1	Magmatic and hydrothermal controls on diverse Nb mineralization associated with					
2	carbonatite-alkaline complexes in the southern Qinling orogenic belt, Central China					
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ABSTRACT

22 Although carbonatite-alkaline complexes are the primary source of the world's Niobium (Nb) supply, the mineralization style is largely variable in these complexes and 23 the processes behind are still poorly understood. Exemplifying with the ~430 Ma Miaova 24 and Shaxiongdong carbonatite-syenite complexes in the southern Qinling orogenic belt, 25 26 central China, our new observations show that Nb mineralization in these two deposits is persuasively throughout the entire complexes on both syenite and carbonatite in 27 disseminated form. Both the magmatic and hydrothermal processes have attributed to Nb 28 29 mineralization in both deposits, despite different in the mineralization style. The 30 Nb-bearing minerals in the mineralized Miaoya syenites include magmatic U-poor 31 pyrochlore, rutile, and ilmenite with minor amounts of columbite, and hydrothermal 32 columbite and rutile, whereas those in the mineralized carbonatites are mainly magmatic 33 U-poor pyrochlore, uranpyrochlore, U-rich betafite, and rutile with minor amounts 34 columbite, and hydrothermal columbite and rutile. On the other hand, the Nb-bearing 35 minerals in the mineralized Shaxiongdong syenites include magmatic U-poor pyrochlore, titanite, rutile, and ilmenite, and hydrothermal fersmite, rutile, and ilmenite, whereas 36 those in the mineralized carbonatites are mainly magmatic U-poor pyrochlore without 37 38 any hydrothermal Nb-bearing minerals. Field observations, whole-rock chemical and Sr-Nd isotopic compositions strongly constrained that assimilation of U-rich rocks (e.g., 39 40 the hosting Yaolinghe and Meiziya Groups) and magma differentiation are responsible for 41 diverse magmatic Nb mineralization in the two deposits. On the other hand, the diverse 2/47

42	assemblages of hydrothermal Nb minerals in Miaoya and Shaxiongdong are mainly
43	controlled by variation in the nature of fluid constrained to be genetically related to the
44	\sim 220 and \sim 420 Ma hydrothermal events, respectively. In summary, both magma
45	evolution (e.g., differentiation, assimilation) and late hydrothermal overprinting are
46	responsible for the diverse Nb mineralogy in carbonatites-alkaline complexes, a situation
47	that is commonly observed worldwide.
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49	Keywords: Pyrochlore group minerals, Columbite, Diverse Nb mineralization, Miaoya,

50 Shaxiongdong, Carbonatite-syenite complexes

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INTRODUCTION

53 Niobium is a relatively rare lithophile transition metal, and its average abundance in the crust is about 8 ppm (Rudnick and Gao 2003). The use of Nb in high-tech 54 applications calls for a comprehensive understanding of the processes that govern the 55 concentration of this element in mineral deposits. Carbonatite-alkaline complexes, the 56 most important Nb (and/or REEs) carriers (Mitchell 2015; Verplanck et al. 2016; 57 Anenburg et al. 2021; Beard et al. 2023), have attracted inordinate attention from 58 researchers. Numerous studies documented that the Nb mineralization (particularly with 59 grade < 1 wt% Nb₂O₅) is commonly concentrated through differentiation of carbonatitic 60 or alkaline melts, even though some of them may have been reworked to various extents 61 by later hydrothermal overprinting (Chakhmouradian et al. 2015; Mitchell 2015; 62 63 Tremblay et al. 2017; Liu et al. 2020). Carbonatite/alkaline rock-related Nb deposits exhibit large varieties of Nb mineral assemblages such as pyrochlore group minerals (e.g., 64 Araxá and Catalão, Brazil; St. Honoré, Canada), columbite (Fe²⁺Nb₂O₆; e.g., Upper Fir 65 Nb-rich 66 and Bayan Obo). rutile $(TiO_2;$ e.g., Seis Lagos), aeschynite ((Y,Ca,Fe²⁺)(Ti,Nb)₂(O,OH)₆; e.g., Bayan Obo), latrappite (Ca(Fe,Nb)O₃; e.g., Oka and 67 Prairie Lake) and loparite ((Na,Ce)TiO₃; e.g., Prairie Lake) (Cordeiro et al. 2011; 68 Chakhmouradian et al. 2015; Mitchell 2015; Tremblay et al. 2017). A better 69 understanding of the processes attributed for the diversity of Nb mineralogy is critical for 70 beneficiation and metallurgy, and for effective targeting of highly-endowed Nb deposits. 71 72 Previous studies show that the diversity of Nb-bearing species in carbonatite or 4 / 47

73	alkaline rocks may imply varying geochemical behaviors of Nb under different magmatic
74	and/or hydrothermal conditions (Mitchell 2015; Liu et al. 2020; She et al. 2021). For
75	example, experimental investigations documented that whether pyrochlore or other
76	Nb-bearing minerals such as columbite, lueshite, or perovskite would crystallize is a
77	function of H ₂ O, Na, and F contents of the parental magmas (Jago and Gittins 1993;
78	Mitchell and Kjarsgaard 2004). However, the roles of different processes (magmatic or
79	hydrothermal) in Nb mineralization remain enigmatic. Moreover, the process controlling
80	the association of REE-Nb in these deposits is still not well constrained (She et al. 2021).
81	Abundant Silurian REE-Nb deposits and prospects distributed along the southern part
82	of the Qinling Orogenic Belt comprise an important REE-Nb metallogenic belt in central
83	China (Zhang et al. 2019a; Wang et al. 2021). Typical examples include the REE-Nb
84	deposits associated with the Miaoya and Shaxiongdong carbonatite-syenite complexes
85	(Xu et al. 2008, 2010; Ying et al. 2017; Chen et al. 2018; Ma et al. 2021; Wu et al. 2021)
86	and Nb-rich trachytes (e.g., Zhuxi) that cover an outcrop of approximately 100 km ² (Nie
87	et al. 2019; Wang et al. 2021; Yan et al. 2021). Despite previous works on the
88	petrogenesis of these complexes (Xu et al. 2008, 2010, 2014, 2015; Zhu et al. 2016; Ying
89	et al. 2017; Chen et al. 2018; Su et al. 2019, 2022; Yan et al. 2021) and the origin of REE
90	mineralization (Cimen et al. 2018; Nie et al. 2019; Zhang et al. 2019a, 2019b; Ying et al.
91	2020; Ma et al. 2021; Su et al. 2021), the styles of Nb mineralization have not yet been
92	well characterized, hindering an understanding of the Nb mineralization process. In this
93	contribution, we investigated the Nb mineralization style and process, and the controlling $5/47$

94 factors, exemplified by the Miaoya and Shaxiongdong REE-Nb deposits in the Qinling 95 belt, through a combined mineralogical and in-situ chemical-isotopic investigation. The 96 new findings provide new insights regarding key factors controlling diverse Nb 97 mineralization associated with carbonatite/alkaline rocks.

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GEOLOGICAL SETTING

100 The Qinling Orogenic Belt is a result of multi-stage tectonic evolution involving arc 101 terrane accretion, arc-continent collision, and continent-continent collision (Fig. 1a; 102 Meng and Zhang 2000; Chen 2010; Dong et al. 2011; Wu and Zheng 2013; Dong and 103 Santosh 2016), followed by the final collision between the North and South China cratons 104 at the Middle Triassic (230-220 Ma) along the Mianlue faults (Meng and Zhang 1999; Dong and Santosh 2016). The final collision was also accompanied by the formation of a 105 106 number of orogenic-type Ag-Au deposits (Pang et al. 2001; Xu et al. 2012; Yue and Deng 2019). The orogenic belt was generally divided into four units including the Southern 107 108 North China Craton, North Qinling, South Qinling, and Northern South China Craton that 109 are separated by the Luanchuan, Shangdan, and Mianlue faults from the north southward 110 (Fig. 1b; Wu and Zheng 2013). 111 The South Qinling unit, where the carbonatite/alkaline rock-hosted Nb-REE

112 mineralization developed, is dominated by a thin-skinned tectonics (Fig. 1b; Meng and

113 Zhang 1999, 2000; Dong et al. 2011; Wu and Zheng 2013). The Precambrian basement in

this unit includes the Wudang Terrane (Wudang and Yaolinghe Groups) in the south, and $\frac{6}{47}$

115	the Douling and Xiaomoling complexes in the north, and they are unconformably
116	covered by Phanerozoic limestones, clastic rocks, shales, and sandstones (Mattauer et al.
117	1985; Ratschbacher et al. 2003; Dong et al. 2011; Wu and Zheng 2013; Liu et al. 2016).
118	The Wudang and Yaolinghe Groups consist of greenschist facies metamorphosed
119	volcanic-sedimentary rocks, and the Douling and Xiaomoling complexes are mainly
120	composed of biotite gneiss and mafic rocks, respectively (Liu et al. 2016). The basement
121	rocks are intruded by mafic-ultramafic dykes and carbonatite-syenite complexes of
122	Silurian ages (Zhang et al. 2007; Xu et al. 2008) and Mesozoic granitoid intrusions (ca.
123	248-190 Ma) (Liu et al. 2011; Yang et al. 2012) (Fig. 1b).

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DEPOSIT GEOLOGY

126 The Miaoya and Shaxiongdong deposits, containing totally >1 Mt Nb ores at 0.1 wt% 127 Nb₂O₅ and 1.2 Mt REE ores at 1.5 wt% REE₂O₃, are located in the southwestern margin 128 of the Wudang Terrane (Fig. 1b). Both deposits are hosted in the Miaoya and 129 Shaxiongdong syenite-carbonatite complexes. The Miaoya complex intrudes both the 130 meta-quartz keratophyre of the Yaolinghe Group and the carbonaceous-sericite schist of the Meiziya Group along the Ankang-Desheng-Fangxian fault (Fig. 1c). The 131 132 spindle-shaped complex consists dominantly of syenites (>90 vol%; composed mainly of 133 K-feldspar) intruded by a number of carbonatitic dykes (>7.5 vol%) (Figs. 1c and 2a), 134 and locally contains abundant xenoliths of the country rocks (Fig. 2d-2e). The

135 carbonatitic dykes were classified as calciocarbonatite and ferrocarbonatite types based 136 on carbonate mineral assemblage (e.g., Ca-rich and Fe-rich carbonates; Su et al. 2019). The contacts between the carbonatites and syenites are generally sharp but locally 137 138 gradational (Figs. 2b-2c). Both the carbonatites and syenites have undergone extensive 139 hydrothermal carbonatization. Such alteration is characterized by the replacement of 140 primary magmatic minerals by fine-grained calcite and dolomite with minor quartz and 141 sulfides, associated with REE minerals-bearing or barren veinlets (Ying et al. 2020; Ma et 142 al. 2021). Notably, veinlets of quartz and graphite are also locally present (Fig. 2f), and 143 the graphite grains are generally disseminated and flaky in shapes (Fig. 3a). On the other hand, the spindle-shaped Shaxiongdong complex intrudes the 144 145 sericite-chlorite-albite schists of the Wudang Group (Fig. 1e). It consists mainly of nepheline syenites (77 vol%), which in turn intruded by calciocarbonatitic dykes (23 146 147 vol%) (10 to > 200 m in length) (Figs. 1e and 2g-2h). Similar to the Miaoya complex, the Shaxiogndong complex has undergone variable hydrothermal alteration, characterized by 148 149 the formation of secondary albite, biotite, baryte, and aegirine.

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151 STYLES OF NIOBIUM MINERALIZATION

152 Nb mineralization in Miaoya

153 The Nb ores in Miaoya are essentially Nb-mineralized syenites and carbonatites with

154	Nb_2O_5 content > 0.08 wt% (Fig. 1d) (Liu et al. 1984), and no clear boundaries between
155	the Nb ores and the host complexes can be defined. This situation is also applicable to the
156	REE ores (REE ₂ O ₃ content > 0.3 wt%) (Fig. 1d). It is notable, however, that the REE and
157	Nb mineralization are not entirely spatially overlapping, and thus the ores can be divided
158	into either REE-Nb or Nb ones (Fig. 1d). The REE minerals are mainly monazite and
159	bastnäsite-(Ce) in veinlet, stockwork, and to a minor extent, disseminated forms (Ying et
160	al. 2017, 2020; Zhang et al. 2019a; Ma et al. 2021). In contrast, the Nb minerals are
161	mainly present in disseminated form throughout the complexes (Figs. 3b-3g and 4), and
162	can be divided into magmatic and hydrothermal assemblages as illustrated below.

163 **Nb-bearing minerals in mineralized syenites.** The Nb-bearing minerals are mainly disseminated pyrochlore, rutile, and ilmenite with minor amount of columbite, which is 164 165 supposed to be magmatic origin due to intergrowths with the major rock-forming minerals such as K-feldspar and albite (Figs. 3d and 3g). These magmatic minerals were 166 hydrothermally overprinted, accompanied with the formation of new hydrothermal 167 168 Nb-bearing minerals, including rutile and columbite. For example, the coarse-grained magmatic pyrochlore grains (up to 1.5 mm), which are generally subhedral to anhedral, 169 170 were variably replaced by hydrothermal columbite and rutile; magmatic rutile grains of 171 bright BSE reflectance being replaced by porous secondary rutile of dark BSE reflectance (Fig. 4g); magmatic, BSE-homogeneous ilmenite is partially replaced by hydrothermal 172 173 rutile and columbite (Figs. 4i-4l). Magmatic columbite grains are relatively minor and 174 presenting as euhedral to subhedral platy oikocrysts, which are also variably 9/47

hydrothermally modified to form pseudohexagonal and porous grains infilled by variable hydrothermal mineral inclusions (e.g., phengite and bastnäsite) (Fig. 4e). In summary, the magmatic Nb minerals in the mineralized syenites of Miaoya are dominated by pyrochlore, rutile, and ilmenite with minor columbite, whereas columbite and rutile are the major hydrothermal Nb minerals.

Nb-bearing minerals in mineralized carbonatites. In this kind of ores, magmatic 180 181 Nb-bearing minerals are mainly disseminated pyrochlore and rutile with minor amount of columbite which are all closely associated with the rock-forming minerals (e.g., calcite 182 183 and apatite; Figs. 3b-3c and 3e-3f). Such an assemblage of magmatic Nb minerals is 184 broadly similar to that of the mineralized syenites, but having an elevated content of pyrochlore and without ilmenite. These minerals have also been hydrothermally 185 186 overprinted. For example, the magmatic pyrochlore grains commonly contain 187 homogenous, massive cores replaced by porous rims infilled by abundant fined-grained inclusions of hydrothermal columbite, rutile, uraninite, thorite, and aeschynite (Figs. 188 189 4a-4c). It is also common that some magmatic pyrochlore grains are partially to completely replaced by hydrothermal columbite and rutile (Figs. 4c-4d and 4f). The 190 191 magmatic rutile exhibits similar textures composed of a BSE-bright core and BSE-dark 192 rims (Fig. 4h). The magmatic columbite grains are similar to those in the mineralized syenites in terms of their pseudohexagonal shapes and porous and inclusion-rich textures, 193 194 albite the mineral inclusions are mainly ankerite and quartz. They are also commonly 195 replaced by hydrothermal rutile (Fig. 4f). In summary, the magmatic Nb-bearing minerals 10/47

in the mineralized carbonatites are dominated by pyrochlore and rutile with minor
columbite, whereas hydrothermal Nb-bearing minerals are mainly columbite and rutile
with trace amounts of aeschynite.

199 Nb mineralization in Shaxiongdong

The Nb ores in Shaxiongdong are also Nb-mineralized syenites or carbonatites, similar 200 201 to those of the Miaoya deposit. The Nb-bearing minerals are disseminated, and closely 202 associated with REE minerals and the major rock-forming minerals such as calcite, 203 ankerite, or K-feldspar (Figs. 3h-31 and 5). It is notable that the REE mineralization in 204 Shaxiongdong is relatively weak, and is characterized mainly by disseminated REE-rich apatite with minor allanite and burbankite. Similar to the Miaoya deposit, the 205 206 assemblages of Nb-bearing minerals in the mineralized syenites and carbonatites of 207 Shaxiongdong are different, but can also be divided into the magmatic and hydrothermal assemblages. 208

Nb-bearing minerals in mineralized syenites. The Nb-bearing minerals in these ores include mainly pyrochlore, rutile, ilmenite, and titanite with trace amounts of aeschynite (Figs. 3h and 3j-3l). They are closely associated with rock-forming minerals such as K-feldspar or nepheline (Figs. 3h and 3j-3l), and thus are supposed to be magmatic origin. These minerals also suffered from variable degrees of hydrothermal modification, and thus exhibit complex internal textures (Figs. 5a and 5c-5k). For example, the altered pyrochlore grains are free of magmatic oscillatory zoning but rich in cracks and pores,

216	and are generally composed of multiple domains with variable BSE intensities (Fig. 5a).
217	The subhedral to euhedral rutile grains also consist of primary BSE-bright and secondary
218	BSE-dark domains (Figs. 5c-5d), of which the latter are commonly full of inclusions such
219	as hydrothermal calcite and albite, and are variably replaced by hydrothermal ilmenite
220	along the rims and cracks (Figs. 5e-5f). The altered ilmenite grains are commonly porous
221	in appearance, and are variably replaced by secondary hydrothermal rutile, fersmite, and
222	titanite (Figs. 5g-5i). The altered titanite is similarly composed of primary, magmatic
223	BSE-bright and secondary BSE-dark domains (Fig. 5j). In summary, the magmatic
224	Nb-bearing minerals in the mineralized syenites include pyrochlore, rutile, ilmenite, and
225	titanite, whereas hydrothermal Nb-bearing minerals include ilmenite, rutile, and fersmite
226	with trace amounts of titanite.

Nb-bearing minerals in mineralized carbonatites. The Nb minerals in these ores are dominated by pyrochlore of which the contents are much higher than those in the mineralized syenites. The pyrochlore grains are generally subhedral to euhedral, appearing in disseminated or aggregate forms. They display conspicuous oscillatory zonation indicative of magmatic in origin (Fig. 5b). Notably, this study did not identify any hydrothermal Nb-bearing minerals in these ores.

Based on the field and petrographic observations, we summarized the paragenetic sequence of the Nb-bearing minerals in the ores as in Figure 6.

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236 SAMPLING AND ANALYTICAL RESULTS

237 Sampling

238	About 95 samples, including ores and host rocks, were collected from Miaoya, while
239	24 ore samples were collected from Shaxiongdong (Figs. 1c and 1e), and the sample
240	locations are illustrated in Figure 1. Chemical compositions of different Nb-bearing
241	minerals and U-Pb ages of titanite were obtained by electron probe micro-analysis
242	(EPMA) and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)
243	techniques, respectively. Bulk-sample major and trace elemental compositions were
244	obtained by X-ray fluorescence (XRF) spectrometry and ICP-MS, respectively. In-situ Sr
245	and Nd isotopic compositions of apatite were obtained by LA Multiple collector
246	(MC)-ICP-MS technique. Detailed analytical methods and results are available in Online
247	Supplemental Methods and Online Supplemental Tables 1-12, respectively.

248 U-Pb ages of titanite in Shaxiongdong

The analyzed titanite grains are from the mineralized syenites in Shaxiongdong, and consist of magmatic, BSE-bright cores and secondary BSE-dark domains. Both domains are characterized similarly by high U but low common Pb concentrations (Table S1). In the Tera-Wasserburg diagram, plots of the BSE-bright domains define a good regression line yielding a lower-intercept age of 432.0 \pm 3.6 Ma (2 σ , n = 71, MSWD = 1.5) with an initial ²⁰⁷Pb/²⁰⁶Pb ratio of 0.7189 (Fig. 7a), whereas the regression line for the BSE-dark

domains yields a slightly younger lower-intercept age of 423.3 \pm 6.6 Ma (2 σ , n = 54, MSWD = 2.7) with an initial ²⁰⁷Pb/²⁰⁶Pb ratio of 0.7395 (Fig. 7b).

257 Mineral compositions of Miaoya and Shaxiongdong

258	Pyrochlore group minerals. Pyrochlore group minerals $(A_{2-m}B_2X_{6-w}Y_{1-n}\cdot pH_2O)$, where
259	m = 0-1.7; $w = 0-0.7$; $n = 0-1$; $p = 0-2$; $X = O$, OH; and $Y = O$, OH, and F) generally have
260	highly variable compositions due to the flexibility in the crystal structures (Nasraoui and
261	Bilal 2000; Zurevinski and Mitchell 2004). According to the relative contents of Nb, Ti,
262	Ta, and U (Table S2), pyrochlore group minerals in Miaoya can be subdivided into
263	U-poor pyrochlore, uranpyrochlore, and U-rich betafite with increasing TiO_2 (2.96 to
264	23.39 wt%) and UO ₂ (0 to 30.14 wt%) but decreasing Nb ₂ O ₅ contents (69.35 to 15.43
265	wt%) (Figs. 8a and 9a). Notably, pyrochlore group minerals in the mineralized syenites of
266	Miaoya are generally U-poor, whereas those in the mineralized carbonatites include
267	U-poor pyrochlore, uranpyrochlore, and U-rich betafite (Figs. 8a and 9a; Xu et al. 2015).
268	This feature is different from those of Shaxiongdong which are mainly U-poor pyrochlore.
269	In the ternary plots of Ca, Na, and A-site vacancies (VA) (Nasraou and Bilal 2000;
270	Lumpkin and Ewing 1995), the pyrochlores in the mineralized syenites of Miaoya plotted
271	in the magmatic field, whereas those in the mineralized carbonatites exhibit magmatic,
272	hydrothermal, and supergene alteration trends (Fig. 8b). On the other hand, the
273	pyrochlores from the Shaxiongdong deposits (including the mineralized syenites and
274	carbonatites) show the magmatic and hydrothermal trends (Fig. 8b). In general, the $14/47$

275 U-poor pyrochlore grains from Miaoya and Shaxiongdong show broadly similar Nb, Ca,

and Ti concentrations (Figs. 9a-9c).

There are negative correlations between Nb and U, and Ti and Ca contents in the 277 278 pyrochlore group minerals of the mineralized carbonatites in Miaoya, whereas the Nb 279 content is positively correlated with that of Ca (Figs. 9a-9c). Similar positive correlation between Ca and Nb contents is also observed for the pyrochlore in Shaxiongdong (Fig. 280 281 9b). To summarize, the pyrochlore group minerals in Miaoya exhibit obviously negative 282 correlations of Ca+Nb contents with U+Ti and LREE+Ti contents but positive 283 correlations of Ca content with Na+LREE contents, whereas those in Shaxiongdong 284 exhibit obviously positive correlations between Ca or Ca+Ti contents and Na+LREE, 285 Na+Nb, or Na+Ta contents (Figs. 9d-9h).

Columbite. The columbite grains analyzed include the magmatic and hydrothermal ones that are only present in the Miaoya deposit (Figs. 4a-4f). They are all ferrocolumbite in compositions, characterized by high FeO (16.52-24.35 wt%) and Nb₂O₅ contents (59.88-77.35 wt%) (Table S3). However, the magmatic columbite grains tend to contain relatively higher Nb content but lower Ta content and Ta/(Nb+Ta) ratios (Fig. 10a). Notably, the contents of Nb₂O₅ and Ta₂O₅ are negatively correlated (Fig. 10b).

292 **Nb-rich rutile.** The magmatic rutile in various ores of Miaoya, including BSE-bright 293 and BSE-dark domains, show broadly similar Ti, Fe, and Nb concentrations (Figs. 294 11a-11b; Table S4). On the other hand, the BSE-bright domains of the magmatic rutile in 295 the mineralized syenites of Shaxiongdong exhibit much higher Nb and Fe but lower Ti $\frac{15}{47}$

contents than the BSE-dark domains or individual hydrothermal rutile grains (Figs. 296 297 11d-11e; Table S4). It is notable that all the rutile grains from both deposits have Fe+Nb content negatively correlated with that of Ti (Figs. 11a and 11d), but the FeO content is 298 positively correlated with that of Nb₂O₅ (Figs. 11b and 11e), indicating that the 299 incorporation of Nb into the rutile is compensated by Fe^{2+} and Fe^{3+} . However, they have 300 different Fe²⁺/Fe³⁺ ratios, which is well reflected in the invariant diagram of FeO versus 301 302 Nb₂O₅ (Figs. 11b and 11e). For example, the rutile grains in Miaoya, regardless of the origin, plotted mostly within the field of Fe/Nb ratios from 0.5 to 1.0, whereas those in 303 304 Shaxiongdong plotted mostly along the Fe/Nb=1.0 line, indicative of relatively high Fe^{3+}/Fe^{2+} ratios (Figs. 11b and 11e). 305

Nb-rich ilmenite. Analyzed ilmenite grains in both deposits are mainly from the mineralized syenites, including those of magmatic and hydrothermal origins. All analyzed grains exhibit broadly comparable concentrations of Mg, V, Cr, Al, or Ti (Figs. 11c and 11f; Table S5), even though the ilmenite grains from Shaxiongdong tend to have Nb contents (Nb₂O₅: 0.1-0.91 wt%) slightly higher than those in Miaoya (0.01-0.70 wt%) (Figs. 11c and 11f).

312 **Nb-rich titanite.** Titanite grains are only present in the mineralized syenites of 313 Shaxiongdong. Both the primary, magmatic BSE-bright and secondary, hydrothermal 314 BSE-dark domains have similarly low F (<1.33 wt%) but variable Nb contents 315 (1673-5603 ppm) (Table S6-7). They are also similarly enriched in LREEs relative to 316 HREEs (Fig. 12a), but have different REE and Nb contents and chondrite-normalized $\frac{16}{47}$

317 REE patterns (Figs. 12b-12d).

Apatite. Both the BSE-bright and BSE-dark domains of the apatite from Shaxiongdong are fluorapatite, characterized by sufficiently high F and Na but low Cl and OH contents (Table S8-9). Composition of apatite from Miaoya is available in the published literature (e.g., Ma et al. 2021), and was analyzed to have high F and Na contents.

323 Bulk-sample major and trace elemental compositions

The bulk major and trace elemental compositions of various ores and host rocks (e.g., 324 325 the Wudang, Yaolinghe and Meiziya Groups) are illustrated in Table S10. The mineralized carbonatites in the Miaoya and Shaxiongdong deposits are characterized by 326 327 relatively high REE but variable Nb contents (3.50-998 ppm), whereas the mineralized 328 syenites contain relatively high Nb but moderate REE concentrations (Figs. 13a-13e). It 329 is notable that the ores sampled from the margins (i.e., close to the country rocks) of the 330 Miaoya complex have relatively high U contents (Fig. 13f). The country rocks, especially 331 those of the Yaolinghe and Wudang Groups, have much lower Nb (< 100 ppm) and REE 332 (< 1000 ppm) contents (Fig. 13e). The rocks of the Yaolinghe and Meiziya Groups have 333 relatively high U contents up to 21 ppm, when compared to that of the Wudang Group (< 334 3 ppm; Fig. 13f).

335 Sr-Nd isotopic compositions of apatite

336	The in-situ Sr-Nd isotopic analysis was only applied to the apatite from the mineralized
337	carbonatites of Shaxiongdong. The results show that these grains, including BSE-dark
338	and BSE-bright domains, have high Sr (> 4180 ppm) but extremely low Rb (< 0.4 ppm)
339	concentrations (Table S9), and thus age correction for initial ⁸⁷ Sr/ ⁸⁶ Sr ratios is not needed.
340	The ⁸⁷ Sr/ ⁸⁶ Sr ratios of the BSE-bright, magmatic domains range from 0.70323 to 0.70360,
341	broadly identical to those of the BSE-dark, secondary domains (0.70312 to 0.70358)
342	(Figs. 14a-14b; Table S11). In addition, the BSE-bright domains have ¹⁴⁷ Sm/ ¹⁴⁴ Nd and
343	143 Nd/ 144 Nd ratios ranging from 0.08498 to 0.15290 and 0.51253 to 0.51269, respectively
344	(Table S12), corresponding to the ϵ Nd(t) values of 2.85 to 5.01 (calculated at ~430 Ma;
345	i.e., the age of titanite obtained in this study). On the other hand, the BSE dark domains
346	have 147 Sm/ 144 Nd and 143 Nd/ 144 Nd ratios varying from 0.13056 to 0.19403 and 0.51262 to
347	0.451275, respectively, corresponding to the calculated $\epsilon_{Nd}(t)$ values of 1.89 to 3.54,
348	similar to those of the BSE-bright domains (Figs. 14c-14d).

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DISCUSSION

351 Controls on diverse Nb mineralization

Recent studies confirmed that late-stage hydrothermal upgrading of early cumulated REEs in magmatic stages is responsible for major economic REE mineralization (the

forms as monazite and bastnäsite) in Miaoya and/or diverse REE mineral assemblages in Miaoya and Shaxiongdong (Zhang et al. 2019a; Ying et al. 2020; Ma et al. 2021; Su et al. 2022). However, the relative roles of the magmatic and late hydrothermal processes on producing the diverse Nb mineralization in both deposits are currently not fully understood (Walter et al. 2018; Ying et al. 2017, 2023; Wu et al. 2021). In the following sub-sections, we will discuss the magmatic and hydrothermal controls on the diverse Nb mineralization styles in the two deposits.

361 Magmatic controls. In both deposits, the magmatic Nb-bearing minerals in the mineralized syenites are similarly dominated by pyrochlore, rutile, and ilmenite, while 362 those in the mineralized carbonatites are mainly pyrochlores (Fig. 6). The differences are 363 that the mineralized syenites of Shaxiongdong contain a higher abundance of titanite with 364 365 trace amounts of aeschynite, whereas those of Miaoya contain minor amount of 366 columbite (Figs. 3-6), and that the mineralized carbonatites of Miaoya contain an addition of minor amounts of rutile and columbite (Fig. 6). In general, the crystallization of 367 368 pyrochlore (instead of perovskite-structured compounds) in magmas is mainly controlled 369 by Na and F contents (>1 wt%) and high F/OH ratios which could stabilize pyrochlore as 370 a primary liquidus phase (Jago and Gittins 1993; Mitchell and Kjarsgaard 2002, 2004). 371 Such a criterion should be fulfilled in both deposits, as the magmatic apatite grains in the 372 mineralized syenites and carbonatites of Miaoya and Shaxiongdong do have similarly high F and Na contents (Table S8-9; Ma et al. 2021). However, the compositions of 373 374 pyrochlore group minerals in different types of ore in the two deposits are different. For 19/47

375 example, the pyrochlore group minerals in the mineralized carbonatites of Miaoya are 376 characterized by an assemblage of U-poor pyrochlore, uranpyrochlore, and U-rich betafite, different from those in other Nb ores of Miaoya and Shaxiongdong which 377 contain only U-poor pyrochlore (Figs. 8a and 9a). This discrepancy is also consistent 378 379 with bulk-ore compositions showing that some samples of the mineralized carbonatites in 380 Miaoya have relatively high U contents (up to 230 ppm; Fig. 13f). Such a high-U feature 381 cannot solely be controlled by a primary mantle source, as previous studies confirmed 382 that the parental magmas for both deposits were similarly derived from a common 383 depleted mantle source (Xu et al. 2008, 2014; Chen et al. 2018; Su et al. 2019, 2022). 384 Instead, subsequent differentiation (such as assimilation and/or fractionation 385 crystallization) could be an alternative factor. Considering that the country rocks of both deposits contain remarkably different U contents, and specifically the host rocks (i.e., the 386 387 Yaolinghe and Meiziya Groups) of the Miaoya deposit have much higher U contents (Fig. 13f), we propose that local assimilation of the U-rich host rocks could be the potential 388 389 cause for the formation of the magmatic U-rich pyrochlore in the mineralized 390 carbonatites. Such proposal is further supported by the fact that the U-rich ores are indeed 391 sampled in the parts where xenoliths of U-rich country rocks are widely present. The 392 Sr-Nd isotopic compositions of these samples are indicative of extensive assimilation 393 (Figs. 14 and 15a). In addition to U, the assimilation of the U-rich silicate rocks also 394 provided a considerable amount of Si that promotes the crystallization of apatite (~ 9.5 395 vol% in Miaoya, ~2.0 vol% in Shaxiongdong (Figs. 4a-4d and 5b-5c; Aenenburg et al. 20/47

396 2020, 2021).

397 In summary, magmas similarly crystallized U-poor pyrochlore at the very beginning, by consuming Na, Ca, REE, and Nb, at both the Miaoya and Shaxiongdong deposits (Fig. 398 399 8). However, subsequent assimilation of U-rich country rocks into the carbonatitic melts 400 at Miaoya has triggered crystallization of Nb-Ca-low but U-Ti-rich pyrochlore, U-Ti-rich 401 betafite, and rutile due to elevated U and Ti contents in the residual magmas (Figs. 9a-9c). 402 On the other hand, crystallization of minor magmatic titanite and columbite in both 403 Shaxiongdong and Miaoya deposits may be attributed to relatively low degree of magma evolution and crystallization of some Fe³⁺-rich minerals (e.g., biotite and magnetite), 404 405 respectively.

406 Hydrothermal controls. Our results show that the hydrothermal Nb-bearing minerals 407 in various ores of the two deposits contain rutile. The major difference is that the Miaoya 408 deposit is in addition rich in columbite with a trace amount of aeschynite, whereas the 409 Shaxiongdong deposit contains minor fersmite and ilmenite with a trace amount of 410 titanite (Figs. 3-6). Previous studies well documented that hydrothermal alteration of pyrochlore could result in columbitization (e.g., Aley and Saint-Honoré deposits) 411 412 (Chakhmouradian et al. 2015; Tremblay et al. 2017). Such a process should be applicable 413 to Miaoya, as the hydrothermal columbite grains mostly form through replacing early magmatic pyrochlore (Figs. 4a-4d and 6). This alteration is also accompanied with the 414 415 formation of fine uraninite, thorite, and aeschynite that present as inclusions in the altered 416 pyrochlores (especially the U-rich ones) (Figs. 4a-4b). For Shaxiongdong, although the 21/47

417 early magmatic pyrochlores also suffered from variable hydrothermal modification, no418 columbite or uraninite was observed to be formed (Figs. 5a-5b).

419 Different alteration products of the magmatic precursors at the two deposits strongly 420 suggested distinguished hydrothermal events that likely involved distinct fluids despite 421 the spatial proximity of the two deposits. Previous dating results of hydrothermal 422 monazite, bastnäsite, and columbite from Miaoya revealed an age of ~220 Ma for the 423 hydrothermal event, remarkably younger than the hosting complex (\sim 430 Ma; Fig. 16; 424 Xu et al. 2014, 2015; Ying et al. 2017; Zhang et al. 2019a; Wu et al. 2021). This event is 425 coeval to the widespread orogenic Au-Ag mineralization in South Qinling, and thus was suggested to be genetically related (Ma et al. 2021). This interpretation is well supported 426 427 by the bulk-carbonatite C-O isotopic data (Xu et al. 2014; Cimen et al. 2018; Su et al. 428 2019; Zhang et al. 2019b) that display a mixing trend between the mineralized or barren 429 carbonatites and the Au-Ag deposits (Fig. 15b). In contrast, this study obtained a distinct U-Pb age of 423.3 ± 6.6 Ma for the BSE-dark, hydrothermal domains of the titanite 430 431 grains from Shaxiongdong, slightly younger than the age of 432.0 ± 3.6 Ma for the 432 BSE-bright, magmatic domains of the titanite (Fig. 7), thus suggesting a hydrothermal 433 event distinct from that in Miaoya. Indeed, carbonatite-like C-O isotopic compositions of 434 the altered ores/rocks in Shaxiongdong (Xu et al. 2008; Chen et al. 2018) (Fig. 15b) 435 strongly indicate that such a hydrothermal event could be authigenic in origin, likely 436 genetically related to the carbonatitic melts.

437 Processes in response to the variety of hydrothermal Nb mineralogy in Miaoya and

438 Shaxiongdong

The different sources and natures of hydrothermal fluids, as revealed earlier, should be 439 440 responsible for the diverse hydrothermal Nb mineralogy (and the associated diverse compositions) in the Miaoya and Shaxiongdong deposits. The pyrochlore grains from 441 Shaxiongdong have compositions generally located in the "magmatic" 442 and 443 "hydrothermal" fields of the VA-Ca-Na triangle diagram (Fig. 8b), whereas those in Miaoya additionally plot in the unexpected "supergene" fields along the "S" evolution 444 445 trend (Fig. 8b; Lumpkin and Ewing 1995; Nasraoui and Bilal 2000). This feature 446 indicates that the Miaoya pyrochlore likely has experienced the secondary alteration more intensive than those in Shaxiongdong, resulting in more leaching of the elements from the 447 A-site to produce more A-site vacancies (VA) in the pyrochlore grains, thus plotting in 448 449 the "supergene" field (Fig. 8b; Zurevinski and Mitchell, 2004).

Generally, the presence of distinctly abundant hydrothermal columbite (FeNb₂O₆) and uraninite (UO₂) in Miaoya (i.e., the replacement products of magmatic uranpyrochlore; Figs. 4a-4c) indicates that the fluid is characterized by a low oxygen fugacity due to high Fe²⁺ and U⁴⁺. Hydrothermal rutile (or BSE-dark domains of the magmatic ones) in Miaoya have compositions plotting close to the line of Fe/Nb=0.5 (Fig. 11b), also suggestive of a relatively reducing condition. This interpretation is further supported by local presences of graphite in hydrothermal veins at Miaoya (Figs. 2f and 3a). Therefore,

457 the replacement of pyrochlore by columbite, involving such reducing, acidic fluids

459 reaction in the presence of sufficient Fe^{2+} (Chakhmouradian et al. 2015):

On the other hand, the formation of minor fersmite and ilmenite instead of columbite in the hydrothermal stage at Shaxiongdong should be related to fluids distinctly rich in Ca but relatively depleted in Fe^{2+} (i.e., relatively oxidized), consistent with the generally Ca-rich and oxidized authigenic fluids derived from carbonatite (e.g., Xie et al. 2015). The oxidizing feature is further supported by the chemical compositions of the hydrothermal rutile from Shaxiongdong, which plot mostly along the line of Fe/Nb=1 in the FeO versus Nb₂O₅ bivariant diagram (Fig. 11e).

468 **Decoupling of Nb and REE mineralization**

Decoupling of REE and Nb during magmatic process. The magmatic REE-rich 469 470 minerals in Miaoya and Shaxiongdong are dominantly apatite and allanite that are closely 471 associated with the magmatic Nb-bearing minerals such as pyrochlore, rutile, ilmenite, and titanite (Figs. 3-5). However, the relative abundances of the magmatic REE-bearing 472 473 and Nb-bearing minerals in different ores are highly variable, indicating that REE and Nb are decoupled during magmatic process. For example, the mineralized carbonatites of 474 475 both deposits have higher abundances of magmatic REE minerals (e.g., apatite and 476 allanite), whereas the mineralized syenites contain more abundant Nb-rich minerals such

as rutile, ilmenite, and titanite (Figs. 6). Such a decoupling of REE and Nb is possibly
ascribed to the immiscibility of the conjugated carbonatitic and syenitic melts (Su et al.
2021, 2022), as the REE and Nb generally tend to favor partitions into carbonatite and
silicate melts, respectively (Wyllie et al. 1996; Suk 2012).

481 Decoupling of REE and Nb during late hydrothermal overprinting. Previous 482 studies documented that the major REE mineralization in Miaoya has formed through 483 secondary remobilization and upgrading of early magmatic REEs dispersed throughout 484 the whole Miaoya complex (e.g., in apatite or calcite, Ying et al. 2020; Ma et al. 2021). 485 These studies also revealed that the remobilized REE finally precipitated as monazite and 486 bastnäsite-(Ce) dominantly in veinlets, supporting an extensive redistribution of REEs 487 during late hydrothermal overprinting. In contrast, the Nb mineralization in Miaoya is 488 dominantly present as disseminated minerals that have closely intergrown with magmatic 489 rock-forming minerals (Fig. 4), and the REE-rich veinlets do not contain any Nb-bearing 490 minerals (Figs. 3-5). These features, in combination with the fact that the hydrothermal 491 columbite and rutile are genetically and spatially associated with the magmatic precursors, 492 strongly indicate that the major Nb mineralization in Miaoya should be primary 493 magmatic in origin and the late-stage external hydrothermal overprinting (i.e., related to 494 the Ag-Au mineralization event) did not essentially produce extensive, large-scale 495 mobilization of Nb but only local redistribution. In particular, bulk-rocks composition 496 shows that the REE contents are in general negatively correlated with the Nb contents 497 (Fig. 13e), further confirming that the REE and Nb were decoupled during the fluid 25/47

metasomatism. On the other hand, both the carbonatites and syenites of Shaxiongdong do
not show expected remarkable REE enrichments (total REE mostly < 1000 ppm) (Fig.
13), and there is a roughly positive correlation between Nb and REE contents (Fig. 13e),
indicating that the authigenic fluids at Shaxiongdong did not extensively remobilize the
REEs in the manner observed at Miaoya, and did not decouple the REE from the Nb.

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IMPLICATIONS

505 Although carbonatites and alkaline rocks host the majority of the world's REE and Nb 506 resources, it was well documented that not all of them are associated with REE and Nb 507 mineralization, particularly for those at convergent belts (Chakhmouradian et al. 2015; 508 Liu and Hou 2017). Our studies provide strong evidence that secondary fluids, no matter 509 the external, reducing or authigenic, oxidizing fluids, cannot essentially remobilize Nb on large scales, and the hydrothermal Nb minerals often formed through in-situ replacement 510 511 of early magmatic precursors, in contrary to the REE which is remarkably remobilized 512 and enriched to ore grade during fluid metasomatism, as well recorded in the Miaoya 513 deposit (Ma et al. 2021). The new findings imply that different behaviors of REE and Nb 514 during hydrothermal processes could be one of the key factors responsible for the spatial 515 decoupling of REE and Nb mineralization associated with carbonatites and alkaline rocks. 516 Our new results thus provide new indicators for REE and Nb resources exploration in 517 such rocks particularly for those suffering extensive hydrothermal overprinting. This 26/47

518 study also highlights that fluid nature could be one of the foremost control on the 519 decoupling of REE and Nb, as exemplified by the Shaxiongdong deposit.

This study also confirmed that both magmatic and hydrothermal processes are able to 520 produce diverse Nb mineralogy in individual Nb deposits, during which multiple 521 522 parameters such as oxygen fugacity, magma composition, and nature of fluid play key 523 roles. Clear understanding of these processes is useful for Nb beneficiation and 524 metallurgy. For example, the common economic Nb minerals are mainly pyrochlore group minerals, whereas columbite and rutile are Nb-rich but currently not optimal for 525 526 metallurgical beneficiation. As such, the hydrothermal overprinting in both deposits, 527 which variably modified the economic, magmatic pyrochlore, would significantly affect the utilization of the Nb ores. On such basis, we propose that the primary magmatic Nb 528 529 deposit without or with only minor hydrothermal alteration would be relatively favorable 530 for Nb beneficiation.

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FIGURE CAPTIONS

FIGURE 1. (a) Tectonic map of China. (b) Geological sketch of the Qinling Orogenic
Belt and the location of the Miaoya and Shaxiongdong deposits (modified from Zhang et

al. 2019a). (c) Simplified geological map of the Miaoya carbonatite-syenite complex

(modified from Liu et al. 1984). (d) Simplified geological plans showing the distributions

of REE and Nb ore bodies (REE₂O₃ > 0.3 wt% and Nb₂O₅ > 0.08 wt%) in the Miaoya

796 complex (modified from Liu et al. 1984). (e) Simplified geological map of the

797 Shaxiongdong carbonatite-syenite complex (modified from Xu et al. 2008).

798 Abbreviations: S-NCC = Southern North China Craton; NQL = North Qinling; SQL =

799 South Qinling; N-SCC = Northern South China Craton.

800

FIGURE 2. Field photos of various rocks/ores in Miaoya and Shaxiongdong. (a)
 Carbonatites intruding syenites in the Miaoya complex. (b-c) The carbonatites are sharp 41/47

(b) or transitional (c) contacts with the syenites in Miaoya. (d-e) rock xenoliths of the
Yaolinghe and Meiziya Groups in the mineralized carbonatites (d) and syenites (e) of
Miaoya. (f) Quartz-graphite veins in syenites and country rocks of Miaoya. (g)
Carbonatites intruding syenites of Shaxiongdong. (h) Carbonatites in Shaxiongdong,
containing abundant biotite aggregates.

808

809 FIGURE 3. Photomicrographs of various Nb mineralogy in the Miaoya and Shaxiongdong deposits. (a) Minor fine-grain graphite present in the mineralized Miaoya 810 carbonatites, associated with magmatic calcite and apatite. (b-c) Medium- to 811 812 coarse-grained pyrochlore crystals are partially replaced by columbite (b) and columbite (c) in the mineralized carbonatites of Miaoya. (d-e) Rutile grains intergrown with 813 814 K-feldspar in mineralized syenites (d) or calcite in carbonatites (e) of Miaoya. (f) 815 Irregular hydrothermal rutile grains intergrown with pyrite in mineralized carbonatites of 816 Miaoya. (g) Regular ilmenite intergrown with allanite in mineralized syenites of Miaoya. (h-i) Anhedral to euhedral pyrochlore grains intergrown with K-feldspar of mineralized 817 818 syenites (h) or apatite in mineralized carbonatites (i) of Shaxiongdong. (j-l) Anhedral to 819 euhedral rutile (j), ilmenite (k), and titanite (l) grains intergrown with K-feldspar, albite, 820 and epidote in mineralized syenites of Shaxiongdong. Abbreviations: Ab = albite; Aln = 821 allanite; Ank = ankerite; Ap = apatite; Cal = calcite; Chl = chlorite; Clb = columbite; Ep 822 = epidote; Gr = graphite; Ilm = ilmenite; Kfs = K-feldspar; Mag = magnetite; Pcl =

823 pyrochlore; Py = pyrite; Qz = quartz; Rt = rutile; Ttn = titanite; Upcl = uranpyrochlore.

824

825	FIGURE 4. BSE images of various Nb ores in the Miaoya deposit. (a-b) Coarse-grained
826	(a) and medium-grained (b) uranpyrochlore grains in mineralized carbonatites. Note that
827	they are in close association with apatite but are variably modified, associated with the
828	presences of abundant inclusions of secondary hydrothermal minerals such as columbite,
829	rutile, uraninite, thorite, and aeschynite. (c-d) The uranpyrochlore grains in mineralized
830	carbonatites are partially (c) or completely (d) replaced by secondary columbite. (e-f)
831	Primary magmatic columbite grains in mineralized syenites are variably disturbed by
832	hydrothermal bastnäsite (e) or rutile (f) along rims and crack. (g-h) Magmatic rutile
833	grains in mineralized syenites (g) and carbonatites (h) have porous or inhomogeneous
834	appearances. (i) Secondary rutile replacing early magmatic ilmenite in the mineralized
835	carbonatites (i1) or quartz veins (i2). (j-k) Magmatic ilmenite grains in mineralized
836	syenites are closely associated with allanite (j) or apatite (k) . (l) Secondary columbite
837	grains present as inclusions in altered ilmenite. Abbreviations: Aes = Aeschynite; Bsn =
838	batnäsite; Mnz = monazite; Ph = phengite; Thr = thorite; Urn = uraninite. Other
839	abbreviations are the same as those in Figure 3.

FIGURE 5. BSE images of various Nb ores in the Shaxiongdong deposit. (a) Pyrochlore
grains in mineralized syenites were altered. (b) Pyrochlore grains in mineralized

842	carbonatites exhibit well-developed oscillatory zoning. (c-d) Magmatic rutile grains in
843	mineralized syenites. Note that they are intergrown with magmatic apatite (c) and pyrite
844	(d), and contain BSE-bright and -dark domains. (e-f) Magmatic rutile in mineralized
845	syenites exhibits porous appearances, and was replaced by secondary calcite (e) or
846	ilmenite (f) along rims. (g-i) Early ilmenite grains in mineralized syenites are partially
847	replaced by rutile, fersmite (g), albite (h), or titanite (i), and exhibit porous appearances.
848	(\mathbf{j}) Magmatic titanite in mineralized syenites contains BSE-bright and dark domains. (\mathbf{k})
849	Fibrous aeschynite grains in mineralized syenites present as aggregates. (1) magmatic
850	apatite in mineralized carbonatites contains BSE-bright and dark domains. Abbreviations:
851	Aeg = aegirine; Anc = ancylite; Brt = baryte; Bt = biotite; Dol =dolomite; Fsm = Fersmite.
852	Other abbreviations are the same as those in Figures 3 and 4.
853	

FIGURE 6. Paragenetic sequences of REE and Nb mineralization in the Miaoya and
Shaxiongdong deposits. The arrows indicate replacing products of related precursors.

856

FIGURE 7. Tera-Wasserburg plots for the U-Pb ages of the BSE-bright (a), and
BSE-dark (b) domains of titanite from the mineralized syenites of Shaxiongdong.

859

860	FIGURE 8. (a) Variation of B-site cations (Nb-Ta-Ti) of the pyrochlore group minerals
861	in the Miaoya and Shaxiongdong deposits (diagram cited from Hogarth 1977). (b)
862	Variation of the A-site cations (Ca-Na) and lattice vacancies (VA) of the pyrochlore group
863	minerals in the Miaoya and Shaxiongdong deposits (diagrams cited from Nasraou and
864	Bilal 2000 and Lumpkin and Ewing 1995). Note that the concepts of P, T, and S trends
865	were described in Lumpkin and Ewing (1992, 1995). The data for the Miaoya pyrochlore
866	is cited from Xu et al. (2015). Abbreviations: MY= Miaoya; SXD = Shaxiongdong; C =
867	Carbonatites; S = Syenites.

868

FIGURE 9. Bimodal plots of U vs. Nb (a), Ca vs. Nb (b), Ca vs. Ti (c), U+Ti vs. Ca+Nb

870 (d), LREE+Ti vs. Ca+Nb (e), Na+LREE vs. Ca (f), Na+Nb vs. Ca+Ti (g), and Na+Ta vs.

871 Ca+Ti (h) for the pyrochlore group minerals from the Miaoya and Shaxiongdong deposits.

872 The data for the Miaoya pyrochlore is cited from Xu et al. (2015).

873

FIGURE 10. Bimodal plots of Ta/(Nb+Ta) vs. Mn/(Fe+Mn) (a) and Ta₂O₅ vs. Nb₂O₅ (b)

875 for magmatic and hydrothermal columbite from the Miaoya deposit.

876

FIGURE 11. Bimodal plots of Ti vs. Fe+Nb, and FeO vs. Nb₂O₅ of rutile in the Miaoya

- 878 (**a**, **b**) and Shaxiongdong (**d**, **e**) deposits, and bimodal plots of TiO_2 vs. Nb_2O_5 of ilmenite
- 879 in the Miaoya (c) and Shaxiongdong (f) deposits.

880

FIGURE 12. Bimodal plots of LREE vs. HREE+Y (a), REE vs. Nb (b), and (La/Yb)_N vs.

882 REE+Y (c), and chondrite-normalized REE patterns (d) for different domains of titanite

in mineralized syenites of Shaxiongdong.

884

FIGURE 13. Plots of CaO vs. REE (a), SiO₂ vs. REE (b), CaO vs. Nb (c), SiO₂ vs. Nb

(d), Nb vs. REE (e), and SiO₂ vs. U (f) for bulk ore/rock samples from the Miaoya and

887 Shaxiongdong deposits. Note that the data of the Wudang and Yaolinghe Groups are

- collected from Ling et al. (2002), Su et al. (2006), Luo et al. (2010), Zhu et al. (2014),
- 889 Zhang (2020), and Zhao et al. (2022).

890

FIGURE 14. Histograms showing 87 Sr/ 86 Sr (**a**, **b**) and $\varepsilon_{Nd}(t)$ (**c**, **d**) values for BSE-bright and BSE-dark domains of apatite from mineralized carbonatites of Shaxiongdong. The data for the Miaoya apatite is cited from Ma et al. (2021). Note that $\varepsilon_{Nd}(t)$ values are calculated by using the age of 430 Ma.

895

896	FIGURE 15. (a) Summary of the previous $\varepsilon Nd(t)$ vs. initial Sr isotopic data of whole
897	rocks from the Miaoya and Shaxiongdong complexes and the Yaolinghe Groups (Xu et al.
898	2008, 2014; Zhu et al. 2014, 2016; Cimen et al. 2018; Su et al. 2019, 2022; Zhang et al.
899	2019b). Note that data of the mantle end-members are from Hart (1988). (b) Summary of
900	previous C-O isotopic compositions of carbonate grains from the Shaxiongdong and
901	Miaoya complexes (Xu et al. 2008, 2014; Chen et al. 2018; Cimen et al. 2018; Zhang et
902	al. 2019b; Su et al. 2019). The data for the Au-Ag deposits are cited from Pang et al.
903	(2001), Zhang et al. (2010), and Yue and Deng (2019).

904

FIGURE 16. Summary of geochronological data showing multi-stage magmatic,
hydrothermal or mineralization events in the region. Geochronological data are collected
from Li et al. (1989), Xu et al. (2008, 2014, 2015), Zhu et al. (2016), Ying et al. (2017,
2020), Chen et al. (2018), Zhang et al. (2019a), Su et al. (2019, 2021), Wu et al. (2021),
and this study.



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Fig. 6



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Fig. 16

	Miaoya	Shaxiongdong	Magmatism/mineralization events
700	Wudang	Group	South Qinling basement
600	Yaolinghe Group		423.3±6.6 Ma BSL bindle domina 423.3±6.6 Ma Difficulture Contraction
500			
400	⁺∙⁺+ + + + +	• • • 😣	Carbonatite-syenite magmatism ~430 Ma
7			
300	¢		
200	• [•] • • • • • • • • • • • • • • • • •	ф Ф	Hydrothermal metasomatism ~220 Ma
Age	(Ma)		