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

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ABSTRACT

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 the processes behind are still poorly understood. Exemplifying with the ~430 Ma Miaoya and Shaxiongdong carbonatite-syenite complexes in the southern Qinling orogenic belt, 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 disseminated form. Both the magmatic and hydrothermal processes have attributed to Nb mineralization in both deposits, despite different in the mineralization style. The Nb-bearing minerals in the mineralized Miaoya syenites include magmatic U-poor pyrochlore, rutile, and ilmenite with minor amounts of columbite, and hydrothermal columbite and rutile, whereas those in the mineralized carbonatites are mainly magmatic U-poor pyrochlore, uranpyrochlore, U-rich betafite, and rutile with minor amounts columbite, and hydrothermal columbite and rutile. On the other hand, the Nb-bearing minerals in the mineralized Shaxiongdong syenites include magmatic U-poor pyrochlore, titanite, rutile, and ilmenite, and hydrothermal fersmite, rutile, and ilmenite, whereas those in the mineralized carbonatites are mainly magmatic U-poor pyrochlore without 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., the hosting Yaolinghe and Meiziya Groups) and magma differentiation are responsible for diverse magmatic Nb mineralization in the two deposits. On the other hand, the diverse
assemblages of hydrothermal Nb minerals in Miaoya and Shaxiongdong are mainly controlled by variation in the nature of fluid constrained to be genetically related to the ~220 and ~420 Ma hydrothermal events, respectively. In summary, both magma evolution (e.g., differentiation, assimilation) and late hydrothermal overprinting are responsible for the diverse Nb mineralogy in carbonatites-alkaline complexes, a situation that is commonly observed worldwide.

**Keywords:** Pyrochlore group minerals, Columbite, Diverse Nb mineralization, Miaoya, Shaxiongdong, Carbonatite-syenite complexes
INTRODUCTION

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 applications calls for a comprehensive understanding of the processes that govern the concentration of this element in mineral deposits. Carbonatite-alkaline complexes, the most important Nb (and/or REEs) carriers (Mitchell 2015; Verplanck et al. 2016; Anenburg et al. 2021; Beard et al. 2023), have attracted inordinate attention from researchers. Numerous studies documented that the Nb mineralization (particularly with grade < 1 wt% Nb$_2$O$_5$) is commonly concentrated through differentiation of carbonatic or alkaline melts, even though some of them may have been reworked to various extents by later hydrothermal overprinting (Chakhmouradian et al. 2015; Mitchell 2015; 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., Araxá and Catalão, Brazil; St. Honoré, Canada), columbite (Fe$^{2+}$Nb$_2$O$_6$; e.g., Upper Fir and Bayan Obo), Nb-rich rutile (TiO$_2$; e.g., Seis Lagos), aeschynite ((Y,Ca,Fe$^{2+}$)(Ti,Nb)$_2$(O,OH)$_6$; e.g., Bayan Obo), latrappite (Ca(Fe,Nb)O$_3$; e.g., Oka and Prairie Lake) and loparite ((Na,Ce)TiO$_3$; e.g., Prairie Lake) (Cordeiro et al. 2011; Chakhmouradian et al. 2015; Mitchell 2015; Tremblay et al. 2017). A better understanding of the processes attributed for the diversity of Nb mineralogy is critical for beneficiation and metallurgy, and for effective targeting of highly-endowed Nb deposits.

Previous studies show that the diversity of Nb-bearing species in carbonatite or
alkaline rocks may imply varying geochemical behaviors of Nb under different magmatic and/or hydrothermal conditions (Mitchell 2015; Liu et al. 2020; She et al. 2021). For example, experimental investigations documented that whether pyrochlore or other Nb-bearing minerals such as columbite, lueshite, or perovskite would crystallize is a function of H$_2$O, Na, and F contents of the parental magmas (Jago and Gittins 1993; Mitchell and Kjarsgaard 2004). However, the roles of different processes (magmatic or hydrothermal) in Nb mineralization remain enigmatic. Moreover, the process controlling the association of REE-Nb in these deposits is still not well constrained (She et al. 2021).

Abundant Silurian REE-Nb deposits and prospects distributed along the southern part of the Qinling Orogenic Belt comprise an important REE-Nb metallogenic belt in central China (Zhang et al. 2019a; Wang et al. 2021). Typical examples include the REE-Nb deposits associated with the Miaoya and Shaxiongdong carbonatite-syenite complexes (Xu et al. 2008, 2010; Ying et al. 2017; Chen et al. 2018; Ma et al. 2021; Wu et al. 2021) and Nb-rich trachytes (e.g., Zhuxi) that cover an outcrop of approximately 100 km$^2$ (Nie et al. 2019; Wang et al. 2021; Yan et al. 2021). Despite previous works on the petrogenesis of these complexes (Xu et al. 2008, 2010, 2014, 2015; Zhu et al. 2016; Ying et al. 2017; Chen et al. 2018; Su et al. 2019, 2022; Yan et al. 2021) and the origin of REE mineralization (Cimen et al. 2018; Nie et al. 2019; Zhang et al. 2019a, 2019b; Ying et al. 2020; Ma et al. 2021; Su et al. 2021), the styles of Nb mineralization have not yet been well characterized, hindering an understanding of the Nb mineralization process. In this contribution, we investigated the Nb mineralization style and process, and the controlling
factors, exemplified by the Miaoya and Shaxiongdong REE-Nb deposits in the Qinling belt, through a combined mineralogical and in-situ chemical-isotopic investigation. The new findings provide new insights regarding key factors controlling diverse Nb mineralization associated with carbonatite/alkaline rocks.

GEOLOGICAL SETTING

The Qinling Orogenic Belt is a result of multi-stage tectonic evolution involving arc terrane accretion, arc-continent collision, and continent-continent collision (Fig. 1a; Meng and Zhang 2000; Chen 2010; Dong et al. 2011; Wu and Zheng 2013; Dong and Santosh 2016), followed by the final collision between the North and South China cratons 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 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 North China Craton, North Qinling, South Qinling, and Northern South China Craton that are separated by the Luanchuan, Shangdan, and Mianlue faults from the north southward (Fig. 1b; Wu and Zheng 2013).

The South Qinling unit, where the carbonatite/alkaline rock-hosted Nb-REE mineralization developed, is dominated by a thin-skinned tectonics (Fig. 1b; Meng and 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
the Douling and Xiaomoling complexes in the north, and they are unconformably covered by Phanerozoic limestones, clastic rocks, shales, and sandstones (Mattauer et al. 1985; Ratschbacher et al. 2003; Dong et al. 2011; Wu and Zheng 2013; Liu et al. 2016). The Wudang and Yaolinghe Groups consist of greenschist facies metamorphosed volcanic-sedimentary rocks, and the Douling and Xiaomoling complexes are mainly composed of biotite gneiss and mafic rocks, respectively (Liu et al. 2016). The basement rocks are intruded by mafic-ultramafic dykes and carbonatite-syenite complexes of Silurian ages (Zhang et al. 2007; Xu et al. 2008) and Mesozoic granitoid intrusions (ca. 248-190 Ma) (Liu et al. 2011; Yang et al. 2012) (Fig. 1b).

**DEPOSIT GEOLOGY**

The Miaoya and Shaxiongdong deposits, containing totally >1 Mt Nb ores at 0.1 wt% Nb₂O₅ and 1.2 Mt REE ores at 1.5 wt% REE₂O₃, are located in the southwestern margin of the Wudang Terrane (Fig. 1b). Both deposits are hosted in the Miaoya and Shaxiongdong syenite-carbonatite complexes. The Miaoya complex intrudes both the 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 spindle-shaped complex consists dominantly of syenites (>90 vol%; composed mainly of K-feldspar) intruded by a number of carbonatitic dykes (>7.5 vol%) (Figs. 1c and 2a), and locally contains abundant xenoliths of the country rocks (Fig. 2d-2e). The
carbonatitic dykes were classified as calciocarbonatite and ferrocarbonatite types based 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 gradational (Figs. 2b-2c). Both the carbonatites and syenites have undergone extensive hydrothermal carbonatization. Such alteration is characterized by the replacement of primary magmatic minerals by fine-grained calcite and dolomite with minor quartz and sulfides, associated with REE minerals-bearing or barren veinlets (Ying et al. 2020; Ma et al. 2021). Notably, veinlets of quartz and graphite are also locally present (Fig. 2f), and the graphite grains are generally disseminated and flaky in shapes (Fig. 3a).

On the other hand, the spindle-shaped Shaxiongdong complex intrudes the 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 vol%) (10 to > 200 m in length) (Figs. 1e and 2g-2h). Similar to the Miaoya complex, the Shaxiongdong complex has undergone variable hydrothermal alteration, characterized by the formation of secondary albite, biotite, baryte, and aegirine.

STYLES OF NI OBIUM MINERALIZATION

Nb mineralization in Miaoya

The Nb ores in Miaoya are essentially Nb-mineralized syenites and carbonatites with
Nb$_2$O$_5$ content > 0.08 wt% (Fig. 1d) (Liu et al. 1984), and no clear boundaries between the Nb ores and the host complexes can be defined. This situation is also applicable to the REE ores (REE$_2$O$_3$ content > 0.3 wt%) (Fig. 1d). It is notable, however, that the REE and Nb mineralization are not entirely spatially overlapping, and thus the ores can be divided into either REE-Nb or Nb ones (Fig. 1d). The REE minerals are mainly monazite and bastnäsite-(Ce) in veinlet, stockwork, and to a minor extent, disseminated forms (Ying et al. 2017, 2020; Zhang et al. 2019a; Ma et al. 2021). In contrast, the Nb minerals are mainly present in disseminated form throughout the complexes (Figs. 3b-3g and 4), and can be divided into magmatic and hydrothermal assemblages as illustrated below.

**Nb-bearing minerals in mineralized syenites.** The Nb-bearing minerals are mainly disseminated pyrochlore, rutile, and ilmenite with minor amount of columbite, which is 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 hydrothermally overprinted, accompanied with the formation of new hydrothermal 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, were variably replaced by hydrothermal columbite and rutile; magmatic rutile grains of bright BSE reflectance being replaced by porous secondary rutile of dark BSE reflectance (Fig. 4g); magmatic, BSE-homogeneous ilmenite is partially replaced by hydrothermal rutile and columbite (Figs. 4i-4l). Magmatic columbite grains are relatively minor and presenting as euhedral to subhedral platy oikocrysts, which are also variably
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 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 and apatite; Figs. 3b-3c and 3e-3f). Such an assemblage of magmatic Nb minerals is broadly similar to that of the mineralized syenites, but having an elevated content of pyrochlore and without ilmenite. These minerals have also been hydrothermally overprinted. For example, the magmatic pyrochlore grains commonly contain homogenous, massive cores replaced by porous rims infilled by abundant fined-grained inclusions of hydrothermal columbite, rutile, uraninite, thorite, and aeschynite (Figs. 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 magmatic rutile exhibits similar textures composed of a BSE-bright core and BSE-dark 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, albite the mineral inclusions are mainly ankerite and quartz. They are also commonly replaced by hydrothermal rutile (Fig. 4f). In summary, the magmatic Nb-bearing minerals
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.

**Nb mineralization in Shaxiongdong**

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

**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,
and are generally composed of multiple domains with variable BSE intensities (Fig. 5a).

The subhedral to euhedral rutile grains also consist of primary BSE-bright and secondary BSE-dark domains (Figs. 5c-5d), of which the latter are commonly full of inclusions such as hydrothermal calcite and albite, and are variably replaced by hydrothermal ilmenite along the rims and cracks (Figs. 5e-5f). The altered ilmenite grains are commonly porous in appearance, and are variably replaced by secondary hydrothermal rutile, fersmite, and titanite (Figs. 5g-5i). The altered titanite is similarly composed of primary, magmatic BSE-bright and secondary BSE-dark domains (Fig. 5j). In summary, the magmatic Nb-bearing minerals in the mineralized syenites include pyrochlore, rutile, ilmenite, and titanite, whereas hydrothermal Nb-bearing minerals include ilmenite, rutile, and fersmite 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.
SAMPLING AND ANALYTICAL RESULTS

Sampling

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

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 ± 3.6 Ma (2σ, n = 71, MSWD = 1.5) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ 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 ($2\sigma$, n = 54, MSWD = 2.7) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.7395 (Fig. 7b).

**Mineral compositions of Miaoya and Shaxiongdong**

**Pyrochlore group minerals.** Pyrochlore group minerals ($A_{2-m}B_2X_{6-w}Y_{1-n}p\text{H}_2\text{O}$, where $m = 0-1.7; w = 0-0.7; n = 0-1; p = 0-2; X = \text{O, OH};$ and $Y = \text{O, OH, and F}$) generally have highly variable compositions due to the flexibility in the crystal structures (Nasraoui and Bilal 2000; Zurevinski and Mitchell 2004). According to the relative contents of Nb, Ti, Ta, and U (Table S2), pyrochlore group minerals in Miaoya can be subdivided into U-poor pyrochlore, uranpyrochlore, and U-rich betafite with increasing TiO$_2$ (2.96 to 23.39 wt%) and UO$_2$ (0 to 30.14 wt%) but decreasing Nb$_2$O$_5$ contents (69.35 to 15.43 wt%) (Figs. 8a and 9a). Notably, pyrochlore group minerals in the mineralized syenites of Miaoya are generally U-poor, whereas those in the mineralized carbonatites include U-poor pyrochlore, uranpyrochlore, and U-rich betafite (Figs. 8a and 9a; Xu et al. 2015). This feature is different from those of Shaxiongdong which are mainly U-poor pyrochlore. In the ternary plots of Ca, Na, and A-site vacancies (VA) (Nasraou and Bilal 2000; Lumpkin and Ewing 1995), the pyrochlores in the mineralized syenites of Miaoya plotted in the magmatic field, whereas those in the mineralized carbonatites exhibit magmatic, hydrothermal, and supergene alteration trends (Fig. 8b). On the other hand, the pyrochlores from the Shaxiongdong deposits (including the mineralized syenites and carbonatites) show the magmatic and hydrothermal trends (Fig. 8b). In general, the
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 pyrochlore group minerals of the mineralized carbonatites in Miaoya, whereas the Nb 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. 9b). To summarize, the pyrochlore group minerals in Miaoya exhibit obviously negative correlations of Ca+Nb contents with U+Ti and LREE+Ti contents but positive correlations of Ca content with Na+LREE contents, whereas those in Shaxiongdong exhibit obviously positive correlations between Ca or Ca+Ti contents and Na+LREE, 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 Nb$_2$O$_5$ 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 Nb$_2$O$_5$ and Ta$_2$O$_5$ are negatively correlated (Fig. 10b).

Nb-rich rutile. The magmatic rutile in various ores of Miaoya, including BSE-bright and BSE-dark domains, show broadly similar Ti, Fe, and Nb concentrations (Figs. 11a-11b; Table S4). On the other hand, the BSE-bright domains of the magmatic rutile in the mineralized syenites of Shaxiongdong exhibit much higher Nb and Fe but lower Ti
contents than the BSE-dark domains or individual hydrothermal rutile grains (Figs. 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 positively correlated with that of Nb$_2$O$_5$ (Figs. 11b and 11e), indicating that the incorporation of Nb into the rutile is compensated by Fe$^{2+}$ and Fe$^{3+}$. However, they have different Fe$^{2+}$/Fe$^{3+}$ ratios, which is well reflected in the invariant diagram of FeO versus Nb$_2$O$_5$ (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 Shaxiongdong plotted mostly along the Fe/Nb=1.0 line, indicative of relatively high Fe$^{3+}$/Fe$^{2+}$ ratios (Figs. 11b and 11e).

**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 (Nb$_2$O$_5$: 0.1-0.91 wt%) slightly higher than those in Miaoya (0.01-0.70 wt%) (Figs. 11c and 11f).

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

**Bulk-sample major and trace elemental compositions**

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

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

DISCUSSION

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.

**Magmatic controls.** In both deposits, the magmatic Nb-bearing minerals in the mineralized syenites are similarly dominated by pyrochlore, rutile, and ilmenite, while those in the mineralized carbonatites are mainly pyrochlores (Fig. 6). The differences are that the mineralized syenites of Shaxiongdong contain a higher abundance of titanite with trace amounts of aeschynite, whereas those of Miaoya contain minor amount of 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 pyrochlore (instead of perovskite-structured compounds) in magmas is mainly controlled by Na and F contents (>1 wt%) and high F/OH ratios which could stabilize pyrochlore as a primary liquidus phase (Jago and Gittins 1993; Mitchell and Kjarsgaard 2002, 2004). Such a criterion should be fulfilled in both deposits, as the magmatic apatite grains in the 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 pyrochlore group minerals in different types of ore in the two deposits are different. For
example, the pyrochlore group minerals in the mineralized carbonatites of Miaoya are 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 contain only U-poor pyrochlore (Figs. 8a and 9a). This discrepancy is also consistent with bulk-ore compositions showing that some samples of the mineralized carbonatites in Miaoya have relatively high U contents (up to 230 ppm; Fig. 13f). Such a high-U feature cannot solely be controlled by a primary mantle source, as previous studies confirmed that the parental magmas for both deposits were similarly derived from a common depleted mantle source (Xu et al. 2008, 2014; Chen et al. 2018; Su et al. 2019, 2022). Instead, subsequent differentiation (such as assimilation and/or fractionation 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 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 cause for the formation of the magmatic U-rich pyrochlore in the mineralized carbonatites. Such proposal is further supported by the fact that the U-rich ores are indeed sampled in the parts where xenoliths of U-rich country rocks are widely present. The Sr-Nd isotopic compositions of these samples are indicative of extensive assimilation (Figs. 14 and 15a). In addition to U, the assimilation of the U-rich silicate rocks also provided a considerable amount of Si that promotes the crystallization of apatite (~9.5 vol% in Miaoya, ~2.0 vol% in Shaxiongdong (Figs. 4a-4d and 5b-5c; Aenenburg et al.
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. 8). However, subsequent assimilation of U-rich country rocks into the carbonatitic melts at Miaoya has triggered crystallization of Nb-Ca-low but U-Ti-rich pyrochlore, U-Ti-rich betafite, and rutile due to elevated U and Ti contents in the residual magmas (Figs. 9a-9c). On the other hand, crystallization of minor magmatic titanite and columbite in both Shaxiongdong and Miaoya deposits may be attributed to relatively low degree of magma evolution and crystallization of some Fe$^{3+}$-rich minerals (e.g., biotite and magnetite), respectively.

**Hydrothermal controls.** Our results show that the hydrothermal Nb-bearing minerals in various ores of the two deposits contain rutile. The major difference is that the Miaoya deposit is in addition rich in columbite with a trace amount of aeschynite, whereas the Shaxiongdong deposit contains minor fersmite and ilmenite with a trace amount of titanite (Figs. 3-6). Previous studies well documented that hydrothermal alteration of pyrochlore could result in columbitization (e.g., Aley and Saint-Honoré deposits) (Chakhmouradian et al. 2015; Tremblay et al. 2017). Such a process should be applicable 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 formation of fine uraninite, thorite, and aeschynite that present as inclusions in the altered pyrochlores (especially the U-rich ones) (Figs. 4a-4b). For Shaxiongdong, although the
early magmatic pyrochlores also suffered from variable hydrothermal modification, no columbite or uraninite was observed to be formed (Figs. 5a-5b). Different alteration products of the magmatic precursors at the two deposits strongly suggested distinguished hydrothermal events that likely involved distinct fluids despite the spatial proximity of the two deposits. Previous dating results of hydrothermal monazite, bastnäsite, and columbite from Miaoya revealed an age of ~220 Ma for the hydrothermal event, remarkably younger than the hosting complex (~430 Ma; Fig. 16; Xu et al. 2014, 2015; Ying et al. 2017; Zhang et al. 2019a; Wu et al. 2021). This event is 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 by the bulk-carbonatite C-O isotopic data (Xu et al. 2014; Cimen et al. 2018; Su et al. 2019; Zhang et al. 2019b) that display a mixing trend between the mineralized or barren 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 grains from Shaxiongdong, slightly younger than the age of 432.0 ± 3.6 Ma for the BSE-bright, magmatic domains of the titanite (Fig. 7), thus suggesting a hydrothermal event distinct from that in Miaoya. Indeed, carbonatite-like C-O isotopic compositions of the altered ores/rocks in Shaxiongdong (Xu et al. 2008; Chen et al. 2018) (Fig. 15b) strongly indicate that such a hydrothermal event could be authigenic in origin, likely genetically related to the carbonatitic melts.
Processes in response to the variety of hydrothermal Nb mineralogy in Miaoya and Shaxiongdong

The different sources and natures of hydrothermal fluids, as revealed earlier, should be responsible for the diverse hydrothermal Nb mineralogy (and the associated diverse compositions) in the Miaoya and Shaxiongdong deposits. The pyrochlore grains from Shaxiongdong have compositions generally located in the “magmatic” and “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 trend (Fig. 8b; Lumpkin and Ewing 1995; Nasraoui and Bilal 2000). This feature 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 A-site to produce more A-site vacancies (VA) in the pyrochlore grains, thus plotting in the “supergene” field (Fig. 8b; Zurevinski and Mitchell, 2004).

Generally, the presence of distinctly abundant hydrothermal columbite (FeNb_2O_6) and uraninite (UO_2) in Miaoya (i.e., the replacement products of magmatic uranopyrochlore; Figs. 4a-4c) indicates that the fluid is characterized by a low oxygen fugacity due to high Fe^{2+} and U^{4+}. 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,
the replacement of pyrochlore by columbite, involving such reducing, acidic fluids (Chakhmouradian et al. 2015; Tremblay et al. 2017), likely proceed through the following reaction in the presence of sufficient Fe$^{2+}$ (Chakhmouradian et al. 2015):

$$\text{NaCaNb}_2\text{O}_6(F_y\text{OH}_{1-y}) + \text{Fe}^{2+} + (1-y)\text{H}^+ = \text{FeNb}_2\text{O}_6 + \text{Na}^+ \text{Ca}^{2+} + y\text{F}^- + (1-y)\text{H}_2\text{O}$$

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 Nb$_2$O$_5$ bivariant diagram (Fig. 11e).

**Decoupling of Nb and REE mineralization**

**Decoupling of REE and Nb during magmatic process.** The magmatic REE-rich minerals in Miaoya and Shaxiongdong are dominantly apatite and allanite that are closely 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 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 both deposits have higher abundances of magmatic REE minerals (e.g., apatite and 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).

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

IMPLICATIONS

Although carbonatites and alkaline rocks host the majority of the world’s REE and Nb resources, it was well documented that not all of them are associated with REE and Nb mineralization, particularly for those at convergent belts (Chakhmouradian et al. 2015; Liu and Hou 2017). Our studies provide strong evidence that secondary fluids, no matter 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 of early magmatic precursors, in contrary to the REE which is remarkably remobilized and enriched to ore grade during fluid metasomatism, as well recorded in the Miaoya deposit (Ma et al. 2021). The new findings imply that different behaviors of REE and Nb during hydrothermal processes could be one of the key factors responsible for the spatial decoupling of REE and Nb mineralization associated with carbonatites and alkaline rocks. Our new results thus provide new indicators for REE and Nb resources exploration in such rocks particularly for those suffering extensive hydrothermal overprinting. This
This study also highlights that fluid nature could be one of the foremost control on the
decoupling of REE and Nb, as exemplified by the Shaxiongdong deposit.

This study also confirmed that both magmatic and hydrothermal processes are able to
produce diverse Nb mineralogy in individual Nb deposits, during which multiple
parameters such as oxygen fugacity, magma composition, and nature of fluid play key
roles. Clear understanding of these processes is useful for Nb beneficiation and
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
metallurgical beneficiation. As such, the hydrothermal overprinting in both deposits,
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
deposit without or with only minor hydrothermal alteration would be relatively favorable
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 (REE$_2$O$_3$ > 0.3 wt% and Nb$_2$O$_5$ > 0.08 wt%) in the Miaoya complex (modified from Liu et al. 1984). (e) Simplified geological map of the Shaxiongdong carbonatite-syenite complex (modified from Xu et al. 2008). Abbreviations: S-NCC = Southern North China Craton; NQL = North Qinling; SQL = South Qinling; N-SCC = Northern South China Craton.

**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
(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.

FIGURE 3. Photomicrographs of various Nb mineralogy in the Miaoya and Shaxiongdong deposits. (a) Minor fine-grain graphite present in the mineralized Miaoya carbonatites, associated with magmatic calcite and apatite. (b-c) Medium- to 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 K-feldspar in mineralized syenites (d) or calcite in carbonatites (e) of Miaoya. (f) Irregular hydrothermal rutile grains intergrown with pyrite in mineralized carbonatites of 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 syenites (h) or apatite in mineralized carbonatites (i) of Shaxiongdong. (j-l) Anhedral to euhedral rutile (j), ilmenite (k), and titanite (l) grains intergrown with K-feldspar, albite, and epidote in mineralized syenites of Shaxiongdong. Abbreviations: Ab = albite; Aln = allanite; Ank = ankerite; Ap = apatite; Cal = calcite; Chl = chlorite; Clb = columbite; Ep = epidote; Gr = graphite; Ilm = ilmenite; Kfs = K-feldspar; Mag = magnetite; Pcl =
pyrochlore; Py = pyrite; Qz = quartz; Rt = rutile; Ttn = titanite; Upcl = uranpyrochlore.

FIGURE 4. BSE images of various Nb ores in the Miaoya deposit. (a-b) Coarse-grained (a) and medium-grained (b) uranpyrochlore grains in mineralized carbonatites. Note that they are in close association with apatite but are variably modified, associated with the presences of abundant inclusions of secondary hydrothermal minerals such as columbite, rutile, uraninite, thorite, and aeschynite. (c-d) The uranpyrochlore grains in mineralized carbonatites are partially (c) or completely (d) replaced by secondary columbite. (e-f) Primary magmatic columbite grains in mineralized syenites are variably disturbed by hydrothermal bastnäsite (e) or rutile (f) along rims and crack. (g-h) Magmatic rutile grains in mineralized syenites (g) and carbonatites (h) have porous or inhomogeneous appearances. (i) Secondary rutile replacing early magmatic ilmenite in the mineralized carbonatites (i1) or quartz veins (i2). (j-k) Magmatic ilmenite grains in mineralized syenites are closely associated with allanite (j) or apatite (k). (l) Secondary columbite grains present as inclusions in altered ilmenite. Abbreviations: Aes = Aeschynite; Bsn = batnäsite; Mnz = monazite; Ph = phengite; Thr = thorite; Urn = uraninite. Other 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
carbonatites exhibit well-developed oscillatory zoning. (c-d) Magmatic rutile grains in mineralized syenites. Note that they are intergrown with magmatic apatite (c) and pyrite (d), and contain BSE-bright and -dark domains. (e-f) Magmatic rutile in mineralized syenites exhibits porous appearances, and was replaced by secondary calcite (e) or ilmenite (f) along rims. (g-i) Early ilmenite grains in mineralized syenites are partially replaced by rutile, fersmite (g), albite (h), or titanite (i), and exhibit porous appearances. (j) Magmatic titanite in mineralized syenites contains BSE-bright and dark domains. (k) Fibrous aeschynite grains in mineralized syenites present as aggregates. (l) Magmatic apatite in mineralized carbonatites contains BSE-bright and dark domains. Abbreviations: Aeg = aegirine; Anc = ancylite; Brt = baryte; Bt = biotite; Dol = dolomite; Fsm = Fersmite. Other abbreviations are the same as those in Figures 3 and 4.

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

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

FIGURE 9. Bimodal plots of U vs. Nb (a), Ca vs. Nb (b), Ca vs. Ti (c), U+Ti vs. Ca+Nb (d), LREE+Ti vs. Ca+Nb (e), Na+LREE vs. Ca (f), Na+Nb vs. Ca+Ti (g), and Na+Ta vs. Ca+Ti (h) for the pyrochlore group minerals from the Miaoya and Shaxiongdong deposits. The data for the Miaoya pyrochlore is cited from Xu et al. (2015).

FIGURE 10. Bimodal plots of Ta/(Nb+Ta) vs. Mn/(Fe+Mn) (a) and Ta2O5 vs. Nb2O5 (b) for magmatic and hydrothermal columbite from the Miaoya deposit.

FIGURE 11. Bimodal plots of Ti vs. Fe+Nb, and FeO vs. Nb2O5 of rutile in the Miaoya
(a, b) and Shaxiongdong (d, e) deposits, and bimodal plots of TiO$_2$ vs. Nb$_2$O$_5$ of ilmenite in the Miaoya (c) and Shaxiongdong (f) deposits.

**FIGURE 12.** Bimodal plots of LREE vs. HREE+Y (a), REE vs. Nb (b), and (La/Yb)$_N$ vs. REE+Y (c), and chondrite-normalized REE patterns (d) for different domains of titanite in mineralized syenites of Shaxiongdong.

**FIGURE 13.** Plots of CaO vs. REE (a), SiO$_2$ vs. REE (b), CaO vs. Nb (c), SiO$_2$ vs. Nb (d), Nb vs. REE (e), and SiO$_2$ vs. U (f) for bulk ore/rock samples from the Miaoya and 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), Zhang (2020), and Zhao et al. (2022).

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

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.
Fig. 1

a) Map showing the Yangtze Block, Cathaysia Block, North China Craton, Tarim Craton, South China Craton, and their respective block boundaries.

b) Map of the North China Craton and South China Craton showing the Longmenshan-Dabashan Fault, Mianlue Fault, Luanchuan Fault, Anfong-Desheng-Fangxian Fault, and other geological features.

Legend:
- Late Jurassic-Early Cretaceous granitoid
- Late Triassic granitoid
- Neoproterozoic granitoid
- Early Paleozoic granitoid
- Neoproterozoic metamorphic rocks

Silurian basaltic rock, Neoproterozoic gabbro and diabase, Precambrian basement, Trachyte.

- REE-Nb deposit

C) Map showing Neoproterozoic meta-quartz Keratophyre (Yaolinghe Group), Silurian Schist (Meiziya Group), Silicified argillite, and other geological features.

Legend:
- Neoproterozoic sericite-chlorite-albite schist (Wudang Group)
- Nepheline syenite
- Carbonatite
- Sample location

Legend for REE and Nb concentrations:
- REE\(_2\)O\(_3\) > 0.3 wt%
- Nb\(_2\)O\(_3\) > 0.08 wt%
- REE\(_2\)O\(_3\) < 0.3 wt%; Nb\(_2\)O\(_3\) < 0.08 wt%

Legend for Sample location:
- (24)
- (95)

e) Map showing Neoproterozoic sericite-chlorite-albite schist (Wudang Group), Nepheline syenite, Carbonatite, and Sample location.

Legend:
- Neoproterozoic sericite-chlorite-albite schist (Wudang Group)
- Nepheline syenite
- Carbonatite
- Sample location

User comments:

- Late Jurassic-Early Cretaceous granitoid
- Late Triassic granitoid
- Neoproterozoic granitoid
- Early Paleozoic granitoid
- Neoproterozoic gabbro and diabase
- Precambrian basement
- Trachyte

- REE-Nb deposit

- Neoproterozoic meta-quartz Keratophyre (Yaolinghe Group)
- Silurian Schist (Meiziya Group)
- Silicified argillite

- REE\(_2\)O\(_3\) > 0.3 wt%
- Nb\(_2\)O\(_3\) > 0.08 wt%
- REE\(_2\)O\(_3\) < 0.3 wt%; Nb\(_2\)O\(_3\) < 0.08 wt%

- Sample location

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Fig. 2
Fig. 3
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Fig. 6

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REE mineralization

Nb mineralization

Syenites Calcocarbonatites Ferrocarbonatites

Syenites Calcocarbonatites
Fig. 7

Intercepts at 432.0 ± 3.6 Ma (N = 71, MSWD = 1.5)

Intercepts at 423.3 ± 6.6 Ma (N = 54, MSWD = 2.7)
Fig. 8
Fig. 9

![Graphs showing various compositional data](image-url)
Fig. 10

(a) Plots of Ta/(Nb+Ta) versus Mn/(Fe+Mn) for Magmatic Clb (red squares) and Hydrothermal Clb (purple circles).

(b) Plot of Nb₂O₅ (wt.%) versus Ta₂O₅ (wt.%) for Magmatic Clb (red squares) and Hydrothermal Clb (purple circles).
Fig. 11

(a) Miaoya

(b) Excessive Fe vs. Nb in NbO_3 (wt.%) for Miaoya.

(c) Miaoya

(d) Shaxiongdong

(e) Excessive Fe vs. Nb in NbO_3 (wt.%) for Shaxiongdong.

(f) Shaxiongdong

Graphs showing the distribution of Ti and Nb in mol, and FeO in wt.% for Miaoya and Shaxiongdong samples.
Fig. 12

(a) LREE vs. HREE+Y (ppm) showing LREE-rich and LREE-enriched domains.

(b) REE vs. Nb (ppm) and Nb vs. REE (ppm) showing distribution patterns.

(c) (La/Yb)_N vs. REE+Y (ppm) highlighting REE loss.

(d) REE profiles with Mineral/Chondrite ratios for BSE-bright and BSE-dark domains.
Fig. 13

(a) CaO (wt.%) vs. REE (ppm)
(b) SiO₂ (wt.%) vs. REE (ppm)
(c) CaO (wt.%) vs. Nb (ppm)
(d) SiO₂ (wt.%) vs. Nb (ppm)
(e) Nb (ppm) vs. REE (ppm)
(f) SiO₂ (wt.%) vs. U (ppm)

Legend:
- Carbonatite (MY)
- Syenite (MY)
- Carbonatite (SXD)
- Syenite (SXD)
- Yaolinghe Group (MY)
- Meiziya Group (MY)
Fig. 14

![Graphs showing Sr isotopic variations and εNd(t) for BSE-bright and dark domains of Shaxiongdong and Miaoya samples.](image-url)
Sedimentary contamination and high T fractionation
Seawater influence
Low T alteration
High T meteoric water influence

Au-Ag deposits in South Qinling unit at Triassic

Fig. 15

δΟ (‰) VSMOW
δC (‰) VPDB

Miaoya
Shaxiongdong
Primary carbonatite field

(DMM) 0.702 0.703 0.704 0.705 0.706 0.707 0.708
(87Sr/86Sr)

ɛNd(t)

HIMU
EMII
Shaxiongdong
Yaolinghe
Miaoya

Sedimentary contamination and high T fractionation
Seawater influence
Low T alteration
High T meteoric water influence

δ18O (‰) VSMOW

Yaolinghe
Miaoya
Shaxiongdong

DMM
HIMU
EMII
Shaxiongdong
Yaolinghe
Fig. 16

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<td>Hydrothermal metasomatism ~220 Ma</td>
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- Zircon U-Th-Pb
- Apatite U-Th-Pb
- Monazite U-Th-Pb
- Columbite U-Th-Pb
- Bastnäsite U-Th-Pb
- Uraninite U-Th-Pb
- Biotite K-Ar
- Feldspar K-Ar
- Titanite U-Pb