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Recycling of subducted upper continental crust: Constraints on the extensive molybdenum mineralization in the Qinling–Dabie orogen



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ABSTRACT

The Qinling-Dabie orogenic belt is the most important molybdenum ore belt in the world, with a proven reserve of over 9 million tons metal Mo. More than 92% of the reserves come from porphyry-skarn type deposits that are closely related to Late Mesozoic granite intrusions (158-101 Ma) occurring mainly along the southern margin of the North China Craton, where the majority of the continental crust was formed before 2.5 Ga with crustal Hf model ages of 2.8 to 3.2 Ga. The granite intrusions, which consist mainly of granodiorite, monzogranite, and syenogranite, intrude an Archean to Paleoproterozoic basement. The granitic rocks are metaluminous to peraluminous with C/CNK values mostly in range of 0.9-1.2, commonly alkaline rich with high-K calc-alkaline and shoshonitic features. The linear trends of major and trace elements on Harker diagrams suggest a common magma source for the granitic rocks. Abundant inherited zircons with Neoproterozoic U-Pb ages and substantial younger crustal Hf model ages (averaging 2.4 Ga and 2.0 Ga for granitic rocks with U-Pb ages older and younger than 125 Ma, respectively) demonstrate that these granitic rocks were probably derived from partial melting of the subducted northern Yangtze continental crust with Hf model age younger than 2.2 Ga. Integrating the recent progresses in geological, geochronological, and geophysical investigations of the Qinling–Dabie orogenic belt, we propose that it is the conjunction of the decoupling of the subducted plate at the easternmost part and the slab rollback and subsequent breakoff at the westernmost part of the orogenic belt that resulted in the westward shallowing continental subduction along the Manlue suture at the southern margin of the Qinling-Dabie orogenic belt. This subduction took place during westward propagating continental collision in the Late Triassic and the prolonged relative rotation of the North China Craton and Yangtze Block that lasted until the Middle Jurassic. The molybdenum source for the extensive Mo mineralization in the Qinling–Dabie orogenic belt was most likely derived from Mo enriched components of subducted continental crust. The decoupling of the subducted plate that occurred in the easternmost part of the orogenic belt, where only less Mo-enriched components of the Yangtze Block have been subducted, may account for the lack of economically significant Mo mineralization there. © 2016 Elsevier B.V. All rights reserved.

1. Introduction

Granitoids are essential in the study of the tectonic evolutions of orogenic belts, which can provide critical constraints on the dynamics of exhumed plate margins and the identity of unexposed basement terranes (Bennett and Depaolo, 1987; Jung et al., 2009). Comprehensive investigations of the petrology, element abundances, and isotope geochemistry of granitoids and the tectonic evolution of the associated orogenic belt will enable us to obtain deeper insight into the petrogenesis of the granitoids and metallogeny of the associated hydrothermal ore deposits. Moreover, an understanding of the anatectic processes in the deep crust will contribute to the understanding of the growth and recycling of continental crust (Arndt, 2013; Condie, 2014).

The Qinling–Dabie orogenic belt, which hosts over 9 Mt of proven Mo metal reserves, is the most important molybdenum ore belt

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http://dx.doi.org/10.1016/j.oregeorev.2016.02.006 0169-1368/© 2016 Elsevier B.V. All rights reserved. worldwide, accounting for one third of the World's total proven Mo reserves (Chen et al., 2013; Mao et al., 2011). Over 92% of the molybdenum reserves in the Qinling–Dabie orogenic belt come from porphyryskarn type Mo deposits associated with the Late Jurassic to Middle Cretaceous granitic intrusions in the East Qinling–Dabie orogenic belt (e.g., Li et al., 2007; Mao et al., 2008). These porphyry-skarn type Mo deposits consist of more than twenty ore deposits and occurrences (Mao et al., 2011; Zeng et al., 2013), among which 7 large deposits make up 78% of the proven reserves, i.e., the Jinduicheng (1.078 Mt), Nannihu-Sandaozhuang (1.337 Mt), Shangfanggou (0.716 Mt), Yuchiling (0.550 Mt), Donggou (0.690 Mt), Qian'echong (0.600 Mt), and Shapinggou (2.20 Mt) deposits. Locations of the 7 large deposits along with 12 representative deposits are shown on the Fig. 1.

The conundrum regarding the petrogenesis of the ore-related Mesozoic granites and source of molybdenum for the mineralization have drawn attentions of many geoscientists, and numerous studies have been carried out in the last two decades (e.g., Bao et al., 2009a; Bao et al., 2014; Chen et al., 2013; Chen et al., 2015; Chen et al., 2000; Gao



Fig. 1. Sketch map showing the distribution of the Late Mesozoic granite intrusions and related porphyry-skarn type molybdenum ore deposits at the southern margin of the North China Craton (modified after Luo et al., 1991).

et al., 2010b; Gong et al., 2009; Li et al., 2012a; Li et al., 2009b; Li et al., 2007; Luo et al., 1991; Mao et al., 2008; Mao et al., 2010; Wang et al., 2014; Ye et al., 2008; Zhang et al., 2014a). Some researchers proposed that these granites were derived from partial melting of the lower crust with input of a juvenile mantle component (e.g., Wang et al., 2015; Wang et al., 2013b; Zhu et al., 2010), while others argued that the Mesozoic granites were solely products of re-melting of the basement or the lower crust of the NCC (e.g., Chen et al., 2000; Wang et al., 2010c; Wei et al., 2010). It has also been proposed that the granites were primarily produced by melting of subducted continental crust at the northern margin of the Yangtze Block (YB) (e.g., Bao et al., 2014; Bao et al., 2009b; Chen et al., 2013; Chen et al., 2015; Gao et al., 2014b; Li et al., 2013a; Liu et al., 2015a). As to the source of the Mo, many researchers suggested that Mo derived mainly from the lower crust or the basement at the southern margin of the NCC (e.g., Lu et al., 2002; Wang et al., 2015), while a few proposed that Mo mainly sourced from the continental crust at the northern margin of the YB (e.g., Bao et al., 2014; Bao et al., 2009b; Li et al., 2012b).

It is widely accepted that the ore metals and hydrothermal fluids responsible for porphyry-skarn ore deposits were primarily derived from the magmatic system itself (e.g., Halter et al., 2005; Hedenquist and Lowenstern, 1994; Pettke et al., 2010; Sun et al., 2015; Sun et al., 2013). Therefore, the petrogenesis, especially the source rocks of the ore related granites in the Qinling-Dabie orogenic belt is of crucial importance to unveil the enigma of the extensive Mo mineralization during the Late Jurassic to Middle Cretaceous. In this contribution, we discuss the petrogenesis of the ore-related granites in relation to the Mesozoic tectonic evolution of the Qinling-Dabie orogenic belt. Our conclusions draw heavily upon compilations of major and trace element geochemistry, zircon dating, and Hf isotope composition data obtained for the Late Mesozoic granites in the Qinling-Dabie Mo ore belt. We propose that the ore-related granites were mainly derived from re-melting of the subducted YB continental crust, while the Mo responsible for the extensive and explosive mineralization was primarily sourced from subducted Mo-enriched sedimentary rocks.

2. Geological background

2.1. Tectonic settings of the ore belt

The Qinling-Dabie Mo ore belt is located in the eastern part of the Central China Orogenic Belt, which extends more than 4000 km from West Kunlun, through Qilian, Qinling, Tongbai, Hong'an, and Dabie, to Sulu on the east (Yang et al., 2010; Zhang et al., 1996). The continuously distributed Qinling, Tongbai, Hong'an, and Dabie orogenic belts are often referred to as Qinling-Dabie orogenic belt in Chinese literatures (Wu and Zheng, 2013). The Mo ore deposits in the Qinling orogen occur along the southern margin of the NCC, which has been involved in the Qinling–Dabie orogeny caused by the Triassic collision between the NCC and YB (e.g., Dong et al., 2011; Meng and Zhang, 2000; Sun et al., 2002a; Sun et al., 2002b; Sun et al., 2002c; Zhang et al., 2014b); while the Mo deposits in the Tongbai-Hong'an-Dabie area occur to the south of the Guishan-Meishan fault, a Paleozoic suture and possibly the east-extension of the Shangdan suture in the Tongbai-Hong'an-Dabie orogen, and north of the Triassic suture between the YB and NCC (Liu and Zhang, 1999; Liu et al., 2015c; Zhang et al., 2001).

The YB and the NCC were separated by a branch of the Paleo-Tethys Ocean in the Early Paleozoic as evidenced by their completely different apparent pole wandering paths that reflect different drift and displacement histories before the Permian (Gilder and Courtillot, 1997; Huang et al., 2008a; Zhu et al., 1998). Paleomagnetic data, sediment distribution, and collision-related deformation and metamorphism indicate that the YB subducted in a northwesterly direction obliquely under the NCC in the Late Permian to Early Triassic. This scissor-like closure of the ocean basin and continental collision propagated westward along the Mianlue suture in the Late Triassic (Chen and Santosh, 2014; Guo et al., 2012; Huang et al., 2008a; Li et al., 2015b; Liu et al., 2015b; Liu et al., 2005; Sun et al., 2002a; Wu and Zheng, 2013; Zhao and Coe, 1987).

Detailed geochronological studies on high pressure (HP) metamorphic rocks show that the subduction started at least in the Carboniferous (Sun et al., 2002b), whereas initial continental subduction first appeared in the Tongbai orogenic belt during the Late Permian to Triassic commencing at ~255 Ma (Cheng et al., 2011; Liu et al., 2010a). Subsequently, when the Hong'an and Dabie orogenic belts to the east were subducted to deep levels and underwent HP and ultra-high pressure (UHP) metamorphisms at ~240 Ma (Li et al., 2000; Li et al., 1994; Li et al., 1993; Zheng et al., 2003), the Tongbai orogenic belt might already have been re-exhumed to middle and upper crustal levels. The seesaw-type subduction/exhumation of the same slices may be triggered by a gradual shallowing of the subducted YB slab towards the west as is evidenced by the absence of UHP rocks in the Tongbai orogen (Liu et al., 2010a; Liu et al., 2013a) and the wide distribution of Triassic granites (Sun et al., 2002a). The west-propagated continent–continent collision between the YB and NCC finalized in the Late Triassic at ca. 225 Ma (Wu and Zheng, 2013).

The NCC rotated 12°-32° counterclockwise with respect to the YB during the Early and Middle Jurassic (Uno and Huang, 2003). The paleomagnetic data and the sedimentary records of the northern Yangtze foreland basin show that the termination of collision and welding of the two blocks took place no earlier than the Middle Jurassic (Gilder and Courtillot, 1997; Huang et al., 2008a; Li et al., 2013c; Liu et al., 2005; Qian et al., 2015; Yang and Besse, 2001). The Early Mesozoic continent-continent collision between the YB and NCC resulted in an overthickened continental crust (Huang et al., 2008b; Huang et al., 2007), followed subsequently in the Middle Jurassic to the Early Cretaceous by uplift and extensional tectonic collapse (Hacker et al., 2000; Qian et al., 2015). A negative Bouguer gravity underneath the UHP terrane has been interpreted as the underthrust YB continental crust stagnating at a middle or lower crust level (Wang et al., 1999). Moreover, there still remains an orogenic root, ca. 5 km thick, beneath the Dabie orogenic belt, suggesting a possibly incomplete collapse and/or delamination of the thickened crust (He et al., 2014; Li et al., 2009a).

2.2. Basement of the ore belt

The Qinling orogen is composed of four tectonic units, which are, from north to south, the southern margin of the NCC, North Qinling (NQ), South Qinling (SQ), and the northern margin of the YB (Fig. 1) (Dong et al., 2011; Meng and Zhang, 2000; Shi et al., 2013).

The basement of the southern margin of the NCC consists of the Neoarchean to Paleoproterozoic Taihua Group, a suite of medium- to high-grade metamorphic rocks consisting of greenstone belts and khondalites. The tonalite-trondhjemite-granodiorite (TTG) gneisses of the Taihua Group are dated at 2.3 to 2.7 Ga by zircon U–Pb methods with crustal Hf model ages ranging from 2.6 to 3.2 Ga (Huang et al., 2010; Huang et al., 2012; Shi et al., 2011; Wang and Liu, 2012). The cover sequences consist of the Paleoproterozoic Xiong'er Group, Mesoproterozoic Guandaokou Group quartzite and schist with intercalated dolomitic marble, and Neoproterozoic Luanchuan Group clastic and carbonate rocks. The Xiong'er Group is composed of mafic to felsic volcanic rocks and minor sedimentary rocks with zircon U–Pb and Sm–Nd isochron ages of 1.75–1.80 Ga and two-stage whole-rock Nd and zircon Hf model ages of 2.7–3.0 Ga and 3.0–3.3 Ga, respectively (Cui et al., 2011; Zhao et al., 2007a).

The NQ is separated from the NCC by the Luonan–Luanchuan Fault. The basement of the NQ consists mainly of the Mesoproterozoic Qinling Group and Neoproterozoic Kuanping Group. The Qinling Group is composed of biotite plagioclase gneiss, granulite, amphibolite, dolomite marble and graphite marble, which were dated to be 1.4 to 1.6 Ga by zircon U–Pb methods (Wan et al., 2011; Yang et al., 2010). The Kuanping Group is composed of meta-basalts, clastic rocks and carbonate rocks (Diwu et al., 2010; Shi et al., 2009).

The SQ crust consists of a basement of Neoarchean to Neoproterozoic meta-volcanic rocks and meta-sedimentary rocks and overlying Cambrian to Triassic sedimentary rocks (Meng and Zhang, 2000). The basement of the SQ is composed of several discrete

metamorphic terrains, including the Neoarchean Yudongzi Group amphibolite–leptite–migmatite (2.66–2.70 Ga, zircon U–Pb age, Zhang et al., 2010) and the Douling Group granitic gneiss–amphibolite–marble (within which the granitic gneiss was dated to be 2.47 to 2.51 Ga by zircon U–Pb method, two-stage zircon Hf model ages of 3.30 to 2.95 Ga) (Hu et al., 2013); the Neoproterozoic volcanic rocks (840–685 Ma, zircon U–Pb method, Ling et al., 2008; Yan et al., 2003).

The basement of the northern margin of the YB consists of the Neoarchean Kongling Group and Neoarchean to Paleoproterozoic Houhe Group metamorphic rocks (Ling et al., 1997; Wei et al., 2009), overlain by a series of Neoproterozoic to Mesozoic volcanic and sedimentary rocks (Chen et al., 2011).

The Tongbai, Hong'an, and Dabie orogenic belts, to the east of the Qinling orogenic belt, are taken as eastern extensions of the Qinling orogenic belt, and mainly of the South Qinling unit (Huang et al., 2006; Kuang and Zhang, 2002; Sun et al., 2002c; Xu et al., 2007; Zhang et al., 2002) or the Qinling and Erlangping Groups of the NQ (Liu et al., 2013b; Mi et al., 2015). These eastern belts are comprised of a Paleozoic collision orogenic belt in the north and a Mesozoic orogenic belt of the HP-UHP rocks in the south. The epidote-amphibolite facies metamorphic rocks in the Hong'an and Dabie orogenic belts have tectonic affinity close to rocks of the northern margin of the YB. These low-grade metamorphic rocks may have been detached and removed from the subducted continental crust of the YB during the initial stage of subduction in the Triassic, and then thrust northward over the Paleozoic metamorphic rocks at the southern margin of the NCC. Alternately, they may have been introduced as foreign slices within the UHP zone during continental collision (Liu and Li, 2008; Liu et al., 2010b).

A continent-collisional lithospheric-wedging model was postulated to interpret the decoupling of the surface and subsurface sutures in the Dabie-Sulu orogen (Li and Yang, 2003). This model is based on the observations that the Early Cretaceous mafic-ultramafic intrusions in the north part of the Dabie orogen have very low $\varepsilon_{Nd}(t)$ values (-15 to -21) and Pb²⁰⁶/Pb²⁰⁴ ratios (<17.3), which are significantly different from those of their counterparts in the YB. Consequently, the lower crust and lithospheric mantle on the south margin of the NCC became wedged into the north margin of the lithosphere of the YB along the Dabie-Sulu collision zone. This scenario could explain the overthrust of the mid-upper continental crust above the exhumed ultrahigh pressure (UHP) metamorphic rocks, and underthrust of the deep lithosphere of the YB (Li and Yang, 2003). Considering the counterclockwise rotation of the NCC during the Late Triassic to Early Jurassic (Yang et al., 2001), the architecture of the Dabie orogenic belt might have resulted from the decoupling of the subducting plate, which is believed to be a common process in continental collision orogenic belts (Willingshofer et al., 2013).

3. Geology and geochemistry of the Late Mesozoic granites in the Qinling–Dabie Mo belt

The Late Mesozoic (Late Jurassic to Middle Cretaceous) granitoids are widespread in the Qinling-Dabie orogenic belt (Fig. 1). These granite intrusions have zircon U–Pb ages that range from 158 Ma to 101 Ma (Table S1, Fig. 2), and commonly intruded the Archean to Mesoproterozoic metamorphic rocks (Taihua and Xiong'er Group) in the East Qinling and the Archean to Neoproterozoic metamorphic rocks (e.g., Dabie complex and Tongbai complex) in the Tongbai, Hong'an, and Dabie orogenic belts (e.g., Bao et al., 2014; Chen et al., 2015; Gao et al., 2014a; Wu et al., 2002). The porphyry -skarn Mo deposits are spatially, temporally, and genetically associated with the granites (e.g., Mao et al., 2011; Mi et al., 2015). The ore related granite porphyries are commonly small in size, with outcrop areas of less than 1.5 km² (Mao et al., 2011). Geophysical investigations indicate that the ore-bearing granite porphyries are likely shallow plutons emanating from deeper batholiths. For example, the Donggou and the Nannihu-Shangfanggou granite



Fig. 2. Histogram of zircon U–Pb ages of the Late Mesozoic granite intrusions in the southern margin of the North China Craton.

porphyries can be linked to their neighboring Taishanmiao and Heyu granite batholiths, respectively, as is supported by their similar zircon U–Pb ages and trace element and isotope geochemical characteristics (e.g., Bao et al., 2014; Mao et al., 2010; Ye et al., 2008).

The rock types of the granite plutons consist mainly of monzogranite, granodiorite, and syenogranite (Fig. 3). The granitic rocks are metaluminous to peraluminous (Fig. 4a), and commonly alkaline rich with features of high-K calc-alkaline and shoshonitic (Table S2, Fig. 4b). The alkaline contents of the rocks increase with increasing SiO₂ showing linear trends on Harker diagrams (Fig. 5a–f). The somewhat dispersed K₂O may be due to late magmatic hydrothermal alteration, particularly for the ore related granite porphyries (Fig. 5f). The petrological and geochemical differences between the ore-bearing granite porphyries and the batholiths are the porphyritic structures and slightly higher SiO₂ and alkaline contents (Table S2). The lack of significant compositional gaps in the Harker diagrams suggests that the main petrogenetic process operative in their origin is likely to be partial melting of source rocks with widely varied chemical compositions.

All of the Late Mesozoic granitic rocks in the Qinling–Dabie Mo belt plot in the post-collisional tectonic field of a Rb versus (Y + Nb)



Fig. 3. TAS plot for the granitic rocks from the southern margin of the North China Craton (after Cox et al., 1979).



Fig. 4. (a) A/NK versus A/CNK and (b) K₂O versus silica diagrams for the Late Mesozoic granitic rocks.

discrimination diagram (Fig. 6) (Pearce, 1996; Pearce et al., 1984), which is consistent with the tectonic evolution of the Qinling-Dabie orogenic belt (e.g., Wu and Zheng, 2013; Zhang et al., 1995). Whole rock Sm-Nd isotope compositions of the Late Mesozoic granitic rocks, which are characterized by very low $\varepsilon_{Nd}(t)$ values varying mainly in the range of -10 to -20, suggest a crustal origin (Table S3). Moreover, the batholiths and granite porphyries have similar Sm-Nd isotope compositions, suggesting a co-magmatic origin. For instance, the $\epsilon_{\text{Nd}}(t)$ values of granitic rocks from the Heyu, Taishanmiao, and Yinjiagou plutons and nearby granite porphyries are quite similar, varying between -14 and -16 for Heyu (Bao et al., 2009b; Gao et al., 2010a), -8 and -18 for Taishanmiao (Dai et al., 2009; Gao et al., 2014a; Li et al., 2013a), and -10 and -14 for Yinjiagou (Li et al., 2013b), and do not change with SiO₂ content (Fig. 7a-c). Similarly, no correlation between the SiO₂ content and $\varepsilon_{Nd}(t)$ value is observed in the Late Mesozoic granites as a whole (Fig. 7d). Most of the Late Mesozoic granites in the Qinling–Dabie Mo belt have $\varepsilon_{Hf}(t)$ ranging between -10 and -30(Table S4), which plot above the 2.0 Ga evolution line of average crust (176Lu/177Hf = 0.015) (Griffin et al., 2002), suggesting that the granitic



O Granites younger than 125 Ma; + Granites older than 125 Ma

Fig. 5. Harker variation diagrams for the Late Mesozoic granitic rocks.

rocks were mainly derived from re-melting of crustal materials with two-stage Hf model ages younger than 2.0 Ga (Fig. 8). Abundant inherited zircons with Paleoproterozoic and Neoproterozoic U–Pb ages further support the probability that the Late Mesozoic granites were derived from recycling of Paleoproterozoic and Neoproterozoic crustal material.

It is strikingly noteworthy that there are abrupt changes in the trace element and Nd–Hf isotope compositions of these granites at about 125 Ma. Granitic rocks younger than 125 Ma have higher contents of large ion lithophile elements (LILEs) and high field strength elements (HFSEs) than rocks older than 125 Ma (Fig. 9a–f). Some granitic rocks (including quartz syenite and syenogranite) with U–Pb ages younger than 125 Ma have characteristics of A-type granite (e.g., Dai et al., 2009; Gao et al., 2014a; Li and Bao, 2010; Mao et al., 2011; Wang et al., 2013b). Also, the whole rock $\epsilon_{Nd}(t)$ values of



Fig. 6. Rb versus (Y + Nb) discrimination diagram for the Late Mesozoic granitic rocks (after Pearce, 1996).

granites younger than 125 Ma are higher than those of the older granites (Fig. 10). Consistent with this, granitic rocks younger than 125 Ma have systematically higher $\varepsilon_{\rm Hf}(t)$ values and lower crustal Hf model ages of 1.6 to 2.6 Ga with an average value of 2.0 Ga (Fig. 11) than for the older ones of 1.8 to 3.0 Ga with an average value of 2.4 Ga (Fig. 12).

4. Discussion

4.1. Subduction of the continental crust of the Yangtze block

Continent-continent collisions frequently play a fundamental role in the evolution of continents (Unsworth, 2010). Although the subduction of continental crust was once held in suspect because of its buoyancy, it is now widely accepted as a common process during plate convergence (Afonso and Zlotnik, 2011; Li, 2014; Molnar and Gray, 1979). Subduction of continental crust has been well illustrated in the Dabie Mountains (Li et al., 1993; Zheng, 2008) and the Tibetan Plateau (Li et al., 2008; Zhao and Nelson, 1993). While subduction recycling of oceanic lithosphere is a well-documented process in plate tectonics, the recycling of continental lithosphere appears to be far more complicated and less well understood (Levander et al., 2014). Unlike oceanic slabs, continental crust is considerably more buoyant than mantle rocks. Consequently, the intrinsic buoyancy of the subducted continental crust would oppose entrainment to greater depth, and therefore the crust might be gravitationally trapped during subduction (Wu et al., 2009 and references therein).

Experimental petrology studies have shown that under certain conditions the upper continental crust can be transported to the lower part of the transition zone. Such a condition might occur when the crust is subducted together with eclogite and/or it is dragged by oceanic subduction exceeding the critical depth of 250 km where conversion to high-pressure phases in the subducted continental crust would lead to a gravitational reversal (Irifune et al., 1994; Wu et al., 2009). Conversely, loss of leading portion of the high-density oceanic lithosphere by slab breakoff of changes in tectonic conditions, such as from compression to extension or transtension, may result in exhumation of deeply buried continental crust (Ernst et al., 1997; Teyssier, 2011). Slices of subducted continental crust may stall in the mantle and rise up to the continental Moho under their buoyancy force (Boutelier et al., 2004; Walsh and Hacker, 2004). In this circumstance, the lower crust and lithospheric mantle could eventually be replaced by the continental lithosphere from an unrelated, accreted continental fragment in a continental



Fig. 7. Plots of whole rock $\varepsilon_{Nd}(t)$ vs. SiO₂ (wt.%) for granitic rocks from the (a) Heyu pluton–related to the Nannihu–Sandaozhuang–Shangfanggou large Mo deposits, (b) Taishanmiao pluton–related to the Donggou large Mo deposit, (c) Yinjiagou pluton–related to the small-sized Yinjiagou Cu–Mo deposit.

collision orogenic belt (Collins et al., 2011). The presence of buried continental crust at depths in continental collision orogens is also supported by seismic tomography and magnetotelluric surveys (e.g., Pous et al., 1995; Schneider et al., 2013; Sippl et al., 2013).

The Triassic continental collision between the YB and NCC along the Huwan suture in the east (Sun et al., 2002b; Sun et al., 2002c) and the Mianlue suture in the west (Dong et al., 2011), first produced the Dabie–Sulu orogenic belt at the east end of the Central China Orogen, forming the famous Dabie–Sulu UHP metamorphic zones (Wu and Zheng, 2013). The subsequent westward propagating continental collision in the Qinling and Tongbai orogenic belts were not accompanied by UHP metamorphic rocks, and only a few outcrops of UHP metamorphic rocks were observed in the Hong'an orogen (e.g., Liu and Liou, 2011; Wu and Zheng, 2013; Zheng et al., 2009). The westward decrease in metamorphic temperatures and pressures from the Dabie–Sulu regions through the Hong'an and Tongbai regions to the Qinling region is interpreted as the results of westward-shallowing subduction (Liu et al., 2010a; Liu et al., 2013a). Relics of subducted continental crust at the middle crust level underneath the UHP metamorphic slice in the



Fig. 8. Plot of $\varepsilon_{\rm Hf}(t)$ versus U–Pb ages for magmatic and inherited zircons from the Late Mesozoic granitic rocks in the southern margin of the North China Craton.

Dabie orogenic belt is evidenced by a negative Bouguer gravity anomaly (Wang et al., 1999).

4.2. Recycling of the subducted continental crust—origin of the Late Mesozoic granites in the Qinling–Dabie orogenic belt

Granitoids, as major post-collisional magmatic rock type found widespread in continental collisional orogens (Dilek and Altunkaynak, 2007), are indispensable sources of information for understanding the evolution of orogenic belts (e.g., Barbarin, 1999) and tracing the unexposed basement terranes at depth (Bennett and Depaolo, 1987; Jung et al., 2012). Studies concerning the timing, rock type, geochemical characteristics, magma sources, and geodynamic settings of postcollisional magmatism have important implications for understanding the recycling of subducted continental lithosphere, the partial melting of deeply subducted continental lithosphere-sometimes stalled in the uppermost part of the upper mantle for tens of millions years, and the tectonic evolution of collision orogens (Jung et al., 2012). From the distinct zircon Hf isotope compositions and the abundant inherited zircons with Neoproterozoic and Paleozoic ages, it can be inferred that the Late Mesozoic granites in the Mo ore belt were unlikely derived from melting of the basement of the southern margin of the NCC.

4.2.1. Origin of the Late Mesozoic granites in the Dabie orogenic belt

Source rocks of the Late Mesozoic granites in the east part of the Central China Orogen, i.e., the Dabie-Sulu orogenic belt, are better constrained than those of the Qinling orogenic belt (e.g., Zhao et al., 2011; Zhao et al., 2007b). The occurrence of the UHP metamorphic rocks in the Dabie-Sulu belt provides robust evidence of the Early Mesozoic continental crust subduction (Wu and Zheng, 2013; Zheng, 2008). Moreover, geophysical evidence suggests that segments of the subducted continental crust still exist at depth in the orogenic belt (Wang et al., 1999). The Late Mesozoic granitic rocks in the belt contain abundant inherited zircons with Neoproterozoic and Triassic U-Pb ages. Moreover, the zircon domains with Triassic U-Pb ages have low Th/U ratios and thus give evidence of a metamorphic origin. Additionally, the granitic rocks have trace element and isotope geochemical signatures similar to the adjacent UHP metamorphic rocks, indicating a tectonic affinity to the northern margin of the YB (Tang et al., 2008; Zheng et al., 2009; Zheng et al., 2005). Existence of subducted continental crust underneath the orogenic belt and the southern part of the NCC is also supported by the banded biotite gneiss xenoliths from lamprophyre dikes having a phlogopite 40Ar/39Ar plateau age of 116 Ma at the southeastern part of the NCC, about 150 km north of the Dabie–Sulu UHP metamorphic belt. Geochemical characteristics of the gneisses demonstrate that the xenoliths represent vestiges of the subducted YB crust underneath the southern margin of the NCC (Wu et al., 2015). Therefore, the Late Mesozoic granitic rocks were probably derived from partial melting of the stagnated subducted continental crust originally at the northern margin of the YB. Partial melting of the stagnated subducted continental crustal materials is possibly related to tectonic collapse of the orogenic roots, through lower crustal delamination or lithospheric delamination, in response to post-collisional lithospheric extension (e.g., He et al., 2011; Wang et al., 2007; Wu et al., 2015; Xu et al., 2012a; Zhao and Zheng, 2009).

4.2.2. Origin of the Late Mesozoic granites in the Qinling, Tongbai, and Hong'an orogenic belts

Different petrogenetic models have been proposed for the Late Mesozoic granites in the Qinling–Dabie Mo belt which include: (1) remelting of the local basement (the Archean–Paleoproterozoic Taihua Group and Paleoproterozoic Xiong'er Group) and possibly the Mesoproterozoic Kuanping Group (Chen et al., 2013; Chen et al., 2000; Fan et al., 1994; Li et al., 2015a); (2) partial melting of ancient crust with input of juvenile mantle material (Dai et al., 2009; Ke et al., 2013; Wang et al., 2015; Zhu et al., 2010); and (3) partial melting of subducted continental crust (Bao et al., 2014; Bao et al., 2009b; Li et al., 2012b). In addition, there are a few researchers who have argued that the ore-bearing granite porphyries and the granite batholiths are genetically different, belonging to I-type and S-type igneous rocks, respectively (Lu et al., 2002; Sun and Liu, 1987).

The similar trace element and Nd–Hf isotope geochemical characteristics of the Late Mesozoic granites (the Qinling, Tongbai, and Hong'an orogenic belts alike) (Figs. 5, 9–10) demonstrate that the rocks might have derived from similar sources. The crustal Hf model ages of the granitic rocks, ranging from 1.6 to 3.0 Ga (average 2.4 Ga for rocks with ages older than 125 Ma and 2.0 Ga for those younger than 125 Ma; Fig. 12) are substantially younger than the 2.8 to 3.2 Ga model ages of the local basement (Diwu et al., 2010; Huang et al., 2010). Moreover, Hf model ages of magmatic zircons from the Late Mesozoic granitic rocks are also significantly younger than those of the Mesozoic felsic igneous rocks, which are attributed to partial melting of the lower crust, found elsewhere in the NCC (2.5–2.7Ga) (Jiang et al., 2013; Yang et al., 2014). Thus, despite the Archean to Mesoproterozoic whole rock Nd and zircon Hf isotope crustal signatures of the granites, their



O Granites younger than 125 Ma; + Granites older than 125 Ma

Fig. 9. Bivariate plots of trace element versus U-Pb ages for the Late Mesozoic granitic rocks.

considerably younger crustal Hf model ages do not support the remelting of the local basement.

SHRIMP zircon U–Pb dating and whole rock Nd isotope studies demonstrate that before ca. 125 Ma the subcontinental mantle beneath the southern margin of the NCC had enriched isotopic compositions. For instance, gabbro and dolerite dikes from the Luanchuan (148 ± 2 Ma), Wenyu–Huashan (127 to 129 Ma), and Huanglongpu (129 ± 2 Ma) areas in the East Qinling orogenic belt and the Jinzai area ($126 \pm$ 3 Ma) in Dabie orogenic belt have $\varepsilon_{Nd}(t)$ values of -6.1 to -7.0, -8.0 to -26, -18 to -20, and -12 to -19, respectively (Table S3) (Bao et al., 2009a; Wang et al., 2010b; Wang et al., 2008; Zhao et al., 2010). To produce granitic magmas with Nd–Hf isotopic signatures like those of the Late Mesozoic granites in the Qinling–Dabie Mo belt, the enriched mantle should have been the predominant end-member of the source rocks, which is not supported by their major element geochemistry.

The Late Mesozoic granites in the Qinling–Dabie Mo belt might have been derived predominantly from partial melting of the geologicallyand geophysically-identified stagnated subducted continental crust at the northern margin of the YB. For instance, the lower crust enclaves composed of high-pressure mafic to felsic granulite and metagabbro from the ~160 Ma Xinyang diatremes in the southern margin of the



Fig. 10. Plots of whole rock $\epsilon_{Nd}(t)$ vs. U–Pb age for the Late Mesozoic granitic rocks.

NCC show geochemical affinity of the YB, suggesting the northward continental subduction of the YB beneath the NCC which extended as far as 400 km laterally (Lu et al., 2003; Lu et al., 2004; Zheng et al., 2008). Moreover, geophysical data show that the lower crust beneath the southern margin of the NCC is thin, and the Moho dips northward, the imaged high velocity volumes in the intralithospheric mantle beneath the southern margin of the NCC was interpreted to be a subduction remnant that still exists in the uppermost mantle, which reveal a flat subduction of the YB beneath the NCC (Zheng et al., 2012, and references therein). It is important to notify that the NCC and YB have distinct histories of crustal growth. The majority of the crust was formed by 2.5 Ga (Hu et al., 2012; Jiang et al., 2010; Wang and Liu, 2012). On the contrary, the northern margin of the YB is characterized by prominent crustal additions in the Mesoproterozoic and Neoproterozoic (Liu et al., 2008; Wang et al., 2010a, 2013a), whereas the Early Paleozoic, Late Triassic, and Early Cretaceous are also important episodes of crustal growth (Yang et al., 2007). Supporting this conjecture, the Nd-Hf isotope compositions of the granites are similar to those of the continental crust at the northern margin of the YB, where major crustal growth occurred in the Paleoproterozoic and Neoproterozoic (e.g., Ling et al., 2008; Wang et al., 2013a; Zhang and Zheng, 2007). Also, the Pb isotope compositions of the granites show affinity to the northern margin of the YB (e.g., Li et al., 2011; Zhang, 1988; Zhao and Zheng, 2009).

Element and isotope characteristics of the granitic rocks in the Mo ore belt show that the ore-bearing granite porphyries are genetically related to the neighboring granite batholiths (Figs. 5, 9), deriving from a similar magma source rather than one of a different genetic type (Bao et al., 2014; Yang et al., 2013). Therefore, the Late Mesozoic granites in the Qinling–Dabie Mo belt were derived predominantly from partial melting of the subducted continental crust originally at the northern margin of the YB. The striking contrast between the NQ and the southern margin of the NCC in Mesozoic Mo mineralization in the Qinling orogen is fascinating, and much work is needed to solve this conundrum. A tentative explanation regarding the difference may be that the crustal structures of the two units were different in the Late Mesozoic, which is possibly related to the intracontinental geodynamic processes such as E–W dextral lateral strike slipping before the Late Mesozoic ore-related magmatism (Dong et al., 2015; Li et al., 2013c). Available data show that the crustal sources for the Late Mesozoic granites in the NQ are different from those of the southern margin of the NCC, for instances, granites in the NQ commonly have lower SiO₂, abundant mafic enclaves, relative higher $\varepsilon_{Nd}(t)$ and $\varepsilon_{Hf}(t)$ values (Wang et al., 2015; Wang et al., 2011). Thus, the less Mo mineralization in the NQ may be due to the absent of the subducted crust of the YB during the Late Mesozoic which might have been removed by unknown tectonic mechanisms.

4.2.3. Coupling of the post-collisional granite magmatism and tectonics of the orogenic belt

As discussed above, geochemical characteristics of the granitic rocks show that the Late Mesozoic granites in the Qinling–Dabie Mo belt were derived primarily from recycling of the subducted continental crust. The abrupt changes of the chemical and isotope compositions of the granitic rocks at 125 Ma (Figs. 9, 10, 11) reflect the onset of an added contribution from upwelling asthenospheric mantle. The upwelling of asthenospheric mantle may have been triggered by the delamination and collapse of the thickened lower crust as a result of Early Mesozoic continental collision. It is also synchronous with and may be genetically related to the destruction of the NCC characterized by lithospheric thinning (e.g., Ling et al., 2013; Meng et al., 2015; Wilde et al., 2003; Wu et al., 2006; Xu et al., 2009; Zhai et al., 2007; Zhou et al., 2002) and the transformation of the Cretaceous plate subduction in the west Pacific



Fig. 11. Plots of (a) $\epsilon_{Hf}(t)$ and (b) crustal Hf model ages (T_{Hf2}) versus U–Pb ages for magmatic zircons from the Late Mesozoic granitic rocks.

(Sun et al., 2007). The replacement of the enriched subcontinental mantle by depleted asthenospheric mantle, as one of the important results of the lithospheric thinning (e.g., Ma et al., 2014; Meng et al., 2015), may be the major factor accounting for the changes of the trace element and isotope compositions of the granites at ca. 125 Ma. The replacement of enriched mantle by depleted upwelling asthenospheric mantle is likely also exemplified by the occurrence of the Tianqiaogou diorite in the East Qinling area (122 \pm 2 Ma, LA-ICPMS zircon U–Pb; $\epsilon_{\rm Hf}(t) = 2.87–6.21$) (Gao et al., 2014a).

Integrating geological, geochronological, and isotopic geochemical results, we propose that the petrogenesis of the Late Mesozoic granite magmatism in the Qinling–Dabie Mo belt and its relationship with the tectonic evolution of the Qinling–Dabie orogenic belt can be inferred as follows:

(1) The initial continental subduction of the YB beneath the NCC took place in the Tongbai orogenic belt at ~255 Ma (Chen et al., 2011). Later on, a protracted deep subduction of continental crust took place within the Hong'an and Dabie orogenic belts east of the Tongbai orogenic belt. Here decoupling of the subducting continental plate might have led

to the deep subduction of the lower crust and lithospheric mantle at the east end of the Qinling-Dabie orogenic belt and westwards shallowing seesaw-type subduction (Liu et al., 2013a; Willingshofer et al., 2013). The Late Permian to early Middle Triassic (250-234 Ma) slab rollback and back-arc basin development at the west end of the Qinling orogenic belt (Li et al., 2014; Pullen et al., 2008) and the subsequent Late Triassic (225-205 Ma) slab breakoff in the Qinling orogenic belt (Bao et al., 2015; Sun et al., 2002a), might also have contributed to the westwards shallowing continental subduction of the Qinling-Dabie orogenic belt. The slab breakoff, and possibly the peel off of the lithospheric mantle of the subducting YB reduced the downward-pulling force for further subduction. Thus, the subsequent continental subduction became flat and shallow because of the buoyancy of the continental crust. The shallow subduction of the continental crust of the YB is attested by the lack of exhumed UHP metamorphic rocks like those found in the Dabie-Sulu area. By contrast, the superficial structures of the Qinling orogen are characterized by southward thrusting of NCC terrains. Therefore, it can be inferred that the decoupling of the subducting continental lithosphere was virtually nonexistent west of the Dabie orogenic belt. Consequently, we, propose



Fig. 12. Histograms of crustal Hf model ages for the Late Mesozoic granitic rocks with U-Pb ages (a) older than 125 Ma; and (b) younger than 125 Ma.

that the upper crust originally at the northern margin of the YB was most likely entrained underneath the lower crust or upper mantle of the NCC, particularly in the Qinling, Tongbai, and Hong'an orogenic belts.

(2) Partial melting of the subducted continental crust stacked underneath the southern margin of the NCC in its post-collisional setting gave rise to the extensive Late Mesozoic granite intrusions. With the progression of partial melting and delamination of the thickened crust in the orogenic belt, the upwelling of asthenospheric mantle took place at about 125 Ma, which is coincident with the lithospheric thinning in the NCC. Involvement of the depleted asthenospheric mantle led to the abrupt changes of the trace element and isotope geochemical signatures of the granitic rocks.

4.3. Source of Mo for the extensive Mesozoic molybdenum mineralization

The source of Mo for the over 9 million tons of molybdenum reserves deposited in a relatively short geological period (~50 Ma) in the Qinling-Dabie Mo belt has been debated for decades. Some researchers speculated that the ore-bearing granite porphyries inherited their Mo rich feature from the basement, i.e., the Taihua and Xiong'er Group (e.g., Chen et al., 2000; Wang et al., 2015). However, the Mo enrichment in the basement rocks at the southern margin of the NCC, such as the Taihua (1.05 ppm), Xiong'er (0.37 ppm) and Kuanping (0.98 ppm) groups, is far from sufficient to account for the large scale molybdenum mineralization (Lu et al., 2002); similarly, the Mo concentration of the lower crust in the southern margin of the NCC (0.90 ppm) is only slightly greater than average continental lower crust (0.6 ppm) (Gao et al., 1998; Wedepohl, 1995). Furthermore, Mo ore deposits related to granites of Proterozoic to Early Mesozoic age, which also involved the reworking of the ancient lower crust, are economically much less significant (e.g., Chen, 2010; Lu et al., 2002; Wang et al., 2013b).

Regarding the genetic link between the porphyry-skarn deposits and the granitic plutons, it seems more plausible to propose that the principal Mo source for the extensive mineralization was related to the recycling of the subducted upper crust of the YB (Bao et al., 2014; Bao et al., 2009b). It is well-known that the upper crust of the YB, which includes widespread black shales, is tremendously enriched in molybdenum. The sulfidic sediments, in particular, have metal contents several hundred times greater than that of sediments in modern euxinic environments (e.g., Lehmann et al., 2007; Xu et al., 2011). The black shales in the YB contain over 100 ppm Mo, and a layer of polymetallic sulfide ores in the Lower Cambrian Niutitang Formation on the southeastern margin of the YB contains extremely high concentration of Mo (up to 7.5 wt.%) (e.g., Coveney and Nansheng, 1991; Xu and Li, 2015).

The Mo isotope composition of the molybdenites from the deposits in the ore belt is also supportive of a contribution from the subducted YB crust. Studies show that Mo isotope fractionation during igneous processing is insignificant (Siebert et al., 2003; Yang et al., 2012), and granites formed by partial melting or assimilation of a sedimentary source should preserve their Mo isotopic signature (Voegelin et al., 2014; Yang et al., 2015; Yang et al., 2012). Recently determined Mo isotope compositions of molybdenite from the Donggou $(\delta^{97}/{}^{95}Mo = -0.53 - 0.47\%)$ and Nannihu $(\delta^{97}/{}^{95}Mo = -0.74 - 0.74 - 0.53 - 0.47\%)$ 0.73‰) large Mo deposits in the Qinling-Dabie Mo belt have a range of variation, which may reflect the signature of the sedimentary source. The similarity between the Mo isotopes of the Mo deposits at the Qinling-Dabie Mo belt and the black shales and sulfidic sediments in the YB (e.g., the Niutitang Formation) that vary between -0.5 and 1.5% (Wen et al., 2011; Xu et al., 2012b), can be considered as collateral evidence supporting our model that the subducted upper continental crust of the YB has been a predominant contributor of Mo for the extensive Mo mineralization in the Oinling-Dabie Mo belt.

As illustrated above, robust evidence shows that the Late Mesozoic ore-bearing granites were derived primarily from partial melting of the Mo-enriched continental crust of the YB that subducted along the Manlue suture at the southern margin of the Qinling–Dabie orogenic belt during the Mesozoic orogenesis. The decoupling of the upper crust from the deep subduction of the lower crust and lithospheric mantle may account for the lack of economically significant Mo mineralization in the eastern part of the Dabie–Sulu orogenic belt. Here the Mo rich upper crust of the YB did not participate in the subduction, and thus was not involved in the generation of the Late Mesozoic granitic magmatism.

5. Conclusion

Geochemical characteristics of the Late Mesozoic granitic rocks at the Qinling–Dabie Mo belt, which are closely related to the extensive molybdenum mineralization, suggest that they were derived from a similar magma source. Nd–Hf isotope compositions of the granites suggest a crustal origin, whereas the substantially younger crustal Hf model ages, and U–Pb ages of inherited zircons—comparable to the continental crust at the northern margin of the YB—further demonstrate that the granitic rocks were most likely derived from partial melting of the stagnated subducted continental crust of the YB.

Trace element and Nd–Hf isotope geochemical signatures of the Late Mesozoic granites changed dramatically in response to the collapse of the thickened lower crust at ~125 Ma, accompanied by simultaneous lithospheric thinning in the NCC and upwelling of the asthenospheric mantle.

Subduction and recycling of the Mo rich upper continental crust of the YB are of crucial importance for the formation of the extensive Late Mesozoic porphyry-skarn molybdenum mineralization.

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Conflict of interest

We, the authors, hereby declare that there is no conflict of interest regarding this manuscript.

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