Mantle metasomatism did not modify the initial H₂O content in peridotite xenoliths from the Tianchang basalts of eastern China

Yan-Tao Hao¹, Qun-Ke Xia^{1, 2}, Zhen-Zhen Tian², Jia Liu²

1 School of Earth Sciences, Zhejiang University, Hangzhou 310027, China

2 School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

Email: ythao@zju.edu.cn, qkxia@zju.edu.cn

Abstract

Metasomatism induced by melts/fluids is ubiquitous in the lithospheric mantle and can potentially modifies the initial water content of the mantle. However, the preservation of correlations between H₂O content and partial melting indices (e.g., Yb content in clinopyroxene, Cr/(Cr+Al) in spinel) and the lack of correlations between H₂O content and metasomatic indices (e.g., La/Yb in clinopyroxene) in peridotite xenoliths from several localities suggest that variations in the initial H₂O content were controlled by partial melting processes rather than by subsequent metasomatic event(s) (Hao et al., 2014; Denis et al., 2015). However, the applied partition coefficients of H₂O between peridotite and melt ($D^{\text{peridotite/melt}}=0.1-0.3$) in the partial melting models cast doubts on the reasonability of such explanations. Whether metasomatism always modifies the initial H₂O content of the lithospheric mantle remained a topic of debate. In this paper, we measure major and trace element concentrations and H₂O contents of minerals in the peridotite xenoliths hosted by the Tianchang Cenozoic basalts in eastern China by using electron microprobe, laser-ablation ICP-MS and Fourier transform infrared spectroscopy, respectively. The H₂O contents (weight in ppm) of clinopyroxene, orthopyroxene and olivine are 70-280 ppm, 35-140 ppm and below detection limit (<2 ppm H₂O), respectively. Although water diffusion during xenolith ascent cannot be excluded for olivine, pyroxenes largely retain the initial H₂O content of the mantle source, as supported by (1) the correlation between H₂O content and major element content of pyroxene, and (2) the equilibrium H₂O partitioning between clinopyroxene and orthopyroxene. The calculated whole-rock H₂O contents range from 14 to 93 ppm (average 52 ± 25 ppm) assuming 0.1 for the H₂O partition coefficient between olivine and clinopyroxene. Although no hydrous minerals are found, the enrichment in light rare earth elements and large ion

lithophile elements of clinopyroxene indicates cryptic mantle metasomatism. However, variations between the H₂O contents of the whole rocks and the metasomatic index (La/Yb ratio in clinopyroxene) are not correlated, suggesting that mantle metasomatism did not modify the initial H₂O contents after the melting event. Instead, the H₂O content correlates with the melting indices demonstrating that partial melting is the primary factor controlling the variations in the initial H₂O contents. Notably, variations in whole rock H₂O contents of the Tianchang peridotites can be modeled as a simple melting process of a MORB mantle source using the reported partition coefficients of H₂O ($D^{\text{peridotite/melt}}=0.005\text{-}0.03$), providing a robust example suggesting that metasomatism does not always change the initial H₂O content in the lithospheric mantle.

Key words: hydrogen; peridotite xenoliths; partial melting; mantle metasomatism; eastern China

1. Introduction

Peridotite xenoliths hosted by alkali basalts and kimberlites are direct samples of the continental lithospheric mantle. The xenoliths largely preserve the geochemical signatures of the mantle source because they rapidly reach the surface (generally within of 50 hours after entrainment in the host magma, O'Reilly and Griffin, 2010). The main constituent minerals of peridotite xenoliths (olivine (ol), orthopyroxene (opx), clinopyroxene (cpx) and garnet) are nominally anhydrous minerals (NAMs) that contain variable amounts of water (as hydrogen) in their crystal defects (Bell and Rossman, 1992), making the lithospheric mantle a potential water reservoir of the Earth (Bell and Rossman, 1992; Hirschmann, 2006; Ingrin and Skogby, 2000). The presence of water in point defects of NAMs greatly affects the physical (e.g., rheology, electrical conductivity and seismic velocity) and chemical (e.g., ionic diffusion and partial melting) properties of mantle domains (Demouchy et al., 2012; Hier-Majumder et al., 2005; Karato and

Jung, 1998; Mackwell et al., 1985; Mei and Kohlstedt 2000a, b). Studies of water distribution in the continental lithospheric mantle show a close connection between the water contents of NAMs and the stabilities of the continents (Lenardic et al., 2013; Li et al., 2008; Peslier et al., 2010; Xia et al., 2013).

Mantle metasomatism by melts or fluids (usually volatile-rich agent) is diffusely occurs in the lithospheric mantle. Studies on peridotite xenoliths from the Kaapvaal cratonic mantle suggest that the H₂O contents of ol, pyroxenes and garnet are enhanced by metasomatic melts (Peslier et al., 2012). Similarly, Doucet et al. (2014) suggest that the high water contents in the Siberian cratonic mantle are the results of interactions between residual, melt-depleted peridotites and silicate melt before entrainment in the host kimberlites and eruption. The low H₂O contents of minerals included in Siberian diamonds suggested that the initial H₂O content of the lithospheric mantle was indeed modified (Novella et al., 2015; Taylor et al., 2016). Moreover, the high H₂O content of ol from the refractory spinel harzburgites of the Ontong Java Plateau is also related to fluid metasomatism linked to a decrease in plume activity (Demouchy et al., 2015).

In our previous study (Hao et al., 2014), we found well-defined correlations between H₂O content and melting indices (such as Yb content in cpx and Cr# in spinel), and no correlation between H₂O content and metasomatic indices (such as La/Yb in cpx) based on Jiande peridotite xenoliths from SE China. Therefore, we proposed that the H₂O contents variations of the peridotites were controlled by partial melting event they experienced and were not modified by later metasomatic event. However, the partition coefficient of H₂O between peridotite and melt ($D^{\text{peridotite/melt}}=0.1$) we applied to fit the partial melting modeling is larger than the experimentally determined partition coefficients currently available ($D^{\text{peridotite/melt}}=0.005-0.03$). Denis et al. (2015)

found similar phenomena in the Massif Central peridotite xenoliths, suggesting that H₂O may behave as a middle incompatible element (i.e., $D^{\text{peridotite/melt}}$ can be up to 0.1-0.3) in some cases. However, Peslier et al. (2015) explained the variation in H₂O content of the Hawaiian peridotite xenoliths as an assimilation and fractional crystallization (AFC) process rather than a partial melting control. However, it is not easy to explain the preservation of the correlations between H₂O content and melting indices in the Hawaiian samples through such a complicated process. Overall, whether metasomatic events always modify the initial H₂O content in the lithospheric mantle remained a matter of debate.

In this study, we focus on peridotite xenoliths from a newfound locality (Tianchang) in eastern China. The samples display similar correlations between H₂O content and melting indices as those from the Jiande (Hao et al., 2014) and Massif Central samples (Denis et al., 2015). However, the H₂O content variations of these samples can be modelled as a simple modal melting process using reasonable partition coefficients ($D^{\text{peridotite/melt}} = 0.01-0.03$) from a MORB source. In addition, coherent variations between the H₂O content and the metasomatic index (La/Yb ratio in cpx) are lacking for these samples. Therefore, this study describes a robust case demonstrating that mantle metasomatism does not always change the initial water content of the lithospheric mantle.

2. Geological setting and samples

The Tianchang volcano is close to the Panshishan, Lianshan and Fangshan Cenozoic volcanoes (Hao et al., 2015; Xia et al., 2010), in the Subei basin on the south edge of the North China Craton (NCC). The NCC, one of the oldest cratons worldwide, is separated from the Mongolian Block by the eastern Central Asian Orogenic Belt to the north and from the South China Block by the Triassic Qinling-Dabie-Sulu orogen to the south and east (Fig. 1). The NCC is

crosscut by two large-scale geophysical and geological linear zones, with the Tan-Lu Fault in the east and the Daxing'anling-Taihangshan Gravity Lineament in the west. The NCC, especially the eastern part, has re-activated since the Phanerozoic, as indicated by a series of thermo tectonic events. The eastern NCC is now underlain by a fertile, high heat-flow and thin lithosphere that have replaced the refractory, low heat flow and thick cratonic type lithosphere. In addition to these dramatic changes, the underlying lithospheric mantle suggests the lithospheric thinning, resulting in destruction of the NCC (Menzies et al., 2007). However, the timing of, spatial and temporal variation of and mechanism for the lithospheric thinning of NCC are strongly debated (Gao et al., 2002; Menzies et al., 2007; Xu, 2001; Zhang et al., 2008; Zheng et al., 1998, 2005).

Fifteen peridotite xenoliths were collected from the Tianchang volcano (GPS coordinates $32^{\circ} 35' 41''$ N and $118^{\circ} 56' 05''$ E) in Anhui province (Fig. 1). Although no age data have been reported, the similar volcanic structure and basalt characteristics (massive alkali basalts) and the wide existence of mantle xenoliths suggest that the Tianchang volcano erupted at the same time as the nearby Fangshan volcano (~9 Ma, Chen and Peng, 1988). The fresh peridotite xenoliths are 10-20 cm in diameter and lack evidence of alteration or host basalt infiltration. The mineral modal contents were estimated by point counting using the scanned digital figures from the thin sections. Most are spinel lherzolites (cpx vol. % = 6-19), with one spinel harzburgite (DFS15, <5 vol. % cpx). Following the naming scheme of Mercier and Nicolas (1975), the textures of Tianchang peridotite xenoliths vary from protogranular to porphyroclastic (Table 1). The coarse-grained ol and opx are 3–5 mm in size, while cpx and spinel exhibit somewhat smaller grains (1-3 mm). In most samples, large grains of ol show kink banding and opx is usually free of inclusions. The spinel commonly forms vermicular crystals inside the opx or between opx and cpx

grains. The modal mineral assemblages of the Tianchang peridotites vary substantially, with ol, opx, cpx, and sp ranging from 45–83 vol. %, 11–36 vol. %, 2–19 vol. % and approximately 1–3 vol. %, respectively. No hydrous phases or spongy rims of minerals were found within these peridotite xenoliths.

3. Methods

3.1 Electron microprobe analysis (EMPA)

The Shimadzu Electron Probe Micro-analyzer (EMPA 1600) at the University of Science and Technology of China (USTC) was used to determine the major elements of the minerals, with operating conditions set as 15 kV and 20 nA. Natural minerals and synthetic oxides **were** used as standards, including SiO₂ for Si, rutile for Ti, pyrope for Al, Cr₂O₃ for Cr, almandine for Fe, bustamite for Mn, olivine for Mg, wollastonite for Ca, jadeite for Na, potassium-feldspar for K and NiO for Ni. A program based on the ZAF procedure (Armstrong, 1989) was used for data correction. Three to four grains of each mineral were analyzed in each sample. The uncertainty of all elements was below 5%, except for Na, for which the uncertainty may be as high as 10%.

3.2 Fourier transform infrared spectrometry (FTIR)

Double-polished thin sections with thicknesses of approximately 0.2 mm were prepared for FTIR analysis. The Nicolet 5700 FTIR spectrometer coupled with a Continuum microscope at USTC was used to obtain unpolarized spectra in the range of 600 to 4500 cm⁻¹. The measurements were collected with a KBr beam splitter and a liquid nitrogen cooled MCT (Hg-Cd-Te) detector. The number of scans was 256 and the aperture size varied from 40×40 to 100×100 μm, with a resolution of 4 cm⁻¹. Optically clean, inclusion-free, crack-free areas (typically the core regions of the selected grains) were selected for measurements. Profile analyses were run for each relatively

large mineral grain. More than 10 different grains (usually 15-20 grains) of each mineral in the same sample were analyzed. A modified form of the Beer-Lambert law is used to calculate the H₂O content of minerals:

$$c=A/(I \times t)$$

where c is the content of the hydrogen species (ppm H₂O wt. %), A is the integrated area (cm⁻²) of the absorption bands in the region of interest, I is the integral specific absorption coefficient (ppm⁻¹ cm⁻²) and t is thickness (cm). Baseline corrections were performed using a linear fit method in the region between 3000 and 3800 cm⁻¹ for cpx and between 2800 to 3800 cm⁻¹ for opx. The OH absorption bands were integrated and were multiplied by 3 to obtain the A values (Kovács et al., 2008). The integral specific coefficients were from Bell et al., (1995) for pyroxenes. The thickness was the average of 20-40 measurements covering the whole section. The linear absorbance is less than 0.2 for all spectra. The average of > 10 unpolarized measurements was used to estimate the true sample value, the uncertainties are relative small for pyroxenes, and an error of less than 10% is expect (Kovács et al., 2008; Withers, 2013).

Uncertainties in the calculated H₂O contents are as following: (1) unpolarized measurements (<10%); (2) baseline correction (<5%); (3) variation of sample thickness (<3%); (4) differences between the absorption coefficients of our samples and those of samples used by Bell et al. (1995) due to different in minerals composition and density (<10%) and (5) due to different proportions of defects (<5%). The total uncertainty is estimated to be less than 20%.

3.3 Laser ablation inductively coupled plasma-mass spectrometry (LA-ICPMS)

Unaltered and inclusion-free cpx grains from a thin section were selected after FTIR analysis. The trace element compositions of cpx were analyzed using a 193 nm Coherent GeoLas Pro ArF

laser system coupled to an Agilent 7700 ICPMS at USTC. The laser was operated using a beam at 10 Hz and 10 J/cm² of energy per pulse with a beam diameter of 60 μm. The ICPMS was operated with an RF power of 1350 W and a nebulized gas flow rate of 0.7 L/min. The results of the sample analyses were processed using LaTEcalc software. NIST 610 silicate glass was used to calibrate the signal intensities (counts per ppm), and the Ca content of the cpx from EMPA was used as an internal standard. Typical analytical precisions are better than 5%. Four to seven cpx grains for each sample were analyzed.

4. Results

4.1 Mineral Chemistry and Thermometry

The EMPA showed that the minerals in the Tianchang peridotites are homogenous (i.e., no chemical variations were observed within a grain or among grains of the same sample) and average values are reported in Table 2. The Mg# ($\text{Mg\#} = 100 \times \text{Mg} / (\text{Mg} + \text{Fe})$, mol%) values of ol, opx and cpx from the Tianchang peridotites range from 89.2 to 91.4, 89.8 to 92.2 and 90.0 to 94.5, respectively. The Cr# ($\text{Cr\#} = 100 \times \text{Cr} / (\text{Cr} + \text{Al})$, mol %) values in spinel vary from 9.5 to 25.9 (Table 2) for all xenoliths, falling in the range of literature data reported for peridotite xenoliths hosted in Cenozoic basalts from the Subei basin and NCC (Lu et al., 2013; Xia et al., 2010; Zheng et al., 1998, 2001). Olivine, opx and cpx generally display Mg# values in equilibrium with each other. The Al₂O₃ content of opx decreased (from 4.57 wt. % to 2.89 wt. %) while Mg# of opx increased (Fig. 2a). The Al₂O₃ content and Na₂O content of cpx decreased while Mg# of cpx increased (Fig. 2b, c). The Cr# of spinel increased from 9.5 to 25.9 when the Mg# of ol increased (Fig. 2d). Tianchang samples generally have fertile compositions compared to the relict lithospheric mantle of the NCC (Fig. 2).

The Ca-in-opx and two-pyroxene Mg-Fe exchange geothermometers proposed by Brey et al. (1990) were used to estimate the equilibrium temperatures assuming a pressure of 1.5 GPa. The temperature estimates range from approximately 800 to 1050°C (Table 1). The lowest temperature obtained by both geothermometers was for the harzburgite DFS15.

4.2 Trace element characteristics of cpx

Clinopyroxene is the most important mineral reservoir because it hosts the largest amount of highly incompatible trace elements in anhydrous spinel peridotites. Multiple grain analyses (4-7 grains) show that the trace element contents of cpx from the Tianchang xenoliths are homogenous within the same sample. The average values are reported in Table 3.

Figures 3 show the rare earth element (REE) contents normalized to C1 chondrite (Sun and McDonough, 1989), and the trace element contents normalized to the primitive mantle (PM, McDonough and Sun, 1995). The REE and trace element patterns can be divided into two groups based on the extent and pattern of LREE enrichment. Group I includes DFS01, DFS03, DFS05, DFS06, DFS10 and DFS11, which are characterized by depletion of LREE and most incompatible elements (Fig. 3a), with $(La/Yb)_n = 0.05-0.51$ ("n" denotes C1 chondrite normalized values). Their HREE to MREE exhibit flat profiles, varying within a small range ($Yb_n = 6.9-13.7$), and the anomalies of Zr and Hf are very weak (Fig. 3b). The remaining samples (DFS02, DFS04, DFS07, DFS08, DFS09, DFS13, DFS14, DFS15 and DFS16) belong to group II, with enriched LREE ($(La/Yb)_n = 1.10-11.57$) and variable HREE contents ($Yb_n = 3.4-11.4$, Fig. 3c). Group II samples also exhibit Th and U enrichments and negative anomalies of high field strength elements (i.e., Zr, Hf, Nb, Ta and Ti) (Fig. 3d). The harzburgite DFS15 displays the lowest HREE content, the highest $(La/Yb)_n$ ratio and the largest negative Zr, Hf and Ti anomalies among the Tianchang

peridotite xenoliths.

4.3 FTIR spectra and H₂O content of peridotite minerals

In all the thin section used, most of the ol in the Tianchang peridotite xenoliths displays no detectable OH peaks, with few grains displaying a very weak OH band. In contrast, all of the analyzed cpx and opx grains are characterized by several typical absorption bands in the OH-stretching vibration region (2800–3800 cm⁻¹). Representative infrared spectra for ol, opx and cpx are shown in Fig. 4a-c. The IR absorption bands of the pyroxenes can be sub-divided into several groups: 3600–3580 cm⁻¹, 3520–3510 cm⁻¹, 3420–3410 cm⁻¹ and 3310–3300 cm⁻¹ for opx; and 3630–3620 cm⁻¹, 3540–3520 cm⁻¹, and 3470–3450 cm⁻¹ for cpx. The positions of these absorption bands are similar to natural samples reported worldwide (e.g., Bell and Rossman, 1992; Demouchy et al., 2015; Ingrin and Skogby, 2000; Peslier et al., 2002, 2012; Skogby and Rossman, 1989; Warren and Hauri, 2014; Xia et al., 2010; Yang et al., 2008a,b). The profile analyses of cpx grains exhibit homogeneity. Some opx grains show that absorbance areas decreased from the core to the rim. The cores retain the initial H₂O content whereas the rims may have undergone hydrogen diffusion upon ascent to the surface (Tian et al., 2016). Spectra collected from mineral core were therefore used to calculate opx H₂O contents.

The H₂O contents of the Tianchang peridotites vary from 70 ppm to 280 ppm for cpx and from 35 ppm to 140 ppm for opx (Fig. 5a, Table 4). The H₂O contents of ol are less than 2 ppm, considering the magnitude of the spectral noise from the background and instrument relative to the absorption of the ol, the absorption coefficient and the thickness of thin section. The H₂O contents of ol do not represent the source value due to possible H loss during ascent (see Discussion). Instead, the initial H₂O content can be retrieved by considering the equilibrium partitioning of

H₂O between the pyroxenes and ol. The $D^{\text{ol/cpx}}$ values of H₂O range from 0.011 to 0.05 under different P-T conditions in experimental studies (Table 5) (Aubaud et al., 2004, 2007; Hauri et al., 2006; Hirschmann et al., 2009; Koga et al., 2003; Tenner et al., 2009; Withers and Hirschmann, 2007, 2008). We recalculated the whole-rock H₂O contents by assuming an ol H₂O content of 1/10 of that of cpx ($D^{\text{ol/cpx}}=0.1$, maintaining consistency with previous works, Hao et al., 2014, 2016; Xia et al., 2010), as shown in Table 4. The whole-rock H₂O contents are calculated based on the H₂O content of ol, opx and cpx and their modal percentage. When $D^{\text{ol/cpx}}=0.1$ is assumed for H₂O, the whole-rock H₂O content represents the maximum estimates. These are generally <20% larger than the minimum estimates (ol H₂O contents ~0 ppm). The Tianchang peridotites exhibit whole-rock H₂O contents ranging from 14 to 93 ppm (average= 52 ± 25 ppm), similar to the low end of the H₂O contents estimated for the MORB source (50-200 ppm, Asimow et al., 2004; Dixon et al., 1988, 2004; Michael, 1988; Saal et al., 2002; Simons et al., 2002; Sobolev and Chaussidon, 1996) and much lower than those estimated for an OIB source (300–1000 ppm, Dixon et al., 1997; Nichols et al., 2002; Seaman et al., 2004; Simons et al., 2002; Wallace, 2002; Workman et al., 2006).

5. Discussion

5.1 The initial H₂O content in the mantle source

The majority of the Tianchang ol grains show no obvious OH absorption peaks, probably because of de-compressional H loss during ascent (Fig. 4a). The experimental results show that the solubility of hydrogen in the nominally anhydrous minerals decreases with decreasing pressure (Keppler and Bolfan-Casanova, 2006; Mierdel et al., 2007), and when peridotite xenoliths are brought to the surface by their host magmas, hydrogen can potentially diffuse out of the mineral

due to decompression. The hydrogen loss phenomena are typically evidenced by the diffusion profiles of the water contents (Demouchy, 2004; Demouchy et al., 2003, 2006; Denis et al., 2013; Peslier and Luhr, 2006; Peslier et al., 2008; 2015). In most of the Tianchang ol, both the rim and the core display H₂O contents below the instrument detection limit (<2 ppm). The hydrogen is suggested to have completely diffused, even if some hydrogen was present in ol at depths within the mantle, similar to other peridotite xenoliths from NCC (Li et al., 2015; Xia et al., 2010, 2013; Yang et al., 2008).

In contrast, pyroxenes were able to preserve their initial H₂O contents from the mantle source surviving the subsequent transport to the surface (e.g., Bell and Rossman, 1992; Denis et al., 2013, 2015; Gose et al., 2009; Grant et al., 2007; Hao et al., 2012, 2014, 2016; Hesse et al., 2015; Peslier et al., 2002, 2015; Skogby et al., 1990; Xia et al., 2010). Pyroxenes of the Tianchang peridotites appear to largely retain the initial H₂O contents of the mantle source as inferred from: (1) the correlation between the H₂O contents and the major element contents of pyroxene grains (Fig. 5b, c); the positive correlation between the H₂O contents of cpx and opx with partition coefficient of cpx relative to opx of ~2 (Fig. 5a), which is in agreement with natural peridotite xenoliths from eastern China (Hao et al., 2014, 2016; Li et al., 2015; Xia et al., 2010; Yang et al., 2008a; Yu et al., 2011) and worldwide (2.3 ± 0.5 , Bell and Rossman, 1992; Denis et al., 2015; Grant et al., 2007; Li et al., 2008; Mosenfelder and Rossman, 2013a, b; Peslier et al., 2002, 2012, 2015; Warren and Hauri, 2014).

5.2 Processes occurred in the Tianchang lithospheric mantle

The Tianchang peridotites display correlations between Mg# in ol and Cr# in spinel (Fig. 2d), and the abundances of the major oxides and moderately incompatible elements in the minerals

vary systematically with of Mg# variations in the minerals (Fig. 2a-c). These trends generally indicate that the peridotite compositions reflect variable degrees of melt extraction from a fertile lherzolite source (Herzberg, 2004; Ionov et al., 2002). Following the method of Norman (1998), the degrees of partial melting for the Tianchang peridotite xenoliths are estimated based on the correlation between the Y and Yb content of cpx, originating either from a depleted MORB mantle source (DMM, Workman and Hart, 2005) or from a primitive mantle source (PM, McDonough and Sun, 1995). The degree of partial melting is approximately 2% higher when estimated from the PM than from the DMM. The Tianchang lherzolites exhibit a degree of partial melting less than 10%. The harzburgite DFS15 has the highest degrees of partial melting (10%-12%, Fig. 6).

The cpx in the group I lherzolites display slightly depleted REE patterns and negative high field strength element (i.e., Nb, Tb, Zr and Hf) anomalies, suggesting that these xenoliths represent the residue of partial melting and have not been significantly metasomatized. In contrast, although no hydrous minerals are found, the LREE, Th and U enrichments in cpx indicate that the group II peridotites (Fig. 3) underwent cryptic mantle metasomatism (Dawson, 1984). The absence of hydrous minerals suggests that a fluid-rich metasomatism agent is not associated with the Tianchang peridotites (Downes, 2001). The trace element patterns of the group II peridotites indicate that the metasomatic fluid/melt may have been enriched in LREE and fluid-mobile elements (e.g., Th, U and Sr). The high Ti/Eu but low La/Yb ratios of most of the group II peridotites (Fig. 7) suggest silicate metasomatism rather than carbonatitic metasomatism, except for DFS15 (Coltorti et al., 1999). The oxygen isotope compositions of the peridotites from the Subei basin (Panshishan, Lianshan and Fangshan, Hao et al., 2015) suggest that recycled oceanic crust-derived materials were involved in the lithospheric mantle of this area and may be

responsible for the metasomatism.

5.3 H₂O content variations: controlled by partial melting

Metasomatic events can be related to fluid/melt circulation in the mantle. Fig. 8a shows that the cpx water contents in the metasomatized samples (group II) are never exceed those of the non-metasomatized peridotites (group I). Moreover, no well-defined correlations are observed between the mineral modal compositions, MREE contents of cpx and H₂O contents of minerals and whole rocks, suggesting that mineral H₂O contents are not associated with the metasomatism.

Figures 8b and 8c show that the melting indexes (such as Cr# of sp and Yb content of cpx) have well-defined correlations with the H₂O contents of the Tianchang peridotites. We found similar correlations between the whole rock H₂O content, the Yb content of the cpx and the inferred melting degrees of the peridotite xenoliths in the Cenozoic basalts of SE China. Additionally, we suggested that the H₂O content variations in these samples were controlled by a partial melting process (Hao et al. 2014). If the DMM is the mantle source, the H₂O content variations can only be modeled by a simple melting process with an H₂O ($D^{\text{peridotite/melt}}$) partition coefficient of 0.1, which is much higher than the $D^{\text{peridotite/melt}}$ values observed in the experiments and natural samples ($D^{\text{peridotite/melt}}=0.005-0.03$, Table 5, Aubaud et al., 2004, 2007; Bell et al., 2004; Danyushevsky et al., 2000; Hirschmann et al., 2009; Hauri et al., 2006; Michael, 1995; Stolper and Newman, 1994; Tenner et al., 2009). Denis et al. (2015) studied the peridotite xenoliths of the Ray Pic volcano from French Massif Central and found that the H₂O content of ol, opx and cpx are correlated with the Yb content of the cpx. Therefore, they suggested that the H₂O content variation of the Ray Pic peridotites was controlled by a partial melting process rather than later metasomatism(s). They modeled the correlations between the H₂O contents and the melting

indices using $\text{H}_2\text{O } D^{\text{peridotite/melt}} = 0.1\text{-}0.25$, suggesting that H in the upper mantle minerals does not behave as a highly incompatible element. Peslier and Bizimis (2015) observed similar correlations between the H_2O contents and the melting indices (Al_2O_3 in pyroxenes and bulk rock, Cr# of sp and Yb content of cpx) for the Hawaiian peridotites. Because they cannot model such correlations using the available experimental $D^{\text{peridotite/melt}}$ values of H_2O , they believed that the variation in the H_2O content was not being controlled by the partial melting process. Instead, they explained the H_2O content variations in the Hawaii peridotites as being due to an AFC process that added a small percentage of a melt. However, in this model, the preservation of the correlations between the H_2O content and the melting indices through such a complex AFC process seems less likely. We show that the H_2O content variation in the Tianchang peridotites can be modeled by a simple fractional melting process using $\text{H}_2\text{O } D^{\text{peridotite/melt}}$ values of 0.01-0.03, providing a robust case against the view that mantle metasomatism always modifies the initial H_2O content of the continental lithospheric mantle.

For the Tianchang peridotites, the whole rock H_2O content variations versus the Yb content of cpx are modeled for PM and DMM sources and shown in Fig. 9. With the assumption that the silicate Earth has a chondritic refractory lithospheric element compositions, the H_2O content of the PM is estimated to be 850-1100 ppm H_2O (Palme and O'Neill, 2003). However, if considering a nonchondritic Earth model, the H_2O content in the PM would be ~650 ppm (Palme and O'Neill, 2014). In the DMM model, the whole rock H_2O content is estimated to be 50 to 200 ppm (MORB source, Workman and Hart, 2005). Experimental studies have shown significant variations in H_2O partition coefficients between the minerals and melt ($D^{\text{mineral/melt}}$) due to the starting materials, P-T conditions, mineral composition of the run products, existence of interstitial melts, etc. The $D^{\text{ol/melt}}$,

$D^{\text{opx/melt}}$ and $D^{\text{cpx/melt}}$ values range from 0.001 to 0.003, from 0.005 to 0.027, and from 0.007 to 0.03, respectively (Table 5, Aubaud et al., 2004, 2008; Grant et al., 2007; Hauri et al., 2006; Koga et al., 2003; Kovacs et al., 2012; O'Leary et al., 2010; Novella et al., 2014; Tenner et al., 2009). Considering the modal compositions of the minerals in the PM (ol:opx:cpx=54:28:18, Johnson, 1990) and DMM (ol:opx:cpx=58:29:13, Workman and Hart, 2005), the $D^{\text{peridotite/melt}}$ of H_2O is estimated to range from 0.003 to 0.014 for both the PM and DMM. This range is broadly similar to the results ($D^{\text{peridotite/melt}} = 0.01$ to 0.03) obtained for natural basalts that compared H_2O with REEs (Danyushevsky et al., 2000; Michael, 1995; Stolper and Newman, 1994). The PM source, which has an excessive initial H_2O content, did not produce the Tianchang peridotite whole rock H_2O contents via a fractional melting process (Fig. 9). As for the DMM source, the whole rock H_2O content variations with the Yb content of cpx and the melting degree (F %) are shown in Fig. 10a and Fig. 10b. Taking into account the error associated with the measured H_2O content (~20%) and the estimated H_2O content of the DMM, as well as the uncertainty of the $D^{\text{peridotite/melt}}$ values of H_2O , the H_2O content of the Tianchang peridotites generally follows a partial melting trend (Fig. 10). Overall, for the Tianchang peridotite xenoliths, we suggest that partial melting rather than later mantle metasomatism mainly controlled the H_2O content variations.

5.4 A newly accreted lithospheric mantle

As discussed above, the major and trace element compositions of the minerals provide evidence that the Tianchang peridotites are residues derived from partial melting of the mantle. The results shown in Fig. 8 and Fig. 10 suggest a fertile source with an Mg# value of 88.5-89 in ol, a Yb content in cpx that is 4.5-5 times primitive bulk mantle values and a whole-rock H_2O content of 50-200 ppm. These characteristics, together with the trace element pattern of the group I

samples, are similar to those of the asthenospheric mantle (Workman and Hart, 2005). Thus, we propose that the lithospheric mantle beneath the Tianchang area was newly accreted from an upwelling and cooled asthenosphere, followed by a small degree of melting.

6. Conclusions

(1) The peridotite xenoliths hosted by the Cenozoic basalts of Tianchang in eastern China were formed by variable degrees of partial melting followed by mantle metasomatism.

(2) The H₂O contents of cpx, opx and ol in the Tianchang peridotite xenoliths are 70-280 ppm, 35-140 ppm and approximately 0 ppm, respectively. The recalculated whole-rock H₂O contents range from 14 to 93 ppm, assuming a partition coefficient for H₂O of 0.1 between the ol and the cpx, which is in the range of the MORB source.

(3) The correlations between the whole rock H₂O contents and the melting indices (such as the Yb content in cpx and Cr# in spinel) suggest that partial melting was the main process controlling the variations of the peridotite H₂O contents. The H₂O content variations can be modelled by a simple melting process using the available partition coefficients of H₂O ($D^{\text{peridotite/melt}}=0.01-0.03$). Combined with the lack of correlations between the H₂O content and the La/Yb ratios in cpx, we suggested that mantle metasomatism did not modify the initial H₂O content in the lithospheric mantle in Tianchang.

Acknowledgements

We thank Sylvie Demouchy, two anonymous reviewers and the editor Marco Scambelluri for the comments and suggestions. We gratefully acknowledge the financial support from the National Science Foundation of China (nos. 41101036 and 41225005). We thank J.L. Xu for EMPA measurements and Z.H. Hou for ICP-MS measurements.

References

- Armstrong, J.T., 1989. CITZAF: Combined ZAF and Phirho(Z) Electron Beam Correction Programs, California Institute of Technology.
- Asimow, P.D., Dixon, J.E., Langmuir, C.H., 2004. A hydrous melting and fractionation model for mid-ocean ridge basalts: Application to the Mid-Atlantic Ridge near the Azores. *Geochemistry, Geophysics, Geosystems* 5, 1–24.
- Aubaud, C., Hauri, E.H., Hirschmann, M.M., 2004. Hydrogen partition coefficients between nominally anhydrous minerals and basaltic melts. *Geophysical Research Letters* 31, 2–5.
- Aubaud, C., Hirschmann, M.M., Withers, A.C., Hervig, R.L., 2008. Hydrogen partitioning between melt, clinopyroxene, and garnet at 3 GPa in a hydrous MORB with 6 wt.% H₂O. *Contributions to Mineralogy and Petrology* 156, 607–625.
- Aubaud, C., Withers, A.C., Hirschmann, M.M., Guan, Y., Leshin, L. a., Mackwell, S.J., Bell, D.R., 2007. Intercalibration of FTIR and SIMS for hydrogen measurements in glasses and nominally anhydrous minerals. *American Mineralogist* 92, 811–828.
- Bell, D.R., Ihinger, P.D., Rossman, G.R., 1995. Quantitative analysis of trace OH in garnet and pyroxenes. *American Mineralogist* 80, 465–474.
- Bell, D.R., Rossman, G.R., 1992. Water in Earth's Mantle: The Role of Nominally Anhydrous Minerals.

Science 255, 1391–1397.

Bell, D.R., Rossman, G.R., Moore, R.O., 2004. Abundance and partitioning of OH in a high-pressure magmatic system: Megacrysts from the monastery kimberlite, South Africa. *Journal of Petrology* 45, 1539-1564.

Bonadiman, C., Hao, Y., Coltorti, M., Dallai, L., Faccini, B., Huang, Y., Xia, Q., 2009. Water contents of pyroxenes in intraplate lithospheric mantle. *European Journal of Mineralogy* 21, 637–647.

Brey, G.P., Kohler, T., Nickel, K.G., 1990. Geothermobarometry in four-phase lherzolites II. new thermobarometers, and practical assessment of existing thermobarometers. *Journal of Petrology* 31, 1353–1378.

Chen, D., Peng, Z., 1988. K-Ar ages and Pb, Sr isotopic characteristics of some Cenozoic volcanic rocks from Anhui and Jiangsu provinces, China. *Acta Petrologica Sinica* 2, 12–16.

Coltorti, M., Bonadiman, C., Hinton, R.W., Siena, F., Upton, B.G.J., 1999. Carbonatite metasomatism of the oceanic upper mantle : evidence from clinopyroxenes and glasses in ultramafic xenoliths of Grande Comore, Indian Ocean. *Journal of Petrology* 40, 133–165.

Danyushevsky, L. V., Eggins, S.M., Fallon, T.J., D.M., C., 2000. H₂O Abundance in Depleted to Moderately Enriched Mid-ocean Ridge Magmas; Part I: Incompatible Behaviour, Implications for Mantle Storage, and Origin of Regional Variations. *Journal of Petrology* 41, 1329-1364.

Dawson, J.B., 1984. Contrasting types of upper mantle metasomatism? In: Kornprobst, J. (Eds.), *Kimberlites II*. Elsevier, Amsterdam, pp. 289–294.

Demouchy, S., Gaillard, F., Stern, C.R., Mackwell, S.2003. Water diffusion as a natural process in olivine crystals from garnet-peridotite xenoliths in basalts. In *EGS-AGU-EUG Joint Assembly* Vol. 1, 3216.

- Demouchy, S., Ishikawa, A., Tommasi, A., Alard, O., Keshav, S., 2015. Characterization of hydration in the mantle lithosphere: Peridotite xenoliths from the Ontong Java Plateau as an example. *Lithos* 212-215, 189-201.
- Demouchy, S., Jacobsen, S.D., Gaillard, F., Stem, C.R., 2006. Rapid magma ascent recorded by water diffusion profiles in mantle olivine. *Geology* 34, 429–432.
- Demouchy, S., Tommasi, A., Barou, F., Mainprice, D., Cordier, P., 2012. Deformation of olivine in torsion under hydrous conditions. *Physics of the Earth and Planetary Interiors* 202-203, 56-70.
- Denis, C., Alard, O., Demouchy, S., 2015. Water content and hydrogen behaviour during metasomatism in the uppermost mantle beneath Ray Pic volcano (Massif Central, France). *Lithos* 236-237, 256–274.
- Denis, C., Demouchy, S., Shaw, C., 2013. Evidence of dehydration in peridotites from Eifel Volcanic Field and estimates of the rate of magma ascent. *Journal of Volcanology and Geothermal Research* 258: 85-99.
- Dixon, J.E., Clague, D. a, Wallace, P., Poreda, R., 1997. Volatiles in alkalic basalts from the North Arch volcanic field, Hawaii: extensive degassing of deep submarine-erupted alkalic series lavas. *J. Petrol.* 38, 911–939.
- Dixon, J.E., Dixon, T.H., Bell, D.R., Malservisi, R., 2004. Lateral variation in upper mantle viscosity: Role of water. *Earth and Planetary Science Letters* 222, 451–467.
- Dixon, J.E., Stolper, E., Delaney, J.R., 1988. Infrared spectroscopic measurements of CO₂ and H₂O in Juan de Fuca Ridge basaltic glasses. *Earth and Planetary Science Letters* 90, 87–104.
- Doucet, L.S., Peslier, A.H., Ionov, D. a., Brandon, A.D., Golovin, A. V., Goncharov, A.G., Ashchepkov, I. V., 2014. High water contents in the Siberian cratonic mantle linked to metasomatism: An FTIR

study of Udachnaya peridotite xenoliths. *Geochimica et Cosmochimica Acta* 137, 159-187.

Downes, H., 2001. Formation and modification of the shallow sub-continental lithospheric mantle: a review of geochemical evidence from ultramafic xenolith suites and tectonically emplaced ultramafic massifs of western and central Europe. *Journal of Petrology* 42, 233-250.

Gao, S., Rudnick, R.L., Carlson, R.W., McDonough, W.F., Liu, Y.S., 2002. Re-Os evidence for replacement of ancient mantle lithosphere beneath the North China craton. *Earth and Planetary Science Letters* 198, 307-322.

Gose, J., Schmädicke, E., Beran, A., 2009. Water in enstatite from Mid-Atlantic Ridge peridotite: Evidence for the water content of suboceanic mantle? *Geology* 37, 543-546.

Grant, K., Ingrin, J., Lorand, J.P., Dumas, P., 2007. Water partitioning between mantle minerals from peridotite xenoliths. *Contributions to Mineralogy and Petrology* 154, 15-34.

Hao, Y., Xia, Q., Dallai, L., Coltorti, M., 2015. Recycled oceanic crust-derived fluids in the lithospheric mantle of eastern China: Constraints from oxygen isotope compositions of peridotite xenoliths. *Lithos* 228-229, 55-61.

Hao, Y.T., Xia, Q.K., Li, Q.W., Chen, H., Feng, M., 2014. Partial melting control of water contents in the Cenozoic lithospheric mantle of the Cathaysia block of South China. *Chemical Geology* 380, 7-19.

Hao, Y.T., Xia, Q.K., Liu, S.C., Feng, M., Zhang, Y.P., 2012. Recognizing juvenile and relict lithospheric mantle beneath the North China Craton: Combined analysis of H₂O, major and trace elements and Sr-Nd isotope compositions of clinopyroxenes. *Lithos* 149, 136-145.

Hao, Y.T., Xia, Q.K., Jia, Z.B., Zhao, Q.C., Li, P., Feng, M., Liu, S.C., 2016. Regional heterogeneity in the water content of the Cenozoic lithospheric mantle of Eastern China. *Journal of Geophysical*

Research 121, 517-537.

Hauri, E.H., Gaetani, G. A., Green, T.H., 2006. Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions. *Earth and Planetary Science Letters* 248, 715-734.

Hellebrand, E., Snow, J.E., Dick, H.J., Hofmann, A.W., 2001. Coupled major and trace elements as indicators of the extent of melting in mid-ocean-ridge peridotites. *Nature* 410, 677-681.

Herzberg, C., 2004. Geodynamic information in peridotite petrology. *Journal of Petrology* 45, 2507-2530.

Hesse, K.T., Gose, J., Stalder, R., Schmädicke, E., 2015. Water in orthopyroxene from abyssal spinel peridotites of the East Pacific Rise (ODP Leg 147: Hess Deep). *Lithos* 232, 23-34.

Hier-Majumder, S., 2005. Water weakening of clinopyroxenite in diffusion creep. *Journal of Geophysical Research* 110, B07406. doi:10.1029/2004JB003414

Hirschmann, M.M., 2006. Water, melting, and the deep Earth H₂O cycle. *Annual Review of Earth and Planetary Sciences* 34, 629-653.

Hirschmann, M.M., Aubaud, C., Withers, A.C., 2005. Storage capacity of H₂O in nominally anhydrous minerals in the upper mantle. *Earth and Planetary Science Letters* 236, 167-181.

Hirschmann, M.M., Tenner, T., Aubaud, C., Withers, a. C., 2009. Dehydration melting of nominally anhydrous mantle: The primacy of partitioning. *Physics of the Earth and Planetary Interiors* 176, 54-68.

Hirth, G., Kohlstedt, D.L., 1996. Water in the oceanic upper mantle: implications for rheology, melt extraction and the evolution of the lithosphere. *Earth and Planetary Science Letters* 144, 93-108.

Ingrin, J., Skogby, H., 2000. Hydrogen in nominally anhydrous upper-mantle minerals: concentration levels and implications. *European Journal of Mineralogy* 12, 543-570.

- Ionov, D.A., Bodinier, J.L., Mukasa, S.B., Zanetti, A., 2002. Mechanisms and Sources of Mantle Metasomatism: Major and Trace Element Compositions of Peridotite Xenoliths from Spitsbergen in the Context of Numerical Modelling. *Journal of Petrology* 43, 2219-2259.
- Johnson, K.T.M., Dick, H.J.B., Shimizu, N., 1990. Melting in the oceanic upper mantle: An ion microprobe study of diopsides in abyssal peridotites. *Journal of Geophysical Research* 95, 2661-2678.
- Karato, S.I., Jung, H., 1998. Water, partial melting and the origin of the seismic low velocity and high attenuation zone in the upper mantle. *Earth and Planetary Science Letters* 157, 193-207.
- Keppler, H., Bolfan-Casanova, N., 2006. Thermodynamics of Water Solubility and Partitioning. *Reviews in Mineralogy and Geochemistry* 62, 193-230.
- Koga, K., Hauri, E., Hirschmann, M., Bell, D., 2003. Hydrogen concentration analyses using SIMS and FTIR: Comparison and calibration for nominally anhydrous minerals. *Geochemistry, Geophysics, Geosystems* 4, 1-20.
- Kovács, I., Green, D.H., Rosenthal, A., Hermann, J., O'Neill, H.S.C., Hibberson, W.O., Udvardi, B., 2012. An experimental study of water in nominally anhydrous minerals in the upper mantle near the water-saturated solidus. *Journal of Petrology* 53, 2067-2093.
- Kovács, I., Hermann, J., O'Neill, H.S.C., Gerald, J.F., Sambridge, M., Horváth, G., 2008. Quantitative absorbance spectroscopy with unpolarized light: Part II. Experimental evaluation and development of a protocol for quantitative analysis of mineral IR spectra. *American Mineralogist* 93, 765-778.
- Lenardic, A., Moresi, L.N., Muhlhaus, H., 2003. Longevity and stability of cratonic lithosphere: insights from numerical simulations of coupled mantle convection and continental tectonics.

Journal of Geophysical Research 108, doi:10.1029/2002JB001859.

Li, P., Xia, Q.K., Deloule, E., Chen, H., Gu, X.Y., Feng, M., 2015. Temporal variation of H₂O content in the lithospheric mantle beneath the eastern North China Craton: Implications for the destruction of cratons. *Gondwana Research* 28, 276-287.

Li, Z.X.A., Lee, C.T. a, Peslier, A.H., Lenardic, A., Mackwell, S.J., 2008. Water contents in mantle xenoliths from the Colorado Plateau and vicinity: Implications for the mantle rheology and hydration-induced thinning of continental lithosphere. *Journal of Geophysical Research: Solid Earth* 113. doi:10.1029/2007JB005540

Lu, J., Zheng, J., Griffin, W.L., Yu, C., 2013. Petrology and geochemistry of peridotite xenoliths from the Lianshan region: Nature and evolution of lithospheric mantle beneath the lower Yangtze block. *Gondwana Research* 23, 161-175.

Mackwell, S.J., Kohlstedt, D.L., Paterson, M.S., 1985. The role of water in the deformation of olivine single crystals. *Journal of Geophysical Research* 90, 11319-11333.

McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. *Chemical Geology* 120, 223-253.

Mei, S., Kohlstedt, D.L., 2000. Influence of water on plastic deformation of olivine aggregates 1. Diffusion creep regim. *Journal of Geophysical Research* 105, 21457-21469.

Mei, S., Kohlstedt, D.L., 2000. Influence of water on plastic deformation of olivine aggregates 2. Diffusion creep regim. *Journal of Geophysical Research* 105, 21471-21481.

Menzies, M., Xu, Y., Zhang, H., Fan, W., 2007. Integration of geology, geophysics and geochemistry: A key to understanding the North China Craton. *Lithos* 96, 1-21.

Mercier, J.C.C., Nicolas, A., 1975. Textures and fabrics of upper-mantle peridotites as illustrated by xenoliths from basalts. *Journal of Petrology* 16, 454-487.

- Michael, P.J., 1995. Regionally distinctive sources of depleted MORB: Evidence from trace elements and H₂O. *Earth and Planetary Science Letters* 131, 301-320.
- Michael, P.J., 1988. The concentration, behavior and storage of H₂O in the suboceanic upper mantle: Implications for mantle metasomatism. *Geochimica et Cosmochimica Acta* 52, 555-566.
- Mierdel, K., Keppler, H., Smyth, J.R., Langenhorst, F., 2007. Water solubility in aluminous orthopyroxene and the origin of Earth's asthenosphere. *Science* 315, 364-368.
- Mosenfelder, J.L., Rossman, G.R., 2013a. Analysis of hydrogen and fluorine in pyroxenes: II. Clinopyroxene. *American Mineralogist* 98, 1042-1054.
- Mosenfelder, J.L., Rossman, G.R., 2013b. Analysis of hydrogen and fluorine in pyroxenes: I. Orthopyroxene. *American Mineralogist* 98, 1026-1041.
- Nichols, A.R.L., Carroll, M.R., Höskuldsson, Á., 2002. Is the Iceland hot spot also wet ? Evidence from the water contents of undegassed submarine and subglacial pillow basalts. *Earth and Planetary Science Letters* 202, 77-87.
- Norman, M.D., 1998. Melting and metasomatism in the continental lithosphere: Laser ablation ICPMS analysis of minerals in spinel lherzolites from eastern Australia. *Contributions to Mineralogy and Petrology* 130, 240-255.
- Novella, D., Frost, D.J., Hauri, E.H., Bureau, H., Raepsaet, C., Roberge, M., 2014. The distribution of H₂O between silicate melt and nominally anhydrous peridotite and the onset of hydrous melting in the deep upper mantle. *Earth and Planetary Science Letters* 400, 1-13.
- O'Leary, J.A., Gaetani, G.A., Hauri, E.H., 2010. The effect of tetrahedral Al³⁺ on the partitioning of water between clinopyroxene and silicate melt. *Earth and Planetary Science Letters* 297, 111-120.
- Palme, H., O'Neill, H.S.C., 2003, Cosmochemical estimates of mantle composition, in: Carlson, R.W.

(Eds.), Treatise on Geochemistry. Elsevier, Oxford, U. K., pp. 1-38.

Palme, H., O'Neill, H.S.C., 2014, Cosmochemical estimates of mantle composition, in: Carlson, R.W.

(Eds.), Treatise on Geochemistry 2nd edition. Elsevier, Oxford, U. K., pp. 1-39.

Peslier, A.H., Woodland, A.B., Bell, D.R., Lazarov, M., Lapen, T.J., 2012. Metasomatic control of water contents in the Kaapvaal cratonic mantle. *Geochimica et Cosmochimica Acta* 97, 213-246.

Peslier, A.H., Bizimis, M., 2015. Water in Hawaiian peridotite minerals: A case for a dry metasomatized oceanic mantle lithosphere. *Geochemistry, Geophysics, Geosystems* 1211-1232.

Peslier, A.H., Luhr, J.F., 2006. Hydrogen loss from olivines in mantle xenoliths from Simcoe (USA) and Mexico: Mafic alkalic magma ascent rates and water budget of the sub-continental lithosphere. *Earth and Planetary Science Letters* 242, 302-319.

Peslier, A.H., Luhr, J.F., Post, J., 2002. Low water contents in pyroxenes from spinel-peridotites of the oxidized, sub-arc mantle wedge. *Earth and Planetary Science Letters* 201, 69-86.

Peslier, A.H., Woodland, A.B., Wolff, J. A., 2008. Fast kimberlite ascent rates estimated from hydrogen diffusion profiles in xenolithic mantle olivines from southern Africa. *Geochimica et Cosmochimica Acta* 72, 2711-2722.

Saal, A.E., Hauri, E.H., Langmuir, C.H., Perfit, M.R., 2002. Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature* 419, 451-455.

Seaman, C., Sherman, S.B., Garcia, M.O., Baker, M.B., Balta, B., Stolper, E., 2004. Volatiles in glasses from the HSDP2 drill core. *Geochemistry Geophysics Geosystems* 5, doi:10.1029/2003GC000596

Simons, K., 2002. Volatiles in basaltic glasses from the Easter-Salas y Gomez Seamount Chain and Easter Microplate: Implications for geochemical cycling of volatile elements. *Geochemistry Geophysics Geosystems* 3. doi:10.1029/2001GC000173

- Skogby, H., 2006. Water in Natural Mantle Minerals I: Pyroxenes. *Reviews in Mineralogy and Geochemistry* 62, 155-167.
- Skogby, H., Bell, D.R., Rossman, G.R., 1990. Hydroxide in pyroxene: variation in the natural environment. *Am. Mineral.* 75, 764-774.
- Skogby, H., Rossman, G.R., 1989. OH⁻ in pyroxene; an experimental study of incorporation mechanisms and stability. *American Mineralogist* 74, 1059-1069.
- Sobolev, A. V., Chaussidon, M., 1996. H₂O concentrations in primary melts from supra-subduction zones and mid-ocean ridges: Implications for H₂O storage and recycling in the mantle. *Earth and Planetary Science Letters* 137, 45-55.
- Stolper, E., Newman, S., 1994. The role of water in the petrogenesis of Mariana trough magmas. *Earth and Planetary Science Letters* 121, 293-325.
- Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders, A.D., Norry, M.J. (Eds.), *Magmatism in Ocean Basins*. Geol. Soc. Spec. Publ., London, pp. 313-345.
- Tenner, T.J., Hirschmann, M.M., Withers, A.C., Hervig, R.L., 2009. Hydrogen partitioning between nominally anhydrous upper mantle minerals and melt between 3 and 5 GPa and applications to hydrous peridotite partial melting. *Chemical Geology* 262, 42-56.
- Tian, Z.Z., Liu, J., Xia, Q.K., Ingrin, J., Ni, H.W., 2015. H concentration profile in nature orthopyroxene: constraints on the preservation of water and dehydration mechanisms in the nature peridotite. *Geology*, in review.
- Wallace, P.J., 2002. Volatiles in Submarine Basaltic Glasses from the Northern Kerguelen Plateau (ODP Site 1140): Implications for Source Region Compositions, Magmatic Processes, and Plateau

- Subsidence. *Journal of Petrology* 43, 1311-1326.
- Warren, J., Hauri, E., 2014. Pyroxenes as tracers of mantle water variations. *Journal of Geophysical Research: Solid* 119, 1851-1881.
- Withers, A.C., 2013. On the use of unpolarized infrared spectroscopy for quantitative analysis of absorbing species in birefringent crystals. *American Mineralogist* 98, 689-697.
- Withers, A.C., Hirschmann, M.M., 2008. Influence of temperature, composition, silica activity and oxygen fugacity on the H₂O storage capacity of olivine at 8 GPa. *Contributions to Mineralogy and Petrology* 156, 595-605.
- Withers, A.C., Hirschmann, M.M., 2007. H₂O storage capacity of MgSiO₃ clinoenstatite at 8-13 GPa, 1,100-1,400C. *Contributions to Mineralogy and Petrology* 154, 663-674.
- Workman, R.K., Hart, S.R., 2005. Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters* 231, 53-72.
- Workman, R.K., Hauri, E., Hart, S.R., Wang, J., Blusztajn, J., 2006. Volatile and trace elements in basaltic glasses from Samoa: Implications for water distribution in the mantle. *Earth and Planetary Science Letters* 241, 932-951.
- Xia, Q.K., Hao, Y.T., Li, P., Deloule, E., Coltorti, M., Dallai, L., Yang, X.Z., Feng, M., 2010. Low water content of the Cenozoic lithospheric mantle beneath the eastern part of the North China Craton. *Journal of Geophysical Research* 115, 1-22.
- Xia, Q.K., Hao, Y.T., Liu, S.C., Gu, X.Y., Feng, M., 2013. Water contents of the Cenozoic lithospheric mantle beneath the western part of the North China Craton: Peridotite xenolith constraints. *Gondwana Research* 23, 108-118.
- Xu, Y.G., 2001. Thermo-tectonic destruction of the archaean lithospheric keel beneath the Sino-Korean

- Craton in China: Evidence, timing and mechanism. *Physics and Chemistry of the Earth, Part A: Solid Earth and Geodesy* 26, 747-757.
- Yang, X.Z., Deloule, E., Xia, Q.K., Fan, Q.C., Feng, M., 2008a. Water contrast between Precambrian and Phanerozoic continental lower crust in eastern China. *Journal of Geophysical Research: Solid Earth* 113, 1-12.
- Yang, X.Z., Xia, Q.K., Deloule, E., Dallai, L., Fan, Q.C., Feng, M., 2008b. Water in minerals of the continental lithospheric mantle and overlying lower crust: A comparative study of peridotite and granulite xenoliths from the North China Craton. *Chemical Geology* 256, 33-45.
- Yu, Y., Xu, X.S., Griffin, W.L., O'Reilly, S.Y., Xia, Q.K., 2011. H₂O contents and their modification in the Cenozoic subcontinental lithospheric mantle beneath the Cathaysia block, SE China. *Lithos* 126, 182-197.
- Zhang, H.F., Goldstein, S.L., Zhou, X.H., Sun, M., Zheng, J.P., Cai, Y., 2008. Evolution of subcontinental lithospheric mantle beneath eastern China: Re-Os isotopic evidence from mantle xenoliths in Paleozoic kimberlites and Mesozoic basalts. *Contributions to Mineralogy and Petrology* 155, 271-293.
- Zheng, J., Griffin, W.L., O'Reilly, S.Y., Liou, J.G., Zhang, R.Y., Lu, F., 2005. Late Mesozoic-Eocene Mantle Replacement beneath the Eastern North China Craton: Evidence from the Paleozoic and Cenozoic Peridotite Xenoliths. *International Geology Review* 47, 457-472.
- Zheng, J., O'Reilly, S.Y., Griffin, W.L., Lu, F., Zhang, M., 1998. Nature and Evolution of Cenozoic Lithospheric Mantle beneath Shandong Peninsula, Sino-Korean Craton, Eastern China. *International Geology Review* 40, 471-499.
- Zheng, J., O'Reilly, S.Y., Griffin, W.L., Lu, F., Zhang, M., Pearson, N.J., 2001. Relict refractory mantle

beneath the eastern North China block: Significance for lithosphere evolution. *Lithos* 57, 43-66.

Figure Captions

Figure 1. Xenoliths hosted by Cenozoic basalts in eastern China and the sample location. DTGL:

Daxing'anling-Taihangshan Gravity Lineament.

Figure 2. Variation plots for major elements in the minerals. Al_2O_3 versus Mg# in opx (a), Al_2O_3

versus Mg# in cpx (b), Na_2O versus Mg# in cpx (c) and Cr# in spinel versus Mg# in ol (d).

Subei basin xenolith data are from Bonadiman et al. (2009) and Xia et al. (2010). Hebi xenolith data are from Zheng et al. (2001).

Figure 3. REE (a, c) and trace element (b, d) patterns of cpx in the Tianchang peridotites. REEs

are normalized to C1 chondrite values (Sun and McDonough, 1989) and identified with a subscript “n”. The trace elements are normalized to the primitive mantle values (McDonough and Sun, 1995) and identified with a subscript “PM”.

Figure 4. Representative IR spectra of ol (a), opx (b) and cpx (c) in the Tianchang peridotites.

Thickness is normalized to 1 cm, and the spectra are stacked for clarity.

Figure 5. H_2O contents in pyroxenes. H_2O contents of cpx (in ppm) versus opx (a), Na_2O versus

H_2O contents in cpx (b) and Al_2O_3 versus H_2O contents in opx (c). Cross line represents the analytical uncertainty. The symbols are the same as those in Fig. 2.

Figure 6. Y and Yb contents of cpx in peridotite xenoliths from Tianchang. A fractional melting

model (Norman, 1998) within the spinel stability field was used with $D^{\text{cpx/melt}}=0.42$ for Y and 0.40 for Yb. The subscript “PM” indicates that concentrations have been normalized to the primitive mantle composition (McDonough and Sun, 1995) with $X_{\text{cpx}}=0.2$. The DMM values for Y and Yb are from Workman and Hart (2005), with $X_{\text{cpx}}=0.17$. The tick marks on curves indicate partial melting percentages (F %).

Figure 7. Plot of $(La/Yb)_n$ versus Ti/Eu of cpx from Tianchang peridotites. The fields for “carbonatitic” and “silicate” metasomatism are from Coltorti et al. (1999).

Figure 8. Variation plots for H_2O content and parameters of Tianchang peridotites. Whole-rock (WR) H_2O content (in ppm) versus $(La/Yb)_n$ in cpx (a) and $Cr\#$ in spinel (b), and H_2O content (in ppm) versus Yb_{PM} in cpx (c).

Figure 9. Modelling of fractional partial melting from PM and DMM. $D^{cpx/melt}=0.40$ for Yb, and $D^{peridotite/melt}$ for H_2O is set to 0.01 (black line) and 0.03 (red line). The starting point of the whole rock H_2O content is 650-1100 ppm for the PM and 50-200 ppm for the DMM, (see text for details).

Figure 10. Modeling of fractional partial melting from the DMM. Degrees of partial melting in (b) are estimated using $Cr\#$ of the spinel as $F\%=10\times Ln(Cr\#)+24$ (Hellebrand et al., 2001).

Table 1 Sample list and information summary of the Tianchang peridotites

Samples	texture	Modal composition				Mg# in Ol	Cr# in sp	Equilibration temp.		REE group
		ol	opx	cpx	sp			BKN	Ca-opx	
DFS01	protogranular	45	36	15	4	89.77	11.36	978	965	I
DFS02	protogranular	62	30	7	1	90.30	17.05	1004	967	II
DFS03	porphyroblastic	51	31	15	3	90.20	14.53	945	939	I
DFS04	protogranular	57	27	14	2	90.43	17.69	978	954	II
DFS05	protogranular	64	26	8	2	90.07	18.97	962	911	I
DFS06	porphyroblastic	51	35	13	1	89.71	11.37	970	935	I
DFS07	porphyroblastic	64	23	12	1	89.82	18.41	895	937	II
DFS08	porphyroblastic	56	27	14	3	89.94	18.62	929	934	II
DFS09	porphyroblastic	83	11	6	0	90.07	21.29	894	927	II
DFS10	protogranular	57	22	19	2	89.93	13.33	1028	938	I
DFS11	protogranular	51	31	16	2	89.18	9.51	1012	943	I
DFS13	protogranular	62	21	15	2	89.91	12.95	946	914	II
DFS14	protogranular	70	21	8	1	89.95	13.22	1031	937	II
DFS15	protogranular	79	18	2	1	91.37	25.90	822	874	II
DFS16	porphyroblastic	67	19	13	1	90.00	14.73	1025	960	II

BKN and Ca-opx are temperature estimates that use the two-pyroxene and Ca-in-opx geothermometers of Brey et al. (1990).

Table 2 Chemical compositions of minerals of the Tianchang peridotite xenoliths

Olivine	DFS01		DFS02		DFS03		DFS04		DFS05		DFS06		DFS07		DFS08		DFS09		DFS10		DFS11		DFS13		DFS14		DFS15		DFS16	
n.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.
SiO ₂	40.79	0.63	41.17	0.45	40.94	0.22	41.26	0.39	40.47	0.11	41.34	0.19	41.23	0.69	40.84	0.20	41.06	0.39	40.34	0.32	40.16	0.18	40.52	0.34	40.47	0.33	44.32	7.53	40.20	0.45
TiO ₂	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.02	0.02	0.01	0.02	0.00	0.00
Al ₂ O ₃	0.03	0.01	0.02	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.02	0.02	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.69	1.35	0.02	0.02
Cr ₂ O ₃	0.22	0.31	0.02	0.02	0.04	0.03	0.03	0.02	0.01	0.02	0.08	0.10	0.03	0.02	0.03	0.03	0.07	0.09	0.00	0.01	0.04	0.03	0.02	0.02	0.25	0.39	0.36	0.36	0.03	0.03
FeO	9.80	0.14	9.31	0.11	9.42	0.09	9.17	0.24	9.62	0.14	9.81	0.12	9.69	0.17	9.61	0.19	9.50	0.42	9.74	0.12	10.43	0.24	9.71	0.11	9.66	0.21	7.72	1.39	9.69	0.07
MnO	0.11	0.02	0.09	0.01	0.11	0.02	0.08	0.04	0.08	0.02	0.09	0.02	0.12	0.02	0.12	0.04	0.14	0.04	0.10	0.04	0.10	0.02	0.10	0.02	0.12	0.02	0.10	0.02	0.11	0.01
MgO	48.28	0.33	48.58	0.13	48.63	0.20	48.59	0.21	48.90	0.17	47.98	0.14	47.97	0.66	48.23	0.20	48.33	0.25	48.76	0.17	48.24	0.23	48.52	0.22	48.48	0.13	45.87	7.52	48.93	0.11
CaO	0.06	0.01	0.06	0.01	0.05	0.01	0.05	0.01	0.02	0.00	0.05	0.01	0.03	0.01	0.04	0.01	0.03	0.01	0.04	0.01	0.04	0.01	0.03	0.00	0.06	0.02	0.12	0.15	0.06	0.01
NiO	0.34	0.04	0.38	0.04	0.37	0.04	0.39	0.02	0.37	0.06	0.41	0.05	0.41	0.08	0.37	0.05	0.37	0.06	0.39	0.01	0.33	0.02	0.40	0.05	0.38	0.04	0.26	0.13	0.39	0.07
TOTAL	99.64	0.40	99.63	0.30	99.57	0.27	99.60	0.36	99.47	0.43	99.76	0.42	99.49	0.70	99.26	0.21	99.52	0.60	99.40	0.31	99.34	0.46	99.30	0.14	99.44	0.51	99.45	0.31	99.42	0.26
Mg#	89.77		90.30		90.20		90.43		90.07		89.71		89.82		89.94		90.07		89.93		89.18		89.91		89.95		91.37		90.00	
Opx	DFS01		DFS02		DFS03		DFS04		DFS05		DFS06		DFS07		DFS08		DFS09		DFS10		DFS11		DFS13		DFS14		DFS15		DFS16	
n.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	3	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.
SiO ₂	55.70	0.83	55.84	0.37	55.60	0.40	55.81	0.25	55.66	0.57	55.07	0.22	55.67	0.56	56.00	0.31	55.64	0.67	55.25	0.59	55.53	0.59	56.25	0.44	55.52	0.59	56.61	0.26	55.87	0.36
TiO ₂	0.20	0.12	0.12	0.02	0.09	0.02	0.09	0.02	0.07	0.02	0.08	0.01	0.06	0.02	0.08	0.02	0.01	0.02	0.10	0.01	0.13	0.01	0.09	0.04	0.09	0.03	0.01	0.02	0.06	0.03
Al ₂ O ₃	4.45	0.16	4.20	0.10	4.17	0.08	4.07	0.07	3.84	0.26	4.26	0.21	3.68	0.08	3.76	0.14	3.47	0.16	4.48	0.15	4.57	0.07	3.96	0.12	4.36	0.10	2.89	0.27	4.21	0.06
Cr ₂ O ₃	0.41	0.07	0.49	0.03	0.42	0.11	0.50	0.04	0.48	0.03	0.38	0.12	0.49	0.28	0.43	0.06	0.37	0.05	0.35	0.04	0.26	0.07	0.32	0.09	0.50	0.18	0.60	0.17	0.41	0.10
FeO	6.26	0.19	5.85	0.07	5.98	0.06	6.02	0.06	5.93	0.22	6.47	0.14	6.27	0.10	6.08	0.13	6.06	0.11	5.95	0.10	6.40	0.15	5.67	0.29	5.87	0.11	5.08	0.26	5.84	0.05
MnO	0.14	0.01	0.13	0.02	0.13	0.02	0.11	0.01	0.10	0.01	0.09	0.06	0.14	0.02	0.12	0.03	0.12	0.02	0.12	0.02	0.11	0.01	0.12	0.03	0.11	0.03	0.10	0.02	0.09	0.02
MgO	31.92	0.16	32.46	0.12	31.98	0.10	31.68	0.11	32.68	0.12	32.16	0.15	32.52	0.24	32.35	0.71	33.50	0.16	32.35	0.47	31.73	0.31	32.79	0.13	32.25	0.23	33.65	0.26	32.49	0.17
CaO	0.69	0.05	0.70	0.03	0.61	0.07	0.65	0.02	0.54	0.06	0.60	0.05	0.61	0.07	0.60	0.09	0.58	0.07	0.61	0.02	0.62	0.03	0.55	0.06	0.61	0.03	0.45	0.03	0.68	0.08
Na ₂ O	0.12	0.03	0.10	0.03	0.08	0.01	0.10	0.02	0.08	0.03	0.08	0.02	0.06	0.02	0.05	0.02	0.01	0.01	0.08	0.01	0.07	0.01	0.07	0.02	0.08	0.01	0.03	0.01	0.10	0.04
K ₂ O	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
NiO	0.07	0.06	0.10	0.04	0.05	0.03	0.11	0.03	0.08	0.02	0.09	0.03	0.08	0.02	0.09	0.03	0.05	0.03	0.07	0.04	0.07	0.04	0.08	0.07	0.11	0.03	0.07	0.03	0.06	0.05
TOTAL	99.97	0.65	100.02	0.30	99.12	0.51	99.16	0.05	99.47	0.48	99.29	0.15	99.58	0.52	99.56	0.66	99.81	0.52	99.36	0.36	99.50	0.51	99.90	0.51	99.51	0.55	99.51	0.33	99.83	0.39
Mg#	90.09		90.81		90.50		90.36		90.77		89.86		90.24		90.47		90.79		90.64		89.84		91.15		90.74		92.19		90.84	
Cpx	DFS01		DFS02		DFS03		DFS04		DFS05		DFS06		DFS07		DFS08		DFS09		DFS10		DFS11		DFS13		DFS14		DFS15		DFS16	
n.	3	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.
SiO ₂	52.36	0.52	52.85	0.37	52.88	0.21	53.01	0.30	52.69	0.32	52.25	0.29	52.32	0.38	52.21	0.78	54.42	0.36	52.65	0.38	52.47	0.78	52.97	0.52	52.78	0.40	53.30	0.40	53.31	0.27
TiO ₂	0.40	0.27	0.36	0.03	0.38	0.04	0.39	0.05	0.32	0.02	0.40	0.04	0.26	0.03	0.35	0.03	0.07	0.01	0.41	0.06	0.58	0.02	0.40	0.03	0.43	0.08	0.05	0.04	0.35	0.04
Al ₂ O ₃	6.62	0.11	6.15	0.08	5.91	0.10	6.22	0.09	6.03	0.10	6.39	0.07	5.02	0.08	5.97	0.23	3.65	0.40	6.60	0.08	7.05	0.12	6.25	0.22	6.57	0.09	3.78	0.09	6.30	0.14
Cr ₂ O ₃	1.01	0.38	1.14	0.12	0.95	0.06	1.05	0.05	1.20	0.06	0.74	0.08	0.92	0.10	1.15	0.13	0.76	0.11	1.00	0.32	0.69	0.09	0.97	0.10	0.85	0.06	1.13	0.12	0.93	0.09
FeO	2.75	0.02	2.55	0.15	2.64	0.13	2.62	0.08	2.28	0.09	2.91	0.15	2.74	0.11	2.43	0.12	2.10	0.26	2.53	0.11	2.73	0.13	2.27	0.11	2.60	0.13	1.64	0.17	2.57	0.02
MnO	0.07	0.02	0.08	0.01	0.06	0.01	0.10	0.04	0.06	0.02	0.08	0.02	0.06	0.02	0.07	0.01	0.05	0.02	0.07	0.01	0.05	0.03	0.06	0.03	0.06	0.02	0.05	0.01	0.07	0.01
MgO	14.52	0.15	14.70	0.33	14.78	0.09	14.33	0.09	14.67	0.07	14.61	0.20	15.11	0.36	14.46	0.20	15.44	0.54	14.64	0.20	14.47	0.24	14.44	0.17	14.33	0.40	15.80	0.21	14.76	0.04
CaO	20.35	0.19	20.18	0.11	20.91	0.11	20.12	0.16	20.69	0.12	20.34	0.13	21.54	0.18	20.70	0.13	21.49	0.69	19.89	0.15	20.07	0.21	20.77	0.21	19.94	0.13	22.73	0.21	20.13	0.05
Na ₂ O	1.63	0.14	1.63	0.15	1.50	0.07	1.80	0.05	1.49	0.05	1.61	0.03	1.16	0.11	1.54	0.05	1.31	0.15	1.64	0.03	1.64	0.11	1.59	0.03	1.57	0.06	0.79	0.03	1.62	0.09
K ₂ O	0.03	0.02	0.02	0.02	0.00	0.00	0.01	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
NiO	0.05	0.04	0.01	0.00	0.03	0.02	0.08	0.06	0.05	0.03	0.04	0.02	0.05	0.03	0.07	0.02	0.04	0.02	0.03	0.02	0.05	0.03	0.02	0.03	0.04	0.05	0.01	0.01	0.05	0.04
TOTAL	99.80	0.47	99.67	0.24	100.04	0.34	99.73	0.25	99.49	0.26	99.37	0.33	99.18	0.17	98.94	0.33	99.34	0.57	99.46	0.35	99.80	0.74	99.74	0.56	99.18	0.51	99.27	0.50	100.09	0.39
Mg#	90.39		91.15		90.90		90.69		91.98		89.96		90.76		91.40		92.91		91.15		90.43		91.90		90.76		94.49		91.11	
Spinel	DFS01		DFS02		DFS03		DFS04		DFS05		DFS06		DFS07		DFS08		DFS09		DFS10		DFS11		DFS13		DFS14		DFS15		DFS16	
n.	4	1s.d.	3	1s.d.	4	1s.d.	4	1s.d.	3	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.	4	1s.d.
SiO ₂	0.10	0.08	0.06	0.05	0.06	0.02	0.09	0.05	0.07	0.05	0.02	0.03	0.02	0.02	0.05	0.02	0.02	0.02</												

Table 3 Trace element content of cpx of the Tianchang peridotite xenoliths

Samples	Rb	Ba	Th	U	Nb	Ta	La	Ce	Pr	Sr	Nd	Zr	Hf	Sm	Eu	Ti	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
DFS01	0.27	0.03	0.02	0.01	0.15	0.02	0.98	3.34	0.72	68.8	4.28	31.06	1.76	1.65	0.71	3,292.32	2.08	0.47	3.55	19.59	0.73	2.15	0.31	2.00	0.27
DFS02	0.04	0.03	0.76	0.16	4.96	0.22	5.07	10.37	1.25	125.3	5.14	20.48	0.69	1.22	0.64	2,316.05	1.76	0.37	2.78	15.63	0.56	1.84	0.25	1.71	0.27
DFS03	0.32	3.52	0.02	0.01	0.05	0.01	0.42	2.08	0.39	43.2	2.91	15.81	0.65	1.18	0.61	2,578.52	2.24	0.41	3.35	18.63	0.66	2.06	0.27	1.90	0.28
DFS04	0.06	1.27	1.32	0.31	4.90	0.19	9.99	22.45	2.36	225.8	8.93	23.92	0.78	2.17	0.71	2,456.58	2.25	0.40	2.61	15.83	0.65	1.84	0.24	1.71	0.26
DFS05	0.08	0.10	0.03	0.01	0.18	0.02	0.83	2.80	0.50	53.7	2.60	17.57	0.59	0.93	0.47	2,016.55	1.62	0.29	2.35	13.47	0.50	1.47	0.20	1.17	0.19
DFS06	0.00	b.d.l.	b.d.l.	b.d.l.	0.01	b.d.l.	0.12	0.73	0.23	31.0	1.94	13.86	0.56	1.12	0.54	2,489.42	2.02	0.39	3.10	18.15	0.65	2.07	0.28	1.87	0.32
DFS07	0.13	0.10	1.22	0.22	1.05	0.02	11.26	22.99	2.56	306.2	9.29	18.56	0.53	1.76	0.63	1,866.59	1.94	0.34	2.16	12.30	0.40	1.24	0.15	1.23	0.15
DFS08	0.23	0.53	0.15	0.05	0.23	0.04	2.73	6.22	0.81	99.9	4.04	23.75	0.74	1.52	0.57	2,266.40	1.93	0.34	2.81	14.77	0.54	1.61	0.22	1.56	0.23
DFS09	0.54	0.74	0.30	0.11	0.24	0.02	4.48	8.76	0.81	56.1	2.99	1.92	0.10	0.56	0.15	488.67	0.53	0.14	1.27	6.85	0.28	0.83	0.14	0.92	0.13
DFS10	0.20	0.05	0.03	0.01	0.11	0.02	1.15	4.42	0.80	82.2	5.72	39.81	1.15	2.11	0.76	3,885.23	3.15	0.54	3.90	22.49	0.86	2.42	0.39	2.32	0.32
DFS11	0.10	b.d.l.	0.02	0.01	0.12	0.02	1.16	4.27	0.75	81.4	4.77	39.80	1.13	2.00	0.72	3,892.89	2.89	0.61	4.02	22.09	0.85	2.43	0.38	2.04	0.25
DFS13	0.04	0.03	0.78	0.20	0.12	0.01	3.07	5.46	0.76	106.1	4.18	27.85	0.91	1.61	0.63	3,022.14	2.75	0.49	3.70	19.49	0.76	2.11	0.27	1.93	0.24
DFS14	0.06	0.03	0.43	0.10	0.29	0.01	2.75	4.04	0.55	93.0	3.98	25.60	0.92	1.52	0.69	3,157.39	2.49	0.50	3.31	18.36	0.74	1.95	0.30	1.79	0.31
DFS15	0.05	0.02	0.99	0.22	0.71	0.06	9.25	15.63	1.57	132.5	6.26	16.87	0.32	0.90	0.42	484.47	0.70	0.11	0.81	4.68	0.19	0.56	0.10	0.57	0.11
DFS16	0.12	b.d.l.	0.88	0.20	0.68	0.02	5.70	8.99	0.80	135.8	4.51	24.31	0.75	1.32	0.62	2,635.09	2.09	0.41	3.07	17.38	0.64	1.91	0.27	1.90	0.23

b.d.l. below detection limit

Table 4 Water contents of orthopyroxene, clinopyroxene and calculated whole rock water contents of the Tianchang peridotites

Samples	Olivine		Orthopyroxene			Clinopyroxene			calculated whole-rock	
	n.	H ₂ O (ppm)	n.	H ₂ O (ppm)	Δ H ₂ O	n.	H ₂ O (ppm)	Δ H ₂ O	H ₂ O (ppm)	Δ H ₂ O
DFS01	10	<2	15	107	21	15	246	49	86	17
DFS02	11	<2	15	80	16	17	185	37	48	10
DFS03	10	<2	16	96	19	20	224	45	75	15
DFS04	10	<2	19	97	19	16	283	57	82	16
DFS05	10	<2	16	40	8	17	136	27	30	6
DFS06	10	<2	23	96	19	17	223	45	74	15
DFS07	10	<2	16	66	13	16	129	26	39	8
DFS08	11	<2	17	46	9	19	103	21	33	7
DFS09	10	<2	22	56	11	19	96	19	20	4
DFS10	10	<2	17	109	22	18	155	31	62	12
DFS11	10	<2	17	137	27	18	238	48	93	19
DFS13	11	<2	19	65	13	17	113	23	38	8
DFS14	10	<2	17	108	22	17	162	32	47	9
DFS15	10	<2	15	36	7	14	72	14	14	3
DFS16	12	<2	16	70	14	17	141	28	41	8

n. are numbers of cpx and opx grains analyzed

Δ H₂O are uncertainties for H₂O contents of opx, cpx and whole rock.

Whole-rock H₂O contents are calculated based on H₂O content and modal percentage of mineral.

Olivine water content is estimated as water partition coefficients $D^{\text{ol/cpx}}=0.1$.

Table 5 Summary of partition coefficients of H₂O among minerals and melt at pressure <6 GPa

Reference	D ^{ol/melt}	D ^{opx/melt}	D ^{cpx/melt}	D ^{grt/melt}	D ^{bulk/melt}	D ^{ol/opx}	D ^{ol/cpx}	D ^{cpx/opx}	D ^{cpx/grt}	Al ₂ O ₃ in opx	Al ₂ O ₃ in cpx	P	T(°C)
Koga et al. (2003)	0.0020 ± 0.0002	0.0245 ± 0.0015				0.083				7.30%		2 GPa	1380
Aubaud et al. (2004)	0.0011-0.0029	0.013-0.027	0.019-0.026		0.009	0.11 ± 0.01	0.08 ± 0.01	1.4 ± 0.3		3.39-8.07%	7.01-9.43%	1-2 GPa	1230-1380
Aubaud et al. (2007)	0.0004-0.0011	0.0055-0.0114	0.014										
Bell et al. (2004)	0.0046-0.0053	0.0059-0.0093	0.013-0.016		0.0051-0.0063							5 GPa	1100-1400
Grant et al. (2006)						0.30-0.44				0-11.9%		1-2 GPa	1320
Hauri et al. (2006)	0.0013-0.0021	0.012-0.034	0.0069-0.034	0.003	0.007		0.054-0.079	0.9-1.42	3.07-3.52	4-9.5%	~3-15%	1-4 GPa	1000-1380
Grant et al. (2007)							0.011, 0.045	2.1±0.1		0.66-5.26%	1.83-7.44%		
Aubaud et al. (2008)			0.023 ± 0.005	0.0018 ± 0.0006	0.015-0.0089				11 ± 3		8.83-13.6%	3 GPa	1150-1325
Tenner et al. (2009)	0.0006	0.009-0.019	0.014-0.021	0.011-0.0033	0.006-0.01		0.037	1.2-2		2.03-6.25%	3.42-7.35%	3-5 GPa	1350-1440
O'Leary et al. (2010)			0.0228-0.0477		0.005-0.013						10.3-14.5%	1.5 GPa	1275
Kovacs et al. (2012)						0.149-0.213		2.7-3.5		2.27-2.78%	1.97-3.67%	2.5-4 GPa	
Novella et al. (2014)	0.0040 ± 0.0006	0.0064 ± 0.0004	0.0115 ± 0.0016	0.0032 ± 0.0008		0.625	0.35	2.34	3.59375	1.17-1.47%	1.81-2.49%	6 GPa	1400