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# **The Dabie-Sulu orogenic peridotites: Progress and key issues**

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Orogenic peridotites in the Dabie-Sulu orogenic belt are commonly subdivided into 'crustal' type and 'mantle' type. They exhibit distinct mineral textures, metamorphic evolution, and whole-rock and mineral compositions. Most 'mantle' type peridotites originated from the subcontinental lithospheric mantle (SCLM) of the North China Craton and thus provide direct evidence of crust-mantle interactions in the continental subduction channel. In garnet peridotites, both garnet and Cr-spinel can be equilibrated at peak pressure conditions. Their stabilities are mainly controlled by the refertilized degree of whole-rock; therefore, spinel composition cannot be used to discriminate the partial melting degree of orogenic peridotites. Refractory mantle-derived dunites contain the textures of low Mg and high Ca olivine veins that crosscut orthopyroxene porphyroblasts, which is considered as evidence for silica-undersaturated melt-rock reactions. Such reactions occurring before subduction may potentially affect Re-Os isotopic compositions. Rutile, Ti-clinohumite and zircon in mantle-derived peridotites or pyroxenites provide direct mineralogical evidence for the transport of high field strength elements (HFSEs) from the subducted crust into the mantle wedge. Based on detailed *in situ* element and isotope analyses, we can constrain the source of metasomatic agents, the metasomatic time and the process of mass transfer. The mantle wedge above continental subduction zones has a wide range of oxygen fugacity values (FMQ=5.50–1.75), showing a roughly negative correlation with the subducted depths. However, the calculated results of oxygen fugacity are significantly affected by mineral assemblages, *P*-*T* conditions and dehydrogenation-oxidation of nominally anhydrous mantle olivine during exhumation. Although significant progress has been made in the study of orogenic peridotites in the Dabie-Sulu orogenic belt, many critical questions remain. With new approaches and advanced technologic applications, additional knowledge of the phase relation in the peridotite-pyroxenite complex system, the mantle geodynamic process before continental subduction, the effects of crustal metasomatism on chemical composition, the oxygen fugacity, and the physical properties of the mantle wedge is anticipated.

**garnet peridotite, subduction channel, subduction zone fluids/melts, crust-mantle interaction, oxygen fugacity** 

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Garnet peridotites commonly occur as lenses, blocks or layers within high- to ultrahigh-pressure (HP-UHP) granitic/ pelitic gneisses in continental subduction-collision zones. These peridotites are generally called 'alpine-type peridotites' or 'orogenic peridotites' (Menzies et al., 2001; Medaris et al., 2005). Compared to the country rocks, these

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orogenic peridotites not only preserve mineralogical evidence for subduction-related UHP metamorphism (>180– 200 km) but also preserve plenary metamorphic evidence for mantle geodynamic processes prior to continental subduction (Zhang et al., 2000; Zheng et al., 2006b, 2014; Yang and Powell, 2008; Ye et al., 2009; Scambelluri et al., 2010). Therefore, although volumetrically minor, their geodynamic setting and UHP origin make orogenic mantle rocks an important window to the geodynamic processes of

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continental subduction-exhumation, mantle evolution, and crust-mantle interaction in a regional scale with global geodynamic implications.

Several garnet peridotite and garnet-pyroxenite bodies occur as meter- to kilometer-sized blocks within the amphibolite-facies gneisses in the Dabie-Sulu UHP terrane (Figure 1). In the past twenty years, many petrological and geochemical investigations have been performed on these rocks, and significant progress has been made concerning their origins, metamorphic evolution and metasomatic processes (Zhang et al., 1995, 2000; Liou and Zhang, 1998; Yang and Jahn, 2000; Malaspina et al., 2006; Ye et al., 2009; Chen et al., 2013a, 2013b). Orogenic peridotites in the Dabie-Sulu collision zone were commonly classified into 'crustal' mafic-ultramafic cumulates and 'mantle' peridotites (Zhang et al., 2000; Zhang et al., 2009). The former was crystallized from mafic magmas that underwent magmatic differentiation in the lower continental crust prior to subduction, such as the Bixiling and the Maobei maficultramafic complex (Zhang et al., 1995; Chavagnac and Jahn, 1996; Zhang R Y et al., 2006, 2010; Zhang Z M et al., 2006; Liu et al., 2008; Zheng et al., 2008). The latter originated from the mantle wedge above the slab and commonly records UHP metamorphism and metasomatism (Zhang R Y et al., 2004, 2009, 2011; Zheng et al., 2005b, 2006b, 2008; Yang et al., 2007; Zhao et al., 2007; Liu et al., 2012). These two types of orogenic peridotites exhibit significant difference in geochemical characteristics. Therefore, orogenic peridotites are usually classified into a Fe-Ti type and an Mg-Cr type based on their geochemical composition (Carswell et al., 1983). The Fe-Ti type corresponds to the 'crustal' peridotite, whereas the Mg- Cr type is consistent with the 'mantle' peridotite. Previous petrological and geochemical studies have indicated that most peridotites in the Dabie-Sulu orogenic belt belong to the 'mantle' type peridotite; they were scraped by the low- density continental crustal rocks along a subduction channel and exhumed back into the Earth's surface (Zheng, 2012).

The Dabie-Sulu orogenic peridotites experienced various degrees of metasomatism by fluids or melts derived from subducted continental crust and developed abundant metasomatic minerals. Therefore, orogenic peridotites and surrounding gneisses may represent a subducted slab-mantle interface (Zheng, 2012), making them the best samples in which to explore the physical chemistry effects of deep crust-mantle interaction in subduction zones (Chen et al., 2013d; Zheng and Hermann, 2014). In this paper, we briefly summarize mineralogical and petrological features, protolith affinity, geochemical characteristics, and crustal metasomatism of the Dabie-Sulu orogenic peridotites. We also suggest and discuss several key issues for the further study of orogenic peridotites.

# **1 Mineralogical and petrological characteristics of orogenic peridotites**

Tens of localities of orogenic peridotites reported for the



**Figure 1** Sketched map showing the distribution of peridotites in the Dabie-Sulu orogen (modified after Zhang et al., 2009).

Dabie-Sulu UHP metamorphic belt (Figure 1). Most are exposed in the Sulu UHP metamorphic belt; only three peridotite bodies from Maowu, Bixiling, and Raobazhai are exposed in the Dabie UHP metamorphic belt. Except for the Maowu mafic-ultramafic complex, orogenic peridotites primarily consist of garnet lherzolite, with minor harzburgite, dunite and wehrlite, and are commonly associated with pyroxenite, eclogite, and amphibolite. They occur as meter- to kilometer-sized lenses or blocks in granitic/ pelitic gneisses; a fault causes some of the peridotites to contact the surrounding gneisses (Xue et al., 1996; Zhang et al., 2009). Most of the basement gneisses are paragneisses (Zhang and Liou, 1998), which are usually enriched in biotite and epidote, and occasionally preserve garnet crystals. Apatite, rutile and zircon are common accessory minerals in the surrounding gneisses. Coesite inclusions were observed in the gneiss zircons, indicating that the basement gneisses also underwent UHP metamorphism (Ye et al., 2001). Several leucosomes were occasionally observed in the basement gneisses, reflecting partial melting processes (Zheng et al., 2011). Because of the extensive mylonitization and serpentinization at the boundary between peridotites and gneisses (Figure 2(a)), we hardly observe perfect modification textures of subducted crust-mantle interactions in this zone. Some phlogopite- and talc-rich layers occasionally occur at the contact boundary, most likely attributable to late-stage metasomatism by shallow crustal fluids. However, the inner part of the peridotite body is relatively fresh, and most garnet and olivine grains have survived here. Coarse-grained orthopyroxene porphyroblasts are very common in fresh orogenic peridotites. Furthermore, pyroxene-, phlogopite-, amphibole-, and Ti-clinohumite-rich, millimeter- to decimeter-thick veins occasionally crosscut the orogenic peridotites (Figure 2(b)–(d)). These veins provide direct samples in which to explore the crust-mantle interactions in continental subduction zones.

## **1.1 Petrological differences between continental and oceanic subduction zone peridotites**

Orogenic peridotites occur both in continental and oceanic subduction zones, and all of them may contain evidence of crustal metasomatism. However, the systematic discrepancies of subducted material, fluid activities, and geothermal gradients between continental and oceanic subduction zones most likely cause significant petrological and geochemical differences in these subduction zone peridotites (Zheng et al., 2013). Thus, the crust-mantle interaction processes in continental and oceanic subduction zones may differ.

The most striking feature of oceanic subduction zone peridotites is their significant serpentinization. Most originated from the cold and hydrated mantle wedge just above



**Figure 2** Photograph of the Dabie-Sulu orogenic peridotites in outcrop and hand specimen. (a) Phlogopite-talc-rich serpentine layer along the contact boundary between dunite and gneiss, Lijiatun. (b) Phlogopite-rich vein developed in the host lherzolite, Raobazhai. (c) Garnet pyroxenite vein occurring in garnet lherzolite, Bixiling. (d) Garnet pyroxenite vein cutting dunite, Maowu.

subducted slabs (Guillot et al., 2001, 2009; Savov et al., 2005, 2007), but a few may have originated from the cold and hydrated lithospheric mantle beneath the subducted oceanic crust (Chalot-Prat et al., 2003; Li et al., 2004). The serpentinized peridotites in oceanic subduction zones usually contain eclogite and blueschist blocks of various sizes and display an important role in the exhumation of oceanic mafic crust (Guillot et al., 2001; Agard et al., 2009; Chen and Ye, 2013). Serpentinized harzburgite is the dominant lithology, with minor clinopyroxene-poor lherzolite and dunite. Because they are moderately depleted in major element compositions and represent shallow parts (<80 km) of oceanic subduction zones, they are mostly spinel-facies peridotites. Garnet peridotites have been rarely reported in oceanic subduction complexes (Enami et al., 2004; Abbott et al., 2007; Hattori et al., 2010b). Therefore, oceanic subduction zone peridotites can only record the information of crust-mantle interactions at shallow depths. The metasomatic minerals in oceanic subduction zone peridotites are primarily low-temperature hydrous minerals such as serpentine, amphibole, chlorite, talc, and phlogopite. Several oceanic subduction zone peridotites occasionally preserve mineralogical evidence of serpentine dehydration and secondary olivine formation (Scambelluri et al., 2001, 2004; Nozaka, 2003; Padrón-Navarta et al., 2011; Spandler and Pirard, 2013). Such prograde metamorphic olivine is typically extremely Mg-rich, with Fo ranging from 94 to 99 (Li et al., 2004; Song et al., 2009; Arai et al., 2012). However, chlorite can be stable under peak metamorphic conditions, indicating that the metamorphic temperatures of the peridotites range from 650 to 800°C (Fumagalli and Poli, 2005; Padrón-Navarta et al., 2010). The fluids derived from serpentine dehydration are important carriers of Cl, Li, B, As, Sb, Sr, Pb, Cs, and U into subduction zones and are also important in the formation of forearc and arc magmatism (John et al., 2011; Kendrick et al., 2011; Kodolányi et al., 2012; Spandler and Pirard, 2013; Scambelluri et al., 2014). Ti-clinohumite-rich veins commonly occur in the peridotites with serpentine dehydration, implying that the fluids can partially transport HFSEs. The source of HFSEs may be derived from subducted oceanic crust or some Ti-rich phases (clinopyroxene and spinel) in oceanic subduction zone peridotites (Rebay et al., 2012; Arai et al., 2012).

Orogenic peridotites in continental subduction zones are entirely garnet peridotites. Most have lower loss-on-ignition (LOI: water dominated total volatiles; <5wt%) relative to oceanic subduction zone peridotites, reflecting weaker serpentinization. Although some continental subduction zone peridotites also show strong serpentinization (LOI>10wt%) (Xie et al., 2013), the serpentine currently circumfuses or crosscuts the matrix olivine and pyroxene and the symplectites after the peak garnet and Ti-clinohumite (Chen et al., 2013a). This feature indicates that the serpentinization of orogenic garnet peridotites is related to the fluid metasomatism at shallow crustal levels. Compared to oceanic subduction zone peridotites, those in continental subduction zones exhibit relatively fertile major element compositions; the peak mineral assemblage is mostly garnet+clinopyroxne+ orthopyroxene+olivine+Cr-spinel±phlogopite±Ti-clinohumite (Zhang et al., 2000, 2009). Most orogenic garnet peridotites underwent UHP metamorphism (3.5–6.5 GPa), corresponding to a 100–200 km mantle depth. Exsolution lamellae are typical textures in orogenic garnet peridotites. For example, olivines from the Maowu and the Zhimafang garnet peridotites develop abundant exsolution lamellae of Fe-Ti oxides, most likely indicating that they were once subducted into very deep mantle (>300 km) (Dobrzhinetskaya et al., 1996). Traditional geothermobarometries and phase modeling yield the peak pressures of orogenic garnet peridotites that can be up to 6–7 GPa (Yang and Jahn, 2000; Ye et al., 2009; Chen et al., 2013a), also implying that they once reached a deep mantle of >200 km. Therefore, orogenic garnet peridotites in continental subduction zones are ideal for providing information on deep crust-mantle interactions. Except for the Raobazhai peridotite, almost all of the Dabie-Sulu orogenic peridotites preserve peak temperatures of <850°C. The Maowu, the Zhimafang, and the Xugou peridotites/ pyroxenites record the peak *P*-*T* conditions corresponding to a very low subducted geothermal gradient (<5°C/km) (Yang and Jahn, 2000; Zhang et al., 2007; Ye et al., 2009; Spengler et al., 2012; Chen et al., 2013a), which is significantly lower than in oceanic subduction zones (Guillot et al., 2009; Chen et al., 2013c, 2013e).

Orogenic garnet peridotites and pyroxenites are commonly characterized by their complex metasomatic processes. They typically exhibit multistage and various metasomatic minerals, such as garnet, rutile, Ti-clinohumite, Ti-chondrodite, pyroxene, amphibole, phlogopite, epidote, sapphirine, magnesite, dolomite, apatite, monazite, celestite, karstenite, zircon and pyrite (Yang and Jahn, 2000; Zhang et al., 2000, 2007; Yang, 2003; Malaspina et al., 2006, 2009a; Ye et al., 2009; Chen et al., 2013a, 2013b). It is widely accepted that continental subduction usually follows oceanic subduction (Song et al., 2009). Therefore, the mantle wedge overlying the subducted continental slab most likely underwent multistage metasomatism from oceanic subduction to continental subduction processes. The metasomatic agents are expected to include melts from asthenospheric mantle, melts or fluids derived from subducted oceanic crust, and aqueous fluids or hydrous melts released from continental crust during subduction or exhumation (Zhang et al., 2005a, 2007; Zheng et al., 2006a, 2014; Ye et al., 2009; Chen et al., 2013a). Generally, two main types of metasomatism have been identified: modal (or patent) metasomatism and cryptic metasomatism (Malaspina et al., 2006; Scambelluri et al., 2006; Zhang et al., 2007; Vrijmoed et al., 2013). Modal metasomatism changes the modal compositions via the introduction of amphibole, chlorite, phlogopite, Ti-clinohumite, carbonate, ilmenite, rutile or zircon at the expense (or not) of the primary minerals

(olivine, pyroxene, spinel/garnet) in peridotites, whereas cryptic metasomatism only results in changes in the primitive mineral composition without the formation of new phases (Zhang et al., 2005a, 2007; Beyer et al., 2006; Malaspina et al., 2006; Zhao et al., 2007; Zhang Z M et al., 2011). Distinguishing these metasomatic processes requires detailed petrographic observations and *in situ* geochemical analyses.

#### **1.2 Spinel-garnet transition (SGT) reaction**

The Dabie-Sulu orogenic peridotites both in the 'crust' and the 'mantle' types are mostly garnet-facies peridotite. Only the Raobazhai ultramafic body is spinel-facies peridotite, representing a shallow origin (<80 km) that did not experience UHP metamorphism. Tsai et al. (2000) argued that the symplectite of spinel+clinopyroxene+orthopyroxene in the Raobazhai peridotite may have been formed by the decomposition of the primary garnet. However, the local bulk composition of the symplectite exhibits higher  $Cr_2O_3$ , CaO, and  $Na<sub>2</sub>O$  and lower  $SiO<sub>2</sub>$  contents relative to the normal composition of garnet in peridotite. Notably, both garnet and spinel peridotites are currently associated with garnet pyroxenites. In garnet peridotites, Cr-spinel typically occurs as inclusions in the peak garnet and pyroxene or as matrix phases showing an equilibrium texture with other minerals (garnet, pyroxene, and olivine). This feature demonstrates that Cr-spinel (or chromite) can be stable under peak pressure conditions. A typical feature of the Cr-spinels in the Dabie-Sulu orogenic peridotites is their high  $Cr^*$ (=Cr/(Cr+Al)>0.60) (Zheng et al., 2005b, Chen et al., 2006a; Ye et al., 2009; Xie et al., 2013; Chen et al., 2013a). Generally, the stabilities of garnet and spinel, as well as their Cr# values, are closely related to bulk-rock Cr# and *P*-*T* conditions (Klemme et al., 2009; Ziberna et al., 2013). Cr is a compatible element and relatively immobile in mantle peridotite. Except for chromitite-bearing peridotites, the Cr contents of most mantle peridotites are not significantly different. However, Al is a relatively mobile element and is preferentially incorporated into a melt (Griffin et al., 2009). Therefore, mantle peridotites refertilized to different degrees show a significant discrepancy in  $Al_2O_3$  content. In this regard, the stabilities and compositions of garnet and spinel would be directly controlled by the bulk  $Al_2O_3$  content.

Both garnet and Cr-spinel are major Al-rich minerals in orogenic garnet peridotites. A peridotite with very low  $Al_2O_3$  content (e.g., depleted dunite) cannot develop garnet even under UHP conditions; accordingly, the spinel in this rock is expected to have very high  $Cr^*$  values. However, a lherzolite with very high  $Al_2O_3$  content, which is attributed to refertilization, would form garnet at relatively low pressures. The spinel in the lherzolite would have relatively low Cr<sup>#</sup> values. For example, two types of peridotites have been identified in the Chinese Continental Scientific Drilling

(CCSD) PP3 (Ganyu): one is fertile garnet peridotite with a high  $Al_2O_3$  content; another is garnet-free peridotite that is depleted in  $Al_2O_3$  (Yang et al., 2009). The Dabie-Sulu orogenic peridotites contain minor chromite-bearing dunites associated with garnet harzburgites or lherzolites. Their peak pressure conditions do not significantly differ. However, chromite in the depleted dunites has a  $Cr^*$  as high as 0.85– 0.90, whereas Cr-spinel in the fertile garnet harzburgites/ lherzolites has a relatively lower  $Cr^*$  of 0.60–0.85 (Zheng et al., 2005b, Chen et al., 2006a; Ye et al., 2009; Xie et al., 2013; Chen et al., 2013a).

Generally, increasing  $Cr^*$  in spinel is typically caused by (1) a high degree of partial melting; (2) silica-undersaturated melt-peridotite reaction; and (3) an SGT reaction. Al prefers to incorporate into melt, but Cr usually is retained in the residual peridotite, and a high-degree partial melting would consequently result in an increase of  $Cr^*$  in spinel. Thus, the spinel  $Cr^*$  is a good indicator of the depleted degree or formation temperature (Dick and Bullen, 1984; Kubo, 2002). Pyroxene usually has higher Cr contents than the equilibrated olivine. As a consequence of the silica-undersaturated melt-peridotite reaction in an open system in which the residual melt is lost from a peridotite, Cr is most likely shifted from the previous pyroxene into the secondary spinel because it is difficult for the newly formed olivine to store such high Cr contents (Morgan and Liang, 2005; Xu et al., 2008; Tursack and Liang, 2012). However, in a closed system in which the residual melt is retained in the peridotite, the  $Cr^*$  of the secondary spinel may decrease because melts always have a very low Cr content and  $Cr^*$ . In the stability fields of garnet and spinel, their compositions are mainly controlled by the reactions as follows:  $MgA1_2O<sub>4</sub>$  $(spinel)+2Mg_2Si_2O_6(\text{orthopyroxene}) = Mg_3Al_2Si_3O_{12}$  (garnet) + $Mg_2SiO_4$  (olivine); (Fe,  $Mg)Cr_2O_4$  (spinel)+2(Mg,  $Fe$ )<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> (orthopyroxene) = (Mg, Fe)<sub>3</sub>Cr<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> (garnet)+ (Mg, Fe)SiO4 (olivine) (Brey et al., 1999, 2008; Girnis et al., 2003; Klemme, 2004). With a pressure increase, the spinel  $\mathrm{Cr}^*$  will also increase (Figure 3) (Brey et al., 1999, 2008). However, in the stability field of garnet without spinel, the garnet  $Cr^*$  does not significantly change (Figure  $3(c)$ , (d)). Therefore, the spinel  $Cr^{\#}$  in spinel peridotites is closely related to the formation temperature or the melt-rock reaction processes, whereas the spinel  $Cr^*$  in garnet peridotites is mainly controlled by pressure (Figure 3(a), (b)). Thus, some discrimination diagrams for spinel that are commonly used to show the degrees of partial melting cannot be applied in garnet peridotites.

Although many experimental studies have been focused on the SGT reaction, most of them were performed in simple CMAS and NCMAS systems (O'Neill, 1981; Gasparik and Newton, 1984; Klemme and O'Neill, 2000; Walter et al., 2002). The effect of bulk rock  $Cr^*$  on the SGT reaction has only been considered in a few studies (Klemme, 2004; Klemme et al., 2009). An increase in bulk rock  $Fe^{2+}$  content corresponding to an  $Mg^*$  decrease would decrease the



**Figure 3** Phase equilibrium relations for fertile and depleted mantle peridotites in the system NCFMACrS (Na<sub>2</sub>O-CaO-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) (modified after Ziberna et al., 2013). (a) Spinel modal and Cr<sup>#</sup> isopleths for fertile peridotite (Al<sub>2</sub>O<sub>3</sub>=4.85wt%, CaO=4.08wt%); (b) spinel modal and Cr<sup>#</sup> isopleths for depleted peridotite (Al<sub>2</sub>O<sub>3</sub>=1.82wt%, CaO=0.29wt%); (c) Cr<sup>#</sup><sub>Grt</sub> isopleths for fertile peridotite with the same composition as (a); (d) Cr<sup>#</sup><sub>Grt</sub> isopleths for depleted peridotite with the same composition as (b). The dark dashed line represents the transition reaction between diamond and graphite. The whole-rock compositions of peridotites are collected from Ziberna et al. (2013). Grt, garnet; Opx, orthopyroxene; Cpx, clinopyroxene; Spl, spinel; Ol, olivine; Esk, eskolaite.

stability field of spinel and shift garnet-in into lower pressures (O'Neill, 1981). However, an increase of bulk rock  $Fe<sup>3+</sup>$  and Cr contents would expand the stability fields of spinel and shift garnet-in into higher pressures (Figure 3) (O'Neill, 1981; Doroshev et al., 1997). Therefore, the SGT reaction is controlled by not only bulk  $Cr^*$  but also bulk  $Mg^{\#}$  and Fe<sup>3+</sup>/ $\Sigma$  Fe (or oxygen fugacity). Because orogenic peridotites commonly underwent various degrees of crustal metasomatism, which is expected to modify bulk rock composition and oxygen fugacity, the composition of garnet and spinel in orogenic peridotites should be carefully considered based on the bulk rock composition and oxygen fugacity.

Petrological investigations on orogenic peridotites commonly show large errors in *P*-*T* estimation and significant discrepancies in *P*-*T* paths, even in a single peridotite body, such as the Zhimafang garnet peridotite (Yang and Jahn, 2000; Zhang R Y et al., 2008; Ye et al., 2009). Orogenic peridotites usually contain multistage garnet, orthopyroxene, and clinopyroxene, and it is difficult for these minerals to reach equilibrium, making their *P*-*T* estimation difficult. Until now, *P*-*T* conditions of orogenic peridotites were commonly calculated using garnet-clinopyroxene thermometers and garnet-orthopyroxene thermobarometers, which only consider the Fe-Mg-Al exchanges and neglect the Cr component. How to choose the garnet and pyroxene composition is a key issue in *P*-*T* estimation. Although several studies calculated the *P*-*T* conditions of orogenic peridotites based on the trace element partition between garnet and clinopyroxene (Zhang et al., 2010), they only yielded semiquantitative results. However, the orthopyroxene-clinopyroxene REE thermometer can effectively overcome the limitations that the Fe-Mg-Al components in orogenic peridotites are easily modified or re-equilibrated during postpeak alterations or metasomatism (Liang et al., 2013; Sun and Liang,2014). Thermodynamic modeling research on ultramafic rocks is very rare, and only a few considered the effect of the Cr component on the phase equilibria. However, the stabilities of common metasomatic minerals such as amphibole, phlogopite, and Ti-clinohumite, as well as partial melting effects, are not well constrained in thermodynamic modeling (Figure 3). Precise constraint of *P*-*T* condi-

tions for orogenic peridotites should be based on careful understanding of phase equilibria in the complex Cr-bearing systems and composition evolution of garnet, spinel and pyroxene.

## **2 The protolith nature of orogenic peridotites**

The two types of orogenic peridotites usually have different compositions and *P*-*T* evolution (Brueckner and Medaris, 2000; Reverdatto et al., 2008; Zhang C et al., 2011). The mantle type always indicates one-stage or multistage highpressure metamorphism in the mantle interior (Brueckner et al., 2004; Spengler et al., 2006, 2012; Ye et al., 2009); it was scraped by the subducted or exhumed continental crusts into the subduction channel and underwent UHP metamorphism (Scambelluri et al., 2008; Zheng, 2012). Except for the exhumation process back to the crust, most processes in the mantle type orogenic peridotites were completed in the mantle. However, some studies suggest that part of the mantle type orogenic peridotites once intruded into the shallow crust levels and underwent significant serpentinization (Yang and Jahn, 2000; Yang et al., 2013). The crustal peridotites were crystallized from mantle magmas that intruded into the lower continental crust prior to continental subduction and usually belong to plagioclase- or spinelfacies peridotites. They were subducted with the continental crust to form garnet peridotites and then exhumed back to the Earth's surface (Krogh and Carswell, 1995; Zhang et al., 1995; Zhang C et al., 2011).

Previous studies indicated that crustal peridotites and pyroxenites typically exhibit complex compositional layers in the outcrop. However, many experimental and natural sample studies have demonstrated that the mantle peridotites metasomatized by the slab-derived fluids or melts also showed complex compositional layers with various lithologies (e.g. Iizuka and Nakamura, 1995; Vrijmoed et al., 2006, 2013). Therefore, it is difficult to identify these two types of orogenic peridotites in a field outcrop. Furthermore, the crustal cumulative peridotites typically have mineral textures that are different from the mantle-derived peridotites. The crustal cumulative peridotites mainly comprise euhedral olivine and pyroxene grains with a well-developed cumulate texture. Euhedral or subeuhedral Cr-spinel grains usually occur as inclusions in olivines. It is worth noting that typical triple junction texture cannot be used to indicate fractional crystallization process, because orthopyroxenes and olivines from several mantle-derived peridotites formed under high-temperature conditions also show such texture (Figure 4(a)) (Tsai et al., 2000; Wang et al., 2005). However, porphyroblastic orthopyroxenes are rarely preserved in cumulative dunites but are universal in mantle-derived peridotites (Figure 4(b)), such as the peridotites from Zhimafang, Ganyu, Lijiatun, Chijiadian, Yangkou and Raobazhai. Such orthopyroxene porphyroblasts usually record the earliest metamorphism and develop clinopyroxene and chromite (or Cr-spinel) exsolution lamellae (Figure 4(d)), most likely resulting from early high-degree partial melting under high-temperature conditions.

Reverdatto et al. (2008) described geochemical criteria to distinguish the two types of peridotites even after the complex history they have been subjected to after their original emplacement. Compared to the crustal cumulative peridotites/pyroxenites, the mantle-derived peridotites/pyroxenites typically have higher MgO, Cr and Ni contents, but lower FeO, TiO<sub>2</sub>, Zr, Nb, and REE contents (Reverdatto et al., 2008). However, to distinguish these two types of orogenic peridotites based on geochemical criteria, we should carefully consider the effect of crustal metasomatism on the bulk rock composition, especially the incompatible elements. For example, the formation of metasomatic phlogopite and amphibole in peridotites would increase the bulk LILE, LREE and HFSE contents (Ionov and Hofmann, 1995; van Achterbergh et al., 2001; Coltorti et al., 2004; Powell et al., 2004; Scambelluri et al., 2006). The formation of metasomatic apatite, zircon and Ti-clinohumite will most likely increase the bulk REE and HFSE contents (Chazot et al., 1996; Zenetti et al., 1999; Zhang et al., 2007; Zhang Z M et al., 2011). The Ni content was most likely lost from the mantle peridotites due to S-bearing melt metasomatism (Fleet et al., 1996; Hattori et al., 2010a). Low-temperature alteration under high oxygen fugacity conditions may result in Cr that is lost from the mantle peridotites (Haggerty, 1995; Griecoa et al., 2004; Mellini et al., 2005). Vrijmoed et al. (2013) investigated the Svartberget garnet peridotite from the northernmost ultrahigh-pressure domain in the Western Gneiss Region (WGR) and showed that a sequence of metasomatic reaction zones developed between the mantle wedge peridotite and the country migmatitic gneiss. In the context of such strong metasomatism, the Svartberget garnet peridotites are likely to simultaneously possess the compositional characteristics of depleted mantle and subducted crust and are even akin to crust-derived peridotite (Vrijmoed et al., 2013). Garnet pyroxenites are the metasomatic products between mantle peridotites and felsic melts or are the metamorphic products of late-stage cumulate that was crystallized from mafic magmas. Refractory orogenic harzburgites or dunites consist primarily of olivine, with minor orthopyroxene and spinel/garnet, and were subjected to the weakest metasomatism by crust-derived agents among orogenic peridotites. The mineral compositions (e.g., olivine) of the orogenic harzburgites/dunites would not notably change during later metamorphism related to subduction and exhumation because little element exchange would occur between the abundant olivine and the few other minerals. Therefore, harzburgites/dunites are the best samples from which to trace the origins of orogenic peridotites. However, recovering their protolith nature also requires excluding the effect of cryptic metasomatism (Zheng, 2012).



**Figure 4** Microphotographs and Back-scattered electron images (BSE) showing mineral textures in the Dabie-Sulu orogenic peridotites. (a) 'Triple junction' texture in mantle-derived peridotite, Lijiatun; (b) coarse-grained orthopyroxene porphyroblast in mantle-derived peridotite, Lijiatun; (c) fine-grained olivine vein cutting orthopyroxene porphyroblast, Lijiatun; (d) chromite and clinopyroxene lamellae in the core of orthopyroxene porphyroblast that is cut by fine-grained olivine vein, Lijiatun; (e) rutile veins along the orthopyroxene boundaries, Maowu; (f) Ti-clinohumite-rich vein in harzburgite, Maowu.

The Dabie-Sulu orogenic peridotites, which were generated by different formation processes, are expected to have a wide compositional range. The mantle-derived peridotites commonly have higher  $Mg^*$  values (85.9–93.8), Ni contents (1441–2926 ppm), and Mg/Si ratios (1.04–1.83), whereas the crustal peridotites (such as the Maobei and the Bixiling peridotites) show relatively lower  $Mg^*$  values (<85), Ni contents (760–1440 ppm), and Mg/Si ratios (0.85–1.51) (Figure 5). In the garnet-facies peridotites, the Mg/Si ratio reflects the proportion of olivine/(pyroxene+garnet) because the Mg/Si ratio is 2 for olivine (Fo), 1 for orthopyroxene and garnet (Pyr), and 0.5 for clinopyroxene (Di). Thus, the Mg/Si ratio in orogenic peridotites can denote the degrees of refertilization. Figure 5 shows that the mantle-derived peridotites in the Dabie-Sulu orogen mostly have compositions similar to the Proterozoic subcontinental lithospheric mantle (SCLM). However, some orogenic mantle peridotites have compositions overlapping the Archean SCLM (Figure 5). Note that Si-rich melt metasomatism is expected to only generate orthopyroxene and would decrease the bulk rock Mg/Si ratios, but the bulk rock  $Mg^*$  values would not significantly change. However, the subducted crusts currently released Si-Al-rich and low Mg granitic melts during the early stage of exhumation. The mantle peridotites metasomatized by such melts are expected to develop metasomatic pyroxene and garnet (Malaspina et al., 2006, 2009a; Chen et al., 2013a), resulting in the decrease of both bulk rock Mg/Si and Mg<sup>#</sup>. Therefore, some Archean SCLM peridotites, which suffered extensional crustal metasomatism with granitic melts, most likely show the chemical characteristics of the Proterozoic SCLM. Notably, the bulk  $Mg^*$ cannot be the only criterion to distinguish the two types of orogenic peridotites. Some cumulative peridotites that were crystallized in the sub-arc mantle also have an Mg<sup>#</sup> higher



Figure 5 Diagrams of Mg<sup>#</sup> vs. Mg/Si (a) and Mg<sup>#</sup> vs. Ni (b) for the Dabie-Sulu orogenic peridotites. Zhimafang (CCSD-PP1) (Zhang et al., 2000, 2007; Yang, 2003; Yang et al., 2007, 2009); Maobei (CCSD-MH) (Liu et al., 2008; Yang et al., 2009; Zhang et al., 2010; Li et al., 2011); Ganyu (CCSD-PP3) (Yang et al., 2009; Raobazhai: Zhi et al., 2004; Zheng et al., 2008; Xugou: Yuan et al., 2007); Yangkou (Chen et al., 2002; Zhang et al., 2005b; Xie et al., 2013); Suoluoshu (Xie et al., 2013); Hujialing (Yang, 2006; Zhang R Y et al., 2011; Xie et al., 2013); Chijiadian (Zhang et al., 2000; Zhao et al., 2007); Jiangzhuang (Zhang et al., 2000; Zhang Z M et al., 2011); Bixiling (Chavagnac and Jahn, 1996; Zheng et al., 2008); Maowu (Jahn et al., 2003; Malaspina et al., 2006; Chen et al., 2013b). Arcton, Proton and Tecton fields are from Griffin et al. (1999).

than 90; however, these peridotites usually contain significantly lower Ni (<1000 ppm) relative to the normal mantle peridotites (Rajesh et al., 2013).

The platinum group element (PGE) is an effective approach to distinguish mantle and crustal orogenic peridotites. PGEs are generally subdivided into two groups: compatible IPGEs (Iridium-group PGE; Os, Ir, Ru) and incompatible PPGEs (Palladium-group PGE; Pd, Pt). IPGEs have been suggested as refractory and to preferentially enter residue during partial melting, whereas PPGEs are mainly concentrated in metal sulfides (e.g., pentlandite and chalcopyrite), which are released into the melt as soon as the sulfides begin to melt (Barnes et al., 1985; Lorand et al., 2013). If peridotites are subjected to metasomatism, the PPGE abundances will increase as PPGE-rich sulfides precipitate from the melts (Ackerman et al., 2013; Wang Z C et al., 2013). Until now, the PGE abundances were only reported in the peridotites from Raobazhai, Bixiling, Ganyu, Hujialing, Suoluoshu, and Yangkou (Chen et al., 2006b; Zheng et al., 2008; Liu et al., 2012; Xie et al., 2013). The mantle orogenic peridotites from Ganyu, Hujialing, Suoluoshu, and Yangkou have IPGE abundances similar to the primitive upper mantle (PUM; Becker et al., 2006). They also have high IPGE/PPGE and Ir/(Pt+Pd) ratios, consistent with the SCLM xenoliths in the North China Craton (Figure 6). However, because of partial melting, the PPGE contents show various degrees of depletion (Righter et al., 2004; Brenan et al., 2005; Chen et al., 2006b; Zheng et al., 2008; Xie et al., 2013). On the other hand, the Bixiling cumulative peridotite has relatively lower IPGE contents, with low IPGE/PPGE and Ir/(Pt+Pd) ratios, similar to other cumulative peridotites in different geological settings (Figure 6).

The two types of orogenic peridotites can also be distinguished based on the compositions of olivine and spinel. The olivines in the mantle-derived peridotites from the Dabie-Sulu orogen have high Fo values (generally >91) and



**Figure 6** Diagram of Ir vs. Ir/(Pt+Pd) for the Dabie-Sulu orogenic peridotites. The whole-rock PGE data for the peridotites are from Ganyu (Chen et al., 2006b); Raobazhai (Zheng et al., 2008); Yangkou, Suoluoshu and Hujialing (Xie et al., 2013); Bixiling (Zheng et al., 2008; Liu et al., 2012). The whole-rock PGE data for the ancient mantle xenoliths from the North China Craton are from Gao et al. (2002), Zheng et al. (2005a), Becker et al. (2006), Zhang H F et al. (2008), Liu et al. (2010, 2011, 2014). The field for the Laiwu cumulative dunite is after Wang et al. (2012). The field of PGE data from the cumulative peridotites in the Kohistan and Talketna arc are after Hattori and Guillot (2007). Primitive mantle value is also shown with dark star (McDonough and Sun, 1995).

NiO contents (0.31wt%–0.45wt%), similar to those in refractory mantle peridotites (Tatsumi, 1986) and in the mantle peridotite xenoliths from the North China Craton (Zheng et al., 2006b, 2008, 2014; Xu et al., 2008). However, the olivines from the crustal type orogenic peridotites have relatively low Fo (<85) (Zheng et al., 2008), with typically lower Ni content and higher Ca, Ti, and Cr contents than the normal mantle olivines (Foley et al., 2013). Note that some olivines in the cumulative peridotites from the sub-arc mantle also have high Fo values (>90) and exhibit a rapid decrease in NiO contents from >0.5wt% to <0.1wt% without a significant change in Fo (Santos et al., 2002; Hattori et al., 2010b; Arai et al., 2012; Rajesh et al., 2013). Furthermore, the spinels from the cumulative peridotites feature a wide range of  $Cr^*$  and  $Mg^*$  values, but their  $Mg^*$  values are commonly lower than those from the mantle-derived peridotites (Arai et al., 2003; Bryant et al., 2007). Because both Cr and Ni are compatible elements, they are expected to be quickly removed from a melt into olivine and spinel during their solidification, resulting in a rapid decrease of these components in the residual melt (Melcher et al., 1997). Moreover, the spinel  $TiO<sub>2</sub>$  contents in the cumulative peridotites are typically higher (up to 0.8wt%) than those from the mantle-derived peridotites (Hattori et al., 2010b; Arai et al., 2012; Rajesh et al., 2013). Although the reactions between peridotite and silica-undersaturated basaltic melt can also increase the  $TiO<sub>2</sub>$  content in spinel from the mantle-derived peridotites (Pearce et al., 2000; Morgan and Liang,  $2005$ ), such spinel usually has a higher  $Mg^*$  than the cumulative spinel.

### **3 Silica-undersaturated melt-rock reactions**

Melt-peridotite reactions are widespread in the upper mantle and are considered to be a key mechanism responsible for the chemical changes and physical property transformations of the ancient SCLM (Gao et al., 2002; Zhang et al., 2003; Shaw et al., 2006; Zheng, 2012; Tang et al., 2013). Based on the melt composition, the melt-peridotite reactions have been classified into two groups: (1) the reaction between the silica-rich melt and the refractory peridotite that is characterized by the partial replacement of olivine by pyroxene and consequently results in the transformation of refractory harzburgite or dunite to relatively fertile lherzolite or pyroxenite (McPherson et al., 1996; Rapp et al., 1999; Le Roux et al., 2007; Uysal et al., 2015); (2) the reaction between the silica-undersaturated melt and the pyroxene-rich (fertile) peridotite that preferentially converts pyroxene to olivine and leads to a modal shift towards dunite (Kelemen, 1990; Kelemen and Dick, 1995; Braun and Kelemen, 2002; Suhr et al., 2003). The silica-undersaturated melt (carbonitic melt or basaltic melt) is commonly considered to be derived from the asthenosphere (Piccardo and Vissers, 2007; Zheng, 2012) or from the lower part of lithospheric mantle (Ackerman et al., 2009). Such silica-undersaturated meltperidotite reactions have been widely investigated in ophiolitic peridotites and peridotite xenoliths from the SCLM, but rarely reported in orogenic peridotites. Relative to peridotite xenoliths from the SCLM, orogenic peridotites appear to possess more information on the group (1) reaction because silica-rich melts are widespread in both oceanic and continental subduction zones.

The Dabie-Sulu orogenic peridotites commonly suffered multistage metasomatism by silica-rich fluids or hydrous melts derived from subducted continental crust (Zhang et al., 2007; Ye et al., 2009; Chen et al., 2013b), which makes distinguishing the silica-undersaturated melt-peridotite reactions difficult. However, parts of the Dabie-Sulu orogenic peridotites were most likely involved in the silica-undersaturated melt-peridotite reactions. For example, several orthopyroxene porphyroblasts in the garnet peridotites from the CCSD main hole were cut by fine-grained olivine veins (Li et al., 2011; Figure 3(d)), suggesting the formation of secondary olivine caused by the reaction between silicaundersaturated melt and orthopyroxene. We have observed a similar texture in several peridotites from the Dabie-Sulu orogen. The Lijiatun dunite also develops secondary olivine veins after orthopyroxene porphyroblasts (Figure 4(c), (d)). Relative to the matrix olivine, the secondary olivine grains have lower  $Mg^*$  values and higher CaO and TiO<sub>2</sub> contents (unpublished data), different from those in the residual peridotites that were generated by a partial melting process. During the reaction between silica-undersaturated melt and orthopyroxene, Ca and Ti are preferentially incorporated into secondary olivine (Thompson and Gibson, 2000), whereas Si is incorporated into the residual melt. Addition-

ally, Cr is a compatible element and would be retained in the olivine veins to form secondary Cr-spinel. Therefore, the secondary olivine formed by the melt-peridotite reaction has a lower  $Mg^*$  (controlled by the melt/rock ratio and the melt  $Mg^{\dagger}$ ) and higher CaO and TiO<sub>2</sub> contents relative to the normal mantle olivine (Xu et al., 2008, 2010; Ackerman et al., 2013; Wang Z C et al., 2013; Yu et al., 2014). Note that the orthopyroxene porphyroblasts developing the secondary olivine veins are always surrounded by LREE- and LILE-enriched and HFSE-depleted clinopyroxene and pargasitic amphibole, which are considered to be the metasomatic products between orthopyroxene and slab-derived fluid or melt. This mineral texture indicates that the silicaundersaturated melt-peridotite reaction most likely took place prior to continental subduction/exhumation. Therefore, orogenic dunites cannot be simply considered as the residue after a high degree of partial melting of the lithospheric mantle. Orogenic lherzolites and pyroxenites, which have been subjected to intensive metasomatism by silicarich melt/fluid during slab subduction/exhumation, are the most widely distributed lithologies and have received the most attention (Liou et al., 2004; Zhang et al., 2005a; Le Roux et al., 2007; Lorand et al., 2008; Ye et al., 2009). However, we should also attach greater importance to orogenic dunites or harzburgites that most likely record the silica-undersaturated melt-peridotite reactions in the SCLM.

The mantle-derived peridotites in the Dabie-Sulu orogen have similar mineral and whole-rock compositions to the Archean SCLM of the North China Craton. Yuan et al. (2007) suggested that the Xugou peridotite originated from the SCLM of the Yangtz Craton based on contrasting younger Paleoproterozoic Re-depletion ages (T<sub>DR</sub>, 1.8–2.0) Ga) and Re-Os model ages ( $T_{\text{MA}}$ , 1.9–2.2 Ga). However, the  $187\text{Os}/188\text{Os}$  data of the Raobazhai (Dabie) (Zheng et al., 2009) and the Xugou (Sulu) peridotites (Yuan et al., 2007) overlap the Os isotopic compositions of both the SCLMs of the Yangtz and the North China Craton. Three direct arguments favor the Dabie-Sulu mantle-derived peridotites derivation from the SCLM hanging wall of the North China Craton during the prograde evolution of a continental subduction zone. (1) The refractory peridotite chemistry with olivine  $F_{\text{O}_{91-93}}$  is similar to that of the refractory mantle xenoliths inferred to be of Archean age in the North China Craton (Zheng et al., 2014). By contrast, the northern margin of the Yangtz Craton, which formed the footwall during the continent-continent collision, has a lower olivine  $F_{\text{O}_{88-91}}$ (Zhang et al., 2001). (2) The mantle-derived orogenic peridotites are currently surrounded by continental supracrustal rocks but are not associated with continental lower crustal rocks. Thus, it is very difficult to use the SCLM of the Yangtz Craton to interpret the mantle source of orogenic peridotites. (3) The peak *P*-*T* conditions of the mantlederived orogenic peridotites were constrained at 3.5–6.5 GPa and ~800°C (Yang and Jahn, 2000; Zhang R Y et al., 2005b, 2011; Spengler et al., 2012; Chen et al., 2013a), corresponding to the mantle wedge environment just above the subducted slab. However, the temperature is significantly lower than that of the Yangtz SCLM (Zhang et al., 2001). Notably, the Dabie-Sulu mantle-derived orogenic peridotites mostly show Paleoproterozoic  $T_{\text{DR}}$  and  $T_{\text{MA}}$ (Chen et al., 2006b; Yuan et al., 2007; Zheng et al., 2009). Re is a moderately incompatible element and is preferentially incorporated into melt, whereas Os is highly compatible with mantle residue. Numerous studies have shown that the Re-Os isotopic system is easily modified during the melt-peridotite reaction due to the breakdown of primary sulfides and reprecipitation from the reactive melt (Becker et al., 2001; Büchl et al., 2002; Ackerman et al., 2013; Wang Z C et al., 2013). The melt-peridotite reaction would increase Re abundance rapidly, which probably induced various increases of  $^{187}$ Re/ $^{188}$ Os and  $^{187}$ Os/ $^{188}$ Os (depending on the reaction age), thereby producing a much younger  $T_{RD}$ age than the actual melting age of the mantle peridotite. The available Re-Os isotopic data consistently yield Paleoproterozoic melting ages for the Dabie-Sulu mantle-derived orogenic peridotites (Chen et al., 2006b; Yuan et al., 2007; Zheng et al., 2009), which are slightly younger than the primary source of Archean SCLM in North China (Gao et al., 2002; Wu et al., 2006) and were previously attributed to the Triassic metasomatism caused by fluids or felsic melts from the subducting continental crust (Zheng et al., 2009; Zheng, 2012). Nevertheless, the refractory dunites that experienced weak metasomatism yield similar T<sub>RD</sub> ages as those of the lherzolites/harzburgites (Chen et al., 2006b; Zheng et al., 2009), indicating that, except for the Triassic metasomatism, the silica-undersaturated melt-rock reactions prior to subduction may potentially affect the Re-Os isotopic compositions.

## **4 HFSE mobilization during crust-mantle interactions**

Element exchange during crust-mantle interactions in the subduction factory is a key geochemical dynamic mechanism for mantle heterogeneity (Zheng, 2012). Most previous studies focused on the effect of crustal metasomatism on LREE and LILE modification in the mantle wedge rocks (e.g., Scambelluri et al., 2004, 2010; Malaspina et al., 2006, 2009a; Zhang et al., 2007; Miller et al., 2009; Spandler and Pirard, 2013). Only a few studies examined HFSE mobilization (Kalfoun et al., 2002; Garrido et al., 2005). Thus, the behavior of HFSEs during crust-mantle interactions in subduction zones is not well constrained. Some metasomatic minerals in the Dabie-Sulu orogenic peridotites, such as rutile, zircon, Ti-clinohumite, and Ti-chondrodite, are important HFSE carriers. These minerals directly provide mineral evidence for the HFSE mobilization from the subducted continental crust into the mantle wedge.

Rutile, Ti-clinohumite, and Ti-chondrodite are Ti-rich phases and commonly occur in garnet peridotites and pyroxenites (Kalfoun et al., 2002; Yang, 2003; Zhang et al., 2007; Rebay et al., 2012; Chen et al., 2013a). Petrological observations indicate that rutile and Ti-clinohumite always occur as fine-grained veins or layers (Figure 4(e), (f)), implying that their formation may be related to fluid/melt metasomatism. The rutile veins were interpreted as direct precipitation from a Ti-bearing fluid/melt (Kalfoun et al., 2002). However, Ti-clinohumite and Ti-chondrodite have similar Mg/Si ratios to olivine; thereby, they are produced by the reactions between the Ti-bearing agent and the olivine (Zhang et al., 2007). Until now, the phase relations among rutile, Ti-clinohumite and Ti-chondrodite in the ultramafic system are not well constrained because of the lack of suitable activity-composition models and thermodynamic data for Ti-clinohumite and Ti-chondrodite. In the Dabie-Sulu orogenic peridotites, Ti-clinohumite is the most common Ti-rich phase that is typically equilibrated with phlogopite, orthopyroxene, magnesite and garnet. This feature indicates that the metasomatic agent is not only enriched in Ti but also enriched in Si, Al, K, and  $CO<sub>2</sub>$  (Zhang et al., 2007, 2009, 2010). The garnet and orthopyroxene equilibrated with Ti-clinohumite mostly provide evidence of metamorphic pressures higher than 4.5 GPa, implying that the metasomatic process occurred under UHP conditions.

An HP-HT experimental study (Iizuka and Nakamura, 1995) that was conducted at 8 GPa and 800°C, showed that Ti-clinohumite- and orthopyroxene-rich layers were observed at the contact boundary between eclogite and dunite. This experimental result indicates that: (1) the Ticlinohumite layer was produced by the metasomatic reaction between peridotite and a Ti-bearing fluid released from eclogite, and (2) Si and Ti show significant fractionation during the metasomatic process. Ti-clinohumite in the Dabie-Sulu orogenic peridotites currently contain various F, which shifts its stability field to higher temperature conditions (Trommsdorff et al., 2001). The F-bearing Ti-clinohumite indicates that the metasomatic agent is also an F-bearing fluid/melt that has a strong ability to mobilize HFSEs (Keppler, 1993; Rapp et al., 2010). Note that the Ti-clinohumites found in continental subduction zone peridotites may have different origins from those in oceanic subduction zone peridotites. In oceanic subduction zone peridotites, Ti-clinohumites commonly occur as lamellae in olivine and are interpreted to be Ti-clinohumite defects in OH- and Ti-bearing olivine (Shen et al., 2014). Several Ti-clinohumite veins also occur in oceanic serpentinized peridotites and are considered as metasomatic products formed by interactions between the pre-existing olivine and the Ti-bearing fluid (Arai et al., 2012; Rebay et al., 2012; De Hoog et al., 2014). However, the source of Ti in fluid is attributed to the Ti-bearing spinel and clinopyroxene in the peridotite interior (Arai et al., 2012; Rebay et al., 2012). The spinel and pyroxene in the continental subduction zone peridotites currently have very low Ti abundance, strongly suggesting that the Ti component in the metasomatic fluid/melt was sourced from other rocks. According to the metasomatic minerals, such as orthopyroxene, phlogopite and magnesite that are equilibrated with Ti-clinohumite, the metasomatic fluid/melt rich in Ti, Si, Al, K, F and  $CO<sub>2</sub>$  was most likely derived from the subducted continental crust (Zhang et al., 2009; Malaspina et al., 2006, 2009a) or an enriched mantle (Zhang et al., 2007).

Zircon in orogenic peridotites is also another important mineral that provides evidence for HFSE mobilization during crust-mantle interactions (Zheng, 2012). It enables us to constrain not only the source of the metasomatic agent but also the metasomatic age (Katayama et al., 2003; Zheng et al., 2003; Zhang et al., 2005a; Hermann et al., 2006; Zhang Z M et al., 2011; Zheng et al., 2014). Zircon grains have been separated from the peridotites from Zhimafang, Jiangzhuang, Chijiadian, Ganyu, Xugou, Raobazhai, Yangkou and Hujialing; some zircon grains can be observed in thin-section. Most zircon-bearing orogenic peridotites also contain abundant metasomatic minerals, such as phlogopite and Ti-clinohumite (Zhang Z M et al., 2011). The mineral inclusions in zircon mainly comprise apatite, with minor garnet, olivine, orthopyroxene, phlogopite, Ti-clinohumite and magnesite, indicating that the metasomatic fluid/melt contains P, Ti, LILEs, LREEs, and Zr. Most zircon grains are rounded and show no internal structure in BSE/CL images, but oscillatory zoning or anhedral relict cores remain in a few (Zheng et al., 2014). Metamorphic zircons record ages mostly in the range of 212–227 Ma (Zhang et al., 2005a; Zheng et al., 2006a, 2008; Yang et al., 2009; Zhang Z M et al., 2011), slightly younger than the UHP metamorphic age of 225–240 Ma (Zheng, 2012). Their Th/U ratios are 0.1–1.17 (Zhang et al., 2005a; Zhang Z M et al., 2011; Zheng et al., 2006a, 2008, 2014), demonstrating that the zircon grains in orogenic peridotites may be crystallized from hydrous melts released by the subducted continental crust during the early stages of exhumation (Zheng, 2012). Few zircon grains indicate old ages from the Proterozoic to the Archean (Yang et al., 2005, 2009; Liu F L et al., 2011; Zheng et al., 2014).

As we know, the primitive mantle is depleted in Zr and zircon cannot be directly crystallized from the depleted mantle. Zircon occurring in mantle peridotite commonly reflects metasomatism. The relict detrital zircon cores were physically extracted by the metasomatic agent from host UHP rocks during the slab-mantle interactions, with their origin from the subducting continental crust (Zheng, 2012). The occurrence of a coesite inclusion in the zircon from the Sulu garnet peridotite (Yang et al., 2003), as well as feldspar, quartz and felsic melt inclusions in the zircon from the Bohemian garnet peridotite (Liati and Gebauer, 2009), indicates that some crustal minerals were physically transported by the crust-derived melt into the mantle wedge peridotites and showed disequilibrium with the mantle minerals.

Hydrous melt commonly has higher viscosity than aqueous fluid and more likely transports the crustal material into the mantle wedge. During the slab-mantle interactions in the continental subduction channel, Si-Al-Na components would rapidly precipitate into the mantle wedge peridotites, resulting in a decrease of the Zr solubility of the metasomatic agent (Zotov and Keppler, 2000; Wilke et al., 2012; Louvel et al., 2013). The metamorphic growth of zircon occurred in the metasomatized peridotites when Zr became oversaturated in the crustal-derived melt. In the Dabie-Sulu orogenic peridotites, the zircons with U-Pb ages older than the Triassic most likely represent the following: (1) relict detrital zircons to be metamorphically recrystallized in the crustal-derived agent (Zheng, 2012; Zheng and Hermann, 2014); (2) newly formed zircons crystallized from the metasomatic melt derived from the asthenospheric mantle (Zheng et al., 2006a, 2014); or (3) early metamorphic zircons formed during the ancient oceanic slab-mantle interactions. Tracing the possible origins of these three types of zircon requires us to carefully distinguish. Therefore, to understand the zircon ages and sources as well as the mechanism of HFSE mobilization, we should investigate the textures of zircon and inclusions involved, zircon trace element and isotopic composition in detail.

# **5 Oxygen fugacity of the mantle wedge in continental subduction zones**

The oxidation state of the Earth's mantle is reflected by its prevailing oxygen fugacity  $(fO_2)$ . Some transitional metals (e.g.,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) are very sensitive to oxygen fugacity. Thus, the Fe<sup>3+</sup>/ $\Sigma$  Fe ratio is an index parameter to reflect the oxygen fugacity of a rock (Christie et al., 1986; Kress and Carmichael, 1991). Metamorphic phase relations are affected by the bulk rock  $\text{Fe}^{3+}/\sum \text{Fe}$  (or  $fO_2$ ) (Rebay et al., 2010; Chen et al., 2013c). Accordingly, mineral assemblages and compositions can also reflect oxygen fugacity.  $fO<sub>2</sub>$  is commonly recorded by the  $Fe<sup>3+</sup>$  contents of mafic minerals or V/Sc and Zn/Fe ratios of the whole-rock (Mattioli and Wood, 1986; Wood and Virgo, 1989; Ballhaus et al., 1991; Lee et al., 2005, 2010). The oxygen fugacity of subduction zone fluid or melt, an important issue in the study of the subduction factory, is closely related to subduction zone magmatism and mineralization (Sun et al., 2004; Lee et al., 2010). The crustal-derived C-O-H fluid or melt in subduction zones generally has variable  $fO_2$ , as shown by the occurrence of diamond, moissanite,  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$  fluid inclusions in HP-UHP metamorphic rocks (Xu et al., 1992, 2003, 2005; Fu et al., 2003; Pan et al., 2003; Wang et al., 2007; Song et al., 2009). The variable  $fO<sub>2</sub>$  in crustal-derived fluid or melt is expected to be directly recorded by the metasomatic mantle minerals during the slab-mantle interactions and then pass the signature to the mafic magmas formed by partial melting of the metasomatized mantle wedge (McCammon et al., 2004). Therefore, study of mantle wedge  $fO_2$  requires carefully considering the mixing effect of crustal metasomatism and following partial melting process.

The *f*O<sub>2</sub>s of mid-ocean ridge basalts (MORB) and arc lavas have now been widely investigated. Relative to the fayalite-magnetite-quartz (FMQ) buffer, MORBs have  $\triangle$ log  $fO_2$  (= $\triangle$ FMQ=log  $fO_2$ <sup>sample</sup>-log  $fO_2$ <sup>FMQ</sup>) values between -2 and 0 log units from the FMQ buffer (hereafter referred to as FMO-2 and FMO), whereas arc lavas have  $\triangle$ log  $fO_2$ s ranging from FMQ to FMQ+6 (Christie et al., 1986; Carmichael, 1991). If these magma  $fO_2s$  directly reflect that of their mantle source regions, it must be concluded that sub-arc mantle is more oxidized than ambient asthenospheric mantle (Parkinson and Arculus, 1999). It is widely accepted that such oxidation is attributed to crustal metasomatism by fluids released from subducting oceanic crust. Many researchers suggest that oceanic subduction zone fluid is oxidized (Wood et al., 1990; Brandon and Draper, 1996; Arai et al., 2003), due to the high  $Fe^{3+}/\Sigma$  Fe of altered oceanic crust (Rebay et al., 2010) and the significant mobility of  $Fe<sup>3+</sup>$  that is preferentially incorporated into the fluid. Note that the mantle xenoliths in arc lavas have lower  $fO_2s$ (from FMQ $-2$  to FMQ $+3$ ) than arc lavas (Lee et al., 2005), probably implying that the mantle xenoliths do not represent the mantle source of arc lavas.

Relative to oceanic subduction zones, the oxygen fugacity of continental subduction zones has been given limited attention. Abundant studies have focused on the  $fO<sub>2</sub>$  of the SCLM peridotite xenoliths (McCammon et al., 2001; Woodland and Koch, 2003; McCammon and Kopylova, 2004; Frost and McCammon, 2008; Creighton et al., 2009; Wang J et al., 2013). However, less data are available on the  $fO<sub>2</sub>$  of garnet peridotites from the mantle wedge (Peslier et al., 2002; Malaspina et al., 2009b), resulting in unclear  $fO<sub>2</sub>$ modification effects of crustal metasomatism on the overlying mantle wedge. The  $fO<sub>2</sub>$  of ultramafic rocks can be calculated on the reactions among spinel/garnet, orthopyroxene and olivine. The redox equilibrium in spinel peridotite is  $6Fe_2SiO_4$  (fayalite)+ $O_2=2Fe_3O_4$  (magnetite in spinel)+  $3Fe<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>$  (ferrosilite) (Mattioli and Wood, 1986; Wood and Virgo, 1989; Ballhaus et al., 1990, 1991), whereas that in garnet peridotite is  $2Fe^{3+} {}_{2}Fe^{2+} {}_{3}Si_3O_{12}$  (skiagite in garnet)=  $4Fe_2SiO_4(fayalite)+2Fe_2Si_2O_6(ferrosilite)+O_2$  (Luth et al., 1990; Gudmundsson and Wood, 1995; Woodland and Koch, 2003). In this paper, we calculated the  $fO_2$ s of the Dabie-Sulu orogenic peridotites based on the mineral compositions reported in the literature. As  $Fe<sup>3+</sup>$  in garnet and spinel were calculated by assuming stoichiometry, the calculated results are semiquantitative.

To compare with other mantle environments, peridotites from various geological settings as well as MORBs are also shown in Figure 7. The peak stage  $fO_2$ s in the Dabie-Sulu orogenic peridotites have a wide range, from FMQ-5.5 to FMQ+1.75, and are negatively correlated with depth



**Figure 7** Ranges and average values of oxygen fugacity relative to FMQ for the Dabie-Sulu orogenic peridotites (black lines) as a function of pressure (depth) (modified after Frost and McCammon, 2008). They are compared with selected samples of spinel and garnet peridotites from various settings: oceanic mantle lithosphere (Bryndzia and Wood, 1990), spinel peridotite massifs (Woodland et al., 1992, 2006), garnet peridotite xenoliths from sub-cratonic mantle (Woodland and Koch, 2003) and spinel peridotite xenoliths from sub-arc mantle (Brandon and Draper, 1996; Parkinson and Arculus, 1999; Peslier et al., 2002). The CCO oxygen buffer  $(C+O_2=CO_2)$  and the C-H<sub>2</sub>O join separating CH<sub>4</sub>- and CO<sub>2</sub>-rich aqueous fluids are from Malaspina et al. (2009b). The mineral compositions for the Dabie-Sulu orogenic peridotites are selected from the same literature as Figure 5. The oxygen fugacity of the Raobazhai peridotite is calculated by the olivine-orthopyroxene-spinel oxygen barometer (Ballhaus et al., 1991), whereas those of other garnet peridotites are calculated by the olivineorthopyroxene-garnet oxygen barometer (Gudmundsson and Wood, 1995).

(Figure 7). Therefore, the mantle wedge above subducted continental crust becomes deoxidized at greater depths, which is consistent with the calculated results in cratonic mantle xenoliths (McCammon et al., 2001; Woodland and Koch, 2003) and HP-HT experiments (Rohrbach et al., 2007; Rohrbach and Schmidt, 2011). At the same depth, the mantle wedge above subducted continental crust appears to have higher oxygen fugacity than that of oceanic lithospheric mantle, SCLM and sub-arc mantle (Figure 7). Moreover, the Zhimafang garnet peridotite shows very low  $fO<sub>2</sub>$  at >4 GPa, which is consistent with the occurrence of diamond in the peridotite (Pan et al., 2003). However, the calculated results of oxygen fugacity are affected by many factors as follows. (1) The peak mineral compositions chosen for  $fO_2$  calculations are different in samples collected from the same locality (e.g., Zhimafang), causing a large  $fO<sub>2</sub>$  discrepancy, up to 4 log units (Figure 8). (2) Magnetite, hematite, ilmenite, and chromite lamellae or rods are common in the Dabie-Sulu garnet peridotites (Zhang et al., 1999; Hwang et al., 2008). The formation of magnetite lamellae or rods was interpreted as exsolution of a peak spinel-solid solution Fe<sub>3</sub>O<sub>4</sub>-(Fe, Mg)<sub>2</sub>SiO<sub>4</sub> (wadsleyite) during exhumation (Zhang et al., 1999) or dehydrogenationoxidation of nominally anhydrous olivine during the early stage of exhumation (Hwang et al., 2008). However, the formation of magnetite-hematite rods or lamellae with both origins would directly decrease  $Fe<sup>3+</sup>$  content in the peak olivine, resulting in underestimating the  $fO<sub>2</sub>$  results. (3) Dehydrogenation of garnet during exhumation would in crease



**Figure 8** Effects of pressure, temperature and mineral composition on the calculated  $fO_2$  ( $\triangle FMQ$ ) results.

"skiagite" activity (Ingrin and Skogby, 2000; McCammon et al., 2004). (4) The calculated  $fO<sub>2</sub>$  results are significantly affected by *P*-*T* conditions. In the Zhimafang garnet peridotite, 1 GPa and 100°C discrepancy will cause approximately 1.3 log units and 0.5 log units in  $fO<sub>2</sub>$  error, respectively (Figure 8).

Cratonic mantle xenoliths commonly have simple 4-phase (spinel-facies) or 5-phase (garnet-facies) mineral assemblages due to their high formation temperatures. They are also similar to the starting material used in experiments to construct  $fO_2$  baraometries. Therefore,  $fO_2$  baraometries are able to yield reliable results in the mantle xenoliths. However, orogenic peridotites have relatively complex mineral assemblages because of multistage metamorphism and metasomatism.  $Fe<sup>3+</sup>$  contents distributed in minerals are highly heterogeneous. Revealing the effects of crustalderived fluid/melt metasomatism on mantle oxygen fugacity requires us to carefully distinguish different stage metasomatic minerals. However,  $Fe<sup>3+</sup>$  distribution in garnet, pyroxene and olivine is related not only to  $fO<sub>2</sub>$  but also to the equilibrated metasomatic minerals. Additionally,  $Fe<sup>3+</sup>$  partitioning among the peridotite mineral phases under different *P*-*T* conditions is often neglected. Previous studies indicated that the Fe<sup>3+</sup>/ $\Sigma$ Fe in garnet was positively correlated with temperature (Canil and O'Neill, 1996; Woodland and Koch, 2003). The increase of  $Fe<sup>3+</sup>$  in garnet with increasing temperature does not depend on the whole-rock  $Fe^{3+}/\Sigma$  Fe but is rather the consequence of redistribution of  $Fe<sup>3+</sup>$  from clinopyroxene into garnet (Canil and O'Neill, 1996). Therefore, the  $Fe<sup>3+</sup>$  enrichment in garnet is not necessarily indicative of high whole-rock oxygen fugacity or the interaction with more oxidized metasomatic agents. Well-constrained interpretation of oxygen fugacity of the mantle wedge above the subducted continental crust should be based on exact ascertainment of the peridotite mineral textures, mineral assemblages, metamorphic stages and involved *P*-*T* conditions.

#### **6 Prospects and conclusions**

In the past twenty years, significant progress in mineralogy, petrology, protolith nature, petrochemistry, metamorphic and metasomatic evolution of the Dabie-Sulu orogenic peridotites has improved our understanding of mantle geodynamic processes and crust-mantle interactions. However, numerous key issues must be investigated further, such as complex phase relations constructed in the peridotitepyroxenite system, mantle processes before subduction, element and isotope mobilization and fractionation during crust-mantle interactions,  $fO<sub>2</sub>$  modification during metasomatism by crust-derived C-O-H fluid/melt, and changes in the physical property of the mantle wedge during crustal metasomatism.

Phase relations in felsic-mafic rocks are now well constrained. However, both HP-HT experiments and thermodynamic modeling for ultramafic rocks have been only performed in a very simple system (Yang and Powell, 2008). Orogenic peridotites commonly have a complex composition due to the addition of various degrees of crustal components. It is necessary to construct phase relations in ultramafic rocks in complex systems, such as Ti- and Cr-bearing systems, which may help us understand mineral assemblages at different depths, mineral composition and proportions under given *P*-*T* conditions, and metamorphic *P*-*T* evolution of the rock. The key is to construct reliable composition-activity models for Cr-Ti-bearing spinel, garnet, pyroxene, phlogopite, Ti-clinohumite and Ti-chondrodite.

Most previous studies on orogenic peridotites focused on HP-UHP metamorphism and metasomatism during subduction; the mantle geodynamic processes that occur before subduction have been given little attention. The mantle processes prior to subduction include the mantle structure of the protoliths of orogenic peridotites, the partial melting and the melt-rock reaction processes. Most of the Dabie-Sulu orogenic peridotites record metamorphism before subduction, and some also present textures for silica-undersaturated melt-rock reactions prior to subduction. Understanding these mantle processes is a prerequisite to investigate crust-mantle interactions. *In situ* geochemical analyses of index textures will provide key information for understanding the mantle history of orogenic peridotites.

Element and isotope fractionations during crust-mantle interactions are always characterized by the formation of metasomatized veins or layers that systematically show diverse mineral assemblages, whole-rock major, trace and isotopic compositions. Determining the degrees of metasomatism requires us to understand the crust-derived fluid/ melt compositions and the protolith nature of orogenic peridotites. Based on the degrees of metasomatism and the distance of metasomatized layers away from the protoliths, we are able to estimate which elements are more mobile, which elements are preferentially precipitated, and the internal relation between element and isotope fractionations.

The oxygen fugacity modification during crust-mantle interactions is also an important issue for further orogenic peridotite research. To investigate the effects of crustal metasomatism on the oxygen fugacity of the metasomatized mantle wedge, we should (1) accurately detect  $Fe<sup>3+</sup>$  contents in garnet, spinel, olivine and pyroxene by using X-ray absorption near edge structure (XANES) or the 'Falnk method' technique with an electron microprobe (Höfer and Brey, 2007); (2) calculate different stage  $fO_2$ s based on careful discrimination of different stages of metasomatic minerals; (3) construct phase equilibrium relations on various whole rock Fe<sup>3+</sup>/ $\Sigma$ Fe to reveal the Fe<sup>3+</sup> partitioning among the peridotite mineral phases under different *P*-*T* conditions; and (4) make a comparison between the calculated  $fO<sub>2</sub>$  and typical C-bearing phases in the peridotites, such as diamond, graphite, magnesite,  $CH<sub>4</sub>$  and  $CO<sub>2</sub>$ .

The effects of crustal metasomatism on the physical properties (such as density, wave velocity, magnetoconductivity and electroconductibility) of the metasomatized mantle wedge remain enigmatic. Relative to the depleted mantle minerals, several newly formed minerals caused by modal metasomatism, such as phlogopite, amphibole, chlorite and talc, currently have lower densities and velocities but higher  $V_P/V_S$  ratios and seismic anisotropy. However, some metasomatic minerals, such as garnet, Fe-rich olivine and pyroxene, and Ti-clinohumite usually have higher densities and velocities but relatively lower seismic anisotropy. To constrain the physical properties of metasomatized mantle wedge rocks at different depths, we should establish the distribution of metasomatized minerals in the subduction factory at different depths, phase equilibrium relations and mineral evolution in peridotite-pyroxenite systems, and elastic parameters of related minerals. The investigations will provide direct petrological constraints on the physical property heterogeneity of the mantle.

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