

# Multistage melt/fluid-peridotite interactions in the refertilized lithospheric mantle beneath the North China Craton: constraints from the Li–Sr–Nd isotopic disequilibrium between minerals of peridotite xenoliths

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**Abstract** Elemental and Li–Sr–Nd isotopic data of minerals in spinel peridotites hosted by Cenozoic basalts allow us to refine the existing models for Li isotopic fractionation in mantle peridotites and constrain the melt/fluid-peridotite interaction in the lithospheric mantle beneath the North China Craton. Highly elevated Li concentrations in cpx (up to 24 ppm) relative to coexisting opx and olivine (<4 ppm) indicate that the peridotites experienced metasomatism by mafic silicate melts and/or fluids. The mineral  $\delta^7\text{Li}$  vary greatly, with olivine (+0.7 to +5.4‰) being isotopically heavier than coexisting opx (−4.4 to −25.9‰) and cpx (−3.3 to −21.4‰) in most samples. The  $\delta^7\text{Li}$  in pyroxenes are considerably lower than the normal mantle values and show negative correlation with their Li abundances, likely due to recent Li ingress attended by diffusive fractionation of Li isotopes. Two exceptional samples have olivine  $\delta^7\text{Li}$  of −3.0 and −7.9‰, indicating the existence of low  $\delta^7\text{Li}$  domains in the mantle, which could be transient and generated by meter-scale diffusion of Li during melt/fluid-peridotite interaction. The  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.5123–0.5139) and  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7018–0.7062) in the pyroxenes also show a large variation, in which the cpx are apparently lower in  $^{87}\text{Sr}/^{86}\text{Sr}$  and slightly higher in  $^{143}\text{Nd}/^{144}\text{Nd}$  than coexisting

opx, implying an intermineral Sr–Nd isotopic disequilibrium. This is observed more apparently in peridotites having low  $^{87}\text{Sr}/^{86}\text{Sr}$  and high  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios than in those with high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$ , suggesting that a relatively recent interaction existed between an ancient metasomatized lithospheric mantle and asthenospheric melt, which transformed the refractory peridotites with highly radiogenic Sr and unradiogenic Nd isotopic compositions to the fertile lherzolites with unradiogenic Sr and radiogenic Nd isotopic compositions. Therefore, we argue that the lithospheric mantle represented by the peridotites has been heterogeneously refertilized by multistage melt/fluid-peridotite interactions.

**Keywords** Peridotite xenoliths · Lithium isotope · Melt/fluid-peridotite interaction · Lithospheric mantle · North China Craton

## Introduction

Lithium element and isotope geochemistry is increasingly being used to trace fluid-related processes (e.g., Huh et al. 1998; Marks et al. 2007; Marschall et al. 2007; Lee et al. 2008; Penniston-Dorland et al. 2010) and geochemical recycling such as the return to the Earth's mantle of crust by subduction (e.g., Tomascak et al. 2000; Kobayashi et al. 2004; Elliott et al. 2006; Agostini et al. 2008; Halama et al. 2008; Košler et al. 2009). The main reason that makes Li a powerful tracer is the great range of  $\delta^7\text{Li}$  from −30 to +50‰ in terrestrial samples (Tomascak 2004; Tang et al. 2007a), which is ascribed to the large relative mass difference between  $^6\text{Li}$  and  $^7\text{Li}$ .

Lithium isotope compositions of mantle materials may be affected by diffusion processes due to the exceptionally

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high diffusivity of Li (Coogan et al. 2005) and faster diffusion of  $^6\text{Li}$  than  $^7\text{Li}$  (Richter et al. 2003). For example, high-temperature diffusive fractionation has been invoked to account for striking  $\delta^7\text{Li}$  variations in country rocks of pegmatite (Teng et al. 2006), within individual phenocrysts (Beck et al. 2006; Parkinson et al. 2007) and intragranular, intergranular and intersample scales in mantle-derived rocks (e.g., Lundstrom et al. 2005; Jeffcoate et al. 2007; Kaliwoda et al. 2008; Aulbach and Rudnick 2009).

In a recent study, it is proposed that significant Li isotopic zoning can occur as a natural consequence of cooling magmatic systems (Gallagher and Elliott 2009). This idea is consistent with the suggestion that  $\delta^7\text{Li}$  variations in lava-hosted peridotites may be related to different cooling times of flows (Ionov and Seitz 2008), rather than the result of diffusive fractionation related to melt/fluid-rock reaction (e.g., Rudnick and Ionov 2007; Aulbach and Rudnick 2009). Despite major advances in Li isotopic geochemistry, the processes responsible for Li isotope fractionation in mantle peridotites, such as diffusion of Li during melt/fluid-peridotite interactions, are still poorly understood.

This paper reports element and Li–Sr–Nd isotopic data for minerals in peridotite xenoliths from the Hannuoba, Fanshi and Hebi localities in the Trans-North China Orogen of the North China Craton (NCC, Fig. 1). These data, together with previous geological and geochemical evidence, allow us to refine the existing models for Li isotopic fractionation in mantle peridotites and to probe the importance of melt/fluid-peridotite interaction in the evolution of lithospheric mantle beneath the NCC.

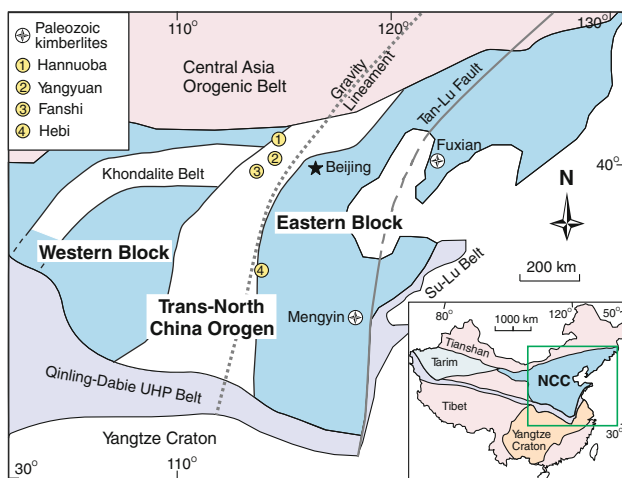
## Geological setting

The NCC (Fig. 1) is one of the world's oldest cratons, containing Archean crustal remnants as old as 3.8 Ga (Liu et al. 1992). It comprises the Eastern Block, the Western Block and the Trans-North China Orogen, which is an ancient orogen formed by the collision between the Eastern and Western Blocks at *ca* 1.85 Ga, marking the final amalgamation of the NCC (Zhao et al. 2008). The NCC experienced multiple circum-craton subductions and collisions, which are manifested by the Paleozoic to Triassic Qinling–Dabie–Sulu ultrahigh-pressure belt in south, the Central Asian Orogenic Belt in north and the Mesozoic–Cenozoic subduction of Pacific plate in east. These subduction and collision events may have affected the compositions and geophysical characteristics of the lithospheric mantle beneath the NCC (Menzies et al. 2007 and references therein) and thus be the key driving force for the transformation of the lithospheric mantle during the Phanerozoic (Zhang et al. 2002, 2003).

Peridotite xenoliths from the Ordovician diamondiferous kimberlites in Mengyin and Fuxian Counties (Fig. 1) represent samples of an ancient mantle lithosphere and indicate a thick (>200 km), cold (geotherm *ca* 40 mW/m<sup>2</sup>) and refractory lithospheric keel beneath the eastern NCC prior to the Paleozoic (e.g., He 1987; Zhang et al. 1989; Dobbs et al. 1994; Meyer et al. 1994; Chi and Lu 1996). Nevertheless, the mantle xenoliths carried in the Cenozoic basalts reveal that the Cenozoic lithosphere is thin (<80 km), hot (geotherm *ca* 80 mW/m<sup>2</sup>) and of fertile composition (e.g., Song and Frey 1989; Fan and Menzies 1992; Tatsumoto et al. 1992; Xu et al. 1998a; Fan et al. 2000; Xu 2001; Zheng et al. 2001). These observations suggest that >100 km of ancient cratonic lithosphere beneath the eastern NCC was lost during the Phanerozoic (e.g., Griffin et al. 1992; Menzies et al. 1993).

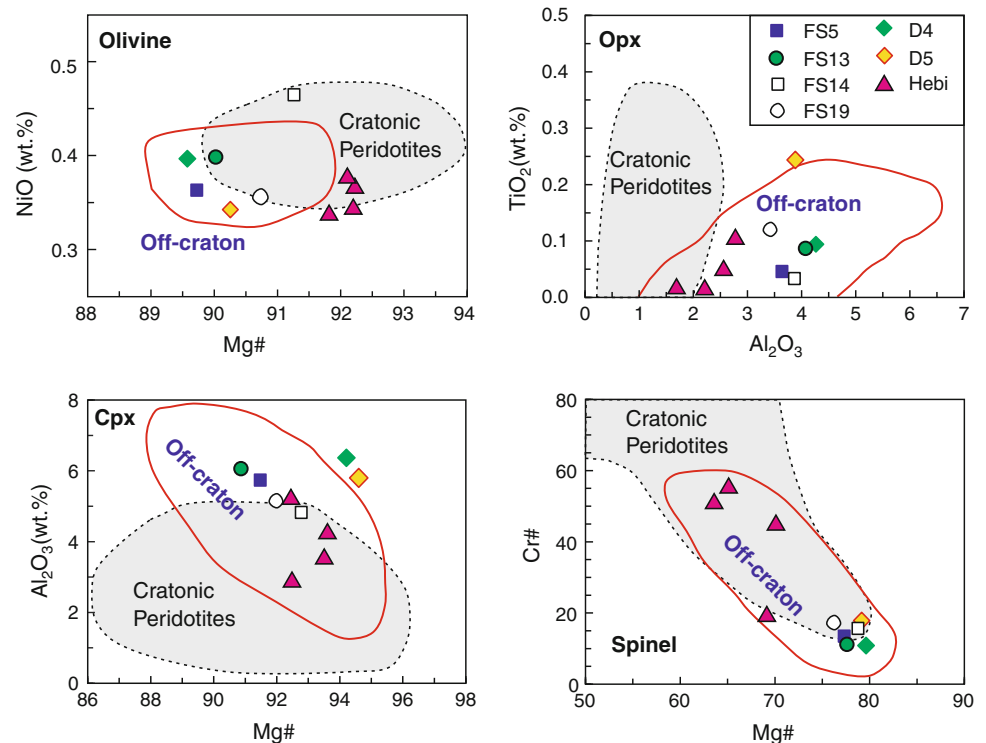
## Sample description

The samples are spinel-facies peridotite xenoliths from the Hannuoba (*ca* 22 Ma, northern margin of the craton), Fanshi (*ca* 25 Ma, northern part of the craton) and Hebi (*ca* 4 Ma, central part of the craton) Cenozoic basalts (Fig. 1). The Hannuoba peridotites gave a Re–Os isochron age of *ca* 1.9 Ga (Gao et al. 2002) and have Re depletion ages as old as 2.2 Ga (Zheng et al. 2007; Xu et al. 2008a; Zhang et al. 2009). When compared to worldwide cratonic peridotites, these peridotites have high  $\text{Al}_2\text{O}_3$  content of cpx and opx, relatively low Mg# of olivine and Cr# of spinel (Fig. 2). These compositions are thus markedly different from cratonic mantle lithosphere found beneath other Archean cratons (Rudnick et al. 2004). It has been suggested that



**Fig. 1** Simplified geological map showing xenolith localities mentioned in the text and tectonic subdivisions of the North China Craton (NCC) (Zhao et al. 2008). The NCC is cut by two major linear zones—Tan-Lu fault zone to the east and south–north gravity lineament to the west. *Inset* shows location of the NCC relative to other blocks and fold belts

**Fig. 2** Mineral compositions for the peridotites. Fields for worldwide off-craton spinel peridotites and cratonic peridotites, including Kaapvaal, east Greenland, Siberia and Tanzania, are from Rudnick et al. (2004)



trace element and Sr–Nd–Os–Li–Fe isotopic compositions of the Hannuoba peridotites reflect considerably recent mantle metasomatic overprinting (Song and Frey 1989; Rudnick et al. 2004; Tang et al. 2007b; Xu et al. 2008a; Zhang et al. 2009; Zhao et al. 2010).

Detailed petrographic descriptions for the Hannuoba samples D4 and D5 have been reported (Tang et al. 2007b). Sample D4 has a porphyroclastic texture. Most olivine and opx grains are *ca* 1–2 mm in diameter with a few up to 3 mm, and large olivine grains are usually kink-banded, indicative of high-temperature plastic deformation (Herzberg 1993). Cpx grains are less than 1 mm in diameter. Sample D5 is coarse-grained and shows coarse-granular and porphyroblastic texture, with mineral mode similar to that of sample D4. Olivine grains are 2–3 mm in diameter with a few grains up to 5 mm. Opx grains are 3–4 mm and cpx *ca* 1 mm.

The Fanshi peridotite xenoliths have Paleoproterozoic Re depletion ages (Xu et al. 2008b). Four lherzolite samples, FS5, FS13, FS14 and FS19, are selected here. These are broadly rounded and range from 5 to 7 cm across. The FS14 is coarse to medium-grained and has porphyroblastic texture. It is relatively poor in modal cpx (8%), similar to the harzburgite xenoliths (cpx < 5%) at this locality (Tang et al. 2008). Samples FS5, FS13 and FS19 are medium to fine grained and have equilibrated textures. Most olivine and opx grains in these samples are 1–2 mm in diameter, and their cpx grains are less than 1 mm in diameter. Cpx modes exceed 10%. The mineral compositions are fertile,

similar to those of the “oceanic” lithospheric mantle in eastern China (Fan et al. 2000; Zhang et al. 2007).

Four Hebi samples HB27, HB30, HB80 and HB81 selected here are coarse-granular harzburgites [olivine: 70–79% (Fo = 91.9–92.3%); opx: 19–25%; cpx: <2%; and trace amounts of spinel; Appendix Table]. They are characterized by high Fo in olivine and interpreted as the relics of old lithospheric mantle (Zheng et al. 2001) with Archean Re depletion ages (as old as 3.0 Ga; Zheng et al. 2007). Compared to Archean lithospheric mantle peridotites (Fo > 92.5), relatively lower Fo values of these harzburgites imply that the old lithospheric mantle has been modified through peridotite–melt interaction, which can transform a major element-depleted peridotite into relatively fertile one (Zhang 2005).

### Analytical methods

Major element compositions of minerals were determined with a Cameca SX51 electron probe micro-analyzer at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Trace element and Sr–Nd–Li isotope analyses were carried out at the Pheasant Memorial Laboratory (PML) for Geochemistry and Cosmochemistry, Institute for Study of the Earth’s Interior, Okayama University at Misasa, Japan.

Fresh xenoliths, without any weathering features by thin section observation, were crushed and sieved with stainless

steel sieves (180–250  $\mu\text{m}$ ). Olivine, opx and cpx separates were handpicked under a binocular microscope and cleaned in an ultrasonic bath in deionized water for 15 min. The separates then were leached by HCl as shown in Tang et al. (2007a). After drying at 110°C, the mineral separates were ground into powders using a silicon nitride mortar.

Trace element analyses of cpx, including Li in olivine and opx, followed the procedures of Moriguti et al. (2004) and Makishima and Nakamura (2006) using an Agilent 7500cs quadrupole ICP mass spectrometer. The analytical reproducibility was <5% (RSD).

The Li chemical separation and isotope analyses by a Neptune MC-ICP-MS have been reported (Moriguti and Nakamura 1998; Tomascak et al. 1999; Tang et al. 2007b). Analytical uncertainty was <0.06‰ ( $2\sigma$  mean). The difference between the  $\delta^7\text{Li}$  of the two L-SVEC standards bracketing each sample was typically <0.4‰ and averaged *ca* 0.2‰. During the course of this study, obtained  $\delta^7\text{Li}$  value of standard rock sample, GSJ JB-2, was  $5.0 \pm 0.5\%$  ( $2\sigma$ ,  $n = 5$ ), consistent with values published previously within analytical error ( $+4.9 \pm 0.7\%$   $2\sigma$  reproducibility, Moriguti and Nakamura 1998;  $5.1 \pm 1.1\%$ , Tomascak et al. 1999;  $4.7 \pm 0.3\%$ , Magna et al. 2008;  $4.7 \pm 1.3\%$ , Halama et al. 2009).

The Sr and Nd isotopic compositions of cpx and opx separates were measured using a Finnigan MAT-262 thermal ionization mass spectrometer following the methods described in Yoshikawa and Nakamura (1993) and Nakamura et al. (2003). The mineral powders were weighed (10–40 mg for cpx and 100–400 mg for opx). Replicate analyses yielded  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.710279 \pm 0.000023$  ( $2\sigma$ ,  $n = 10$ ) for the NBS 987 and  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.511738 \pm 0.000012$  ( $2\sigma$ ,  $n = 10$ ) for in-house standard, PML Nd, which corresponds to  $^{143}\text{Nd}/^{144}\text{Nd} = 0.5118740$  of La Jolla standard. The total procedural blanks are 4, 22, 1 and 7 pg for Rb, Sr, Sm and Nd, respectively.

## Analytical results

### Major and trace elemental compositions

The minerals (olivine, opx and cpx) are homogeneous in major oxides based on analyses from core to rim. The average composition is reported in Table 1. The forsterite contents (Fo) or Mg# range from 89.6 to 92.3, and most of them are significantly lower than those of typical Archean lithospheric mantle (Fo > 92.5; Boyd 1989). The Hebi harzburgites have higher Fo ( $\sim 92$ ) than the Fanshi and Hannuoba (90–91), and most of them plot in the fields for cratonic peridotites. However, the minerals compositions for the Fanshi and Hannuoba lherzolites are generally similar to those of global off-craton spinel peridotites and different from those of typical old cratonic peridotites (Fig. 2;

Rudnick et al. 2004). Some peridotite xenoliths from this region have  $\text{SiO}_2$  contents higher than the primitive mantle (Fig. 3) and cannot be the residue of melt extraction.

The cpx show a large variation in chondrite-normalized rare earth element (REE) patterns from light REE (LREE)-depleted to LREE-enriched profiles (Fig. 4). Most Hebi and Fanshi samples have relatively high LREE contents and positive primitive mantle-normalized Li anomaly, whereas the Hannuoba samples show lower LREE contents and Li depletion (Table 2; Fig. 4). Some of the Fanshi samples have heavy-REE (HREE) contents higher than the Hannuoba and Hebi samples. Two samples from the Hebi (HB27 and HB30) show very low HREE and are characterized by a prominent trough from Gd to Tm, showing at least a two-stage feature of a partial melting followed by mantle metasomatism. In addition, the cpx display Rb and Ba depletion but weak enrichment of Sr.

Li contents in the coexisting minerals vary greatly (Table 3; Fig. 5). The Fanshi cpx are the highest in Li contents (13–24 ppm), followed by opx (4–7 ppm) and olivine (2–4 ppm). Compared with the Fanshi peridotites, the Hannuoba samples are lower in Li contents in cpx (2.4–2.7 ppm), opx (1.4–1.9 ppm) and olivine (1.4–1.5 ppm). For the Hebi harzburgites, Li contents in olivine (1–2 ppm) are similar to the normal mantle, but those in opx (4–8 ppm) and cpx (7–13 ppm) are apparently higher than the normal mantle (Fig. 5).

### Sr, Nd and Li isotope ratios of mineral separates

Sr and Nd isotopic compositions of cpx and opx separates show a large variation (Table 4), ranging from depleted mantle (DM) to enriched mantle (EM1)-like Sr–Nd isotopic characteristics (Fig. 6), which are consistent with those documented in the previous investigations (Rudnick et al. 2004; Tang et al. 2008). The cpx in most peridotites are lower in  $^{87}\text{Sr}/^{86}\text{Sr}$  and higher in  $^{143}\text{Nd}/^{144}\text{Nd}$  than coexisting opx (Fig. 6). The peridotites with strongly different Sr–Nd isotopic compositions between cpx and opx are lower in  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7018–0.7034) and higher in  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.5131–0.5139) than those whose Sr–Nd isotope compositions in cpx and opx are closer (Table 4).

Li isotopic compositions of the mineral separates show extremely large variations, with  $\delta^7\text{Li}$  ranging from +5.4 to  $-7.9\%$  in olivine,  $-4.4$  to  $-26\%$  in opx and  $-3.3$  to  $-21\%$  in cpx (Table 3). For most of the samples, olivine has higher  $\delta^7\text{Li}$  ( $>+0.7\%$ ) than coexisting opx and cpx ( $<-10\%$ ). In sample FS5, olivine has  $\delta^7\text{Li}$  of  $-7.9\%$ , which is isotopically lighter than the coexisting opx ( $-5.3\%$ ), but heavier than the coexisting cpx ( $-8.4\%$ ). Remarkable fractionations of Li isotopes between coexisting minerals are observed. The maximum between pyroxenes and olivines is 27‰ (Table 3).

**Table 1** Major element composition (wt%) of minerals in the peridotites (average value of *n* analyses)

Sample	FS13										FS14						FS19						D4																		
	Sp-lherzolite										Sp-lherzolite						Sp-lherzolite						Sp-lherzolite																		
	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp													
SiO <sub>2</sub>	41.24	52.64	55.22	40.87	51.82	55.53	41.89	53.69	56.98	41.49	53.09	55.63	41.00	52.09	55.36	41.89	53.69	56.98	41.49	53.09	55.63	41.00	52.09	55.36	41.49	53.09	55.63	41.00	52.09	55.36	41.00	52.09	55.36	41.00	52.09	55.36					
TiO <sub>2</sub>	0.45	0.04	0.10	0.6	0.09	0.15	0.24	0.04	0.11	0.40	0.12	0.14	0.52	0.10	0.07	0.24	0.04	0.11	0.40	0.12	0.14	0.52	0.10	0.07	0.40	0.12	0.14	0.52	0.10	0.07	0.12	0.14	0.14	0.52	0.10	0.07					
Al <sub>2</sub> O <sub>3</sub>	5.74	3.67	53.63	6.07	4.1	57	4.82	3.87	52.53	5.18	3.42	50.00	6.55	4.25	58.34	4.82	3.87	52.53	5.18	3.42	50.00	6.55	4.25	58.34	3.42	50.00	50.00	6.55	4.25	58.34	3.42	50.00	50.00	6.55	4.25	58.34					
Cr <sub>2</sub> O <sub>3</sub>	0.94	0.28	13.06	0.78	0.34	11.79	0.78	0.37	15.55	1.01	0.34	16.78	0.79	0.33	9.53	0.78	0.37	15.55	1.01	0.34	16.78	0.79	0.33	9.53	0.34	16.78	16.78	0.79	0.33	9.53	0.34	16.78	16.78	0.79	0.33	9.53					
FeO	10.00	2.58	6.28	9.97	2.64	6.15	8.57	2.25	5.35	9.05	2.47	5.82	10.08	1.64	6.58	9.43	8.57	2.25	5.35	9.05	2.47	5.82	10.08	1.64	6.58	9.43	2.47	5.82	5.82	10.08	1.64	6.58	2.47	5.82	5.82	10.08	1.64	6.58	9.43		
MnO	0.14	0.05	0.10	0.12	0.1	0.16	0.11	0.13	0.08	0.15	0.10	0.15	0.09	0.09	0.14	0.09	0.11	0.13	0.08	0.15	0.10	0.15	0.10	0.09	0.09	0.14	0.09	0.10	0.15	0.15	0.10	0.09	0.09	0.10	0.15	0.15	0.10	0.09	0.09	0.14	0.09
MgO	48.51	15.51	33.02	49.71	15.61	33.85	49.83	16.02	33.47	49.37	15.67	33.36	48.01	14.92	32.54	20.29	49.83	16.02	33.47	49.37	15.67	33.36	48.01	14.92	32.54	15.67	33.36	33.36	48.01	14.92	32.54	15.67	33.36	33.36	48.01	14.92	32.54				
CaO	0.06	19.28	0.60	0.08	20.77	0.58	0.07	20.08	0.70	0.03	20.55	0.64	0.06	20.49	0.57	0.07	20.08	0.70	0.03	20.55	0.64	0.06	20.49	0.57	20.55	0.64	0.64	0.06	20.49	0.57	20.55	0.64	0.64	0.06	20.49	0.57					
Na <sub>2</sub> O	1.39	0.08		1.57	0.09		1.25	0.08		1.39	0.09		1.76	0.09		1.25	0.08		1.39	0.09		1.76	0.09		0.09			1.76	0.09		0.09			1.76	0.09						
NiO	0.36	0.00	0.29	0.39	0.03	0.36	0.47	0.06	0.40	0.36	0.17	0.23	0.40	0.05	0.40	0.47	0.06	0.40	0.36	0.17	0.23	0.40	0.05	0.40	0.17	0.23	0.23	0.40	0.05	0.40	0.17	0.23	0.23	0.40	0.05	0.40					
Total	100.3	98.6	99.3	101.1	100.0	100.9	101.0	99.1	101.0	100.4	99.9	99.7	99.6	100.0	98.2	101.0	99.1	101.0	100.4	99.9	99.7	98.4	99.6	100.0	98.2	99.9	99.7	99.7	98.4	99.6	100.0	99.9	99.7	99.7	98.4	99.6	100.0	98.2			
Mg#	89.7	91.5	90.4	90.0	91.4	90.8	91.3	92.8	91.8	90.8	92.0	91.2	89.6	94.3	89.5	91.3	92.8	91.8	90.8	92.0	91.2	89.6	94.3	89.5	92.0	91.2	91.2	89.6	94.3	89.5	92.0	91.2	91.2	89.6	94.3	89.5					
Cr#			14.2			12.3			16.8			18.6			10.0			16.8			18.6			10.0			18.6			10.0			18.6			10.0					

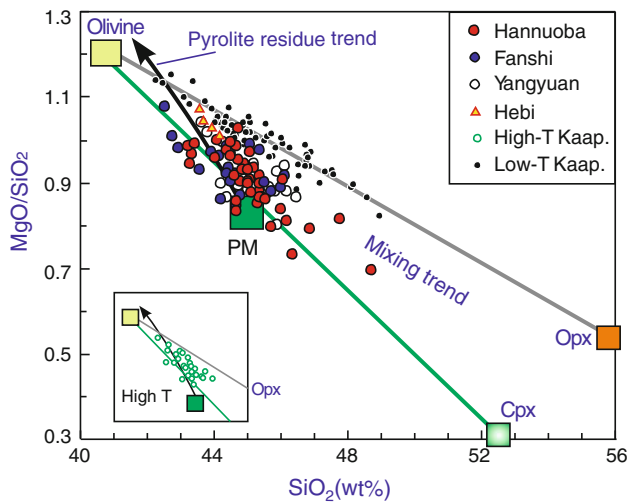
  

Sample	HB27						HB30						HB80						HB81																				
	Sp-harzburgite						Sp-harzburgite						Sp-harzburgite						Sp-harzburgite																				
	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp	Ol	Cpx	Opx	Sp											
SiO <sub>2</sub>	41.34	52.62	55.59	40.32	52.38	55.1	40.87	52.9	56.02	40.8	53.39	56.83	40.16	53.52	57.52	40.87	52.9	56.02	40.8	53.39	56.83	40.16	53.52	57.52	53.39	56.83	56.83	40.16	53.52	57.52	53.39	56.83	56.83	40.16	53.52	57.52			
TiO <sub>2</sub>	0.26	0.36	0.07	0.03	0.12	0.31	0.22	0.04	0.04	0.02	0.01	0.07	0.08	0.01	0.32	0.22	0.04	0.04	0.02	0.01	0.07	0.08	0.01	0.32	0.01	0.07	0.07	0.08	0.01	0.32	0.01	0.07	0.07	0.08	0.01	0.32			
Al <sub>2</sub> O <sub>3</sub>	5.81	3.69	52.46	4.16	2.98	25.03	5.38	2.86	29.23	3.45	2.46	23.9	2.43	1.76	25.44	5.38	2.86	29.23	3.45	2.46	23.9	2.43	1.76	25.44	2.46	23.9	23.9	2.43	1.76	25.44	2.46	23.9	23.9	2.43	1.76	25.44			
Cr <sub>2</sub> O <sub>3</sub>	1.12	0.34	15.71	1.06	0.92	40.62	1.85	0.7	36.22	1.29	0.79	42.22	2.3	0.63	41.98	1.85	0.7	36.22	1.29	0.79	42.22	2.3	0.63	41.98	0.79	42.22	42.22	2.3	0.63	41.98	0.79	42.22	42.22	2.3	0.63	41.98			
FeO	9.52	1.57	5.69	7.55	2.11	4.19	7.99	2.31	4.95	7.78	2.28	4.85	7.82	2.41	4.96	15.96	7.99	2.31	4.95	7.78	2.28	4.85	7.82	2.41	4.96	15.96	2.28	4.85	4.85	7.82	2.41	4.96	2.28	4.85	4.85	7.82	2.41	4.96	15.96
MnO	0.10	0.13	0.16	0.12	0.09	0.11	0.09	0.08	0.1	0.12	0.06	0.11	0.02	0.1	0.13	0.02	0.09	0.08	0.1	0.12	0.06	0.11	0.02	0.1	0.13	0.02	0.06	0.11	0.11	0.02	0.1	0.13	0.06	0.11	0.11	0.02	0.1	0.13	0.02
MgO	48.97	15.08	32.91	50.2	17.17	34.2	50.62	15.99	33.8	50.8	17.88	34.31	50.83	16.48	34.68	15.71	50.62	15.99	33.8	50.8	17.88	34.31	50.83	16.48	34.68	17.88	34.31	34.31	50.83	16.48	34.68	17.88	34.31	34.31	50.83	16.48	34.68		
CaO	0.04	20.67	0.47	0.07	20.31	0.78	0.05	18.59	0.81	0.09	20.6	0.77	0.05	21.09	0.6	0.05	18.59	0.81	0.09	20.6	0.77	0.05	21.09	0.6	20.6	0.77	0.77	0.05	21.09	0.6	20.6	0.77	0.77	0.05	21.09	0.6			
Na <sub>2</sub> O	1.73	0.07			0.91	0.04		1.61	0.21		0.52	0.04		0.08			1.61	0.21		0.52	0.04		0.08		0.52	0.04	0.04		0.08		0.52	0.04	0.04		0.08				
NiO	0.34	0.11	0.34	0.36	0.09	0.22	0.33	0	0.15	0.34	0.1	0.24	0.37	0.1	0.18	0.33	0	0.15	0.34	0.1	0.24	0.37	0.1	0.18	0.1	0.24	0.24	0.37	0.1	0.18	0.1	0.24	0.24	0.37	0.1	0.18			
Total	100.4	99.0	99.4	98.7	98.3	98.5	100.0	99.0	99.6	100.0	99.6	100.3	99.4	99.3	100.5	99.6	100.0	99.0	99.6	100.0	99.6	100.3	99.4	99.3	100.5	99.6	99.6	100.3	100.3	99.4	99.3	100.5	99.6	100.3	100.3	99.4	99.3	100.5	99.6
Mg#	90.3	94.5	91.2	92.3	93.6	93.6	91.9	92.6	92.5	92.2	93.4	92.7	92.1	92.5	92.6	63.9	91.9	92.6	92.5	92.2	93.4	92.7	92.1	92.5	92.6	63.9	93.4	92.7	92.7	92.1	92.5	92.6	93.4	92.7	92.7	92.1	92.5	92.6	63.9
Cr#			16.9			52.5			45.7			54.6			52.9			52.5			45.7			54.6			54.6			52.9			54.6			52.9			

Major element composition (wt%) of minerals in the peridotites (average value of *n* points)

Ol olivine, *opx* orthopyroxene, *cpx* clinopyroxene, *sp* spinel, Mg# = 100 × molar Mg/(Mg + Fe), Cr# = 100 × molar Cr/(Cr + Al). Blank is below detection limit. Data for D4 and D5 are from Tang et al. (2007a)





**Fig. 3** MgO/SiO<sub>2</sub> versus SiO<sub>2</sub> (wt%) showing peridotites from the North China Craton relative to the residue trend for pyrolite and to mixing trends between olivine and opx (Walter 1998) and between olivine and cpx. Data sources for the Chinese peridotites: Fan and Hooper (1989), Song and Frey (1989), Chen et al. (2001), Rudnick et al. (2004), Ma and Xu (2006), Tang et al. (2008), Xu et al. (2008b) and this study. High-temperature and low-temperature peridotites from Kaapvaal, southern Africa and fields for olivine and opx are taken from Walter (1998). Field for cpx represents the average composition of cpx in Hannuoba peridotites and primitive mantle (PM) taken from McDonough and Sun (1995)

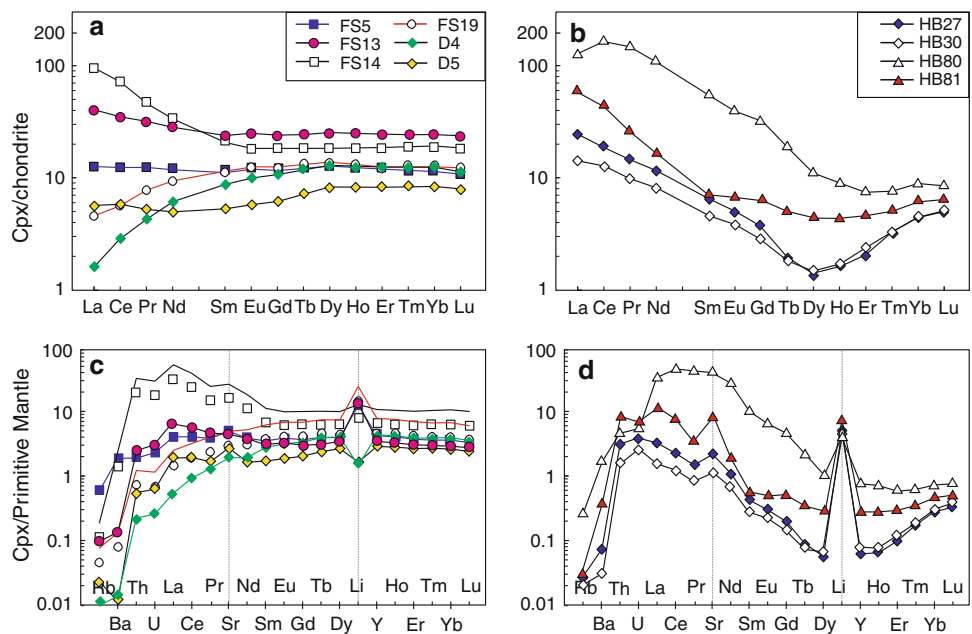
## Discussion

### Elemental geochemistry

Mafic melt extraction from a fertile peridotite will form a relatively refractory lherzolite or harzburgite (Kushiro 2001). Thus, the residue is variously depleted in basaltic

components such as Al, Ca, Ti and Na. A typical feature of Archean mantle is the presence of highly refractory harzburgites and cpx-poor lherzolites (Boyd 1989). Inversely, many xenoliths and xenocrysts data suggest that the lithospheric mantle beneath Archean/Proterozoic areas has been extensively refertilized by metasomatic processes, with the addition of melts rich in basaltic components (including Al, Ca and Fe) to originally depleted peridotites (Griffin et al. 2003; Carlson et al. 2004; Simon et al. 2007; references therein). Most of the Fanshi and Hannuoba samples are plotted in the field for off-craton peridotites due to their relatively fertile mineral compositions (Fig. 2) and lower Fo of olivines (<91.5) than typical old cratonic peridotites (>92) although the NCC is an Archean craton. This indicates different-extent refertilization of the old lithospheric mantle beneath the NCC by melt addition (Tang et al. 2008; Zhang et al. 2009, 2010), by which some peridotites are relatively fertile in mineral compositions and thus bear a resemblance to the newly accreted lithospheric mantle (Fan et al. 2000). Most of the Hebi harzburgites dropped in the fields for global cratonic peridotites due to their high Mg# in olivine and cpx, and high Cr# in spinel, and thus they were interpreted as the relics of old lithospheric mantle (Zheng et al. 2001, 2007). Compared to Archean lithospheric mantle peridotites (Fo > 92.5), relatively lower Fo values and higher Al<sub>2</sub>O<sub>3</sub> contents (Fig. 2) of these harzburgites imply that the Archean lithospheric mantle has been refertilized by melt addition. In contrast, the Hebi samples experienced less-degree refertilization than the others, which is also evidenced in Fig. 3, showing the correlation of MgO/SiO<sub>2</sub> ratio with SiO<sub>2</sub> in cratonic peridotites from the North China Craton and the Kaapvaal craton, southern Africa. Compositions of the low-temperature peridotite

**Fig. 4** Chondrite-normalized REE patterns (a, b) and primitive mantle-normalized spidergram (c, d) for cpx from the Hannuoba, Fanshi and Hebi peridotites. Normalization values: chondrite (Anders and Grevesse 1989), primitive mantle (McDonough and Sun 1995)



**Table 2** Trace element compositions (ppm) of cpx

Sample	FS5	FS13	FS14	FS19	HB27	H30	HB80	HB81	D4	D5
Rb	0.385	0.062	0.072	0.029	0.014	0.013	0.181	0.019	0.006	0.015
Ba	13.6	0.898	10.3	0.563	0.525	0.207	13.5	2.65	0.098	0.080
Th	0.167	0.207	1.73	0.063	0.270	0.153	0.434	0.815	0.019	0.049
U	0.050	0.064	0.386	0.015	0.080	0.055	0.121	0.149	0.006	0.014
La	2.90	4.85	22.7	1.06	2.39	1.06	26.0	8.86	0.382	1.34
Ce	7.49	10.3	43.1	3.49	4.29	2.24	98.7	14.3	1.71	3.57
Pb	0.328	0.466	2.57	0.354	0.174	0.138	1.07	0.090	0.049	0.060
Pr	1.10	1.31	4.19	0.684	0.429	0.242	12.4	1.03	0.374	0.475
Sr	108	116	348	64.4	57.4	25.6	994	211	41.5	59.6
Nd	5.41	5.68	15.3	4.36	1.61	0.97	42.9	2.64	2.74	2.31
Sm	1.62	1.42	3.07	1.70	0.214	0.128	4.78	0.252	1.28	0.783
Eu	0.675	0.584	1.03	0.709	0.059	0.039	1.16	0.083	0.551	0.325
Gd	2.26	1.92	3.69	2.51	0.136	0.087	3.05	0.308	2.08	1.25
Tb	0.447	0.368	0.674	0.495	0.009	0.009	0.258	0.039	0.441	0.268
Dy	3.00	2.54	4.55	3.37	0.039	0.042	0.799	0.212	3.1	2.03
Y	20.0	17.0	30.2	22.1	0.304	0.336	3.71	1.45	20.5	13.6
Ho	0.692	0.573	1.06	0.763	0.011	0.012	0.133	0.046	0.722	0.478
Er	1.85	1.58	3.00	2.06	0.047	0.059	0.287	0.142	1.93	1.33
Tm	0.276	0.246	0.475	0.304	0.014	0.014	0.048	0.026	0.300	0.207
Yb	1.85	1.60	3.24	2.04	0.150	0.149	0.390	0.238	2.02	1.34
Lu	0.253	0.223	0.459	0.275	0.027	0.029	0.062	0.039	0.271	0.185
ΣREE	29.8	33.2	106	23.8	4.8	5.1	191	28.2	17.9	15.9
(La/Yb) <sub>N</sub>	1.08	2.10	4.85	0.36	10.10	4.92	46.10	25.7	0.13	0.69

Data for D4 and D5 are from Tang et al. (2007a)

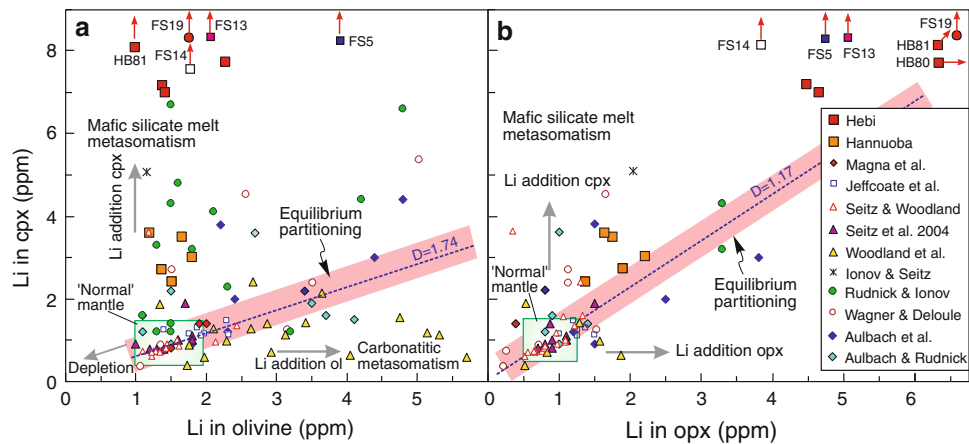
**Table 3** Li concentrations and isotopic compositions of mineral separates in the peridotites

Sample	Olivine			Opx			Cpx		
	Li (ppm)	$\delta^7\text{Li}$	$2\sigma$	Li (ppm)	$\delta^7\text{Li}$	$2\sigma$	Li (ppm)	$\delta^7\text{Li}$	$2\sigma$
FS5	3.88	-7.89	0.04	4.73	-5.29	0.03	20.8	-8.43	0.03
FS13	2.06	-2.96	0.04	5.09	-16.45	0.04	23.55	-11.55	0.04
FS14	1.87	1.20	0.04	3.78	-15.41	0.05	12.7	-19.69	0.03
FS19	1.87	3.38	0.04	6.60	-23.47	0.04	24.2	-17.38	0.05
HB27	1.40	0.72	0.05	4.48	-20.19	0.03	7.3	-18.21	0.02
HB30	1.41	2.91	0.04	4.79	-23.20	0.06	7.0	-20.29	0.03
HB80	2.29	0.70	0.04	7.71	-25.98	0.03	7.9	-11.40	0.04
HB81	0.98	0.21	0.04	7.96	-23.71	0.03	13.1	-21.41	0.03
D4	1.51	5.35	0.04	1.37	-5.27	0.05	2.41	-3.25	0.06
D5	1.37	5.20	0.04	1.89	-4.35	0.05	2.72	-7.54	0.05

Data for D4 and D5 are from Tang et al. (2007a)

xenoliths from Kaapvaal show mixing trends between olivine and opx (Walter 1998), while the peridotites from the North China Craton have the compositions displaying mixing trend between olivine and cpx (Fig. 3). This possibly reflects the introduction of cpx into the peridotites during melt metasomatic events, similar to that recognized by Simon et al. (2007).

The variation of cpx REE patterns (Fig. 4) may reflect the effect of melt/fluid-peridotite interaction. LREE enrichments in some cpx (e.g., HB80, FS13 and FS14) indicate mantle metasomatism. Chromatographic migration of LREE-enriched melts through LREE-depleted peridotites is an efficient mechanism (Navon and Stolper 1987). This type of melt–rock interaction produces REE patterns



**Fig. 5** Li abundance in cpx versus coexisting **a** olivine and **b** opx. Field for ‘normal’ mantle is represented by fertile to moderately depleted peridotites (Seitz and Woodland 2000). The dashed field represents equilibrium partitioning of Li between minerals based on the new partition coefficients  $D^{\text{ol/cpx}} = 1.74$  and  $D^{\text{cpx/opx}} = 1.17$  (Ottolini et al. 2009). *Inset* shows extend diagrams including samples with extremely high Li contents in minerals. Higher Li contents are ascribed to Li ingress by mafic silicate melt metasomatism or/and

carbonatitic metasomatism (Seitz and Woodland 2000). Three Hannuoba samples plotted are from Tang et al. (2007a). Data shown for comparison are from the literature (Seitz and Woodland 2000; Seitz et al. 2004; Woodland et al. 2004; Magna et al. 2006; Jeffcoate et al. 2007; Rudnick and Ionov 2007; Wagner and Deloule 2007; Aulbach et al. 2008; Ionov and Seitz 2008; Aulbach and Rudnick 2009)

**Table 4** Sr and Nd isotopic compositions for cpx and opx separates in the peridotites

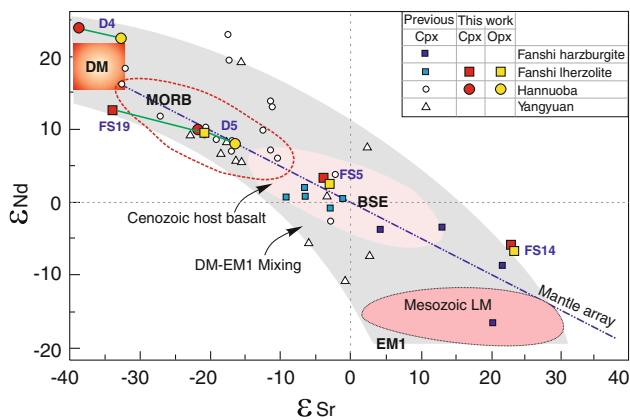
Sample	Weight (mg)	Rb (ppm)	Sr (ppm)	Sm (ppm)	Nd (ppm)	$^{143}\text{Nd}/^{144}\text{Nd}$	$2\sigma$	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma$
Cpx									
D4	43.50	0.005	41.7	1.35	2.73	0.513890	5	0.701770	6
D5	41.51	0.007	57.0	0.78	2.25	0.513159	5	0.702998	7
FS5	10.85	0.362	107	1.79	5.61	0.512762	4	0.704241	6
FS14	11.10	0.051	353	3.24	15.7	0.512270	5	0.706138	5
FS19	13.09	0.021	64.8	1.84	4.44	0.513292	4	0.702102	6
Opx									
D4	403.04	0.002	0.147	0.013	0.016	0.513849	31	0.702203	6
D5	314.89	0.001	0.121	0.006	0.010	0.513105	28	0.703357	7
FS5	68.37	0.347	2.19	0.041	0.125	0.512792	10	0.704314	6
FS14	103.16	0.145	2.28	0.040	0.122	0.512306	5	0.706166	6
FS19	97.52	0.147	0.602	0.035	0.066	0.513202	16	0.703133	5

with extremely variable LREE enrichment, which is typical of that observed in the FS5, D5, HB27 and HB30 (Fig. 4). Although the LREE depletions in D4 and FS19 show a partial melting process, they are the likely consequence that the cpx reach approximate equilibrium with LREE-depleted melts as documented by Xu et al. (1998b) because of their high FeO and TiO<sub>2</sub> contents (Table 2; Fig. 2). The variation observed for the HREE contents likely reflects the variable degrees of partial melting. The positive anomalies of Sr and Li (Fig. 4) may be due to later enrichments related with small-volume melts as described by Bodinier et al. (2004) or fluid-induced overprinting of the mantle (Halama et al. 2009). The negative Li anomaly in Hannuoba peridotites D4 and D5 may reflect (1) the preference of olivine to incorporate Li relative to REE (Tang et al.

2007a) and (2) these peridotites approached equilibrium with LREE-depleted melt/fluid and their Li abundances are close to the normal mantle values.

The Li compositional ranges in olivine and pyroxenes in the normal mantle are 1–1.8 and 0.5–1.3 ppm, respectively (Seitz et al. 2004; Woodland et al. 2004; Jeffcoate et al. 2007). According to the Li partition coefficients of  $D^{\text{ol/cpx}} = 1.74$  and  $D^{\text{cpx/opx}} = 1.17$  (Ottolini et al. 2009), Li partitioning in equilibrated peridotites is olivine > cpx > opx. However, Li partitioning observed in peridotites from this study deviates strongly from such an equilibrium trend (Fig. 5). Based on an empirical observation, the preferential Li enrichment in cpx relative to olivine, similar to that of peridotites from Finero, Italy (Seitz and Woodland 2000), far-east Russia (Rudnick and Ionov 2007), French





**Fig. 6** Variation of  $\epsilon_{\text{Sr}}$  and  $\epsilon_{\text{Nd}}$  for cpx and opx in the studied peridotites, together with the published data for peridotite xenoliths (Song and Frey 1989; Tatsumoto et al. 1992; Fan et al. 2000; Rudnick et al. 2004; Ma and Xu 2006; Tang et al. 2008), Cenozoic Fanshi basalts (Tang et al. 2006) from the studied region and for the Mesozoic lithospheric mantle (LM) beneath the Trans-North China Orogen (Zhang et al. 2004; Wang et al. 2006). These data are calculated back to 20 Ma when the host basalts erupted. DM, MORB, BSE and EM1 end members are from Zindler and Hart (1986). The analytical uncertainties for the data are less than the symbols. The values used for today's  $(^{87}\text{Rb}/^{86}\text{Sr})_{\text{BSE}}$ ,  $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{BSE}}$ ,  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{BSE}}$ , and  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{BSE}}$  are 0.0847, 0.7045, 0.1967 and 0.512638, respectively. The field roughly drawn denotes the DM-EM1 mixing trend

Massif Central (Wagner and Deloule 2007) and Tanzanian Labait volcano (Aulbach et al. 2008), indicates that these peridotites could have been affected by the infiltration of mafic silicate melt. Nevertheless, from available cpx-fluid experimental partitioning data (Brenan et al. 1998), it cannot be ruled out that the metasomatizing agent was a fluid. The preferential Li enrichment in cpx relative to opx (Fig. 5) suggests that the cpx are more susceptible to the melt/fluid infiltration than coexisting opx and olivine due to faster diffusion of Li in cpx than in olivine (Dohmen et al. 2010).

#### Sr–Nd isotopic characteristics and melt–peridotite interaction

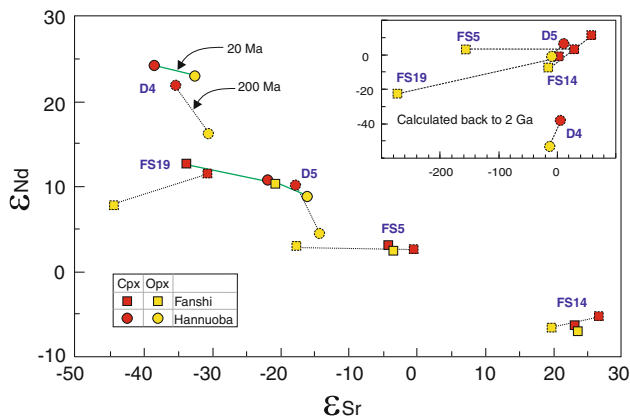
The linear trend on Sr–Nd isotope diagrams for mantle-derived rocks from the DM end member to and beyond BSE (Fig. 6), known as “mantle array”, was traditionally explained by metasomatism of ancient melting residues by asthenospheric and other components enriched in incompatible elements (e.g., Menzies and Murthy 1980). Thus, the radiogenic Sr and unradiogenic Nd isotopic compositions in the Fanshi and Yangyuan peridotites reflect ancient enrichment processes of the subcontinental lithospheric mantle, as previously documented for xenoliths from this region (Ma and Xu 2006; Tang et al. 2008; Xu et al. 2008b). Large variation in the Sr–Nd isotopic ratios of cpx (Fig. 6), from DM to EM1-like signature, indicates that the

lithospheric mantle reflected by these peridotites could have been previously modified by melts/fluids that increased the Rb/Sr and decreased Sm/Nd ratios in the old lithosphere and then experienced a secular evolution (Wang et al. 2006; Tang et al. 2008). The ancient enrichment event was suggested to have been closely related with the Paleoproterozoic subduction/collision between the Eastern Block and the Western Block of the NCC occurred at *ca* 1.85 Ga (Wang et al. 2006; Zhao et al. 2008).

Unradiogenic Sr and radiogenic Nd isotopic compositions in the Hannuoba and FS19 lherzolites (Fig. 6) could be the products of recent asthenospheric melt–peridotite interaction (Tang et al. 2008; Zhang et al. 2009), i.e., old lithospheric mantle with highly radiogenic Sr and unradiogenic Nd isotopic compositions refertilized by the addition of asthenospheric melt. Because the melt derived from the asthenosphere is low in  $^{87}\text{Sr}/^{86}\text{Sr}$  and high in  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, the products should be low in  $^{87}\text{Sr}/^{86}\text{Sr}$  and high in  $^{143}\text{Nd}/^{144}\text{Nd}$  relative to their precursors from the old lithosphere having radiogenic Sr isotopic ratios (Zhang et al. 2004). Further evidence for the melt–peridotite interaction is that some peridotite xenoliths from the region (including Hannuoba, Yangyuan and Fanshi localities) have Sr–Nd isotopic compositions that plot to the right of the “mantle array” (Fig. 6) because the decoupling of Sr and Nd isotopes in some peridotites could be due to “chromatographic” effects of melt percolation as indicated by numeric modeling (Ionov et al. 2002). Moreover, the samples D4, D5 and FS19 are higher in  $\epsilon_{\text{Nd}}$  and lower in  $\epsilon_{\text{Sr}}$  than FS5 and FS14, indicating that the former experienced higher degrees of interaction with the asthenospheric melts than the latter. This is consistent with their depleted REE patterns  $(\text{La}/\text{Yb})_{\text{N}} < 1$  (Table 2) because the elemental and isotopic patterns of the mineral could have been partly or totally reset upon interaction of peridotites with asthenospheric melts.

The difference in Sr and Nd isotope compositions between the coexisting cpx and opx may reflect isotopic disequilibrium. In order to cover a wide time span, we correct the Sr and Nd isotope ratios back to the time of 20, 200 Ma and 2 Ga, respectively (Fig. 7). The apparent difference in the isotope compositions between cpx and opx can be still observed at each time. If the formation age of the peridotites is assumed to be 2 Ga, the isotope difference between cpx and opx is very large. Therefore, the Sr–Nd isotopic differences between cpx–opx pairs cannot be explained by radiogenic ingrowth since the peridotites formed, and thus represent intermineral isotopic disequilibrium caused by later processes.

Intermineral isotopic disequilibrium in some mantle peridotite, for example, Sr isotopic differences between coexisting minerals like cpx and opx or cpx and olivine, has been observed in early studies of mantle xenoliths (e.g., Paul 1971; Burwell 1975; Jagoutz 1988). In most cases,



**Fig. 7**  $\epsilon_{\text{Sr}}$  versus  $\epsilon_{\text{Nd}}$  diagram for the cpx and opx in the studied peridotites. The shown data are calculated back to the time of 2 Ga, 200 and 20 Ma. Normalized  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  values are 0.7045 and 0.512638, respectively

coexisting phases were found to be in Nd isotopic equilibrium, but opx and olivine showed more radiogenic Sr than coexisting cpx. This phenomenon was ascribed to late-stage contamination, i.e., the data for low Sr concentration phases (opx or olivine) are biased toward values for ubiquitous contaminants, either on grain boundaries or associated with fluid inclusions, unless extreme care is taken to obtain minerals of high optical purity (Jagoutz et al. 1980; Menzies and Murthy 1978; Stosch et al. 1986; Zindler and Jagoutz 1988). For example, Jagoutz et al. (1980) found that opx and cpx were in Nd isotopic equilibrium although the Sr isotope ratio of opx (0.7036) was significantly higher than that in the cpx (0.7023) in a spinel lherzolite from Kilbourne Hole. The authors considered that the higher  $^{87}\text{Sr}/^{86}\text{Sr}$  in the opx was likely the result of secondary contamination, which had not been totally removed during sample preparation.

However, both Sr and Nd isotopic disequilibria between coexistent phases in some mantle peridotites were recognized and attributed to recent mantle metasomatic component addition or redistribution without re-equilibration (Richardson et al. 1985; McDonough and McCulloch 1987; Jagoutz 1988). Even reaction with enclosing magma in the case of xenoliths may result in the different isotopic compositions in constituent minerals of peridotites (Basu and Murthy 1976; Zindler and Jagoutz 1988). There are two possible scenarios for the isotopic disequilibrium: (1) all minerals had the same isotopic composition before the late metasomatic event, which may have involved introduction of a melt/liquid that equilibrated with the outermost parts of minerals; (2) isotopic equilibration could occur within given “domains” (possibly in some minerals prior to the metasomatism) of the peridotite but may not have occurred between “domains”, i.e., incomplete equilibration or local resetting of isotopes during the mantle metasomatism (Jagoutz 1988).

In this study, the Sr and Nd isotopic disequilibria between coexisting cpx and opx in the peridotites with radiogenic Nd isotopic compositions (Fig. 6) can be ascribed to the interaction between asthenospheric melt and peridotites since secondary contamination mentioned above was removed by a combination of leaching and handpicking. The inter-mineral isotopic disequilibrium, i.e., incomplete diffusive re-equilibration within the xenoliths indicates that the interval between the metasomatic event and sampling by basaltic magmas is relatively short. Equilibrium should be established after 30 Ma on a cm scale of mineral (Jagoutz 1988) based on experimental determination of Sr and Sm diffusion coefficients ( $1 \times 10^{-15} \text{ cm}^2/\text{s}$ ) in natural cpx at mantle temperature of 1,200°C (Sneeringer et al. 1984). In other words, the event of asthenospheric melt–peridotite interaction possibly occurred recently (shortly before the eruption of host basalts).

The modification of lithospheric mantle by recent asthenospheric melt–peridotite interaction is progressive and comprehensive from the interior to the northern margin of the NCC (Tang et al. 2008). More intensive modification could make the Hannuoba peridotites more radiogenic Nd than those from Yangyuan and Fanshi (Fig. 6). Since the most depleted sample should have low modal cpx content if there was only one ancient depletion event, the observation that most samples having radiogenic Nd isotopic compositions are high in modal cpx contents (11–15%) may indicate that cpx crystallization is related to the melt infiltration (i.e., more isotopic overprint related to the asthenospheric melt coupled with an increase in modal cpx). The cpx separates have more radiogenic Nd and unradiogenic Sr than the coexisting opx, indicating that the cpx could be newly generated or highly modified by the recent asthenospheric melt–peridotite interaction relative to the opx. Thus, the cpx are more susceptible to the asthenospheric melt–peridotite interaction than the opx. This is consistent with the indication based on the Li partitioning between cpx and opx although the time scales of Li and Sr–Nd disequilibrium may be different due to the vastly faster diffusion of Li relative to Sr and Nd.

#### Origin of Li isotopic fractionation in the peridotites

Diffusion is an important mechanism for the Li isotopic variation in mantle peridotites (Richter et al. 2009). However, the nature of Li diffusion processes, such as the cooling of magmatic systems (Beck et al. 2006; Ionov and Seitz 2008), interaction of peridotites or xenoliths with percolating melts and/or host magmas (Rudnick and Ionov 2007; Magna et al. 2008; Zhang et al. 2010) and recycled melt with low  $\delta^7\text{Li}$  (Nishio et al. 2004; Tang et al. 2007b), is currently disputed although these processes are not mutually exclusive. Given that these processes can

produce isotopic fractionation, it is important to discuss them before considering a possible explanation for our observations.

#### Redistribution of Li during cooling of magmatic system

Basically most of olivines have relatively low Li contents and normal mantle-like  $\delta^7\text{Li}$ , similar to MORB (Tomascak et al. 2008), whereas the cpx and opx have high Li abundances but low  $\delta^7\text{Li}$  (Fig. 8). The low  $\delta^7\text{Li}$  in the pyroxenes could be generated by diffusion-driven kinetic isotope fractionation due to Li ingress from melt or host magma (e.g., Rudnick and Ionov 2007) and/or from coexisting olivine by subsolidus intermineral Li-redistribution during slow cooling (e.g., Ionov and Seitz 2008). This should be a recent event (shortly before emplacement of the xenolith-bearing magma) because the isotopic disequilibrium between olivine and pyroxenes would rapidly disappear or be obscured due to the fast diffusivity of Li at magmatic temperatures (Rudnick and Ionov 2007). For example, Li equilibration of small (1–2 cm width) veins or melt conduits can be achieved within  $10\text{--}10^5$  years at mantle wedge temperature (Halama et al. 2009).

However, the model of cooling of magmatic systems (e.g., Gallagher and Elliott 2009) cannot sufficiently explain the observations in this study. This model describes Li isotopic fractionation by diffusion during the grain-scale redistribution related to cooling. In this model, cpx may have low  $\delta^7\text{Li}$ , while olivine primarily retains normal mantle-like (or high)  $\delta^7\text{Li}$  due to the faster diffusion of  $^6\text{Li}$  than  $^7\text{Li}$  from olivine to cpx during cooling (e.g., Ionov and Seitz 2008). Thus, this model can explain the high  $\delta^7\text{Li}$  in

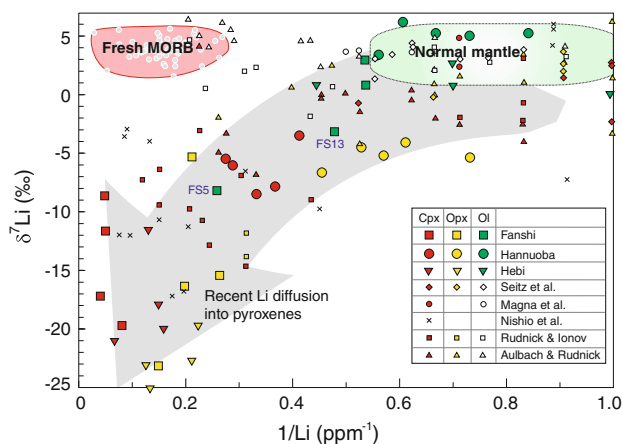
olivine and low  $\delta^7\text{Li}$  in cpx. However, the olivine  $\delta^7\text{Li}$  in a few samples (e.g.,  $-7.9\text{‰}$  in FS5 and  $-3.0\text{‰}$  in FS13), much lower than the normal mantle, is not consistent with the aforementioned model. In addition, the high Li contents (Table 3) and Li partitioning between minerals suggest Li addition possibly by melt infiltration, rather than a simple cooling process.

#### Influx of recycled melt with low $\delta^7\text{Li}$

Several previous studies suggested the existence of recycled materials with low  $\delta^7\text{Li}$  in the mantle (Zack et al. 2003; Nishio et al. 2004; Tang et al. 2007b). One can assume that the  $\delta^7\text{Li}$  of coexisting olivine should be also low if the low  $\delta^7\text{Li}$  of pyroxenes was the effect of low- $\delta^7\text{Li}$  melt. However, the olivines in most peridotites have normal mantle-like  $\delta^7\text{Li}$  (Fig. 8), which does not favor this assumption. Moreover, it has been proposed that dehydration can only produce  $\delta^7\text{Li}$  decrease of  $\leq 3\text{‰}$ , and the deeply subducted eclogites could be higher in  $\delta^7\text{Li}$  than the mantle (Marschall et al. 2007). This is supported by the high  $\delta^7\text{Li}$  of HIMU lavas (Chan et al. 2009; Vlastélic et al. 2009), which are thought to derive from a mantle source into which oceanic crust has been recycled. Thus, this assumption is short of cogent evidence.

#### Interaction of peridotites or xenoliths with percolating melts and/or host magmas

Diffusion-driven kinetic Li isotope fractionation during the Li ingress into minerals from percolating melts or host magmas suggests that the Li enrichment occurred shortly before or coincident with the entrainment into the host magmas and the transport of the xenoliths to the surface (Rudnick and Ionov 2007). This model can explain the relatively high  $\delta^7\text{Li}$  in olivine and low  $\delta^7\text{Li}$  in cpx with high Li abundance since Li diffusion into cpx is faster than into olivine (Dohmen et al. 2010). In order to explore models of late-stage Li enrichments by percolating mafic melts, Magna et al. (2008) studied Li abundances and isotopes in three xenoliths containing quenched mafic melts of mantle origin and found slightly higher Li (2.6–4.5 ppm) than normal mantle (*ca* 1–2 ppm) and only moderately fractionated Li isotopes ( $-3.0$  to  $+2.5\text{‰}$ ) in those melt pockets. The results of Magna et al. (2008) cannot well address our observations: (1) much higher Li abundances and larger fractionation of Li isotopes (Table 3) and (2) the low  $\delta^7\text{Li}$  in olivine ( $-7.9\text{‰}$ ) and cpx ( $-8.4\text{‰}$ ) in the sample FS5, showing an approximate intermineral isotopic equilibrium, which may require a bulk ingress of light Li and a relatively long retention time in the mantle. There are two possibilities accountable for the inconsistency between the previous results and our observations: (1) the mechanism of Li



**Fig. 8** Variation of  $\delta^7\text{Li}$  with Li concentration for minerals in the studied peridotite xenoliths, compared with published data for fresh MORB (Chan et al. 1992; Tomascak and Langmuir 1999, 2008; Elliott et al. 2006) and peridotites (Nishio et al. 2004; Seitz et al. 2004; Magna et al. 2006; Tang et al. 2007b; Rudnick and Ionov 2007; Aulbach and Rudnick 2009). Gray arrow shows the trend for recent Li diffusion into pyroxenes

isotopic fractionation (Li behavior) in mantle peridotites and xenoliths is not very clear and (2) present-day observations are fairly limited, for example, only three pockets were analyzed in the previous study. Thus, the actual fractionation of Li isotopes in mantle peridotites or xenoliths may be still highly unconstrained.

*Combined effects of diffusive kinetic fractionation during melt/fluid-peridotite interaction and cooling of magmatic system*

Based on the aforementioned discussions, our observations may reflect the combined effects of diffusion-driven kinetic fractionation of Li isotopes during melt/fluid-peridotite interactions and the cooling of host magmas. The most likely explanation for the low  $\delta^7\text{Li}$  in the samples FS5 and FS13 is that light Li domains may be existent in the mantle although they cannot persist for extended period of time (Halama et al. 2008; Dohmen et al. 2010). These domains could be produced by diffusion on a large scale of meters because large-scale heterogeneity could survive diffusion of Li isotopes over time scales longer than the small (Vlastélic et al. 2009). Diffusive influx of Li from melt channels into the surrounding lithospheric mantle at depth could produce Li concentration profiles on meter scale, probably similar to the model of alkali diffusion and melt extraction proposed by Lundstrom et al. (2005), who observed that the maximum distance for changes in  $\delta^7\text{Li}$  is around 3 meters. A similar process, Li diffusion from pegmatite into country rock, described by Teng et al. (2006), produced  $\delta^7\text{Li}$  variations to a maximum distance of *ca* 50 m. Therefore, the scale of low- $\delta^7\text{Li}$  domains caused by diffusion of Li from melt channels into wall rock can be tens of meters. Xenoliths, which represent fragments ripped off from the wall rock of melt channels, will record the bulk enrichment and diffusively fractionated  $\delta^7\text{Li}$  (e.g., low  $\delta^7\text{Li}$  in sample FS5). Other samples may be close enough or far enough from the Li source, so that they show normal mantle values or even higher  $\delta^7\text{Li}$  (see Lundstrom et al. 2005). This explanation is consistent with the recent asthenospheric melt–peridotite interaction suggested by the petrology, trace element and Sr and Nd isotopic characteristics of the peridotites from this region.

A very recent study suggested that the effective diffusion coefficients of many elements (e.g., Li, Ca and Y) in olivine fell within a factor of three of the Mg–Fe interdiffusion coefficient (Qian et al. 2010), in agreement with the results from experiments at higher temperatures that the diffusion rate of Li into olivine is similar to that of the divalent cations (Dohmen et al. 2010; Parkinson et al. 2007; Spandler and O'Neill 2010). Thus, the diffusion coefficient of Li can be similar to that of Sr, indicating that Li, Sr and Nd isotope systems in the peridotites could have been reset by the same event of recently occurred asthenospheric melt/fluid-peridotite interaction.

It should be underlined that the diffusive fractionation of Li isotopes on the grain scale during cooling of the xenoliths, due to temperature-dependent partition coefficient of Li (Coogan et al. 2005; Wunder et al. 2006; Gallagher and Elliott 2009), could have further lowered the  $\delta^7\text{Li}$  in the pyroxenes by Li ingress from host magma and coexisting olivines (subsolvus intermineral Li-redistribution). This probably happened during xenolith entrainment, ascent, eruption and cooling of host magma.

*Implication of melt/fluid-peridotite interaction*

The transformation of old lithosphere beneath the NCC is not only the large-scale thinning of the lithosphere but also the great change of the lithospheric mantle from highly refractory to fertile in mineral compositions and from high  $\varepsilon_{\text{Sr}}$  and low  $\varepsilon_{\text{Nd}}$  to low  $\varepsilon_{\text{Sr}}$  and high  $\varepsilon_{\text{Nd}}$  in isotopic compositions (Zhang 2005; Menzies et al. 2007; Tang et al. 2008). Because the peridotite xenoliths hosted in the Cenozoic basalts from the eastern NCC have “oceanic-like” geochemical characteristics (fertile in mineral compositions and radiogenic Nd isotopic compositions), they are considered to represent newly accreted lithospheric mantle (Fan et al. 2000; Xu 2001; Ying et al. 2006). One can speculate that if all the “oceanic-like” mantle peridotite xenoliths are newly accreted, they should be young rather than old, which is conflicting with the facts that the Hannuoba peridotites have Proterozoic Re depletion ages (Gao et al. 2002; Zheng et al. 2007; Zhang et al. 2009), and Yangyuan, Fanshi and Hebi peridotites (Fig. 1) have Neoproterozoic to Paleoproterozoic Re depletion ages (Zheng et al. 2007; Xu et al. 2008a, b). This indicates that not all the peridotitic xenoliths bearing a resemblance to “oceanic-like” mantle are newly accreted and some are still old lithospheric samples. Now the question is what process changed the elemental and isotopic compositions of the old lithospheric mantle?

Asthenosphere–lithosphere and mantle–crust interactions have been used to account for the changes of subcontinental lithospheric mantle beneath ancient cratons (such as Kapvaal) in the world (Downes 2001; Foley 2008), including the NCC (e.g., Menzies et al. 1993). Coupled with previous studies, the Sr–Nd–Li isotopic disequilibria between the peridotite minerals provide further evidence that the lithospheric mantle beneath the NCC experienced multistage melt/fluid-peridotite interactions. During early stage, the initial melt/fluid-peridotite interaction resulted in unradiogenic Nd isotopic compositions in the modified lithospheric mantle; during later stages, asthenospheric melt/fluid interacted with the old peridotites and led to the great change of the lithospheric mantle (Zhang 2005; Tang et al. 2008; Zhang et al. 2008, 2009), concomitant  $\varepsilon_{\text{Nd}}$  increase. Recent melt/fluid-peridotite interaction may also cause the change of mineral  $\delta^7\text{Li}$  recorded by the peridotite xenoliths.



Recent investigations suggest that melt/fluid-rock interactions may be widely existent in the mantle beneath the whole craton, including the northern (Zhang et al. 2003), the eastern (Zhang 2005; Zhang et al. 2010), the southern (Zheng et al. 2006) and the western (Xu et al. 2005) part of the craton. Therefore, melt/fluid-peridotite interaction could be a key mechanism triggering the compositional change and large-scale thinning of the lithospheric mantle.

## Conclusions

The coexisting minerals in the peridotites from the NCC display remarkable Li elemental and Sr–Nd–Li isotopic disequilibria. The cpx have the highest Li contents, followed by opx and olivine, and the mineral Li abundances are significantly higher than the normal mantle. Most olivine  $\delta^7\text{Li}$  are similar to the normal mantle, whereas the  $\delta^7\text{Li}$  of coexisting pyroxenes are very low ( $-3.3$  to  $-23\%$ ), suggesting recent diffusive ingress of Li into the pyroxenes. Two peridotites have olivine  $\delta^7\text{Li}$  of negative values, much lower than the normal mantle, which may reflect the existence of low  $\delta^7\text{Li}$  domain in the mantle, perhaps generated by meter-scale diffusion of Li during melt/fluid-peridotite interaction.

The  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.5123–0.5139) and  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7018–0.7062) in the cpx and opx separates show a large variation, from DM- to EM1-like compositions. The cpx are lower in  $^{87}\text{Sr}/^{86}\text{Sr}$  and slightly higher in  $^{143}\text{Nd}/^{144}\text{Nd}$  than coexisting opx. This Sr–Nd isotopic disequilibrium is more apparent in peridotites with radiogenic Nd isotopic compositions than in those with unradiogenic Nd isotopic compositions. Such an observation suggests a recent interaction between an ancient lithospheric mantle and asthenospheric melt, which

transferred the relatively refractory peridotites with highly radiogenic Sr isotopic compositions to the fertile lherzolites with Sr–Nd isotopic compositions approaching the DM end member, although ancient metasomatic event(s) of small volume LREE-enriched melt(s) were required to produce the original mantle with an EM1 composition before the interaction. In the meanwhile, the recent melt/fluid-peridotite interaction may also cause the intermineral Li elemental and isotopic disequilibria.

Collectively, the lithospheric mantle beneath the NCC has been heterogeneously refertilized by multistage melt/fluid-peridotite interactions with the more comprehensive refertilization from the central craton (Hebi area) toward the craton margin (Hannuoba area), which could be a key mechanism producing the transformation of the lithospheric mantle.

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## Appendix

See Table 5.

**Table 5** Estimated mineral mode (%) and major elemental compositions in the peridotites

Sample	FS5	FS13	FS14	FS19	HB27	HB30	HB80	HB81	D4	D5
Mode										
Olivine	62	66	60	63	70	72	79	73	55	63
Opx	24	21	17	24	27	25	19	24	30	20
Cpx	13	12	8	11	2	1	1	1	13	15
Spinel	1	1	5	2	1	2	1	2	2	2
SiO <sub>2</sub>	45.67	44.85	43.30	45.33	44.15	43.96	43.56	43.66	45.93	45.05
TiO <sub>2</sub>	0.07	0.09	0.03	0.08	0.04	0.01	0.02	0.02	0.10	0.12
Al <sub>2</sub> O <sub>3</sub>	2.16	2.16	3.67	2.39	1.15	1.37	0.75	0.96	3.29	2.67
Cr <sub>2</sub> O <sub>3</sub>	0.32	0.28	0.90	0.53	0.70	0.94	0.62	1.02	0.39	0.57
MgO	40.22	41.99	42.88	41.23	44.89	45.42	46.99	45.91	38.51	40.09
CaO	2.69	2.67	1.77	2.43	0.67	0.42	0.42	0.39	2.87	3.22
MnO	0.12	0.13	0.12	0.14	0.12	0.09	0.12	0.10	0.10	0.12
FeO	8.14	8.30	7.57	7.59	6.60	7.29	7.24	7.24	7.92	7.56
NiO	0.23	0.27	0.36	0.27	0.28	0.28	0.29	0.30	0.24	0.25
Na <sub>2</sub> O	0.20	0.21	0.11	0.17	0.04	0.08	0.01	0.03	0.25	0.27
Total	99.8	100.9	100.7	100.2	99.6	99.9	98.6	99.6	99.6	99.9
Mg#	89.9	90.1	91.1	90.7	92.3	91.9	92.2	92.1	89.7	90.5

Data for D4 and D5 are from Tang et al. (2007a)



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