org.









Data Repository for

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

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A1. Deposit Geology, Sample location and details

At the Xinqiao deposit, the stratabound ore body (Fig. DR1) strikes NE-SW and dips (~45°) northwest, with horizontal and vertical extensions and an average thickness of 2550 m, 1810 m, and 21 m, respectively (Xu and Zhou, 2001). The stratabound ore body (Fig. DR2A) predominantly comprises Cu-bearing massive euhedral pyrite (py1, Figure 2A and DR2B) and colloform pyrite (py2, Figure 2B and DR2C), although massive chalcopyrite and anhedral pyrite are also present. The Jitou diorite (SIMS U-Pb zircon age of ~138.5 ± 1.0 Ma; Li et al., 2017) was emplaced into the Carboniferous-Permian carbonate units, which is associated with intense skarn garnet-diopside-epidote alteration (Zhang et al., 2017), that is crosscut by ~1 cm wide pyrite ± chalcopyrite veins (py3, Figures 2C and DR2D). Beneath the stratabound ore body, the Gaolishan Formation sandstone is extensively fractured (Fig. DR2E), and hosts vertical to sub-vertical Aubearing pyrite stockworks (py4, Fig. 2D) with ~1 – 10 cm wide silicified and sericite-bearing selvages (Guo et al., 2011).

Sample locations are illustrated in Figure 1B and Figure DR3. In Figure DR3, the portion that has been removed/mined is the stratabound ore body. All samples were collected from the outcrops in the open pit. Euhedral pyrite (XQ15-9, py1) and colloform pyrite (XQ15-4, py2) samples of the stratabound orebody were collected from fresh outcrop (Fig. DR1, DR1A) exposed during the mining process. The outcrop is located in the southwest wall of the open pit, where the colloform pyrite ore and euhedral pyrite ore have a sharp contact relationship (Fig. DR2A). No direct relationship between the stratabound ore and country rocks was observed at Xinqiao. The colloform pyrite (py2) also contains carbonate veins (<1mm – 1cm, Figs. 2B, DR2A and DR2C), but according to the sharp contact relationship between py1 and py2, a recrystallization origin of py1 from py2 is unlikely.



Figure DR1. A photo image of the open pit of Xinqiao, with highlighted deposit geology and sample locations.

The euhedral pyrite ore predominately comprises euhedral to sub-euhedral pyrite (<0.5 to several cm in size, Fig. 2A, DR2B) with a volume percentage of ~80%, the cements are calcite (15%) and quartz (<5%). Pyrite veins (XQ15-5, py3) hosted by the garnet-bearing skarn ore was collected from the northwest wall of the open pit where the Jitou stock intrudes limestone of Permian Qixia Formation (Fig. DR1). The sample predominately contains brown-red garnet grains (<1 cm in size), and is crosscut by pyrite veins, which in turn have been crosscut by quartz veins (Fig. 2C, DR2D). The skarn-pyrite vein (~0.5 cm width) contains sub-euhedral pyrite grains (<1 cm in size). Pyrite veins (XQ15-8, py4) beneath the stratabound orebody were collected from the southeast wall of the open pit (Fig. DR1). The veins are of variable width (<1 cm and >15 cm) and are hosted by sandstone of Carboniferous Gaolishan Formation (Fig. DR2E). The sandstone is

intensively fractured, and extensively silicified. The pyrite grains generally are euhedral, with grain sizes of 0.2 cm to 1 cm, and show open space filling features (Fig. 2D, DR2F). With the exception of silicification and sericitization, no other alteration type is observed or is documented.



Figure DR2. Samples utilized in this study. A), The sharp contact relationship between the colloform pyrite and euhedral pyrite ores from the stratabound orebody; B), Euhedral pyrite ore (py1); C), Colloform pyrite ore (py2); D), Garnet bearing skarn ore crosscut by quartz and pyrite veins (py3); E), Pyrite veins hosted by Gaolishan Formation sandstone; F), Pyrite-quartz veins (py4) hosted by sandstone show open space filling features.

In most cases, no direct contact relationship is documented/observed between the colloform ore and sedimentary rocks, but colloform pyrite veins cross cuts the Permian limestone are observed locally (Fig. DR3). Beneath the stratabound ore bodies are vertical to sub-vertical Aubearing pyrite stockworks hosted by the Early Carboniferous Gaolishan Formation sandstone (Guo et al., 2011; Zhang et al., 2017).



Figure DR3. Colloform pyrite ores cross-cutting Permian marble/limestone at the Dongguashan deposit (A) and the Wushan deposit (B).

A2. Pyrite Re-Os isotope analytical method

After petrographic examination, pyrite-bearing samples were crushed to 20-30 mesh and handpicked under a microscope; estimated pyrite purity is better than 98 %. The purified pyrite samples were mounted in epoxy resin for further petrographic examination (Fig. 2A) with an aim to document the texture and association with alteration assemblages. The pyrite Re-Os analytical method utilized is the same as previously documented (Selby et al., 2009; Li, et al., 2017) and is briefly outlined here. Purified pyrite aliquots were accurately weighted and loaded into a Carius tube with known amounts of a mixed Re-Os tracer solution containing ¹⁸⁵Re and ¹⁹⁰Os. The bottom part of the Carius tube was frozen in a mixture of ethanol and dry ice, and 11.5 N HCl (3 ml) and 15.5 N HNO₃ (8 ml) were added. The Carius tube was sealed from the top by a hydrogen-oxygen

torch and then kept in a steel jacket. Sample digestion and sample-spike equilibrium was achieved in an oven at 220 °C for 48 hours. Once cooled, the outside of the Carius tube was rinsed with MQ. The bottom part was frozen again in ethanol-dry ice slurry before being opened from the top by a hydrogen-oxygen torch. Osmium was isolated from the acidic digestion medium using solvent (CHCl₃*3 times) extraction, and then was back extracted by HBr, and finally purified through microdistillation. Rhenium was separated by solvent extraction (NaOH-acetone) from the acidic medium and then was further purified via anion exchange chromatography. The purified Re and Os were loaded onto Ni and Pt filaments, respectively, and the isotopic measurements were conducted using negative thermal ionization mass spectrometry on a Thermo Electron[@] TRITON mass spectrometer (Creaser et al. 1991; Völkening et al. 1991) at Durham University. The Os data was collected via a secondary electron multiplier in peak-hopping mode, and Re data was collected with static Faraday collectors. Total procedural blanks were monitored over the course of study. Blanks for Re and Os were 2.6 ± 0.4 and 1.5 ± 1.6 pg, respectively, with an average ¹⁸⁷Os/¹⁸⁸Os value of 0.21 ± 0.10 (2σ , n = 5). For the samples of this study, the presented uncertainties are fully propagated to include uncertainties in Re and Os isotopic compositions measurements, blank abundances and isotopic compositions, spike calibrations and the reproducibility of Re and Os standards. The Re-Os isochron graphs were plotted using Isoplot v4.15 program (Ludwig 2003), with the ¹⁸⁷Re decay constant of ¹⁸⁷Re of 1.666 x 10 ⁻¹¹a⁻¹ (Shirey and Walker 1998; Selby et al. 2007). For pyrite samples hosted by sandstone of Gaolishan Formation, given the extremely low to absence of common Os detected, in addition to using the 185 Re + 190 Os enriched spike, we also run duplicated analyses using an ¹⁸⁵Re + normal Os spike as used for molybdenite analysis (Selby and Creaser 2001; Li et al. 2017b). For the same sample, the two methods yield similar data, however, they do not overlap within analytical uncertainty (Table DR1). This indicates that Re-Os

systematics of py4 are not homogeneous, as further supported by their element budgets (Table DR2). Nevertheless, the Re abundances and model dates of py4 from both analytical methods fall on the same trend (Fig. 2F, see main text discussion).

A3. Re-Os data and initial ¹⁸⁷Os/¹⁸⁸Os values

For py1, py2 and py3, their initial ¹⁸⁷Os/¹⁸⁸Os values are determined through isochron regression of the ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os data (Fig. 2B), and also recalculated at 138.5 Ma in Table DR1. The two approaches yield indistinguishable results within uncertainties. For py4, the ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os values are highly radiogenic (70930-170383 and 265-943; Table DR1) and imply that the bulk of the Os is ¹⁸⁷Os. The Re-Os isotope data of py4 do not yield any meaningful Re-Os isotopic data and thus their initial ¹⁸⁷Os/¹⁸⁸Os value is not known. In this case, an initial ¹⁸⁷Os/¹⁸⁸Os value must be assumed in order to calculate the best estimate for the percentage of radiogenic Os, and thus to yield an accurate and precise Re-Os model age. For the py4 sample set, owning to their exceptionally high rhenium abundances and high percentage of radiogenic Os, the overall accuracy of the percentage of radiogenic ¹⁸⁷Os/¹⁸⁸Os values (Table DR2).

In order to put tight constraints on the genesis of py4, we further investigate the two proposed genetic scenarios as follows. If we consider py4 are Carboniferous in age (i.e., 320 Ma), then the initial ¹⁸⁷Os/¹⁸⁸Os values of these samples would need to be highly variable (-223 and 59), but the presence of both positive and negative values is a geological unlikely scenario. A Cretaceous age (i.e., 138.5 Ma) would also require the sample set to possess highly variable initial ¹⁸⁷Os/¹⁸⁸Os values (54 to 549). But the initial ¹⁸⁷Os/¹⁸⁸Os values are geologically possible, which could be generated through the interaction with ¹⁸⁷Os-rich phases (e.g., molybdenite; see main text for discussion). Such a hypothesis is further supported by the correlation between the Re-Os model

ages, rhenium abundances and Co + Ni + Ag + Ba + Au + Tl values (Figs. 2F and 3C; see main text for discussion), suggesting that a higher degree of interaction with Re- and ¹⁸⁷Os-rich phases resulted in the inheritance of more Re, ¹⁸⁷Os and trace elements. To summarize, we consider a Carboniferous age is unlikely for py4, and instead propose that a Cretaceous age is the most plausible scenario, which is in accordance with the Re-Os age constrains of py1, py2, py3 and geological observations.

A4. Pyrite trace element analytical method

Trace-element abundances were determined using a modification of the procedure of Ottley et al., (2003). Pyrite grains (~100 mg) were digested in 6ml inverse aqua-regia (2:1 mix of 15.5N HNO₃ and 11.5N HCl) in Teflon beakers at 220 °C for 24 h and then evaporated to dryness at 80 °C. At this stage, 1 ml 16N HNO₃ was added and evaporated to near dryness. This process was repeated for three times, and followed by the addition of 10 ml 4N HNO₃. The sample was capped and heated overnight at 100 °C. Once cooled, the solution was transferred to a 50ml centrifuge tube and brought up to 50 ml MQ H₂O. A 1:10 dilution of the sample solution was made prior to sample analysis. Trace elements were analyzed using the Thermo[@] XSERIES 2 mass spectrometer at Durham University. In-house and international reference materials (W-2, BHVO-1, AGV1) were used for calibration and multiple blank analysis were included for each sample set. Reproducibility of elemental runs is estimated to be better than 5% (2 SD).

A5. List of tables and figures

Table DR1. Synopsis of the Pyrite Re-Os data from the Xinqiao deposit.

Table DR2. Synopsis of the pyrite trace element data from the Xinqiao deposit.

Figure DR3. Colloform pyrite ores intruded into Permian marble/limestone at Dongguashan deposit (A) and Wushan deposit (B).

Figure DR2. A photo image of the open pit of Xinqiao, with highlighted deposit geology and sample locations.

Figure DR2. Samples utilized in this study. A), The sharp contact relationship between the

colloform pyrite and euhedral pyrite ores from the stratabound orebody; B), Euhedral pyrite ore

(py1); C), Colloform pyrite ore (py2); D), Garnet bearing skarn ore crosscut by quartz and pyrite

veins (py3); E), Pyrite veins hosted by Gaolishan Formation sandstone; F), Pyrite-quartz veins

(py4) hosted by sandstone show open space filling features.

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Table DR1, Pyrite Re-Os data from Xinqiao deposit

Sample	Weight (g)	Re (ppb)	2σ	Os (ppt)	2σ	192Os (ppt)	2σ	187Re/188Os	2σ	187Os/188Os	2σ	rho	% ¹⁸⁷ Osr	Osi @ 138.5 Ma	2σ
Py1, euhedral pyrite from stratabound orebody															
XQ15-9-1	0.42	1.47	0.01	7.76	0.24	2.18	0.13	1343.42	82.83	3.72	0.27	0.820	76.6	0.63	0.46
XQ15-9-2	0.41	2.58	0.02	14.11	0.27	3.95	0.13	1299.34	42.92	3.75	0.15	0.823	76.8	0.76	0.24
XQ15-9-4	0.43	2.03	0.01	7.32	0.21	1.71	0.10	2367.32	141.74	6.01	0.38	0.929	85.5	0.56	0.71
XQ15-9-5	0.40	1.58	0.02	10.29	0.19	3.06	0.11	1024.68	38.02	3.11	0.12	0.891	72.0	0.75	0.21
XQ15-9-6	0.41	3.59	0.02	12.94	0.25	2.96	0.10	2412.85	84.13	6.29	0.23	0.940	86.2	0.73	0.42
													weighted mean	0.73	0.14
Py2, colloform pyrite fr	om strataboui	nd orebody													
XQ15(coarse)-4-1	0.40	9.28	0.03	68.95	0.74	19.81	0.21	932.11	10.26	3.47	0.05	0.649	65.5	1.33	0.08
XQ15(coarse)-4-2	0.41	5.62	0.02	116.49	0.95	38.25	0.35	292.47	2.88	2.10	0.03	0.670	42.9	1.43	0.03
XQ15(coarse)-4-3	0.45	2.44	0.01	26.12	0.61	8.09	0.29	599.77	21.53	2.67	0.15	0.614	55.1	1.29	0.20
XQ15(coarse)-4-4	0.41	3.22	0.02	45.09	0.55	14.48	0.24	442.86	7.64	2.31	0.05	0.687	48.1	1.29	0.07
XQ15(coarse)-4-5	0.45	6.89	0.02	18.02	0.66	2.88	0.23	4762.58	356.88	12.28	0.99	0.928	90.2	1.32	1.81
XQ15(fine)-4-0	0.40	1.20	0.02	7.37	0.25	2.01	0.14	1184.49	80.40	4.04	0.32	0.819	70.3	1.32	0.51
XQ15(fine)-4-1	0.40	7.64	0.02	56.07	0.62	16.05	0.20	947.50	12.09	3.52	0.06	0.729	65.9	1.34	0.09
XQ15(fine)-4-2	0.43	8.14	0.03	133.26	1.75	43.35	0.57	373.75	5.17	2.19	0.06	0.448	45.2	1.33	0.07
XQ15(fine)-4-3	0.40	2.22	0.02	36.16	0.49	11.76	0.17	375.33	6.10	2.20	0.06	0.441	45.4	1.33	0.08
XQ15(fine)-4-4	0.41	3.93	0.02	51.21	0.51	16.31	0.19	478.98	6.02	2.40	0.04	0.657	50.0	1.30	0.05
XQ15(fine)-4-5	0.41	5.47	0.03	38.80	0.67	11.02	0.24	987.86	21.49	3.61	0.12	0.625	66.7	1.33	0.17
													weighted mean	1.36	0.02
Py3, euhedral pyrite fro	m garnet bea	ring skarn or	е												
XQ15-5-3	0.41	1.55	0.02	7.66	0.42	2.07	0.31	1490.23	73.57	4.18	0.21	0.961	71.3	0.74	0.27
XQ15-5-4	0.40	1.35	0.02	5.67	0.41	1.41	0.31	1904.13	137.40	5.16	0.38	0.980	69.8	0.77	0.49
													weighted mean	0.74	0.24

Py4, euhedral pyrite from the quartz-pyrite stockworks hosted by Gaolishan Formation sandstone ¹⁹²Os (ppt) 187Re/188Os ¹⁸⁷Os/¹⁸⁸Os %¹⁸⁷Osr¹ 187Re (ppb) 187Osr (ppt)1 Osi for 138.5 Ma Osi for 320 Ma Name Re (ppb) 2σ Os (ppt) 2σ 2σ 2σ 2σ rho 2σ 2σ Age 2σ XQ15-8-1 942.81 18.42 0.953 330.8 549.2 32.0 0.10 3692.22 11.19 230.79 170382.78 3252.10 7.03 66.36 12902.16 43.11 0.81 2320.69 12825.12 99.87 1.7 XQ15-8-2 0.10 525.56 1.59 1615.55 54.30 10.54 0.78 99163.29 7351.46 480.52 35.66 0.997 330.33 1.00 1596.71 7.45 99.75 289.4 1.3 251.4 -49.5 531.51 34.78 0.996 359.0 XQ15-8-3 1010.06 327.1 58.6 0.20 267.88 0.80 1020.06 32.32 6.02 0.39 88465.51 5778.02 168.37 0.50 5.14 99.85 1.8 XQ15-8-4 0.30 124.95 0.37 367.80 12.53 3.50 0.27 70929.58 5410.18 327.72 25.03 0.997 78.54 0.23 361.54 1.91 99.63 275.7 1.5 163.9 -51.4 XQ15-8-5 1359.73 8.84 230.37 1343.93 349.2 41.5 0.20 366.51 1.09 36.10 0.40 82464.29 3754.56 482.29 22.03 0.992 0.69 6.50 99.75 1.7 291.8 XQ15-8-6 0.41 71.81 0.21 182.67 8.55 1.37 0.20 104594.60 15084.31 418.85 60.45 0.999 45.14 0.13 180.40 1.14 99.81 239.4 1.5 177.2 -140.3 XQ15-8-7 91223.10 19240.35 0.30 57 79 0.17 107.23 6.08 1 26 0.27 264.84 55.91 0.999 36.32 0.11 104.98 1.01 99.55 173.2 17 54.1 -222.8

1, Abundances and percentage of radiogenic 187Os are estimated with an initial ¹⁸⁷Os/⁴⁸⁰Os value of 1.2, see main text and DR for discussions.

Py4, euhedral pyrite from the quartz-pyrite stockworks hosted by Gaolishan Formation sandstone, re-analysed using a spike enriched in 185 Re with a normal Os composition as used for molybdenite

 Sample	wt	Re(ppb)	2σ	187Re(ppb)	2σ	187Os(ppt)	2σ	Age	2σ
XQ15-8-1	0.15	2172.54	7.32	1365.48	4.60	8641.73	23.47	378.7	1.6
XQ15-8-5	0.25	346.61	2.46	217.85	1.55	1296.32	8.85	356.1	3.5
XQ15-8-6	0.44	75.34	1.53	47.35	0.96	187.66	3.78	237.4	6.8
XQ15-8-7	0.16	59.32	2.97	37.29	1.87	120.07	6.01	193.0	13.7

Common Os cannot be detected with S/N spike.

Table DR2, Pyrite trace elements data from Xinqiao deposit

		Mn	S	b Cu	Pb	Zn	Mo	W	Ag	Au	Ba	Co	Ni	TI	Co+Ni+Ag-	+Ba+Au+Tl Cu+Zn+	Cu+Zn+Mo+W+Pb		Re Age	
	weight/g	ppm	р	pm ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	М	a	
Py1, euhedral pyrite	e from strataboı	und oreboa	ly																	
XQ15-9-1		0.1	2466.1	0.0	155.5	8.3	10.7	0.0	36.7	4.1	0.0	0.0	0.0	0.0	0.0	4.2	211.2	1.5	135.3	
XQ15-9-2		0.1	1329.7	0.0	111.4	3.6	6.9	0.0	18.2	0.9	0.0	0.0	0.0	0.0	0.0	0.9	140.0	2.6	135.3	
XQ15-9-4		0.1	2817.3	0.0	555.4	6.7	4.9	0.0	12.3	0.9	0.0	0.0	0.0	0.0	0.0	0.9	579.3	2.0	135.3	
XQ15-9-5		0.1	2678.3	0.0	407.9	6.4	6.5	0.0	34.5	1.0	0.0	0.0	0.0	0.0	0.0	1.0	455.4	1.6	135.3	
XQ15-9-6		0.1	2814.8	0.0	52.2	7.7	16.4	0.0	40.6	1.0	0.0	0.0	0.0	0.0	0.0	1.1	116.8	3.6	135.3	
Py2, colloform pyri	te from stratabo	ound orebo	dy																	
XQ15(fine)-4-0		0.1	5318.4	110.7	769.3	1249.6	190.0	25.7	0.0	27.3	0.0	0.0	0.0	0.0	0.0	53.0	2234.6	1.2	137.0	
XQ15(fine)-4-1		0.1	498.2	137.1	648.0	1054.8	11.0	19.9	0.0	25.8	0.0	0.0	0.0	0.0	0.0	45.7	1733.7	7.6	137.0	
XQ15(fine)-4-2		0.1	2299.2	193.6	981.2	1601.8	20.9	42.5	0.0	30.6	0.0	0.0	0.0	0.0	0.0	73.2	2646.5	8.1	137.0	
XQ15(fine)-4-3		0.1	835.5	124.4	552.2	1077.8	5.1	14.6	0.0	16.5	0.0	0.0	0.0	0.0	0.0	31.1	1649.6	2.2	137.0	
XQ15(fine)-4-4		0.1	2967.5	153.8	1549.3	1193.0	25.4	31.8	0.0	28.0	0.0	0.0	0.0	0.0	0.0	59.8	2799.5	3.9	137.0	
XQ15(fine)-4-5		0.1	148.4	0.6	753.2	129.7	7.4	7.3	0.0	5.6	0.0	0.0	0.0	0.0	0.0	13.0	897.6	5.5	137.0	
XQ15(coarse)-4-1		0.1	632.7	139.9	724.4	1100.6	30.8	20.2	0.0	25.5	0.0	0.0	0.0	0.0	0.0	45.7	1876.0	9.3	137.0	
XQ15(coarse)-4-2		0.1	2200.9	181.0	984.2	1642.7	16.1	35.5	0.0	29.4	0.0	0.0	0.0	0.0	0.0	64.9	2678.5	5.6	137.0	
XQ15(coarse)-4-3		0.1	1070.7	118.4	581.2	1107.0	6.8	15.4	0.0	15.9	0.0	0.0	0.0	0.0	0.0	31.3	1710.5	2.4	137.0	
XQ15(coarse)-4-4		0.1	2045.6	140.0	748.1	1043.5	16.5	24.7	0.0	22.0	0.0	0.0	0.0	0.0	0.0	46.7	1832.8	3.2	137.0	
XQ15(coarse)-4-5		0.1	139.5	0.6	555.9	159.5	4.8	0.4	0.0	7.0	0.0	0.0	0.0	0.0	0.0	7.4	720.7	6.9	137.0	
Py3, euhedral pyrite	e from garnet be	earing skai	n ore																	
XQ15-5-3		0.1	1897.4	0.0	11.1	7.3	18.9	0.0	44.9	0.9	0.0	0.0	0.0	0.0	0.0	0.9	82.2	1.6	138.0	
XQ15-5-4		0.1	1625.0	0.0	22.4	3.7	12.0	0.0	20.6	1.0	0.0	0.0	0.0	0.0	0.0	1.0	58.7	1.4	138.0	
Py4, euhedral pyrite	e from the quart	tz-pyrite st	ockworks ho	sted by Gaolishan	Formation sands	stone														
XQ15-8-1		0.1	83.5	60.3	185.8	458.2	95.8	0.0	0.0	17.1	0.3	36.4	76.2	101.0	135.9	290.7	739.8	3692.2	378.7	
XQ15-8-2		0.1	42.0	43.9	155.4	422.4	31.6	0.0	0.0	16.1	0.4	81.0	76.5	79.1	67.5	244.1	609.3	525.6	289.4	
XQ15-8-3		0.1	95.3	54.9	217.4	414.2	61.9	0.0	0.0	27.9	0.1	12.2	35.1	68.2	164.0	272.3	693.5	267.9	359.0	
XQ15-8-4		0.1	37.6	13.8	281.8	182.5	14.3	0.0	0.0	5.8	0.6	28.3	203.5	193.2	8.5	236.4	478.7	125.0	275.7	
XQ15-8-5		0.1	73.3	44.3	209.4	396.0	74.2	0.0	0.0	22.8	0.1	69.4	63.6	96.2	102.4	290.9	679.7	366.5	356.1	
XQ15-8-6		0.1	18.6	17.7	230.1	233.6	34.6	0.0	0.0	5.1	0.3	7.9	62.6	93.8	34.2	141.3	498.3	71.8	239.4	