

Multiple metasomatism in Sulu ultrahigh-P garnet peridotite constrained by petrological and geochemical investigations

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ABSTRACT The pre-pilot hole (PP1) of the Chinese Continental Scientific Drilling Project (CCSD) recovered drill core samples from a 118 m-thick section of peridotites located at Zhimafang in the southern Sulu UHP terrane, China. The peridotites consist of phlogopite-bearing garnet lherzolite, harzburgite, wehrlite and dunite. Some peridotite layers contain magnesite and Ti-clinohumite, and are characterized by LREE and LILE enrichment and HFSE depletion. Phlogopite (Phl) occurs in the peridotite matrix and is LILE-enriched with low Zr/Hf ratios (0.19–0.60). Phlogopite shows a mantle signature in H and O isotopes ($\delta^{18}\text{O}$: +5.4‰ to +5.9‰, and δD : –76‰ to –91‰). Ti-clinohumite (Ti-Chu) is Nb and Ta-enriched and has higher Ti and HREE concentrations than phlogopite. Magnesite (Mgs) occurs as megacrysts, as a matrix phase, and as veins ($\pm\text{Phl} \pm \text{Ti-Chu}$), and contains low REE^{total} contents (<0.3 ppm) with a flat REE pattern. The $\delta^{18}\text{O}$ values (+5.5‰ to +8.0‰) of magnesite are in the range of primary carbonatite, but the $\delta^{13}\text{C}$ values (–2.4‰ to –3.4‰) are slightly more positive than those of the mantle and of primary carbonatite. Petrochemical data indicate that the Zhimafang peridotite was subjected to three episodes of metasomatism, listed in succession from oldest to youngest: (1) crystallization of phlogopite in the mantle caused by infiltration of K-rich hydrous fluid/melt; (2) formation of Mgs and Mgs $\pm$ Phl $\pm$ Ti-Chu veins possibly caused by infiltration of mantle-derived carbonatitic melt with a hydrous silicate component; and (3) replacement of magnesite, garnet and diopside by dolomite and secondary hydrous phases caused by a crust-related, CO₂-bearing, aqueous fluid. Stable isotopic compositions of phlogopite and magnesite indicate metasomatic agents for events (1) and (2) are from an enriched mantle. Multiple metasomatism imposed on mantle peridotite of variable composition led to significant compositional heterogeneity at all scales within the Zhimafang peridotite.

Key words: carbonate; garnet peridotite; metasomatism; pre-pilot hole; stable isotope.

INTRODUCTION

Metasomatism, both cryptic and patent, has been increasingly recognized in ultramafic xenoliths from kimberlites and basalts and in orogenic peridotites from high-pressure (HP)/ultrahigh-pressure (UHP) metamorphic terranes. The metasomatism of orogenic peridotites may take place in a subducting slab, in the mantle wedge above the slab, or in the crust (e.g. Brueckner & Medaris, 1998; Zanetti *et al.*, 1999; Lee *et al.*, 2000b; Brueckner *et al.*, 2002; Kogarko *et al.*, 2001; Laurora *et al.*, 2001; Rampone & Morter, 2001; Downes *et al.*, 2004). Hydrous phases and carbonates are widespread in the Dabie-Sulu garnet peridotites (Zhang *et al.*, 1995, 2004; Liou & Zhang, 1998). The formation of hydrous phases, and the inconsistencies posed by the depleted ‘fertile’ major

element concentrations and the enriched LREE and LILE trace element concentrations for peridotite have commonly been attributed to metasomatism by hydrous fluids or water-rich melts (Peacock, 1990; Tatsumi & Eggins, 1995; Jahn, 1998; Zanetti *et al.*, 1999). Primary carbonates (calcite, dolomite and magnesite) were identified in mantle-derived rocks from various tectonic environments suggesting a different agent for metasomatism (e.g. McGetchin & Besancon, 1973; Zhang & Liou, 1994; Zhang *et al.*, 1995; Gorrington & Kay, 2000; Lee *et al.*, 2000b; Kogarko *et al.*, 2001; Laurora *et al.*, 2001). Carbonatites are frequently invoked as the metasomatizing agents in the mantle and some peridotites show features consistent with carbonatitic metasomatism (Bizimis *et al.*, 2003). High whole-rock LILE and LREE and low HFSE concentrations, high Ca/Al, Zr/Hf, Nb/Ta and very low Ti/Eu

ratios have been considered to be characteristics of carbonatitic metasomatism (Gorring & Kay, 2000; Laurora *et al.*, 2001). However, there is a long-standing debate about whether carbonatite melts are products of liquid immiscibility or can be derived directly from melting of the mantle (or both) (Downes *et al.*, 2005).

The Zhimafang garnet peridotite from Donghai, within the southern Sulu UHP terrane, has been studied petrochemically (Yang *et al.*, 1993; Zhang *et al.*, 1994, 2000; Zheng *et al.*, 2005) and geochronologically with Sm–Nd and Rb–Sr analyses (Yang & Jahn, 2000) using a few core samples provided by the local county geological team. These investigations indicated the Zhimafang peridotite was derived from the mantle, was subjected to UHP metamorphism, and underwent metasomatism. A Sm–Nd mineral whole-rock isochron age of 378 ± 24 Ma is not considered meaningful because of possible isotopic disequilibrium (Yang & Jahn, 2000). Many fresh garnet peridotite samples from Zhimafang have been recovered recently from the first pre-pilot hole (PP1) of the Chinese Continental Scientific Drilling Project (CCSD) (Fig. 1); the core samples of peridotite contain abundant, randomly distributed magnesite, phlogopite and Ti-clinohumite (Ti-Chu, other mineral abbreviations after Kretz, 1983). In the present study a petrological study of peridotites is combined with geochemical data, including trace element and stable isotopic compositions of hydrous phases and carbonate, to constrain the origin of carbonate and hydrous phases and the nature of metasomatism that formed these phases.

The details of petrogenesis are described in the paper by Yang *et al.* (2007).

SULU UHP TERRANE AND PP-1 UHP GARNET PERIDOTITE

The Triassic Sulu UHP terrane is an eastern extension of the Qinling–Dabie collision zone between the Yangtze and Sino-Korean cratons, and consists of a HP belt and a UHP belt (Fig. 1). The UHP belt is composed of gneiss, amphibolite, and minor marble and quartzite, which were intruded by Mesozoic granites. Coesite-bearing eclogites occur abundantly as lenses and layers in gneiss, and also in minor amounts in marble and ultramafic rocks. The protolith ages of most eclogites and their country-rock gneisses range from 800 to 600 Ma, and their UHP metamorphic ages are 240–220 Ma (e.g. Li *et al.*, 1993; Ames *et al.*, 1996; Liu *et al.*, 2004, 2005). Widespread orogenic peridotite bodies occur as blocks and lenses in gneiss, and rarely in eclogite. Except for the Macaokuang harzburgite–dunite body, all Sulu peridotites contain garnetiferous assemblages that recrystallized at 750–950 °C and 4.0–6.7 GPa (Yang *et al.*, 1993; Zhang *et al.*, 1994, 2000, 2003, 2005a; Yang, 2006).

The 432.1 m deep PP1 drill hole of the CCSD recovered peridotite cores from 138.5 to 256.4 m depths and gneissic rocks above and below the peridotites. The peridotite samples consist of lherzolite (64 vol.%), harzburgite (17 vol.%) and subordinate wehrlite and dunite, and were subjected to Triassic (221 ± 3 Ma) UHP metamorphism (Zhang *et al.*, 2005b). All PP1

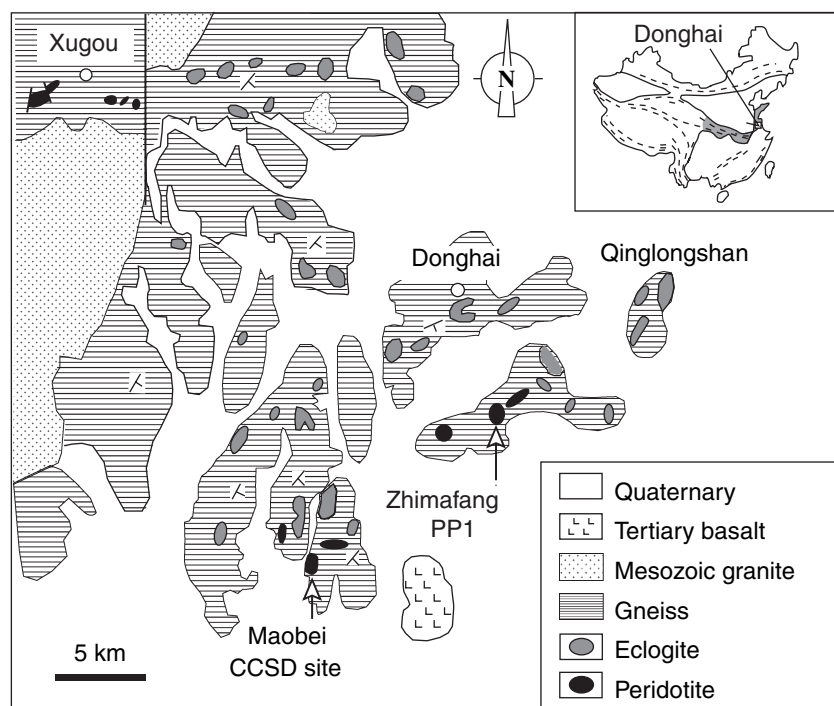


Fig. 1. Geological sketch map of the Donghai area showing the location of the Dabie–Sulu UHP terrane (shaded area in the inset) and locality of the Zhimafang peridotite body and PP1 drill hole.

peridotite core samples contain trace to >15 vol.% phlogopite; more than 90% of the peridotites contain 2–15 vol.% garnet. Except for the serpentinized cores at the contacts with gneiss, most peridotites are fresh without or with little serpentinization, and consist of variable amounts of olivine, enstatite, diopside, garnet, chromite, and phlogopite with additional Ti-clinohumite, magnesite, apatite and zircon in some layers. Two or more mineral assemblages may occur within an individual thin section, such as Ol + Phl (dunite) and Ol + En + Phl (harzburgite). Garnet lherzolite, the most abundant rock type, shows a porphyroblastic texture (Fig. 2a), with rounded coarse-grained garnet of 2 to >10 mm set in a fine-grained (average 1.5 mm) matrix of olivine (Fo_{91–93}), enstatite (En_{92–93}), diopside [Mg/(Mg + Fe): 0.93–0.95] and garnet. Garnet (Ura_{4–12}Prp_{62–73}Alm_{14–24}Grs_{1–10}Sps_{0–2}) is rimmed by amphibole + Cr-spinel (or Cr-rich magnetite) fibres with or without an outer rim of phlogopite. Some garnet in altered rocks, however, is totally replaced by

chlorite ± tiny calcite or by euhedral chlorite flakes, phlogopite and opaque dust (Cr-magnetite). Diopside is overprinted by tremolite and Cr-spinel in retrogressive peridotites. Some enstatite grains are partially replaced by talc. Ti-clinohumite and carbonate are heterogeneously distributed in the peridotite (Fig. 2b), indicating that this body has been subjected to various degrees of metasomatism. The occurrences and the compositions of these phases are described below.

Hydrous minerals

Phlogopite is the dominant hydrous mineral in the Zhimafang peridotite, and shows three occurrences: as matrix (Phl-1); in magnesite veins (Phl-2); and as a secondary phase after garnet (Phl-3). The Phl-1 and Phl-2 occurrences are characterized by high MgO content [24.95–26.66 wt%; Mg/(Fe + Mg) = 0.94–0.95] and low TiO₂ (0.00–0.19 wt%) and Cr₂O₃ (0.07–0.49 wt%) (Table 1). Al₂O₃ contents vary from

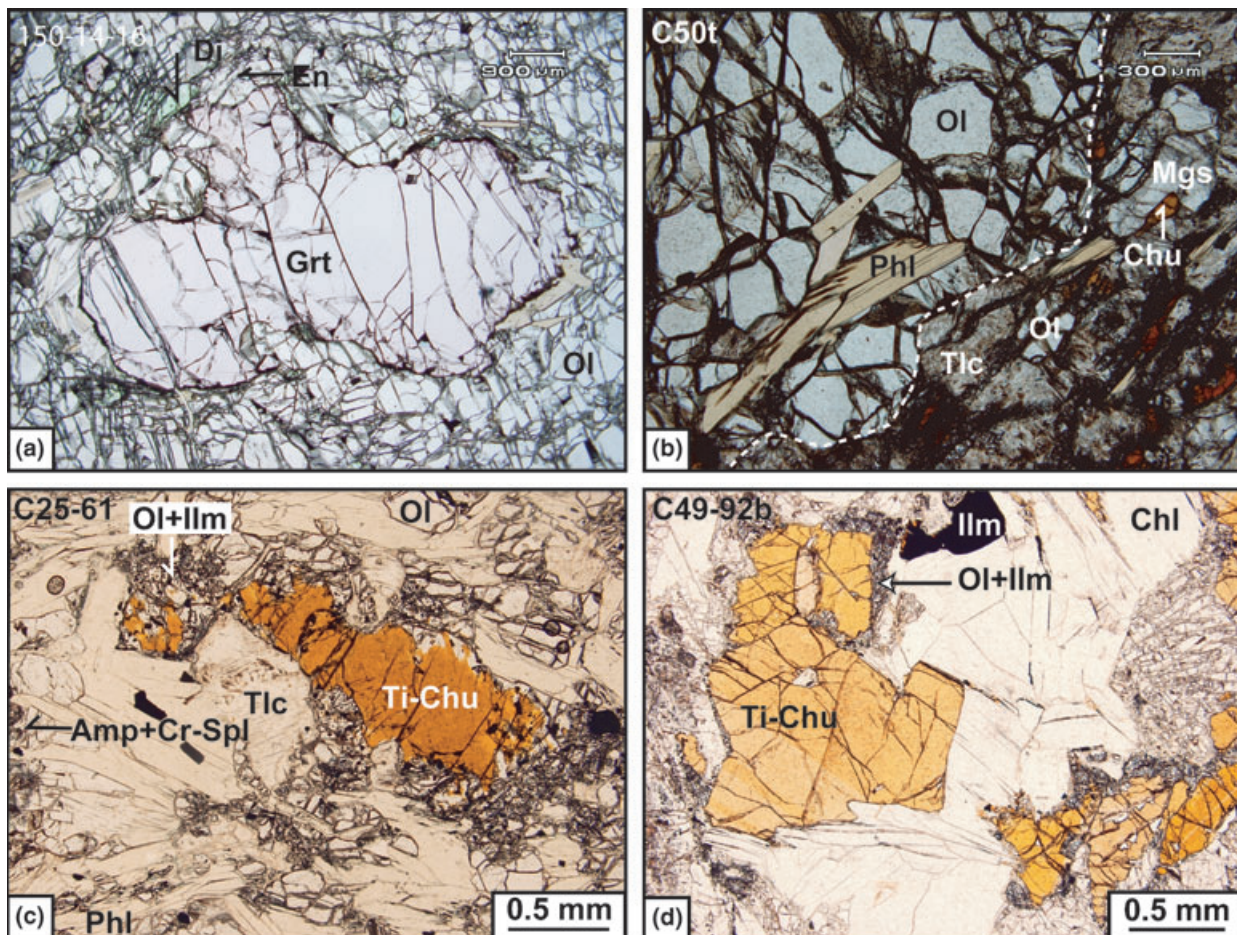


Fig. 2. Photomicrographs showing porphyroblastic garnet lherzolite (a) and occurrences of Ti-clinohumite and magnesite (b–d); all are plane polarized. (b) Metasomatic dunite, left side is Phl-bearing dunite, right side is a vein of Mgs + Phl + Ti-Chu; in the right domain, olivine is replaced by talc with or without relics. (c) Ti-clinohumite (median size, some grains of >4 mm are out of picture) in wehrlite is replaced by Ol + Ilm at its margins, and diopside by Amp + Cr-Spl. (d) Ti-clinohumite is in the vein of Ti-Chu + Chl; chlorite is a pseudomorph after phlogopite.

Table 1. Average compositions of phlogopite and Ti-clinohumite.

Sample:	C24-59				C25-60	C25-61	C27-64		C31t	C41-83		C49-92a	C50-93		C50t
Rock:	Grt lher				Grt lher	wehr	dun + wehr		mt-band	grt lher		dun	dun		dun
Mineral:	Phl	Phl	Ti-Chu	Ti-Chu	Phl	Ti-Chu	Phl	Ti-Chu	Phl	Phl	Phl	Phl	Phl	Ti-chu	Phl
Note:	mtx	gs	mtx	inc	mtx	por	mtx	por	vein	mtx	inc	in mgs	mtx	mtx	vein*
SiO ₂	43.04	37.89	37.60	37.42	42.30	36.68	42.60	37.10	41.63	42.98	42.58	43.07	42.39	36.59	42.56
TiO ₂	0.00	0.13	2.70	3.21	0.09	2.46	0.12	1.96	0.08	0.01	0.00	0.04	0.03	2.49	0.11
Cr ₂ O ₃	0.26	1.22	0.08	0.06	0.36	0.11	0.26	0.18	0.27	0.07	0.09	0.27	0.07	0.03	0.21
Al ₂ O ₃	12.21	17.78	0.01	0.01	13.22	0.00	11.59	0.01	12.09	10.99	11.05	10.91	11.37	0.00	11.68
FeO	2.48	2.43	9.17	8.77	2.55	9.92	2.68	8.99	3.01	2.45	2.44	2.66	2.83	9.39	2.34
MnO	0.00	0.00	0.02	0.08	0.00	0.11	0.00	0.11	0.02	0.00	0.00	0.08	0.00	0.12	0.00
MgO	25.98	23.26	47.72	47.26	26.20	48.02	26.34	48.98	26.56	26.50	26.59	26.00	26.65	48.13	27.12
CaO	0.00	0.00	0.00	0.00	0.03	0.00	0.06	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00
Na ₂ O	0.54	0.77	0.00	0.00	0.71	0.04	0.47	0.00	0.31	0.48	0.39	0.31	0.45	0.01	0.43
K ₂ O	8.43	8.55	0.00	0.00	8.60	0.00	9.23	0.00	9.02	8.96	9.19	9.18	9.46	0.00	9.71
Totals	92.94	92.02	97.30	96.82	94.04	97.32	93.36	97.34	92.98	92.45	92.34	92.56	93.25	96.75	94.15
Si	3.061	2.747	4.040	4.036	2.984	3.967	3.041	3.991	2.988	3.085	3.067	3.095	3.036	3.97	3.017
Ti	0.000	0.007	0.218	0.261	0.005	0.200	0.006	0.159	0.004	0.001	0.000	0.002	0.002	0.20	0.006
Cr	0.015	0.070	0.007	0.005	0.020	0.009	0.015	0.015	0.015	0.004	0.005	0.015	0.004	0.00	0.012
Al	1.024	1.519	0.001	0.001	1.099	0.000	0.975	0.001	1.023	0.930	0.938	0.924	0.960	0.00	0.976
Fe	0.148	0.147	0.825	0.791	0.150	0.897	0.161	0.809	0.181	0.147	0.147	0.160	0.170	0.85	0.139
Mn	0.000	0.000	0.002	0.008	0.000	0.010	0.000	0.010	0.001	0.000	0.000	0.005	0.000	0.01	0.000
Mg	2.754	2.513	7.644	7.598	2.755	7.742	2.802	7.855	2.842	2.836	2.854	2.785	2.845	7.79	2.866
Ca	0.000	0.000	0.000	0.000	0.002	0.000	0.005	0.000	0.000	0.000	0.000	0.003	0.000	0.00	0.000
Na	0.075	0.108	0.000	0.000	0.096	0.007	0.066	0.000	0.043	0.067	0.055	0.043	0.063	0.00	0.059
K	0.765	0.790	0.000	0.000	0.774	0.000	0.840	0.000	0.826	0.820	0.844	0.842	0.864	0.00	0.878
Total	7.840	7.901	12.738	12.700	7.887	12.832	7.911	12.842	7.923	7.891	7.911	7.875	7.944	12.83	7.952

Formula of Phl and Ti-Chu is based on O₁₁ and O₁₇, respectively. dun, dunite; lher, lherzolite; wehr, wehrlite; mt-band, metasomatic band; Ti-Chu, Ti-clinohumite; inc, inclusion; gs, symplectite after garnet; mtx, matrix; por, porphyroblast.

10.99 to 14.35 wt%. In comparison with Phl-1 and Phl-2, Phl-3 has much higher contents of Al₂O₃ (17.78 wt%) and Cr₂O₃ (1.22 wt%), and lower contents of SiO₂ and MgO.

Ti-clinohumite is minor, and present in only a few Phl-rich peridotites. Three occurrences are identified: (1) as minute inclusions (Ti-Chu-pre1) in garnet, pyroxene, olivine and rarely in magnesite; (2) as fine- to coarse-grained crystals in the matrix (Ti-Chu-1) (Fig. 2c); and (3) as a vein mineral (Ti-Chu-2) in veins of Mgs–Ti-Chu–Phl or Ti-Chu–Chl. Chlorite is probably a pseudomorph after phlogopite. A lot of fine-grained Ti-Chu and Tr + Spl pseudomorphs after

diopside occur near the veins (Fig. 2d). The TiO₂ content of Ti-Chu ranges from 1.96 to 3.58 wt% (Table 2), $X_{\text{Fe}} = 0.10\text{--}0.11$ and $X_{\text{Ti}} = 0.16\text{--}0.29$. No F was detected by Energy dispersive spectrometer, EDS.

Carbonates

Magnesite in the Zhimafang peridotite occurs (1) as megacrysts (Mgs-1, Fig. 3a), (2) as a relatively fine-grained matrix phase (Mgs-1), and (3) as a vein mineral (Mgs-2) in harzburgite, wehrlite, dunite and rarely in lherzolite. Megacrystic magnesites up to 5 × 15 mm in size contain inclusions of phlogopite (common) and

Table 2. Average compositions of carbonate^a.

Sample:	C24-59	C25-60	C26-62	C27-64			C31t		C41-83	C49-92		C50-93		C50t
Mineral:	Dol	Dol	Mgs	Mgs	Dol	Cal	Mgs	Dol	Mgs	Mgs	Dol	Mgs	Mgs	
Note:	mtx	mtx	mtx	mtx	sec	sec	vein	sec	vein	mega	sec	mtx-c	mtx-r	vein ^b
FeO	0.33	0.79	3.91	4.23	0.76	0.23	5.02	1.22	3.94	4.81	0.89	4.84	4.97	5.07
MnO	0.42	0.04	0.065	0.11	0.26	1.45	0.11	0.10	0.16	0.20	0.09	0.05	0.12	0.11
MgO	22.02	21.56	38.93	38.70	21.32	1.61	43.43	23.29	42.66	38.07	21.15	38.27	38.33	43.15
CaO	31.33	29.82	0.13	0.11	30.52	58.80	0.11	32.77	0.21	0.11	31.56	0.06	0.08	0.16
Total	54.09	52.21	43.035	43.14	52.87	62.08	48.67	57.38	46.98	43.19	53.69	43.22	43.51	48.50
Fe	0.004	0.010	0.053	0.058	0.010	0.003	0.061	0.014	0.049	0.066	0.011	0.066	0.068	0.062
Mn	0.005	0.001	0.001	0.002	0.003	0.018	0.001	0.001	0.002	0.003	0.001	0.001	0.002	0.001
Mg	0.490	0.496	0.943	0.939	0.486	0.036	0.936	0.489	0.945	0.929	0.476	0.932	0.929	0.934
Ca	0.501	0.493	0.002	0.002	0.500	0.943	0.002	0.495	0.003	0.002	0.511	0.001	0.001	0.003
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Mg/Fe + Mg			0.945	0.942			0.939		0.950	0.933		0.933	0.932	0.938

mtx, matrix; c, core; r, rim; sec, after magnesite.

^aCation calculation is based on total cation = 1.

^bIn the vein of Mgs + Phl + Ti-Chu.

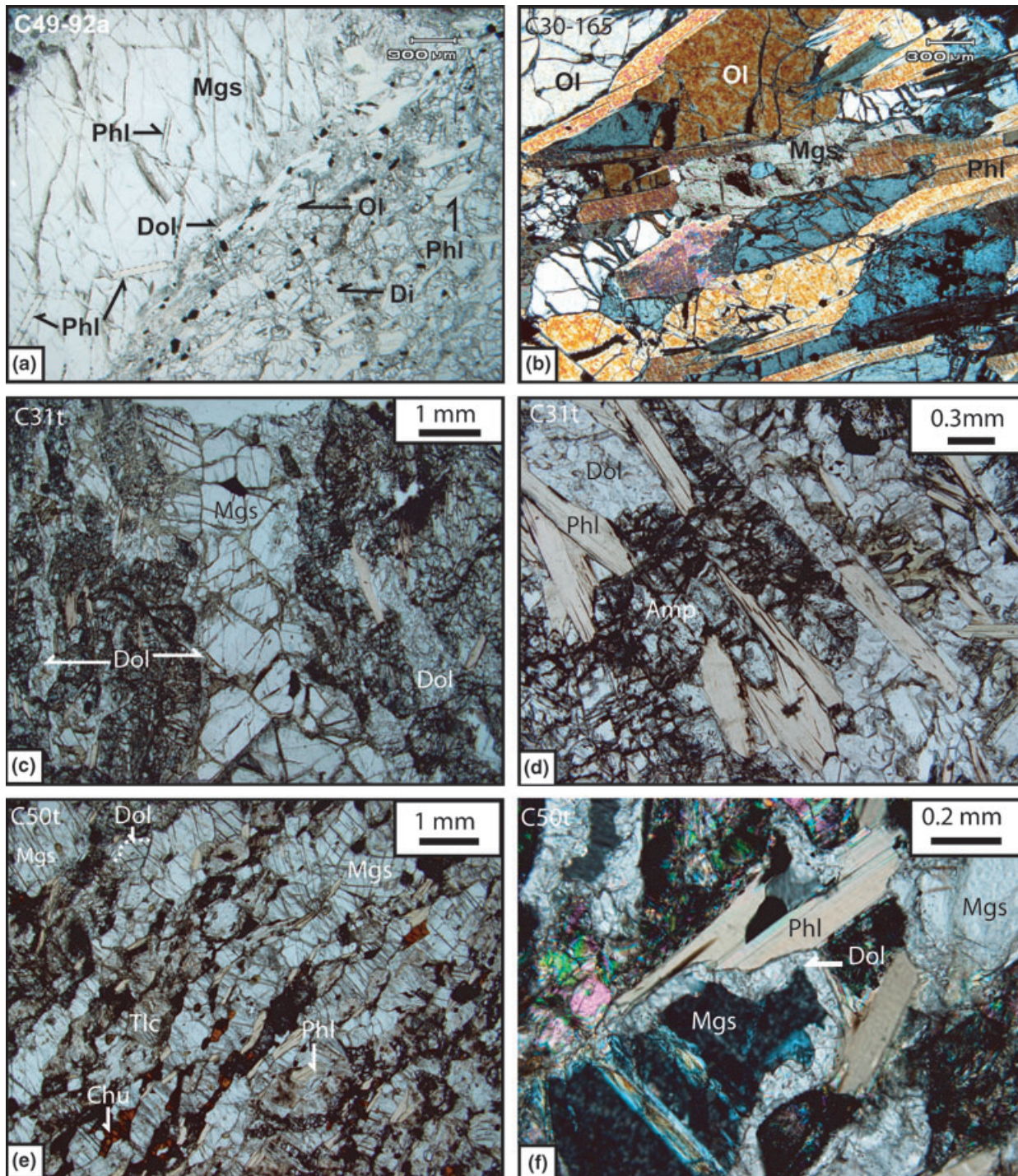


Fig. 3. Photomicrographs showing occurrences of magnesite in the Zhimafang peridotite, all images are plane polarized except for (b) and (f). (a) Megacrystal magnesite in the matrix of olivine, diopside and phlogopite. Magnesite contains phlogopite inclusions. (b) Magnesite occurs as a matrix phase in Phl-rich peridotite (crossed polars). (c) Magnesite vein in a metasomatic band. Fine-grained, well recrystallized dolomite aggregates distributed along vein's margins; both sides of vein show fine-grained dolomite packets + phlogopite with relict magnesite. (d) Large view of dolomite packets in Fig. 3c; secondary amphibole is also present in the domain. (e) Vein consisting of Mgs + Phl + Ti-Chu in dunite shown in Fig. 2b. (f) Large view of Fig. 3e showing magnesite rimmed by dolomite (crossed polars).

Ti-clinohumite (rare), and are partially rimmed by fine-grained dolomite. Matrix magnesite is smaller in size than those in veins, ranging from 0.4 to 1.2 mm, and

shows equilibrium with other peridotitic phases (Fig. 3b). Magnesite veins 2–6 mm wide are composed of coarse-grained crystals 0.9–5 mm in diameter. In

most cases, fine-grained (0.05–0.2 mm in size), well-recrystallized aggregates of dolomite develop along the margins of magnesite veins or occur as small veins or packets with or without magnesite relics in the peridotite (Fig. 3c,d). Some magnesite veins also contain up to 10 vol.% Ti-clinohumite and phlogopite (e.g. sample C50t, Fig. 3e). Magnesite in the multi-mineral veins ranges from 0.5 to 1 mm in size, smaller than in pure magnesite veins (Fig. 3e,f). In patent metasomatic bands or domains, secondary tremolite and talc are associated with dolomite and the Ti-clinohumite is replaced by ilmenite and olivine at its margins.

The average compositions of carbonates are shown in Table 2. Magnesite, including megacrysts, and that from veins and matrix are nearly Ca-free (CaO, 0.06–0.23 wt%) and have high Mg/(Mg + Fe) ratios of 0.93–0.95; some matrix and megacryst magnesite shows slightly lower Mg/(Mg + Fe) values of 0.93. Fine-grained dolomite rims after magnesite contain 0.76–1.22 wt% FeO, and secondary calcite contains minor MnO (1.45 wt%) and MgO (1.61 wt%).

BULK-ROCK GEOCHEMISTRY

Analytical method

Major and trace elements of whole rock were analysed at the National Analytical Center, Chinese Academy of Geological Sciences (CAGS). Analyses of most major elements were carried out on a fused glass disc by X-ray fluorescence (XRF, Rigaku 3080E) and FeO, H₂O⁺ and CO₂ by ICP-AES, JIA IRIS; analytical uncertainties for all major elements are <0.5%. The samples for trace element analyses (Zr, Nb, V, Cr, Sr, Ba, Ni, Rb and Y) were made as a compressed powder discs and analysed by XRF (Rigaku-2100) with analytical uncertainties of <3% except Ba (<5%). Other trace elements were analysed by ICP-MS, TJA-ExCell; the uncertainties are 1–5% for elements of >1 ppm or up to 5–10% for elements of <1 ppm. Rare earth elements (REE) were separated using cation exchange techniques, and their analytical uncertainties are 10% for REE with abundances <10 ppm, and ~5% for those >10 ppm.

Results

The data on major and trace elements of whole rocks are listed in Table 3. Three major elements (Al₂O₃, CaO and Na₂O) v. MgO plots of six representative carbonate and hydrous phase-bearing peridotites are shown in Fig. 4(a). The six samples show a wide compositional range in major elements and show a pronounced negative correlation of these elements with MgO content. These relationships suggest the peridotites were somewhat to extremely depleted in Al₂O₃, CaO and Na₂O presumably by the extraction of melts. Most peridotites, however, are depleted in TiO₂, and enriched in K₂O (>0.05 to 3.22 wt%) compared with

Table 3. Major (wt%) and trace (ppm) element analyses of representative PPI peridotite.

Sample: Rock:	C25-60 grt-lher	C25-61 wehr	C27-63 grt-lher	C27-64 dun + wehr	C41-83 grt-lher	C50-93 dunite
SiO ₂	41.93	42.08	42.71	42.21	42.16	36.60
TiO ₂	0.03	0.30	0.01	0.02	0.01	0.01
Cr ₂ O ₃	0.42	0.39	0.40	0.47	0.39	0.44
Al ₂ O ₃	3.55	3.31	1.91	1.31	2.18	0.52
FeO [†]	7.30	6.65	6.69	7.32	6.60	16.07
MnO	0.12	0.10	0.11	0.12	0.11	0.17
MgO	38.17	34.91	43.92	45.00	39.55	40.97
CaO	2.41	3.15	1.02	0.73	2.32	0.25
Na ₂ O	0.24	0.20	0.06	0.11	0.09	0.03
K ₂ O	0.46	3.09	0.23	0.06	0.37	0.40
NiO	0.20	0.19	0.28	0.24	0.22	0.32
LOI	4.58	3.98	2.70	1.90	5.72	2.42
Total	99.41	98.35	100.04	99.49	99.72	98.20
Rb	18.30	79.30	5.76	2.08	7.23	13.70
Ba	337.00		289.00	109.00	229.00	
Th	10.60	10.30	1.02	1.02	2.71	0.74
U	0.71	1.96	0.16	0.06	0.20	0.17
Ta	0.21	0.57	0.01	0.14	0.33	0.09
Nb	0.41	6.86	0.18	0.37	1.86	0.58
La	2.96	34.90	1.61	10.60	5.30	5.50
Ce	7.20	67.60	3.01	17.40	12.50	19.70
Sr	62.20	441.00	51.10	25.30	35.10	236.00
Nd	2.23	27.80	1.11	7.53	3.99	2.01
Zr	3.01	49.60	7.00	0.86	2.16	2.67
Hf	0.20	3.65		0.04	0.15	0.03
Sm	0.05	5.13	0.20	1.52	0.78	0.36
Eu	0.18	1.37	0.08	0.37	0.25	0.18
Gd	0.61	3.89	0.21	0.74	0.07	0.43
Dy	0.86	1.91	0.18	1.22	0.49	0.28
Ho	0.24	0.41	0.05	0.29	0.12	0.07
Er	0.46	0.73	0.09	0.53	0.22	0.12
Y	4.71	9.40	1.02	6.70	2.48	1.57
Yb	0.60	0.68	0.12	0.60	0.25	0.15
Lu	0.10	0.11	0.02	0.09	0.04	0.03
Sc	19.70	19.10	6.70	11.10	13.40	7.37
V	30.90	60.00	28.70	27.10	28.00	44.70
Co	88.10	87.80	54.30	110.00	85.60	194.00
Ca/Al	1.4	1.3	0.7	0.8	1.4	0.7
Nb/Ta	2.0	12.0	18.0	2.6	5.6	6.4
Th/U	14.9	5.3	6.4	17.0	13.6	4.4
Zr/Hf	15.1	13.6		21.5	14.4	89.0
Ti/Eu	1000.0	1312.8	749.4	324.3	239.8	333.1

Rock abbreviations are same as Table 2.

primitive mantle; neither TiO₂ nor K₂O show a correlation with MgO content (Li *et al.*, 2003). All rocks, either with or without carbonate, Phl-rich or Phl-poor, show LREE-enriched, slightly to highly fractionated REE patterns with (La/Yb)_N ratios of 3.18–52.99. HREE, however, are flat or slightly increase from Er to Lu. These geochemical characteristics suggest that all peridotites experienced metasomatism some time after their depletion (Li *et al.*, 2003). ICP-MS trace element analyses of the six carbonate and hydrous phase-bearing peridotites are characterized by very low Ti/Eu (234–1313), high Zr/Hf (14–89), and variable Ca/Al (0.65–1.44) and Nb/Ta (2–18) ratios (Table 3, Figs 4b & 5). Total REE contents of these rocks, even though they were collected from the same depth (e.g. C25-60 with C25-61, and C27-63 with C27-64) show pronounced variations in chemistry due to variable contents of modal minerals and variable extents of metasomatism. Samples C25-61 (Phl-rich, Ti-Chu- and Ap-bearing wehrilite) and C27-63 (Phl- and

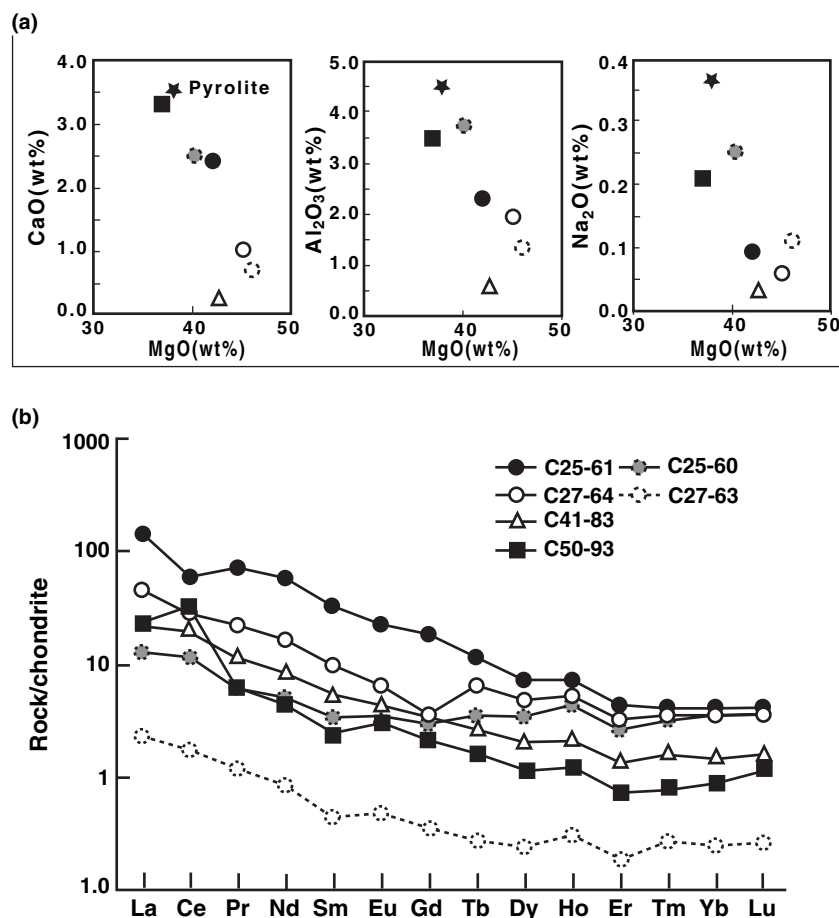


Fig. 4. (a) Major elements v. MgO plots of six representative metasomatized PP1 peridotites. (b) REE patterns for the six peridotites, which show a clear REE variation within short distances from 155 m (sample C25-60) to 159 m (sample C27-63). C25-60, C27-63 and C41-83: Grt lherzolite; C25-61, Phl-rich, Ti-Chu-bearing wehrlite; C27-63, Phl-bearing peridotite (Phl-bearing dunite + Phl-rich wehrlite); C50-93, Mgs-bearing dunite. All abundances normalized to the chondrite composition of Sun & McDonough (1989).

Mgs-bearing Grt-lherzolite) have, respectively, the highest and lowest total REE contents among all PP1 peridotites (Fig. 4b). Wehrlite (C25-61), Grt-lherzolites (C41-83 & C27-63) and Mgs-rich dunite (C50-93) have roughly parallel, LREE-enriched patterns except C25-61 with negative and C50-93 with positive Ce anomalies. Garnet-lherzolite C25-60 and peridotite C27-64 (Phl-bearing dunite + Phl-rich wehrlite bands) display wide v-shaped REE pattern, with REE decreasing from La to Gd, slightly increasing from Gd to Lu, although there is a decrease from Ho to Er. These features clearly indicate that these rocks have been subjected to metasomatism by LREE-enriched fluids. All measured trace elements of these peridotites are plotted in Fig. 5. These peridotites are LILE- (such as Rb & Ba) and LREE-enriched, and have low HFSE concentrations (e.g. Nb, Zr, Hf & Ti) with negative Nb, Zr and Ti anomalies relative to LILE and LREE suggesting carbonatitic metasomatism (Gorring & Kay, 2000; Laurora *et al.*, 2001). Potassium abundances vary with phlogopite content [$(K)_N = 5-100$]. Some peridotites (e.g. C41-83 & C27-64) display negative Sr anomalies whereas no negative Sr anomalies occur in other samples. These characteristics indicate a complex metasomatic history.

TRACE ELEMENTS OF PHLOGOPITE, Ti-CLINOHUMITE AND CARBONATE

Analytical method

In situ trace element analyses of selected hydrous and carbonate phases were conducted at the University of Saskatchewan laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) laboratory using a Micromass Platform ICP-MS coupled with a CETAC LSX-200 266 nm Nd:YAG laser ablation system. The spot sizes of ablation varied from 50 to 200 μ m in diameter depending on the grain size and homogeneity, although smaller spot size of 20 μ m were attempted on fine-grained dolomite. The analysis of each mineral was preceded by (1) measurement of background counts and (2) analysis of NIST-612 and BCR-2 glasses and ended with re-analysis of NIST-612 and BCR-2 glasses. Data reduction of the ICP-MS signals included: (1) subtraction of background counts and (2) calibration using NIST-612 as an external standard. The CaO content of minerals determined by electron microprobe analysis, was used as an internal standard for Ca-bearing minerals, whereas Fe was used as the internal standard for Ca-poor minerals.

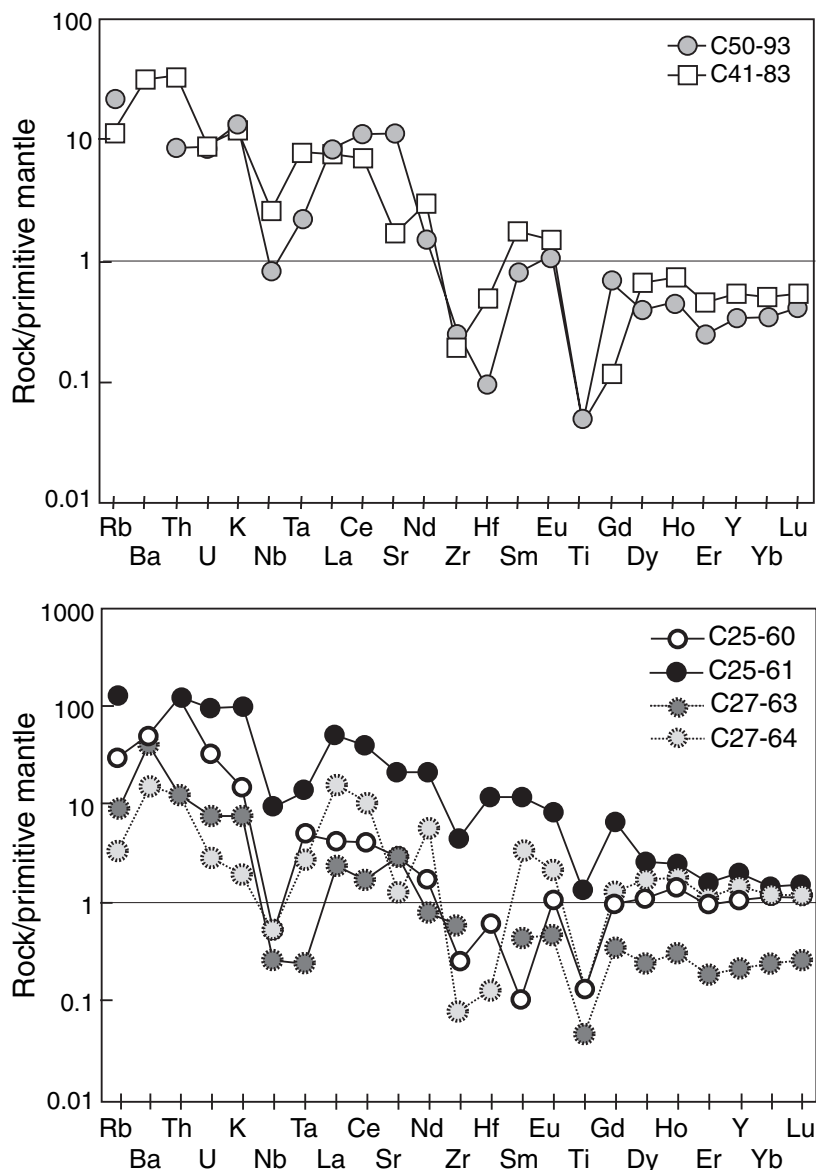


Fig. 5. Primitive mantle normalized trace element patterns of selected PP1 peridotites. The primitive mantle composition is after Sun & McDonough (1989).

Detection limits for each individual laser ablation ICP-MS analysis were calculated from the Ar-gas background and apparent sensitivity of the calibration standard following the approach of Longerich *et al.* (1996). For example, detection limits are approximately 2 ppm for Sc but vary from 0.01 to 0.05 ppm for individual REE. Analytical results and recommended values for BCR-2 glass (used as a quality-control standard; Govindaraju, 1994) show that agreements are better than 5% for all REE, Sr, Y, Zr and Th, 10% for Nb and Ba, and 20% for Sc, V and Hf.

Results

Trace element abundances of magnesite, dolomite, phlogopite and Ti-clinohumite are shown in Table 4.

All minerals except dolomite are characterized by low total REE contents: Mgs, 0.17–0.29, Phl, 2.43–3.97, Ti-Chu, 0.73 and Dol, 106–117 ppm. The low total REE content of magnesite is similar to those of many carbonates from mantle xenoliths worldwide (Lee *et al.*, 2000b). These minerals display distinct REE and trace element patterns (Figs 6 & 7). Phlogopite is characterized by negative Ce and positive Eu anomalies; if the anomalies are ignored it would have a sinusoidal REE pattern. As shown in the primitive mantle normalized trace element pattern (Fig. 7), phlogopite is extremely enriched in Ba and Th with abundances of 2100–2556 ppm [(Ba)_N = 308–365] and 5.65–108.26 ppm [(Th)_N = 66–1273], respectively. In addition, phlogopite has a negative Nb anomaly and low Zr/Hf ratios (0.19–0.60) in comparison with carbonates (11.61–35.00). For Ti-clinohumite, the abundances

Table 4. Trace element analyses of carbonate and hydrous minerals (ppm).

Sample:	C31t					C50t			
Rock:	mt-band					dunite			
Mineral: Occurrence:	Mgs-1 vein	Mgs-2 vein	Dol-1 sec	Dol-2 sec	Phl matrix	Mgs-1 vein	Mgs-2 vein	Phl matrix	Ti-Chu vein ^a
Ti	0.00	0.00	59.95	59.95	119.9	0.00	0.00	359.7	18105
Sc	0.66	0.62	53.29	60.19	3.21	1.32	1.04	3.77	<17.38
V	0.02	0.03	117.05	140.82	23.43	0.04	0.04	14.53	89.28
Sr	0.56	0.55	225.06	249.37	9.23	0.87	0.90	11.27	6.65
Y	0.03	0.03	12.88	15.86	0.30	0.04	0.05	0.70	3.12
Zr	2.80	2.49	5.92	7.49	0.49	3.13	3.45	3.05	13.02
Nb	0.01	0.02	0.86	1.12	1.25	0.02	0.03	1.86	84.80
Ba	3.75	3.99	7.20	19.79	2152.05	6.18	6.33	2556.33	3.65
La	0.04	0.03	7.17	5.46	0.49	0.05	0.06	0.64	0.14
Ce	0.06	0.07	25.46	28.97	0.20	0.11	0.11	0.43	0.12
Pr	0.01	0.01	6.49	7.19	0.09	0.01	0.01	0.13	0.03
Nd	0.03	0.04	36.18	39.18	0.60	0.06	0.05	0.60	<0.35
Sm	0.01	0.01	12.25	13.75	0.14	0.01	0.01	0.17	<0.15
Eu	0.00	0.00	2.77	3.16	0.51	0.01	0.01	0.96	<0.05
Gd	0.01	0.01	8.11	9.36	0.21	0.01	0.01	0.62	<0.21
Tb	0.00	0.00	1.08	1.37	0.01	0.00	0.00	0.02	<0.03
Dy	0.01	0.01	3.33	4.59	0.03	0.01	0.01	0.09	<0.15
Ho	0.00	0.00	0.50	0.62	0.01	0.00	0.00	0.01	<0.04
Er	0.00	0.00	1.17	1.37	0.03	0.01	0.01	0.07	0.18
Tm	0.00	0.00	0.15	0.20	0.01	0.00	0.00	0.02	<0.03
Yb	0.00	0.01	1.23	1.42	0.09	0.01	0.01	0.18	0.26
Lu	0.00	0.00	0.19	0.19	0.01	0.00	0.00	0.03	<0.03
Hf	0.08	0.08	0.51	0.58	2.55	0.09	0.10	5.10	0.15
Ta	0.00	0.00	0.07	0.06	8.51	0.00	0.00	16.23	2.71
Th	0.01	0.01	0.53	0.40	5.65	0.01	0.02	108.26	<0.02
Total REE	0.17	0.19	106.08	116.83	2.43	0.29	0.29	3.97	0.73
Zr/Hf	35.00	31.13	11.61	12.91	0.19	34.78	34.50	0.60	86.80

mt-band, metasomatic band; sec, after magnesite.

^aIn Mgs-Phl-Ti-Chu vein.

of most MREE are below the detection limits of the LA-ICP-MS technique, but Nb, Ta and Ti are enriched relative to adjacent elements and form peaks rather than valleys. Magnesite has a flat REE pattern. Dolomite shows a humped REE pattern with a peak at Sm, and contains much higher Sr (225–249 ppm) than the other minerals (<11 ppm). These data suggest that LREE-enrichment of whole rock is directly related to metasomatism by remaining fluids/melts, rather than directly resulting from the formation of hydrous phases and magnesite. Enrichment-LILE of whole rock, however, is attributed to the occurrence of phlogopite.

STABLE ISOTOPES

Analytical method

Phlogopite was analysed for oxygen isotopes with a CO₂ laser fluorination system in the Geophysical Laboratory, Washington, DC. Reported values of $\delta^{18}\text{O}$ are averages of duplicate determinations with a precision of 0.1–0.2‰. The details of this method have been described (e.g. Rumble & Hoering, 1994; Rumble & Yui, 1998). Hydrogen isotope analyses of phlogopite were performed at the Institute of Earth Sciences, Academia Sinica, Taipei after the method of Godfrey (1962) with a precision of $\pm 2\text{‰}$. The results are reported as δD values relative to V-SMOW. Analyses of NBS-30 (biotite) during this study gave an average δD value of -63‰ (recommended value = -64‰).

All magnesite samples for C isotope analyses were ground to $< 60\text{ }\mu\text{m}$ and then reacted with H₃PO₄ at 120 °C overnight. Carbon and oxygen isotopes of extracted CO₂ were analysed on a Finnigan MAT 252 mass spectrometer at Lehigh University. Oxygen isotope compositions of the magnesite were calibrated from those of CO₂ according to the relationship by Das Sharma *et al.* (2002). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported with reference to the V-PDB and V-SMOW standards, respectively. The reproducibility of measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values was better than 0.2‰.

Results

The oxygen and hydrogen isotopic compositions of nine phlogopite separates collected from depths of 155–235 m are listed in Table 5. Oxygen isotopic composition is rather homogeneous over 80 m; the $\delta^{18}\text{O}$ values of most phlogopite are from $+5.0\text{‰}$ to $+5.9\text{‰}$ indicating a mantle signature except for two samples (Fig. 8). These $\delta^{18}\text{O}$ values are consistent with O isotopic compositions of anhydrous phases (olivine, 5.3–5.4‰; garnet, 5.7‰ and enstatite, 5.7–5.9‰) from PP1 core samples of peridotite (Zhang *et al.*, 2005c) and distinctly higher than those of hydrous minerals from Dabie-Sulu eclogites and paragneisses (Zheng *et al.*, 2003). Samples of phlogopite weighing 1 mg yielded 2.42–2.81 μmol H₂, and δD values of the extracted gases range from -76‰ to -91‰ , which lie in the range of mantle phlogopite (Bell & Ihinger,

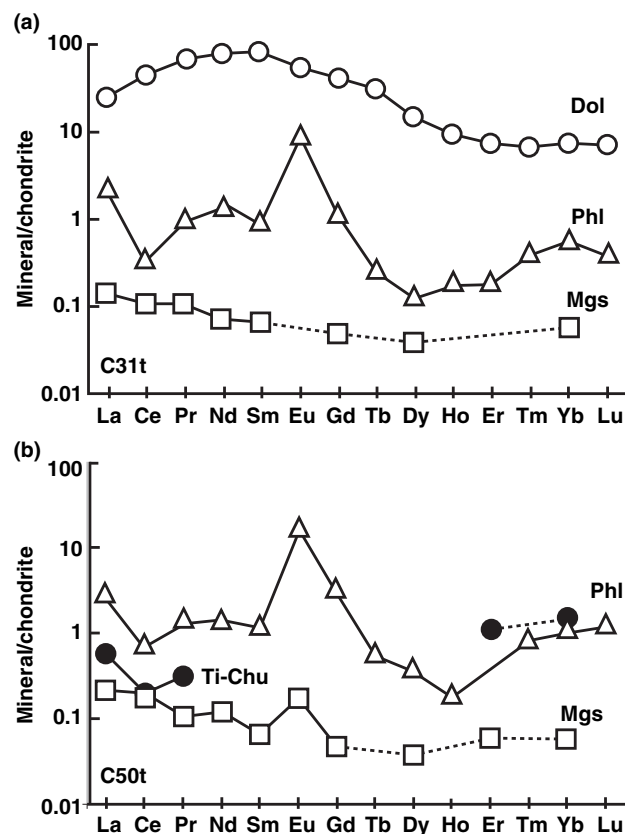


Fig. 6. Chondrite normalized REE patterns for dolomite (Dol), phlogopite (Phl) and magnesite (Mgs) from a metasomatic band (C31t) (a), and for phlogopite, Ti-clinohumite (Ti-Chu) and magnesite from a dunite with metasomatic band shown in Fig. 2b (C50t).

2000) (Fig. 9). Two phlogopite separates have slightly lower $\delta^{18}\text{O}$ (+4.2‰ and +4.4‰) and δD values (about -90‰); these values may be attributed to chlorite replacement along microfractures and margins of phlogopite during exhumation of the UHP slab.

The carbon and oxygen isotopic compositions of six magnesite separates from the PP1 peridotite are also listed in Table 5. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of magnesite range from -2.2‰ to -3.4‰ and from +5.5‰ to +8‰, respectively. The $\delta^{18}\text{O}$ values of magnesite are in the range of primary carbonatites (+5‰ to +10‰, Keller & Hoefs, 1995). Magnesite $\delta^{13}\text{C}$ values are higher than the mantle and primary carbonatites (Fig. 10), but distinctly lower than the Dabie-Sulu UHP marbles in C and O isotopic compositions (Rumble *et al.*, 2000; Zheng *et al.*, 2003).

DISCUSSION

Previous studies have indicated that the Zhimafang peridotite has been subjected to metasomatism (e.g. Yang & Jahn, 2000; Zhang *et al.*, 2000; Zheng *et al.*, 2005). These studies, however, could not provide

details of the metasomatic processes, such as the number of metasomatic events or the nature of metasomatic agents and their sources due to limited samples and study methods. In the present study, new petrographic observations and geochemical data provide convincing information for proposing complex metasomatic processes.

Multiple metasomatic events

Major element contents of the Zhimafang PP1 peridotite, such as CaO , Al_2O_3 and Na_2O , have a clear negative correlation with MgO concentrations indicating that the peridotite has experienced different degrees of partial melting and melt extraction (Zhang *et al.*, 2000; Li *et al.*, 2003). However, the depletion of 'fertile elements' is not consistent with the observed LILE and LREE enrichments of the whole rocks, which cannot be explained by a single process of melt extraction. It requires, instead, a metasomatic effect of LREE and LILE enrichment superimposed on the initially LREE-depleted pattern (Jahn *et al.*, 2003). These features are similar to those observed in mantle xenoliths in kimberlite; the decoupling of major and trace elements is commonly attributed to metasomatism by melt derived from asthenospheric mantle (Griffin *et al.*, 1999, 2000). Trace element analysis of diopside from one Zhimafang garnet lherzolite sampled by Zheng *et al.* (2005) indicates the Zhimafang peridotite requires < 30% partial melting of primitive mantle source to produce the trace element concentrations for the studied sample. The Zhimafang diopside is LREE rich [$(\text{La}/\text{Yb})_{\text{N}} = 94$], and shows a sinusoidal REE pattern with flat HREE, has negative Zr, Ti, and Nb anomalies and a positive Pb anomaly, and deviates from fractional melting curves in plots of trace elements (e.g. Gd & Zr v. Yb). These characteristics together with high $(\text{La}/\text{Yb})_{\text{N}}$ and low Ti/Eu ratios suggest that the Zhimafang peridotite has been subjected to carbonatitic metasomatism (Zheng *et al.*, 2005). Zircon with a metamorphic age of 221 ± 3 Ma (Zhang *et al.*, 2005) from the PP1 peridotite has low trace element concentrations, and their distribution patterns of trace elements have a kimberlitic or carbonatitic signature. Furthermore, a low $^{176}\text{Hf}/^{177}\text{Hf}$ ratio (0.28221 ± 0.00003), negative ϵ_{Hf} values (-16.3 to -13.8), and depleted mantle model ages (T_{DM}) of 1.39–1.48 Ga suggest that the PP1 peridotite represents a piece of ancient mantle and experienced Mesoproterozoic metasomatism. The metasomatic fluids/melts recorded in the zircon were derived from the asthenospheric mantle rather than from subducted continental crust (Zheng *et al.*, 2006). The presence of phlogopite and the low $\text{CaO}/\text{Al}_2\text{O}_3$ of whole rocks also suggest the effect of silicate metasomatism on the peridotite (Zheng *et al.*, 2005). It is worth noting that a high $\text{CaO}/\text{Al}_2\text{O}_3$ ratio is a feature of Ca-carbonatite rather than Mg-carbonatite metasomatism as the later process does not produce high $\text{CaO}/\text{Al}_2\text{O}_3$ ratios.

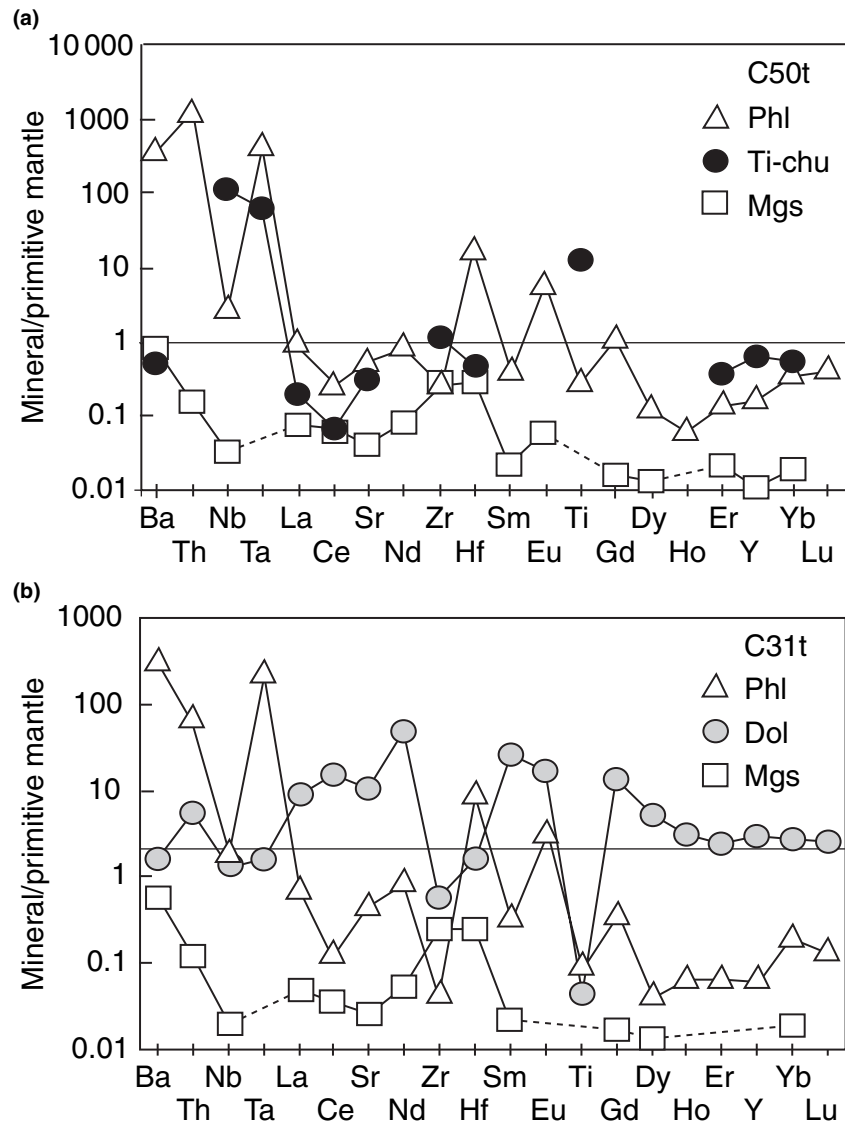


Fig. 7. Primitive mantle normalized trace element patterns of minerals from sample C50t (a) and C31t (b).

Table 5. Stable isotopic compositions of phlogopite and magnesite.

Sample no.	Depth (m)	Rock (magnesite)	Occurrence	Magnesite		Phlogopite	
				δO^{18}	δC^{13}	δO^{18}	δD
C24-59	151.7	Grt-lherzolite	mtx			5.4	-77
C25-60	155.2	Grt-lherzolite	mtx			5.5	-81
C25-61	155.2	Ti-Chu-wehrlite	mtx			5.4	-85
C26-62	156.7	Harzburgite	mtx	7.2	-3.2	5.2	-76
C27-63	159.0	Grt-lherzolite	vein, mtx	7.5	-3.0	5.0	-77
C31-68	168.0	Grt harzburgite	vein, mtx	8.0	-2.2		
C37-78	189.6	harzburgite				4.4	-90
C41-83	205.0	Grt lherzolite	mega, mtx	5.5	-2.5	4.2	-91
C48-91	226.3	Grt-wehrlite				5.9	-81
C49-92	226.8	Dunite ($\pm$ En)	mega, mtx			5.6	-91
C50-93	229.8	Dunite	vein, mtx	7.5	-3.4		

Mega: megacrystal; mtx: matrix. Precision of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for magnesite is $\pm 0.2\text{‰}$. Precision of $\delta^{18}\text{O}$ and δD for phlogopite is $\pm 0.1\text{‰}$ and $\pm 0.2\text{‰}$, respectively.

Sm–Nd and Rb–Sr isotopic compositions of whole rock including initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.709–0.710 and negative $\epsilon_{\text{Nd}}(t)$ of –4 to –5 (even lower if recal-

culated to 200 Ma) for two garnet peridotites indicate the Zhimafang peridotites were either enriched in Rb/Sr and Nd/Sm ratios for a long time or they were

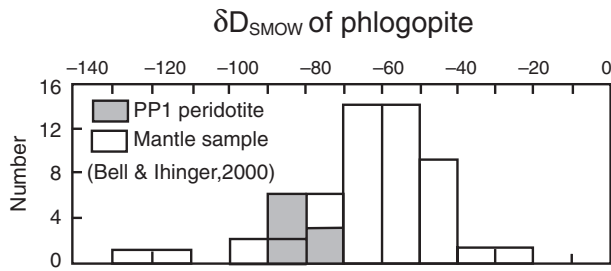


Fig. 8. Frequency distributions of hydrogen isotopic composition in phlogopite from the PP1 peridotites. The mantle phlogopite data were summarized by Bell & Ihinger (2000).

contaminated by radiogenic continental material (Yang & Jahn, 2000).

The petrogenesis of minerals such as phlogopite, Ti-clinohumite and carbonate in the Zhimafang peridotite already requires at least two metasomatic events. We propose three successive metasomatic events defined by (1) the growth of Phl-1 coexisting with olivine, enstatite, diopside and garnet, (2) the formation of coarse-grained magnesite and slightly later veins of Mgs $\pm$ Phl-2 $\pm$ Ti-Chu-2, and (3) the growth of dolomite after magnesite, tremolite after diopside, and talc after olivine by reaction with fluids. As described above, matrix phlogopite forms euhedral flakes and appears to be in textural equilibrium with other peridotitic minerals. In addition, euhedral phlogopite occur as inclusions within magnesite megacrysts and do not show preferred orientation (Fig. 3c), although a few Phl-rich peridotites were deformed, probably during exhumation. Such features suggest that the growth of Phl-1 took place in the mantle wedge prior to UHP metamorphism. Magnesite megacrysts contain phlogopite inclusions that

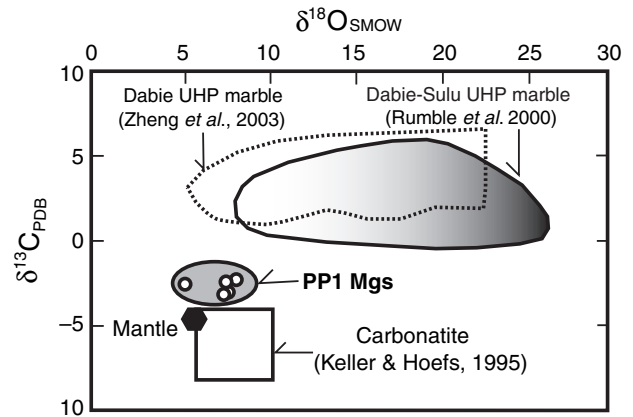


Fig. 10. Stable isotope analyses of magnesite from PP1 peridotites. Carbon isotopic ratios are relative to PDB standard and oxygen ratios are relative to SMOW. Stable isotope data of Dabie-Sulu marbles are also shown.

have the same composition as matrix phlogopite; this fact suggests that the megacrystic or coarse-grained magnesite in the matrix was formed later than Phl-1. Veins of magnesite and Mgs-2 + Phl-2 $\pm$ Ti-Chu were formed at the same time or slightly later than coarse-grained magnesite. It is not apparent from textural relationships when the rare, coarse-grained, matrix Ti-clinohumite crystallized. Considering, however, the stability of F-free Ti-clinohumite and the replacement by Ilm + Ol at Ti-Chu margins, the Ti-Chu is not a secondary phase.

Magnesite is rimmed by fine-grained dolomite, and is associated with talc after olivine and tremolite after diopside in strongly metasomatized band, or domains. These secondary carbonates and hydrous phases (talc and tremolite) were formed during a third metasomatic

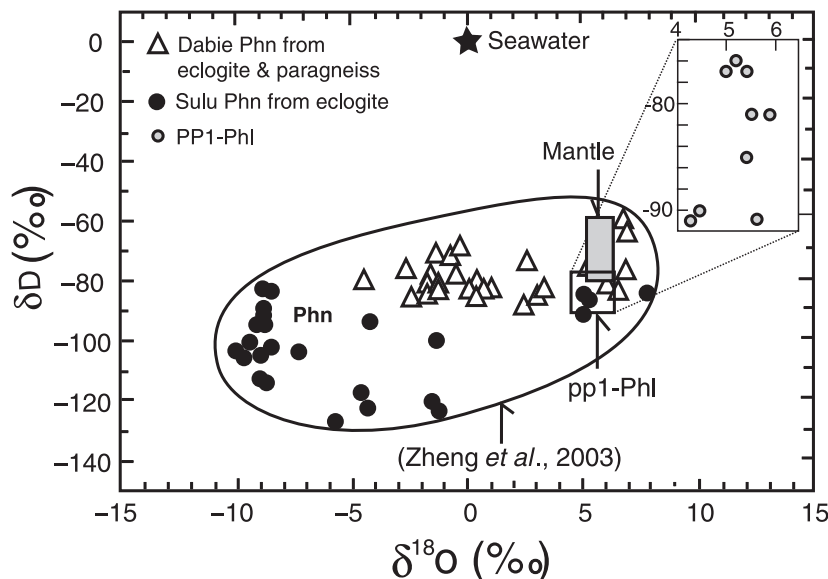


Fig. 9. Hydrogen and oxygen isotopic compositions of phlogopite from the PP1 peridotites. The Dabie-Sulu phengite data were summarized by Zheng *et al.* (2003).

lherzolite at moderate to high pressures, and that carbonatitic melt may exist in equilibrium with mantle peridotite at pressures > 2.2 GPa (e.g. Thibault *et al.*, 1992; Dalton & Wood, 1993; Lee *et al.*, 2000a) and up to 7 GPa (Dalton & Presnall, 1998). These melts are more Mg-rich than the Ca-rich carbonatites observed in extrusive lava flows (Woolley & Kempe, 1989). However, there is debate over whether carbonate inclusions in peridotite xenoliths are crystalline precipitates or quenched liquids (Lee *et al.*, 1994, 2000b). Some textural features, such as globular shapes and curved menisci, have been interpreted as evidence for quenched liquids (e.g. Kogarko *et al.*, 1995; Norman & Person, 1998).

It is known that carbonatite has high total REE with significantly LILE and LREE-enriched pattern (Woolley & Kempe, 1989; Downes *et al.*, 2005). Carbonates in mantle xenoliths have compositions clustered at end-member magnesite, calcite or stoichiometric dolomite and have low total REE contents. These characteristics are interpreted as evidence for their origin as crystalline precipitates from a carbonate melt (Ionov, 1998; Lee *et al.*, 2000b). Magnesite from the Zhimafang peridotite occurs as megacrysts, matrix and veins; all are nearly Ca-free, pure magnesite with high Mg/(Mg + Fe) ratios (0.93–0.95) without a continuous compositional variation, and have very low total REE contents (0.17–0.29 ppm). These compositional characteristics are consistent with an origin as crystalline cumulates from mantle-derived carbonatite melts.

CONCLUSION

Drill core samples from the CCSD-PP1 drill hole show that the Zhimafang peridotite consists of phlogopite-bearing garnet lherzolite (major rock type), harzburgite, wehrlite and dunite; some rocks contain additional Ti-clinohumite and magnesite. The petrochemical data described above have led to the following conclusions.

1. The Zhimafang peridotite was subjected to multiple metasomatic events in the mantle wedge prior to its incorporation into the subducted slab and again during exhumation. Three metasomatic events have been identified: (i) crystallization of phlogopite in the mantle wedge is due to infiltration of K-rich hydrous fluid/melt; (ii) the formation of magnesite and slightly later veins of magnesite and $\text{Mgs} + \text{Phl} \pm \text{Ti-Chu}$ is attributed to Mg-carbonatitic metasomatism; (iii) replacement of mantle minerals by dolomite and other secondary hydrous phase resulted from interactions with a crust-related CO_2 -bearing hydrous fluids at the crust during exhumation.
2. Stable isotopic compositions of phlogopite and magnesite indicate the source of metasomatic agents is an ancient enriched mantle that probably had been contaminated by continental material.

3. The nearly pure magnesite with low total REE abundance is inferred to be a crystalline cumulate from carbonatitic melts.

4. The compositional heterogeneity of the Zhimafang peridotite results largely from two processes: different degrees of partial melting of the mantle protoliths and variable extents of metasomatism at various scales.

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