Fragments of asthenosphere incorporated in the lithospheric mantle underneath the Subei Basin, eastern China: Constraints from geothermobarometric results and water contents of peridotite xenoliths in Cenozoic basalts

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Anhydrous, medium/coarse-grained spinel bearing mantle xenoliths from the Subei Basin, Eastern China have mineral arrangements that reflect low energy geometry. Because of clinopyroxene modal contents, they are grouped into cpx-rich lherzolites (cpx \textgtr 14\% percentage), lherzolites (8 < cpx \textless 14\%), cpx-poor lherzolites (6 < cpx \textless 8\%) and harzburgites (cpx up to 4\%), without relevant textural differences from the most fertile to the most depleted lithotypes. The cpx-rich lherzolites have mineral chemistry close in composition to Primitive Mantle (PM), whereas cpx-poor lherzolites (and lherzolite) and harzburgite groups cannot be considered as a result of direct melting of the PM source. In addition, the high LREE, Th and U contents, coupled with a Sr enrichment of clinopyroxenes in these lithotypes, indicate the circulation of a silicate melt (with crustal components) in a variably depleted mantle sector well before the entrapment of the xenoliths by the host basalt.

Despite the large differences in refractory lithophile element contents (i.e. Ca, Al and REE), the equilibrium temperatures never exceed 1021 °C with a constant difference (\textless 200 °C) from harzburgites to cpx-rich lherzolites. Measured mineral water contents indicate that the whole rock contains, on average, 19 ± 7 ppm of H$_2$O without any systematic variation among rock types nor correlation with Al$_2$O$_3$, light-REE and Yb (or Y) contents of cpx. The cpx H$_2$O contents of cpx-rich lherzolites (41–96 ppm) are, on average, one order of magnitude lower than those theoretically expected (214–530 ppm) for a residuum after a maximum of 3\% of PM fractional (= bulk) melting in the spinel stability field.

The proposed dehydration model suggests that the cold highly refractory harzburgites and cpx-poor lherzolites (and lherzolites?) may represent old cratonic lithospheric mantle modified at depth by the interaction with silicate melts, which may also have involved crustal components. In turn, cpx-rich lherzolites constitute fragments of upwelling fertile asthenosphere, which caused the removal/erosion of the lowermost part of the lithospheric mantle. This asthenosphere portion may have been incorporated in the lithospheric region since the Jurassic and it may have progressively cooled down after one (or more) partial melting episodes. The water depletion can be accounted for a continuous loss by diffusion during the subsolidus chemical-physical readjustment, well after (> 5My, based on modelled H$_2$O solid-solid diffusion rate) the occurrence of the last melting episode.

\textbf{1. Introduction}

The North China Craton (NCC), characterized by crustal remnants older than 3.8 Ga (Liu et al., 1992), represents a unique large craton of eastern Eurasia and its formation and subsequent evolution are well preserved in the Phanerozoic geology of eastern China. In recent years, geological, geophysical and geochemical studies have converged to suggest that the Eastern Block of the North China Craton (NCC) has lost > 100 km in thickness of its lithospheric root (Windley et al., 2010; Menzies et al., 2007 and references therein). However, currently the subject of debate, is how and when the Archaean sub-continental lithospheric mantle was delaminated/thinned (e.g. Griffin et al., 1998, 2009; Xu, 2001; Zhang et al., 2003; Rudnick et al., 2004; Wu et al., 2006; Deng et al., 2004; Gao et al., 2004; Ying et al., 2013; Tang et al., 2019).

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and trace element chemistry (including H2O) of peridotite minerals xenoliths hosted by the Cenozoic basalts from Lianshan (LS). The major basin, eastern China, through a detailed geochemical study of peridotite oxene (cpx), we characterize the mantle domain beneath the Subei and their possible relationship with the asthenosphere, but also to shed not only the nature of the sub-continental lithospheric mantle subsequently, the peridotite xenoliths from the Subei basin have the potential to reveal not only the nature of sub-continental lithospheric mantle’s relics, rather than a juvenile accreted asthenospheric mantle (Xia et al., 2010; Hao et al., 2012).

One critical line of investigation that may be used to address the questions regarding the nature and evolution of the sub-continental lithospheric mantle of the NCC is to examine the mantle-derived peridotite xenoliths. In fact, the majority of peridotite xenoliths, which formed in the sub-continental lithospheric mantle, are rapidly transported to the surface, along with their host magmas, in a matter of few hours/days. Thus, they represent snapshots of the sub-continental lithospheric mantle and have the great potential of unravelling the nature and evolution of their source. The Subei basin occupies a critical position at the southern edge of the NCC and is located within the collision zone between the NCC and the South China Block (SCB), with a northward-directed subduction (Li, 1994; Chung, 1999). Consequently, the peridotite xenoliths from the Subei basin have the potential to reveal not only the nature of the sub-continental lithospheric mantle and their possible relationship with the asthenosphere, but also to shed light on the metasomatic processes associated with subduction.

In this paper, with obtained new trace element data of clinopyroxene (cpx), we characterize the mantle domain beneath the Subei basin, eastern China, through a detailed geochemical study of peridotite xenoliths hosted by the Cenozoic basalts from Lianshan (LS). The major and trace element chemistry (including H2O) of peridotite minerals provides a coherent petrological history of this geodynamically complex region.

2. Geological background

The geological architecture of the eastern part of China resulted from the amalgamation of two large tectonic blocks, the NCC and the SCB. The latter can be divided into the Yangtze block to the northwest and the Cathaysia block to the southeast. The NCC is separated from the Xing-Meng Block by the Central Asia Orogen to the north and from the Yangtze block by the Triassic Qinling-Dabie orogen to the south. A continental scale Tan-Lu fault cuts both the Xing-Meng block and the NCC. The eastern part of NCC experienced widespread lithospheric thinning and evolved from a thick (∼200 km), cold (∼40 mW/m²) and highly refractory lithospheric mantle in the mid-Ordovician to a thin (60–80 km), hot (60–80 mW/m²) and fertile lithospheric mantle after the late Mesozoic (Menzies et al., 2007, and references therein).

From Early Triassic to Late Jurassic, the SCB and the NCC converged, forming the Qinling-Dabie-Sulu orogen and a large ultra-high pressure suture zone (e.g., Li et al., 1993). This was transected during middle Triassic to early Cretaceous by the Tan-Lu sinistral strike slip fault, which moved the Sulu orogeny northward (Zhu et al., 2009). The superficial tectonics indicates that the suture between the SCB and the NCC eastward of the fault is placed slightly north of the Sulu terrain. However, based on linear aeromagnetic anomalies, deep seismic profiles and regional geology, Li (1994) proposed a crustal detachment model. This model postulates that during the mid-Mesozoic a collision between the two continental blocks occurred: the upper crust of the SCB in the Subei Basin-Yellow Sea region was detached from the lower crust and thrust over the NCC for more than 400 km, whereas the lower part of the lithosphere was subducted under the NCC along a subsurface suture located east of Nanjing (Fig. 1). Recently, Su et al. (2013) proposed a similar subsurface boundary, based on the study of Sr–Nd–Pb–Hf isotopic systems of Cretaceous granitic plutons. The Subei basin is located east of Tanlu fault, just north of the proposed subsurface suture. It is still unclear whether the mantle lithospheric roots beneath the Subei basin belong to the NCC or the SCB.

The Subei basin experienced widespread Cenozoic volcanism, which can be either directly or indirectly related to the lithospheric thinning of the NCC. The volcanism includes minor tholeiitic products mainly erupted during the early Paleogene, and xenolith-bearing alkali basalts extensively erupted during the Neogene (Fig. 1). The integration of sulfide and whole-rock Re–Os data suggests that the oldest part of the lithospheric mantle sampled by the peridotite xenoliths beneath Subei basin may be Paleoproterozoic in age, and subsequently modified during Mesoproterozoic and Phanerozoic times (Reisberg et al., 2005; Xu et al., 2008).

Fig. 1. Simplified map of Eastern China (a) main tectonic lines separating the actual lithospheric blocks (after Xia et al., 2010) and location of the Subei Basin. (b) distribution of the Subei Basin Cenozoic mantle xenolith bearing volcanism; in red, the LS sample locality of this study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
basin, located in northwestern Jiangsu Province (Fig. 1) and are contained in the alkali basalts of the Huanggang volcanic group, dated between 10 and 12 Ma (Shao et al., 1989).

3. Material and analytical methods

3.1. Petrography and modal composition

The LS sample collection is entirely constituted by spinel-bearing peridotite without any evidence of hydrous phase. Twenty-two samples out of about forty xenoliths were selected for this study, based on xenolith size and representativeness of the different lithology. They range in size from 5 to 10 cm and do not show any evidence of alteration or host basalt infiltration.

As the thin section includes just a small amount of the xenoliths in relation to the grain size, mass balance calculations between whole rock and mineral major element compositions are generally preferred in determining modal percentages of the minerals. However, for the LS xenoliths, whole rock analyses were possible for seven samples only, thus the mineral proportions of all samples were estimated by thin section point counting (Table 1). This method can be confidently applied, since the grains are all < 3 mm in size; because of the good match between the two methods observed for seven samples, we felt confident in classifying the entire sample collection by point counting.

The majority of the samples are lherzolites. The samples can be subdivided in three groups depending on the clinopyroxene (cpx) modal contents: cpx-poor lherzolites (6 < cpx ≤ 8%), lherzolites (8 < cpx < 14%) and cpx-rich lherzolites (cpx ≥ 14%), with LS04 being the most fertile with up to 18% cpx) and harzburgites (up to 4% cpx). This last group is represented by only two samples (LS26 and LS16).

According to Mercier and Nicolas (1975), the most common texture shown by the LS xenolith population is the protogranular type and, generally, they do not show any pronounced fabric orientation. No hydrous phases, nor metasomatic textures, glassy patches and sieved-spongy crystals were observed. The peridotite samples are textually remarkably different from those studied by Lu et al. (2013) and sampled in the same area; the latter have dominantly “porphyroclastic fine-grained microstructures” and evident superimposed metasomatic textures (i.e.: spongy cpx, containing CO2 fluid inclusions and secondary minerals). Relatively coarse olivine and orthopyroxene (opx) grains (3–5 mm) show curvilinear crystal boundaries. Due to strain, the crystals may be polygonized in medium-grained substructure, with evidence of recrystallization (LS06, Fig. 2) from a previous coarse-grained assemblage (LS17, Fig. 2). Large grains of olivine in almost all samples show kink banding. The orthopyroxenes do not show evident degree of deformation, they are texturally homogeneous except for the samples LS01 and LS31, where the grains are particularly coarse (up to 5 mm) and exsolved fine lamellae of cpx were observed (LS31; Fig. 2). Clinopyroxene and spinel occur as fairly smaller grains (< 3 mm) and blebs either within orthopyroxene or in contact with it (LS26; Fig. 2). In samples LS01, LS06 and LS23, the spinel is anomalously large (up to 4 mm), sometimes aligned and with the typical “holly-leaf” outline. No relevant textural differences were observed from the most fertile to the most refractory lithotype.

3.2. Analytical techniques

Trace element compositions of cpx were obtained by LA-ICP-MS on separate grains fixed in epoxy mounts at the University of Science and Technology of China. Mineral grains were ablated in situ with GeoLas pro ArF excimer laser system with beam wavelength 193 nm at 10 Hz repetition rate and 10 J/cm² energy per pulse. The ablation crater diameters were about 60 µm in size and the sample aerosol was carried to PerkinElmer DRCII ICP-MS by high purity Helium with flow rate of 0.3 L/min. The analysis consists of 80–100 replicates within 80–100 s and was processed by LiTEcalc software. The commercial software GLITTER 4.0 (Macquarie University; Griffin et al., 2008) was used for data reduction with NIST 610 silicate glass as external standard and 44Ca as the internal standard using values for CaO from the electron microprobe analyses for clinopyroxene. USGS glass BCR-2G was measured as an unknown in every session as quality control and always yielded values within 10% of the published values. Despite the general primary protogranular characters of all the lithotypes, in any case care was taken to analyze only unaltered grain areas, which was an issue with the clinopyroxenes. Prior to each spot analysis the target area was checked in reflected and in transmitted light to ensure clear, crack-free and unaltered spots. The time-resolved signals for each individual analysis were screened for inclusions or cracks (identified by spikes in the time-resolved signal) and affected areas or complete analyses were discarded accordingly.

Major element compositions of LS peridotite minerals were determined using a JEOL Superprobe (JXA 8100) at Nanjing University (China). Detection limits were generally between 0.01 and 0.07 wt%. The operating accelerating voltage was 15 kV and 20 nA and 10 to 20 s counting time for all phases; the beam size was 2 µm. Natural minerals and synthetic oxides were used as standards for calibrations. ZAF procedure was used for data correction.

4. Results

4.1. Mineral chemistry

The average values of major elements for olivine, cpx, opx and spinel of most LS peridotites are reported in Xia et al. (2010, in Tables 1–4). In the paper, we report the detail analysis of spots for each minerals in Table S1.

4.1.1. Olivine, orthopyroxene and spinel

Olivine shows in all groups the same textural features and within individual sample has similar inter-grain compositions. Mg# (Mg2+/ (Mg2++Fe2+) *100, all Fe was assumed as Fe2+) values range from 89.15 (lherzolites, LS22) to 91.90 (harzburgite, LS16). NiO contents vary from 0.21 to 0.48 wt% (weight percent), with, on average, a positive correlation with Mg#. The majority of samples are coherent with the Ni contents of residual olivine after the extraction of partial melts (e.g. Mysen, 1978). Olivine from spinel peridotites typically has 0.31–0.43 wt% of NiO, with an average value of 0.37 wt% (Korenaga and Kelemen, 2000). The NiO contents for Primitive Mantle (PM) olivine are 0.28–0.30 wt%. In this range fall the great majority of olivine from cpx-rich lherzolites (Fig. 3).

Orthopyroxene in lherzolites groups and harzburgite shows restricted inter-grain compositional variations. Mg# values vary between 89.44 (lherzolites LS22) and 92.44 (harzburgite LS16); Al2O3 contents range from 1.63 wt% (harzburgite LS16) to 4.65 wt% (cpx-rich lherzolites LS04), showing a negative correlation with Mg# (Fig. 4). Interesting to note, LS opx in cpx-rich lherzolites are all < 4.65 wt% Al2O3 contents, in spite of any Mg# values variation (Fig. 4a). An ideal negative correlation between Al2O3 contents and Mg# are observed. Opx shows low to very low TiO2 contents (< 0.2 wt%), which decrease with increasing Mg# (Fig. 4b). The low CaO contents (< 0.71 wt%) show no correlation with Mg#, but are roughly correlated with Na2O contents (< 0.18 wt%).

Spinel grains from individual samples are homogeneous within analytical error, with less than 10% intra-grain compositional variations for Cr# (Cr/(Cr + Al)*100) and Mg#. They vary from 10.48 to 49.03 and 66.16 to 79.77, respectively. These two ratios show the usual negative correlation similar to residual abyssal, plagioclase-free peridotite (Dick and Bullen, 1984). TiO2 contents are less than 0.15 wt% and, just in harzburgite LS26 up to 0.27 wt%. Moreover, the correlation of spinels from cpx-rich lherzolites (LS 23) and lherzolites (LS22, LS20, LS06; LS05), with the bulk rock composition (Al2O3 = 1.72–3.37 wt%; TiO2 = 0.06–0.16 wt%) is consistent with variable extents of PM melt.

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Table 1
Mineral modal, temperature and oxygen fugacity estimate of Lianshan peridotites and summary of geochemical parameters.

| Sample  | rock type | Mode (%) point counting | Mode (%) mass balance | WR Mg# | Mg# ol | Temperature | Δlog fO2 | OH (ppm wt) |
|---------|-----------|-------------------------|-----------------------|--------|--------|-------------|----------|-------------|
|         |           | ol opx cpx sp           | ol opx cpx sp         |        |        |             |          |             |
| LS16    | hz        | 75 19 4 2               |                       | 91.83  | 833*** | 883         | −1.1     | 57 19       |
| LS26    | hz        | 72 20 4 4               |                       | 90.93  | 837    | 907         | −0.8     | 57 19       |
| LS03    | cpx-poor lh| 72 20 6 2              | 70 20 8 2 91.13***    | 91.47  | 941    | 905         | −0.5     | 41 17       |
| LS12    | cpx-poor lh| 74 15 8 3              |                       | 91.75  | 916    | 925         | −0.2     | 78 32       |
| LS15    | cpx-poor lh| 69 21 7 3              |                       | 91.32  | 858    | 908         | −1.3     | 78 32       |
| LS17    | cpx-poor lh| 73 18 8 1              | 75 16 7 1 93.75***    | 91.74  | 884    | 1012        | −0.6     | 37 17       |
| LS19    | cpx-poor lh| 66 26 7 1              |                       | 90.52  | 856    | 932         | −1.2     | 89 45       |
| LS21    | cpx-poor lh| 78 13 6 3              |                       | 91.49  | 895    | 894         | −1.6     | 16 0        |
| LS01    | lh        | 55 28 12 5              |                       | 90.09  | 849    | 929         | −1.1     | 55 18       |
| LS05    | lh        | 56 29 13 2              | 60 28 11 1 91.10***   | 90.37  | 810    | 998         | −0.7     | 90 34       |
| LS06    | lh        | 60 26 11 3              | 65 24 10 2 91.98***   | 89.84  | 969    | 1021        | −1.3     | 73 32       |
| LS08    | lh        | 66 20 10 4              |                       | 90.13  | 888    | 973         | −1.0     | 42 15       |
| LS09    | lh        | 65 20 11 4              |                       | 90.30  | 802    | 911         | −1.2     | 21 16       |
| LS20    | lh        | 74 14 11 1              | 79 10 10 1 92.27***   | 90.33  | 1015   | 876         | −1.7     | 84 34       |
| LS22    | lh        | 59 26 13 2              | 63 24 12 2 90.57***   | 89.23  | 903    | 930         | −1.6     | 102 41      |
| LS30    | lh        | 62 24 12 2              |                       | 89.84  | 970    | 917         | −2.0     | 92 29       |
| LS02    | cpx-rich lh| 52 30 14 4             |                       | 89.79  | 890    | 982         | −1.8     | 41 13       |
| LS04    | cpx-rich lh| 50 29 18 3             |                       | 89.55  | 1001   | 1004        | −0.9     | 56 28       |
| LS07    | cpx-rich lh| 57 27 14 2             |                       | 89.97  | 970    | 988         | −1.3     | 96 30       |
| LS23    | cpx-rich lh| 60 24 14 2             | 62 22 15 2 91.42***   | 89.71  | 1014   | 875         | −2.2     | 73 32       |
| LS24    | cpx-rich lh| 45 34 17 4             |                       | 89.89  | 968    | 1013        | −1.2     | 80 34       |
| LS31    | cpx-rich lh| 53 27 17 3             |                       | 89.32  | 829    | 940         | −1.1     | 55 16       |
| average | hz        | 91.38 ± 0.45 835 ± 2 895 ± 12 −1.0 ± 0.2 57 19 11 | | 38 ± 0.86 891 ± 36 929 ± 36 −0.9 ± 0.7 61 ± 24 25 ± 9 15 ± 6 |
|         | cpx-poor lh| 90.02 ± 0.79 901 ± 39 944 ± 68 −1.3 ± 0.7 | 97 ± 35 29 ± 11 21 ± 11 |
|         | cpx-rich lh| 89.70 ± 0.38 945 ± 116 967 ± 92 −1.4 ± 0.8 | 67 ± 26 26 ± 13 22 ± 10 |

* Data from Bonadimann et al. (2009).
** Data from Xia et al. (2010).
*** Whole rock X-ray Florescence (XRF) analyses on a pressed powder dish were carried out at the Department of Physics and Earth Science, University of Ferrara, on advant-X Thermo ARL mass balance: see text for full description.
depletion (Workman and Hart, 2005; Craddock et al., 2013). Spinels from cpx-rich lherzolites are analog to the most fertile spinel of the abyssal field (Craddock et al., 2013).

4.1.2. Clinopyroxene

Clinopyroxene in LS xenoliths displays a textural equilibrium with opx, but reflects a larger intra-grain zonation for FeO contents, sensitively affecting Mg# (i.e. lherzolites LS22, (Fig. 5). On average Mg# varies between 89.59 (cpx-rich lherzolites LS04) and 94.07 (harzburgite LS16). By contrast, TiO2 and Al2O3 contents are very homogeneous among grains of the same sample. Both oxides show a negative correlation with Mg#, with Al2O3 contents varying from 7.15 to 1.73 wt% and TiO2 from 0.79 wt% to detection limit (Fig. 5a and b). The Al2O3 contents in cpx-rich lherzolites do not exceed a cpx value of 7.15 wt%. Na2O contents follow the same geochemical behavior of Al2O3, being buffered at 2.0 wt% in cpx-rich lherzolites (Fig. 5c). This indicates that, at least for the most “fertile” LS lherzolite, the Al2O3 (and Na2O) contents result saturated by the bulk peridotite system. In cpx-rich lherzolites, cpx-poor lherzolites LS21 and harzburgite LS16, Na2O is constant at 1.47–1.99 wt%, independent of Mg# values (Fig. 5c). On the other hand, for lherzolites, cpx-poor lherzolites and harzburgite LS26, Na2O contents systematically decrease (down to 0.12 wt%) with increasing Mg#.

Clinopyroxene is the most important phase hosting trace element in anhdyous spinel peridotites. In the majority of LS peridotite xenoliths, the differences between individual analyses of the same mineral are within analytical error, except for LS08 and LS30, which show some heterogeneity in Light Rare Earth Elements LREE (Table 2).

Fig. 6a and b shows REE and incompatible trace element distributions of harzburgite and cpx-poor lherzolites groups. Harzburgite LS16 shows a highly enriched REE pattern from Er to light (L) REE with La about 40 times chondrite and (La/Yb)Ch = 10.8. The sample presents strong Ti and Zr negative anomalies (Ti* = 0.33, Ti* = 2 × TiPM/(EuPM + GdPM) and Zr* = 0.64, Zr* = 2 × ZrPM/(NdPM + SmPM)), a feeble Sr positive anomaly (Sr* = 1.85, Sr* = 2 × SrPM/(PrPM + NdPM) and, together with the cpx-poor lherzolites LS15 and LS17. It presents the highest contents of Th and U (15 and 20 times primitive mantle value respectively) of the entire LS xenolith population. By contrast, the other harzburgite (LS26) shows the lowest trace elements (including REE) contents. This sample is characterized by flat REE pattern with (La/Yb)Ch about 0.80 and (Sm/Yb)Ch about 0.6, with Ti, Zr and Sr, which mimic the same anomalies observed in harzburgite LS16 (Ti* = 0.32, Zr* = 0.41 and Sr* = 1.56). Despite the well-equilibrated textural types, cpx in cpx-poor lherzolites and lherzolites groups records extremely heterogeneous intergroup incompatible trace element contents and distributions (Fig. 6a, b, c and d). Cpx in cpx-poor lherzolites records variable degrees of depletion, with YbCh varying from 3.3 to 6.4 (Fig. 6a). Four samples out of six show positive fractionated REE patterns (Fig. 6a, (La/Yb)Ch = 3.25–18.82) and high Th and U contents (ThPM = 6.82–55.17 and UPM = 8.41–24.07; Fig. 6b). Conversely, cpx-poor lherzolites LS12 and LS19 show slightly depleted LREE patterns ((La/Yb)Ch = 0.20–0.65), comparable to the majority of cpx in lherzolites group (Fig. 6c) but at lower Heavy (H) REE and highly depleted Th and U contents (ThPM = 0.08–1.18 and UPM = 0.15–2.03). The cpx of this group presents ubiquitous negative Ti (Ti* = 0.17–0.42) and positive Sr (Sr* = 1.42–4.01) anomalies (Fig. 6b).

Clinopyroxene from lherzolites group has higher HREE contents (YbCh = 8.34–11.48) than cpx-poor lherzolites with homogenously flat profiles, which evolve from highly depleted (LS09-LS05) to slightly enriched (LS20), with (La/Yb)Ch ratios ranging between 0.4 and 4.42 (Fig. 7c). The LREE highly depleted cpx are associated with the general depletion trend of the most incompatible elements and feeble Zr and Ti negative anomalies (Zr* = 0.25–0.59; Ti* = 0.54–0.56). The progressive LREE increase is accompanied by remarkable Th, U enrichments and variable Sr contents (Sr* = 0.64–2.31).

The cpx-rich lherzolites group is characterized by flat HREE and Middle (M) REE, ((Sm/Yb)Ch = 0.79–1.02), with YbCh contents ranging from 10.51 to 13.04 and a regularly decrease from Sm to La (LaCh = 4.7–5.1), with the LS31 cpx showing the steepest decrease (LaCh = 1.39). The cpx of this group contain systematically low Th and U contents always lower than the PM reference value, weak Ti negative anomaly Ti* = 0.52–0.6 and negligible Zr negative and Sr positive anomalies.

4.2. Mineral equilibrium, temperature, oxygen fugacity and water content estimates

The LS peridotites are texturally well equilibrated with grain boundaries slightly curved or with 120° triple junctions, geometry of
| Sample   | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Rock type |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Hz       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Cpx-poor |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Lh       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| n.       | 5  | 5  | 6  | 5  | 5  | 4  | 8  | 6  | 10 | 8  | 10 | 8  | 10 | 8  |
| Sn.      |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| La       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ce       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| La       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ce       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Pr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Nd       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Zr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Hf       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sm       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Eu       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ti       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Gd       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Tb       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Dy       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Y        |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ho       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Er       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Tm       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Yb       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Lu       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sample   | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ |
| Rock type |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Hz       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Cpx-poor |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Lh       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| n.       | 5  | 10 | 4  | 10 | 7  | 4  | 9  |    |    |    |    |    |    |    |
| Sn.      |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| La       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ce       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Pr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Nd       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Zr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Hf       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sm       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Eu       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ti       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Gd       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Tb       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Dy       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Y        |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ho       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Er       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Tm       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Yb       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Lu       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sample   | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ | 1σ |
| Rock type |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Hz       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Cpx-poor |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Lh       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| n.       | 10 | 5  | 10 | 5  | 10 | 5  | 10 | 5  | 10 | 5  | 10 | 5  | 10 | 5  |
| Sn.      |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| La       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ce       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Pr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Nd       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Zr       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Hf       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Sm       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Eu       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ti       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Gd       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Tb       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Dy       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Y        |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Ho       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Er       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Tm       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Yb       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Lu       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

(continued on next page)
Table 2 (continued)

| Sample | 1o | LS01 | 1σ | LS05 | 1o | LS06 | 1σ | LS08 | 1o | LS09 | 1σ | LS20 | 1σ | LS22 | 1o |
|--------|----|------|----|------|----|------|----|------|----|------|----|------|----|------|----|
| Y      | 0.6 | 16.2 | 0.3 | 18.3 | 1.8 | 17.2 | 0.5 | 15.4 | 0.8 | 11.9 | 0.3 | 14.6 | 0.5 | 20.5 | 0.5 |
| Ho     | 0.017 | 0.656 | 0.043 | 0.730 | 0.086 | 0.675 | 0.032 | 0.633 | 0.052 | 0.416 | 0.039 | 0.399 | 0.576 | 0.036 | 0.795 | 0.037 |
| Er     | 0.036 | 1.810 | 0.068 | 2.964 | 0.290 | 1.812 | 0.107 | 1.706 | 0.181 | 1.366 | 0.090 | 1.445 | 0.052 | 2.138 | 0.148 |
| Tm     | 0.010 | 0.263 | 0.009 | 0.300 | 0.042 | 0.265 | 0.018 | 0.251 | 0.024 | 0.204 | 0.013 | 0.209 | 0.008 | 0.304 | 0.012 |
| Yb     | 0.081 | 1.673 | 0.063 | 2.039 | 0.291 | 1.737 | 0.042 | 1.627 | 0.097 | 1.403 | 0.142 | 1.459 | 0.073 | 1.979 | 0.117 |
| Lu     | 0.021 | 0.242 | 0.005 | 0.281 | 0.038 | 0.247 | 0.013 | 0.235 | 0.022 | 0.212 | 0.013 | 0.211 | 0.012 | 0.292 | 0.021 |

| Sample | 1o | LS30 | 1σ | LS04 | 1σ | LS07 | 1σ | LS23 | 1σ | LS24 | 1σ | LS31 | 1σ |
|--------|----|------|----|------|----|------|----|------|----|------|----|------|----|
| Rock type | lh | cpx-rich lh | n. | 11 | 7 | 6 | 4 | 12 | 11 |
| Ba     | 0.731 | 0.374 | 0.058 | 0.003 | 0.049 | 0.025 | 0.055 | 0.047 | 0.814 | 0.422 | 1.044 | 0.622 |
| Th     | 0.201 | 0.071 | 0.015 | 0.009 | 0.011 | 0.007 | 0.015 | 0.009 | 0.017 | 0.009 | 0.034 | 0.050 |
| U      | 0.072 | 0.041 | 0.021 | b | b.d. | b.d. | 0.022 | 0.018 | 0.010 | 0.006 |
| Nb     | 0.182 | 0.032 | 0.118 | 0.037 | 0.119 | 0.031 | 0.109 | 0.019 | 0.080 | 0.029 | 0.073 | 0.059 |
| Ta     | 0.012 | 0.006 | 0.017 | 0.013 | 0.006 | 0.006 | 0.013 | 0.005 | 0.014 | 0.010 | 0.006 | 0.003 |
| La     | 1.37 | 0.44 | 1.08 | 0.06 | 1.11 | 0.06 | 1.18 | 0.04 | 1.23 | 0.05 | 0.33 | 0.04 |
| Ce     | 2.85 | 0.32 | 4.01 | 0.10 | 4.13 | 0.11 | 4.27 | 0.03 | 4.46 | 0.24 | 1.77 | 0.21 |
| Pr     | 0.487 | 0.020 | 0.714 | 0.030 | 0.736 | 0.016 | 0.770 | 0.018 | 0.803 | 0.035 | 0.429 | 0.039 |
| Sr     | 68.9 | 7.4 | 81.9 | 1.0 | 79.0 | 0.9 | 84.5 | 1.2 | 85.2 | 2.5 | 55.4 | 3.6 |
| Nd     | 3.26 | 0.34 | 4.48 | 0.27 | 4.42 | 0.15 | 4.65 | 0.26 | 4.96 | 0.35 | 3.30 | 0.30 |
| Zr     | 24.3 | 0.6 | 35.0 | 0.7 | 33.8 | 1.2 | 34.1 | 0.6 | 35.2 | 1.0 | 27.6 | 1.1 |
| Hf     | 0.787 | 0.053 | 1.105 | 0.072 | 1.026 | 0.117 | 0.964 | 0.089 | 1.087 | 0.107 | 0.987 | 0.167 |
| Sm     | 1.290 | 0.133 | 1.860 | 0.060 | 1.784 | 0.108 | 1.818 | 0.190 | 1.901 | 0.157 | 1.579 | 0.171 |
| Eu     | 0.585 | 0.041 | 0.762 | 0.015 | 0.728 | 0.036 | 0.766 | 0.064 | 0.787 | 0.048 | 0.726 | 0.092 |
| Ti     | 2460 | 51 | 3498 | 22 | 2882 | 66 | 3554 | 77 | 3554 | 133 | 3110 | 84 |
| Gd     | 2.09 | 0.11 | 2.70 | 0.08 | 2.47 | 0.13 | 2.73 | 0.13 | 2.68 | 0.18 | 2.76 | 0.40 |
| Tb     | 0.404 | 0.024 | 0.500 | 0.017 | 0.453 | 0.025 | 0.498 | 0.008 | 0.499 | 0.032 | 0.500 | 0.046 |
| Dy     | 2.93 | 0.18 | 3.44 | 0.10 | 3.10 | 0.10 | 3.38 | 0.09 | 3.39 | 0.16 | 3.61 | 0.32 |
| Y      | 16.7 | 0.2 | 19.5 | 0.4 | 17.6 | 0.7 | 19.1 | 0.4 | 19.5 | 0.4 | 20.3 | 0.5 |
| Ho     | 0.602 | 0.025 | 0.754 | 0.035 | 0.662 | 0.025 | 0.728 | 0.010 | 0.764 | 0.042 | 0.806 | 0.052 |
| Er     | 1.845 | 0.088 | 2.999 | 0.074 | 1.920 | 0.088 | 2.078 | 0.059 | 2.142 | 0.113 | 2.210 | 0.198 |
| Tm     | 0.263 | 0.020 | 0.306 | 0.012 | 0.268 | 0.010 | 0.302 | 0.008 | 0.313 | 0.025 | 0.327 | 0.037 |
| Yb     | 1.718 | 0.109 | 2.027 | 0.103 | 1.787 | 0.094 | 1.992 | 0.064 | 2.072 | 0.116 | 2.217 | 0.272 |
| Lu     | 0.252 | 0.024 | 0.285 | 0.015 | 0.253 | 0.019 | 0.292 | 0.018 | 0.296 | 0.033 | 0.316 | 0.039 |

Rock type as in Table 1.

n.: numbers of averaged samples when variations are within the analytical errors.

b.d.: below detection limits.

b: just one cpx available for the element average. See text for full description.
low energy for mineral arrangement at mantle depth. The textural equilibrium was chemically tested by Fe-Mg distributions among minerals (Fig. 7), with the equilibrium lines derived from equations experimentally obtained by Brey and Köhler (1990) and Liermann and Ganguly (2003) between silicate minerals and spinel. The equilibrium lines were calculated at pressure of 20 Kbar, with T of 800, 900 and 1100°C. Taking into account Fe/Mg equilibrium models for olivine-opx and olivine-spinel pairs, the LS cpx-rich lherzolites reflect the ideal Fe/Mg distribution at the temperature and pressure reference conditions (Fig. 7a and b). With respect to Fe/Mg opx-cpx equilibrium lines (Fig. 7c), “disequilibrium” is evident for the two harzburgite, cpx-poor lherzolites LS17 and lherzolites LS05, which lay outside the equilibrium region, towards low temperatures, with respect to the validity of the experimental formulations. Considering the different Fe-Mg diffusion rates among peridotite minerals, temperatures were calculated (pressure arbitrarily assumed as 20 Kbar) with both Brey and Köhler (1990, \(T_{BKN}\)) and O’Neill and Wall (1987), as modified by Ballhaus et al. (1991, \(T_{NW}B\)) formulae, based on Fe and Mg exchanges between opx-cpx and olivine-spinel respectively (Table 1). The results of the two methods, as expected, large T differences, generally exceeding the error of the methods (±30°C). Besides, the LS xenoliths coherently record increasing temperatures from cpx-poor lherzolites and harzburgite (\(T_{BKN} = 833–895°C\); \(T_{NW}B = 883–894°C\)) to cpx-rich lherzolites (\(T_{BKN} = 829–1001°C\); \(T_{NW}B = 875–1004°C\)).

Oxygen fugacity (fO2) values were obtained from the equilibrium: 6\(\text{Fe}_2\text{SiO}_4\) (olivine) + \(\text{O}_2\) (fluid) = \(\text{Fe}_3\text{O}_4\) (spinel) + 3\(\text{Fe}_2\text{Si}_2\text{O}_6\) (opx) based on the semi-empirical oxygen barometer calibrated by Ballhaus et al. (1991), using \(X_{\text{Fe}}\) in spinel as \(\text{Fe}^{3+}/\text{total R}^{3+}\), pressure of 20 Kbar and \(T_{NW}B\). The intrinsic errors of the formula as well as the errors derived by the \(\text{Fe}^{3+}\) calculated by the stoichiometry of minerals are as

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**Table 3**

Parameters used for modelling original H2O contents in bulk rocks and cpx.

| Partition coefficients | ol/melt | ref (opx/melt) | ref (ol/opx)** | ref (ol/cpx) | ref (cpx/opx) | ref |
|------------------------|---------|----------------|----------------|--------------|---------------|-----|
| Kd H2O                 | 0.0014  | 2              | 0.018          | 2, 3         | 0.12          | 1   |
| H2O (wt%) of primary melts | 0.68    | 1.5            | 2.6            | 1            | 0.06          | 2   | 1 |
| Modes                  | OI      | Opx            | Cpx            | Sp           |
| PM                     | 0.52    | 0.27           | 0.87           | 0.03         | 5             |
| Melt                    | -0.05   | 0.08           | 0.10           |              |

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**Table 4**

Rock and clinopyroxene water concentration in the upper mantle.

| H2O contents of primary melts (wt%) | From off-craton lithospheric mantle | 0.68–1.5 |
|-----------------------------------|------------------------------------|-----------|
| H2O concentration of PM and cpx (ppm) (\(F = 3\%\)) | Minimum estimate | 328    |
|                                   | Maximum estimate (off-craton) | 722   |
|                                   | Maximum estimate (on-craton) | 923   |
|                                   | Average | 813   |
|                                   | (\(F = 8\%\)) | Minimum estimate | 653    |
|                                   | Maximum estimate (off-craton) | 1440  |
|                                   | Average | 813   |

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\* \(F = 8\%\) PM on-craton maximum estimates has not petrological meaning.
discussed in Bonadiman et al. (2014).

The fO2 values of LS samples, in terms of difference from the fayalite-magnetite-quartz buffer (ΔFMQ), always result below FQM buffer (ΔFMQ = −0.2 to −2.2), with the highest values recorded in the harzburgite and cpx-poor lherzolites groups (ΔFMQ range from −0.9 ± 0.7 to −1.0 ± 0.2) and the lowest values recorded in the cpx-rich lherzolites group (ΔFMQ = −1.4 ± 0.5, Table 1).

To better frame the volatile circulation in the LS mantle domain, we also reported the water contents measured in the nominally anhydrous minerals (olivine, opx and cpx) of these samples (Table 1). Detailed discussions of the data are reported in Bonadiman et al. (2009) and Xia et al. (2010). On the whole, the water contents (H2O wt. %) in opx and cpx range from 13 to 45 ppm and from 37 to 102 ppm, respectively; it is negligible in olivine (in all samples it is always below the detection limits). In order to minimize the effect of H diffusion in ol, the partitioning between olivine, opx and cpx was used to calculate the whole-rock water contents (Bonadiman et al., 2009; Xia et al., 2010). This calculation refers to the modal contents (Table 1), and to KdH2O ol/opx and KdH2O ol/cpx, based on a combination of available data from natural and experimental samples (Hauri et al., 2006; Novella et al., 2014; Tenner et al., 2009; Warren and Hauri, 2014), and assigns, as expected, the wettest lithology to the cpx-rich lherzolites (on average 22 ± 10 ppm; Table 1).

5. Discussion

5.1. Melting models

The abundance of the most fusible elements in the LS minerals systematically varies with Mg#. Such trends are usually interpreted as indicators of residues from different degrees of partial melting and melt extraction from a fertile lherzolite source.

The melting degrees (F) are provided by the major element mineral compositions following the experimental melting results in the CSMA (Fe) peridotitic system (Herzberg, 2004; Bonadiman and Coltorti, 2011). Theoretical melting curve for cpx was obtained for Si, Al, Fe, Mg and Ca from the McDonough and Sun (1995) primitive mantle major element composition, using the mass-balance calculation between the four peridotite phases (PM bulk composition olivine:opx:cpx:spinel = 52:27:18:3) and progressive melting residua derived from the experimental results of Herzberg (2004). The curve was calculated considering the ideal basaltic melting behavior in the pressure range of the anhydrous spinel stability field (10–20 Kbar). In this model, the cpx is consumed at ∼30% of PM melting. Among the basaltic elements, Al, HREE (and Y) are the most sensitive to the melting degree (Ionov and Hofmann, 2007), thus Al2O3 versus MgO and YbPM versus YPM were chosen to describe the melting process (Fig. 8a and b). Since a complete data set (major and trace elements) is provided for cpx only, we refer to this phase to evaluate the residual character and processes of the LS mantle domain. In Al2O3 versus MgO diagram LS cpx grade towards the hypothetical melting curve with the harzburgite group coherently indicating the highest melting degrees (18–24%) and lherzolites-group/cpx-rich lherzolites groups showing the lowest (4–15% and 0–9%). In the spinel stability field, the Al2O3 contents of cpx at the beginning of melting (F < 10%; Al2O3 = 7.00–6.57 wt%) are not able to clearly discriminate in the curve a reduction of modal contents from 18% (PM) to 14% melting (Fig. 8a). In fact, the whole cpx-rich lherzolites group (modal cpx = 18–14%) coherently plots in this region of the curve. On the other hand, theoretically, a rapid Al2O3 decrease is expected for F exceeding 10%. According to the model, the cpx of lherzolites group, with cpx modal contents confined in the range 8–14%, should reflect a
residuum after theoretical melting degrees between ∼16 and ∼12%, but they span between 15 and 4% F (Fig. 8a). The same occurs for the cpx-poor lherzolites group (cpx=6–8% corresponding to an ideal PM melting degree in the range of ∼20–22% F), which are placed in the curve between 16 and 20% F (Fig. 8a). Only LS15 and LS17 represent a residuum (F∼20% PM melting) coherent with the observed cpx modal contents. In this model the cpx of two harzburgites (cpx=4%) present higher Al₂O₃ and lower MgO contents to be considered a direct melting of the PM source.

These results were compared to those obtained applying the more conventional near-fractional melting numerical model Zou (1998) to the cpx HREE (and Y) compositions (i.e. Johnson et al., 1990; Hellebrand et al., 2002; Liang and Peng, 2010) in the spinel stability field. As for the Al₂O₃-MgO model, the starting fertile cpx composition is calculated using the PM composition of McDonough and Sun (1995), cpx=18%, and model parameters as in Bonadiman et al. (2005) and Faccini et al. (2013).

A calculation approximation to the simple ideal, fractional melting equation of Johnson et al. (1990) is applicable to ≤0.1 residual porosity (Zou, 1998). In fact, the HREE (Yb) and Y of the cpx of the entire LS suite were reproduced by the simplest fractional melting model (Fig. 8b). In agreement with the Al₂O₃-MgO melting model, the estimated degrees of partial melting for the cpx-rich lherzolites are less than 3%, leaving an estimated residue which contains a modal clinopyroxene comparable to that measured in the samples (cpx = 14–18%). LS31 represents (trace and major melting modeling) the most fertile sample of the entire collection with the cpx modal content close to PM values (18%). The model assigns to the lherzolites group (cpx = 10–13%) a melting degree spanning between F < 3% and ~7%, slightly lower than that predicted by the Al₂O₃-MgO model. LS05 and LS22 (cpx = 13%) have Yb and Y contents close to the PM values (Fig. 8b) approaching the modal composition of the cpx-rich lherzolites group. Except for LS15 and LS17, which represent a residuum (~17% PM melting) consistent with their cpx contents (7% and 8% respectively), and analogously to what observed for the major element melting model (Fig. 8a), the cpx-poor lherzolites contain cpx with Yb and Y contents corresponding to those of a residuum after ~20% PM melting, but the real abundance is lower than that theoretically predicted (~5% vs. 15–12% F). The harzburgite HREE (and Y) reproduce a residuum after a maximum of 21% degree of melting of PM cpx, too low with respect to the measured cpx modal content (4%), which would suggest a F > 25%. Following the fractional melting model at 4% of modal cpx, in fact, YbPM should be as low as ~0.15–0.20 (F > 25%, rapidly approaching the cpx disappearing) with respect to the real YbPM content of LS26 (0.52–0.70).

To summarize, both the cpx major and trace element melting models, independently indicate that only cpx-rich lherzolites represent extremely fertile (close to the PM) mantle fragments fitting with the proper lithotypes (i.e. cpx modal contents).

Applying the same melting models (major and trace) to the cpx of Lu et al. (2013) xenoliths, it is evident that for all their studied samples the residual character was modified by enrichment events (Fig. 8a). In particular, cpx modal contents vs. Al₂O₃ and Y (and Yb) contents cannot be explained by any melting model, including the one proposed by the authors (Hellebrand et al., 2002). These peridotites may have been metasomatized, and resemble the lherzolites and cpx-poor lherzolites groups of our xenolith collection.
5.2. Metasomatism

As shown in the previous section, most of the clinopyroxenes of lherzolites, cpx-poor lherzolites and harzburgite reflect anomalous Al$_2$O$_3$ and REE enrichments with respect to the contents theoretically expected for residual cpx according to the melting models (Fig. 8). In terms of Refractory Lithophile Element (RLE), the high LREE, Th, and U contents, coupled with variable Sr enrichments of cpx in these lithotypes (Fig. 6), indicate that a variably depleted mantle sector interacted with metasomatic melts. Lu et al. (2013) report abundant CO$_2$ fluid inclusions in spongy cpx, which present convex-down REE patterns and high contents of highly compatible elements (Th, U, Sr and LREE). The authors argue that a refractory mantle system interacted with silicate-to carbonatitic-melt/s at the time of the host basalt entrapment. In our sample collection the absence of carbonate, hydrous mineral phases (i.e. mica, amphibole or apatite), as well as metasomatic textures (i.e. spongy and/or secondary crystals, and/or glassy patches), rules out melt circulation at depth during, or before, the host basalt eruption (Coltorti et al., 1999; Ionov et al., 2002). Since no modal metasomatic minerals were observed and all lherzolites, cpx-poor (and harzburgite)

lithotypes are texturally well equilibrated, the geochemistry (major and trace elements) of clinopyroxenes is the solely indicator of the metasomatic event(s) occurred in the LS mantle domains. Trace element patterns of hypothetical liquids in instantaneous equilibrium with the most enriched cpx (harzburgite and cpx-poor lherzolites) were calculated with D$_{cpx}$/melt using the partition coefficients of Ionov et al. (2002). The theoretical compositions reflect the imprinting of the circulating melt, since in this xenolith population cpx is the sole mineral that can accommodate the incoming trace element budget (Fig. 9). The resulting melts do not show any correspondence with the compositional range of basalts from the region (Chung 1999; Zou et al., 2000), in particular regarding the remarkable Nb (and Ta) and Ti negative anomalies that were not observed in the Subei Basin basalts (Fig. 9).

5.3. Modeling the original water contents

Under the assumption that the Earth has a chondritic RLE composition and that the H in the PM is associated with O in hydroxyl (OH) in minerals or, in minor amounts, in the form of structurally bound water molecules (H$_2$O) (e.g. McDonough and Sun, 1995; Lodders, 2003; Drake and Righter, 2002; Klepe and Jephcoat, 2006), the PM total abundance of H$_2$O is estimated in the range of 850–1100 ppm wt. (Mottl et al., 2007; Palme and O’Neill, 2003). These values were determined by considering the hydrosphere (oceans, pore water in sediments and ice; $1.6 \times 10^{21}$ kg) as the water originally contained in the 50% degassed mantle (Mottl et al., 2007) and a subsequent ingassing
contribution by the recycled crust into the mantle (ca. 200 ppm; Hirschmann, 2006), since the beginning of the Earth’s evolution (Palme and O’Neill, 2003; Arevalo et al., 2009). Alternatively, for a non-chondritic Earth’s model (i.e. O’Neill and Palme, 2008), which estimates that K abundances in the mantle were only about half of that expected from the chondritic model, 40Ar (as mainly derived by 40K) in the atmosphere would correspond to degassing of the entire mantle, not just 50% of it. Consequently, the PM water abundance would be 425–675 ppm, including the contribution of the recycled crust in the mantle (Palme and O’Neill, 2003).

A quantitative insight into the mantle H2O contents may also be obtained by measuring the water contents in mantle-derived magmas. This approach would immediately confine the discussion to the Earth’s upper mantle, but if referring to the whole mantle convection, it can ultimately reflect the PM water contents. Taking into account the instantaneous equilibrium melts. Basalts from Subei basin (Chung et al., 2012; Doucet et al., 2014). Based on experimentally determined contents of primary melts from on-craton lithospheric mantle (Peslier et al., 2012; Xia et al., 2010; Hao et al., 2012; Doucet et al., 2014). Conversely, peridotites ridge basalts (MORB; Michael, 1995; Hauri et al., 2006; Green et al., 2010) have H2O contents of 0.05 to 1.60wt% (Table 4). This range is obtained assuming that the PM source produced melt in the spinel stability field. In terms of H2O contents these cpx residua should contain H2O in the range of 214–530 ppm. Taking into account the measured H2O contents in cpx from cpx-rich lherzolites, an unrealistic 7% of F would be envisaged for this lithotype (Table 1; Fig. 10).

The calculation of H2O contents of residual peridotite (or its cpx), determined by the application of conventional REE melting models, intrinsically has a large source of error. In fact, H2O does not follow the same melting model as REE, as erroneously supposed, considering the relatively constant H2O/Ce ratio in cpx (and whole rock) of mid-ocean ridge basalts (MORB; Michael, 1995; Hauri et al., 2006; Green et al., 2010; Xia et al., 2013; Hao et al., 2014). Conversely, peridotites show a considerable range of H2O/Ce ratios at both mineral and bulk rock levels. This discrepancy is partially due to the variable petrological models which link the mantle source to its basic melts (i.e. polybaric melting histories and fluid refertilization), but the principal source of error is due to the mineral/melt and bulk/melt H2O partition coefficients applied (Hirschmann, 2006; Warren and Hauri, 2014). The various set of published mineral/melt H2O partition coefficients are not always internally consistent: i.e. D H2O/Melt/D H2O/Melt ≠ D H2O/Melt (Warren and Hauri, 2014). This discrepancy is likely due to the different reactivity of water in minerals during melting. In fact the calculation of H2O also depends on the mineral composition, which changes at higher degrees of melting (Zou, 1998), thus H2O activities are not the same as those imposed by the full peridotite assemblage as applied in the equation of Novella et al. (2014). In order to better frame the H2O behavior of cpx during melting, we modeled the melting of the initial cpx (cpxPM) using the fractional melting equation of Shaw (1970), but calculating the global distribution coefficients (D H2O/min/melt and P H2O/min/melt) considering the activity model (Zou, 1998; Till et al., 2010). On the basis of major and trace (lithophile) element cpx modelling, the LS cpx-rich lherzolites correspond to a residuum after a maximum of 3% of PM fractional (= bulk) melting in the spinel stability field. In terms of H2O contents these cpx residua should contain H2O in the range of 214–530 ppm, depending on the model applied (Fig. 10). The cpx H2O contents of LS cpx-rich lherzolites (41–96 ppm) are, on average, one order of magnitude lower than those of theoretically expected at 3% F (214–530 ppm). Taking into account the measured H2O contents in cpx from cpx-rich lherzolites, an unrealistic 7% of F would be envisaged for this lithotype (Table 1; Fig. 10).

The low to very low H2O contents should discharge the potential hydrogen addition from the host magma. The absence of water addition to the xenolith from the host magma is coherent with the mechanism of exhumation by fast ascent of the magma (several hours/days according to estimates of alkaline magma ascent rate) leaving no time for significant exchange of water with the entrapped xenoliths. Moreover, the homogenous H2O content within single pyroxene grains and the equilibrium H2O partitioning between the clinopyroxene and orthopyroxene (Bonadiman et al., 2009; Xia et al., 2010) disclaim a potential H-loss during the xenolith ascent. This difference outmatches the model uncertainties, therefore the measured H2O in cpx (at least in the center of the mineral grains) represent the H2O contents they had in the mantle prior to sampling by the host basalt.

5.4. Heat and H diffusivities

H diffusivities in mantle minerals (ol, cpx and opx) are very high
mantle domains, probably adjacent at the time of basalt capturing. On the basis of the petrology and geochemical data reported above and accordingly to what proposed by Lu et al. (2013) it is reasonable to infer that a cold highly refractory harzburgite and cpx-poor lherzolites could represent the old cratonic lithospheric mantle modified by interaction with metasomatic melts, involving crustal components. Cpx-rich lherzolites constitute fragments of upwelling cooled fertile asthenosphere after the removal/erosion of the base of the lithospheric mantle. This asthenospheric portion had higher T, lower FO2 and higher water contents than the pristine lithosphere.

Since heat and H are the highest diffusive components (8–10 orders of magnitude higher than the highest diffusive RLE) and highly dependent on T, it would take < 5 Ma for a mantle portion about 1 km² in size to re-equilibrate with the surrounding old and cold lithosphere after the last partial melting episode.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jaesx.2019.100006.

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(D = 10⁻¹⁰–10⁻¹¹ m²/s at 900 °C; Ingrin and Blanchard, 2006; Farver, 2010; Bizimis and Peslier, 2015), and mainly controlled by volume diffusion (vacancy diffusion) through the crystal lattice (Farver, 2010). In turn, cation diffusion processes mainly control the trace element (REE) abundances in olivine (and pyroxene). Cation diffusion through minerals is slow (REE in diopside: 8 log units lower than H), consequently, the solid/melt interactions (metasomatic event) would produce a chemical zoning (i.e. REE) of minerals which characterizes the solid until a new mantle process occurs. Moreover, despite the large differences in RLE contents of LS pyroxenes, the T° values from cpx-poor lherzolites (and harzburgite) to cpx-rich lherzolites, are in the narrow interval of 200 °C and never exceed 1021°C (Table 1).

The thermal diffusivity of mantle rocks is known to remain almost constant (D = 4.7 × 10⁻⁷ m²/s; Gibert et al., 2003) when measured in polycrystalline systems between 750 and 1350 °C, with local increase due to the reactive processes. The pressure dependence is expected to be low (Katsura, 1995; Gibert et al., 2003). Applying the simplest diffusion equation of Crank (1975), valid for homogeneous diffusion rate on a finite isotropic plane medium at constant diffusion coefficient, we calculated that the residuum cpx (500 µm length) after 3% of PM melting progressively loses its initial H2O content (Co H2O 214–530 ppm; calculated that the residuum cpx (500µm length) after 3% of PM melting progressively loses its initial H2O content (Co H2O 214–530 ppm; Fig. 10) to reach 50 ppm (average of measured contents) in 40,000–70,000 years. If we extrapolate this punctual data to a column of mantle sector as large as the area of xenolith samples (1Km²), we can estimate homogenous H2O contents (50 ppm) in a time span of 1.5–2.4 My. Taking into account the reduction of the parameters used for the calculations, these values contain large uncertainties; nevertheless, they give important information on the time scale of the dehydration process.

6. Conclusions

Within the LS xenoliths population, the cpx-rich lherzolites group shows the most fertile compositions: Mg# and NiO contents of olivine similar, on average, to the ODeo estimates (McDonough and Sun, 1995); the Al2O3, TiO2, and Na2O contents of pyroxenes and Cr# of spinel are also close to the ideal PM values. The melting degrees estimated by clinopyroxene major and trace elements are very low (always < 3%), with coherent cpx modal contents (Fig. 8). Cpx trace element and RREE patterns indicate no metasomatic effects for this lithotype.

In turn, harzburgite together with cpx-poor lherzolites (and lherzolites) reflect variable enrichments superimposed on a variably depleted (8–23% of partial melting) mantle. The metasomatic event/s introduce Al2O3, LREE, even HREE, modifying the expected cpx/whole chemistry residual relationship. The reconstructed trace element profiles (Fig. 9) of the hypothetical metasomatic melt/s show negative Ti, Nb-Ta and positive Sr anomalies as well as Th, U high contents; this, associated with Al2O3 and HREE enrichments in cpx, would indicate the circulation of a silicate melt with crustal components (i.e.: Faccini et al., 2013).

The LS peridotites contain, on average, 22 ppm H2O, with the highest values up to 30 ppm recorded in cpx-rich lherzolites. In terms of major and trace element geochemistry, LS cpx-rich lherzolites reflect a mantle domain, which does not seem to have acted as magma source, or at least it represents a residuum of < 3% of PM melting in the spinel stability field. Comparing the water contents of cpx-rich lherzolites with the PM water estimates, it is evident that, while the RLE composition (i.e. REE and Al) of this lithotype perfectly fits the PM model (Fig. 8), the H2O contents are significantly lower than the theoretical values (Fig. 10). Water contents of LS peridotites are even lower than the mantle source (H2O ~ 80 ppm; DMW, Workman and Hart, 2005) of the “driest” MORB (H2O ~ 0.05 wt%; Luth, 2013). Overall, water contents of LS peridotites show no systematical variation among rock types (Table 1) and no correlation with Yb (and Y) or Al2O3 contents of cpx. For instance, the harzburgite LS26 and cpx-rich lherzolites LS31 have similar water contents (57 vs. 55 ppm), but they represent different
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