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Highly siderophile and chalcophile element behaviour in abyssal-type and supra-subduction zone mantle: new insights from the New Caledonia ophiolite

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Highly siderophile and chalcophile element behaviour in abyssal-type and supra-subduction zone mantle: new insights from the New Caledonia ophiolite / Secchiari, Arianna; Gleissner, Philipp; Li, Chunhui; Goncharov, Alexey; Becker, Harry; Bosch, Delphine; Montanini, Alessandra. - In: LITHOS. - ISSN 0024-4937. - 354-355:(2020), pp. 105338.1-105338.17. [10.1016/j.lithos.2019.105338]

Availability: This version is available at: 11381/2868206 since: 2024-12-24T07:53:09Z

*Publisher:* Elsevier B.V.

Published DOI:10.1016/j.lithos.2019.105338

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#### Elsevier Editorial System(tm) for Lithos Manuscript Draft

Manuscript Number:

Title: Highly siderophile and chalcophile element behaviour in abyssaltype and supra-subduction zone mantle: new insights from the New Caledonia ophiolite

Article Type: VSI:EMAW- Mantle Paradigms

Keywords: Re-Os geochemistry Highly siderophile elements New Caledonia ophiolite Sub-arc mantle Depleted mantle sections

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Abstract: The New Caledonia Ophiolite hosts one of the largest obducted mantle sections worldwide, offering a unique opportunity to investigate key mantle processes. The ophiolite comprises refractory harzburgites, locally overlain by mafic-ultramafic cumulates, and minor lherzolites. Previous geochemical studies indicated that the lherzolites are akin to abyssal-type peridotites, while the harzburgites underwent multiple melting episodes in MOR and supra-subduction zone environments, followed by late stage metasomatism.

In this work, Os isotopes, highly siderophile (HSE) and chalcophile element data are reported for the New Caledonia peridotites, in order to constrain the behaviour of these elements in abyssal-type and fore-arc mantle.

The variably serpentinised lherzolites (LOI = 6.4 - 10.7 %) yield slightly subchondritic to suprachondritic initial Os isotopic compositions (1870s/1880si = 0.1273-0.1329) and subchondritic to chondritic Re/Os ratios (0.04-0.11). The gently sloping HSE patterns with increasing depletion towards Au show concentrations in the range of other lherzolites from MOR or continental setting. Sulphur contents are high and variable (202-1268 ppm), and were likely increased during serpentinisation. By contrast, Se/Te ratios and concentrations are within the range of primitive mantle (PM) values, meaning that these elements were not significantly mobilised during serpentinisation. Despite displaying homogenous petrographic and geochemical features, the harzburgites are characterised by extremely heterogeneous Re-Os and HSE compositions.

Type-A harzburgites exhibit subchondritic 1870s/1880si (0.1203-0.1266) and low Re/Os ratios (0.01-0.04). The strong IPGE-PPGE fractionations (PdN/IrN = 0.21-0.56) coupled with positive Pt anomalies and S-Se-Te abundances often below the detection limit suggest high melt extraction

rates, resulting in sulphide consumption and Os-Ru metal alloy stabilisation.

Type-B harzburgites possess strongly fractionated, Os-Ir-Pt poor (Os = 0.003-0.072 ng/g, Ir = 0.0015-0.079 ng/g) and Pd-Re enriched patterns, associated with chondritic to suprachondritic measured 1870s/1880s (0.127-0.153). These characters are uncommon for highly depleted mantle residues. Interaction with an oxidised component does not appear as a viable mechanism to account for the IPGE-depleted patterns of type-B harzburgites, as calculated oxygen fugacities are close to the FMQ buffer (Log  $\Delta$ FMQ= 0.20 to 0.48). The lower fO2 conditions register by type-B harzburgites compared to type-A likely records fO2 lowering due to continued melt extraction at un-buffered fO2 conditions. Type-B patterns may thus derive from slightly higher melting degrees, finally leading to Os-Ir-Pt release into the silicate melt. We propose that HSE geochemistry of the New Caledonia peridotites reveals superimposition of geochemical characters related to the recent Eocene evolution on a mantle source bearing a long term (> 1 Ga) evolution.

### Abstract

The New Caledonia Ophiolite hosts one of the largest obducted mantle sections worldwide, offering a unique opportunity to investigate key mantle processes. The ophiolite comprises refractory harzburgites, locally overlain by mafic-ultramafic cumulates, and minor lherzolites. Previous geochemical studies indicated that the lherzolites are akin to abyssal-type peridotites, while the harzburgites underwent multiple melting episodes in MOR and supra-subduction zone environments, followed by late stage metasomatism.

In this work, Os isotopes, highly siderophile (HSE) and chalcophile element data are reported for the New Caledonia peridotites, in order to constrain the behaviour of these elements in abyssal-type and fore-arc mantle.

The variably serpentinised lherzolites (LOI = 6.4 - 10.7 %) yield slightly subchondritic to suprachondritic initial Os isotopic compositions (<sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub> = 0.1273-0.1329) and subchondritic to chondritic Re/Os ratios (0.04-0.11). The gently sloping HSE patterns with increasing depletion towards Au show concentrations in the range of other lherzolites from MOR or continental setting. Sulphur contents are high and variable (202-1268 ppm), and were likely increased during serpentinisation. By contrast, Se/Te ratios and concentrations are within the range of primitive mantle (PM) values, meaning that these elements were not significantly mobilised during serpentinisation.

Despite displaying homogenous petrographic and geochemical features, the harzburgites are characterised by extremely heterogeneous Re-Os and HSE compositions.

Type-A harzburgites exhibit subchondritic  ${}^{187}$ Os/ ${}^{188}$ Os<sub>i</sub> (0.1203-0.1266) and low Re/Os ratios (0.01-0.04). The strong IPGE-PPGE fractionations (Pd<sub>N</sub>/Ir<sub>N</sub> = 0.21-0.56) coupled with positive Pt anomalies and S-Se-Te abundances often below the detection limit

suggest high melt extraction rates, resulting in sulphide consumption and Os-Ru metal alloy stabilisation.

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A comprehensive Re-Os, highly siderophile and chalcophile element investigation of the New Caledonia peridotites is presented.

HSE patterns of the Iherzolites reflect low partial melting degrees of a mantle source that previously experienced melt percolation and radiogenic Os ingrowth.

Based on HSE and Os isotopic signature, two big groups of harzburgites (*type-A and B*) can be identified.

HSE and Re-Os systematics of type-A harzburgites are consistent with high melt extraction degrees, resulting in sulphide exhaustion and Os-Ru metal alloys stabilisation.

The HSE and Re-Os features of type-B harzburgites may record higher partial melting degrees and Os-Ir-Pt release into silicate melt after continued melt extraction.

1

# 2 1. Introduction

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Highly siderophile elements (HSE: PGE+ Au-Re) are powerful geochemical tracers that 4 can provide useful information for a variety of mantle processes, such as mantle 5 melting, metasomatism and melt-fluid/mantle interaction (e.g. Luguet et al., 2001, 6 2003, 2007; Lorand et al., 2008; Ackerman et al., 2009). However, our knowledge 7 concerning the behaviour of HSE in mantle source rocks of primitive arc magmas and 8 9 the role of the subduction zone environment on HSE partitioning (i.e. hydrous melting, melt/fluid-mantle interaction) still remains quite fragmentary. Furthermore, although 10 abundant HSE data are now available for different types of mantle peridotites, HSE 11 data on fore-arc peridotites are remarkably scarce (e.g. Becker and Dale, 2016). 12

The New Caledonia ophiolite (Peridotite Nappe) hosts one of the largest and best 13 preserved mantle sections worldwide, providing an excellent opportunity to 14 investigate upper mantle processes. The rock exposures are dominated by harzburgite 15 tectonites bearing a supra-subduction zone affinity (Marchesi et al., 2009; Ulrich et 16 al., 2010; Pirard et al., 2013; Secchiari et al., 2019a). The main geochemical and 17 isotopic features of these rock-types reflect a complex polyphase evolution, including 18 several melting episodes in different geodynamic settings and subduction zone 19 metasomatism (Marchesi et al., 2009; Ulrich et al., 2010; Secchiari et al., 2019a). 20 Minor abyssal-type spinel and plagioclase lherzolites, with compositions similar to 21 abyssal peridotites, occur as discrete bodies in the north-western part of the island. 22 23 The lherzolites record a different history compared to the extremely refractory harzburgites, as highlighted by their different geochemical signature (Ulrich et al., 24 2010; Secchiari et al., 2016). 25

In this work, a set of fully characterised peridotites (i.e. whole rock and in situ major 26 and trace element contents, Sr-Nd-Pb isotopes) from New Caledonia (Secchiari et al., 27 2016, 2019a) has been used to investigate Re-Os, HSE and chalcophile element (S-28 29 Se-Te) systematics. The main aims of this work are: 1) to examine the behaviour of these elements in the lherzolites (i.e. presumed abyssal peridotites) and in the ultra-30 depleted harzburgites, which may represent rocks from a former supra-subduction 31 zone mantle wedge; 2) to constrain the behaviour of HSE and chalcophile elements 32 during subduction zone processes. 33

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35 2. Geological setting and petrological background

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New Caledonia is a NW–SE elongated island located in the SW Pacific region, between 37 the eastern margin of Australia and the Vanuatu archipelago (Fig. 1a). The island 38 39 represents the emerged portion of the submarine Norfolk Ridge and it is composed by 40 a mosaic of volcanic, sedimentary and metamorphic terranes, ranging in age from Permian to Miocene (Aitchison et al., 1995; Cluzel et al., 2001, 2012; Lagabrielle et 41 al., 2013). These terranes were amalgamated during two major tectonic events: 1) an 42 Early Cretaceous tectonic convergence phase (Paris, 1981) and 2) a Paleocene to Late 43 Eocene subduction culminated in the obduction of the ophiolite. Both events were 44 characterized by high-pressure low-temperature (HP-LT) metamorphism in connection 45 46 with plate convergence. New Caledonia can be sub-divided into four main geological domains (Cluzel et al., 2001; see Fig. 1): (i) the Basement units (pre-Late Cretaceous 47 basement and Late Coniacian-to-Late Eocene sedimentary cover), (ii) the Cenozoic 48 HP-LT metamorphic belt, (iii) the basaltic Poya Terrane and (iv) a large slab of 49 peridotites, i.e. the Peridotite Nappe. 50

The Peridotite Nappe represents an allochtonous sheet of oceanic lithosphere belonging to the former South Loyalty basin thrust on the continental basement of the Norfolk Ridge at the end of the Eocene subduction. The emplacement of the ophiolitic nappe resulted from the failed subduction of the Norfolk Ridge tip in a NE-dipping subduction zone, which culminated in the obduction of the Loyalty subarc lithosphere ~ 34 Ma ago (Cluzel et al. 2012).

The Peridotite Nappe has an extension of about 8000 km<sup>2</sup> and is mostly exposed in 57 the Massif du Sud, where a thick harzburgite-dunite unit, locally overlain by 58 kilometre-scale lenses of mafic and ultramafic intrusives, crops out. The sequence is 59 believed to represent a crust-mantle boundary that records the onset of Eocene 60 61 subduction in a nascent arc setting (Marchesi et al., 2009; Pirard et al., 2013; Secchiari et al., 2018). Recent geochemical studies have shown that the ultramafic 62 intrusives (i.e. dunites and wehrlites) crystallised from variably depleted melts with 63 island arc basalt affinity, after massive interactions with the underlying harzburgite 64 (Marchesi et al., 2009; Pirard et al., 2013). In contrast, the mafic rocks (i.e. 65 gabbronorites) rather have a cumulate origin (Marchesi et al., 2009; Pirard et al., 66 2013; Secchiari et al., 2018) and derive from crystallization of primitive, non-67 aggregated, ultra-depleted melts showing involvement of a subduction-related 68 component in their source (Secchiari et al., 2018). 69

The harzburgites are also exposed in the northern Tiébaghi massif (Ulrich et al., 2010) or as sparse tectonic klippen in the central part of the island (e.g. Kopeto, Poya, Koniambo), where exceptionally fresh peridotites display primary mineral assemblages similar to the more serpentinised rocks of the Massif du Sud.

The New Caledonia harzburgites bear an overall ultra-depleted composition, inherited from a complex multistage evolution linked to the development of the Eocene subduction system (Marchesi et al., 2009; Ulrich et al., 2010; Secchiari et al., 2019a). Geochemical studies have proposed that the harzburgites formed by high degrees of

fluid-assisted melting (up to 20-25 % in a supra-subduction zone environment, see 78 Marchesi et al., 2009; Ulrich et al., 2010). More recently, the work of Secchiari et al. 79 (2019a) provided further constraints on the evolution of the harzburgites, tracking 80 81 their history from melting to late stage metasomatism. Accordingly, the harzburgites underwent two partial melting episodes in the spinel stability field: a first melting 82 phase in a MOR setting (15% melting degrees), followed by hydrous melting in a 83 supra-subduction zone setting (up to 18% fluid-assisted melting). Post-melting 84 cooling and re-equilibration at lithospheric conditions was accompanied by interaction 85 with slab-derived hydrous melts bearing an ultra-depleted composition (Secchiari et 86 al., 2019a,b). These metasomatic processes in the harzburgites are indicated by the 87 widespread occurrence of secondary metasomatic phases (i.e. thin films of Al<sub>2</sub>O<sub>3</sub>-, 88 CaO- poor orthopyroxene, and low Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O clinopyroxene), L-MREE and Zr-Hf 89 bulk rock enrichments, as well as by the unradiogenic Nd isotopic ratios shown by 90 some samples (Secchiari et al., 2019a). 91

22 Compared to the harzburgites from the central and the southern massifs, Tiébaghi 23 samples display a more fertile nature, as indicated by higher trace element 24 concentrations as well as by the occurrence of a small fraction (up to 4 vol.%) of 25 clinopyroxene (see Ulrich et al., 2010; Secchiari, PhD thesis).

96 The main geochemical and petrological features of the spinel and plagioclase 97 Iherzolites are thought to reflect moderate melting degrees (8-9%) in a MOR 98 environment, followed by refertilisation by depleted MORB-type melts, yielding 99 plagioclase Iherzolites. The main petrological and geochemical features of these 100 lithotypes have been described in detail by Secchiari et al. (2016).

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102 2.1 Sample description

In this contribution, seventeen samples of peridotites fully characterised for lithophile element geochemistry (i.e. major, trace element and Sr-Nd-Pb isotope compositions) were analysed for mass fractions of all PGE, Re, Au, S, Se and Te and <sup>187</sup>Os/<sup>188</sup>Os. Detailed descriptions of the lherzolites and harzburgites, including trace element chemistry and Sr-Nd-Pb isotopes, are provided in Secchiari et al. (2016) and Secchiari et al. (2019a, b), respectively.

Lherzolite samples are from the Poum and Babouillat areas, while the harzburgites were collected from several outcrops and mine zones along the island: Yaté, Kopeto, Poya, Poro and Tiébaghi (Fig. 1b and Table 1). The Iherzolites include serpentinised (LOI= 6.9 - 10.7 %) spinel and plagioclase Iherzolites, while the harzburgites are typically not or only little serpentinised (LOI = 0 - 3 %), except for samples YA1, TI1 and TI2 (LOI = 6.0 - 9.0 %).

Both Iherzolites and harzburgites are low strain mantle tectonites, showing dominant 116 porphyroclastic textures (Fig. S1a-b) and local protomylonite development. Spinel 117 118 Iherzolites have 7-8 vol.-% clinopyroxene and display a typical abyssal-type REE signature. The plagioclase lherzolites show melt impregnation microstructures (Fig. 119 120 S1b) and are slightly enriched in incompatible trace element enrichments (REE, Ti, Y, and Zr) with respect to the spinel lherzolites. Harzburgites are extremely depleted 121 rocks, as highlighted by the general absence of clinopyroxene (with the exception of 122 sample TI2, where clinopyroxene is  $\sim$  4 vol. %, Fig. S1c) and the very low 123 incompatible trace element contents (Secchiari et al., 2019a). The primary mantle 124 paragenesis is composed of olivine, orthopyroxene and spinel. The occurrence of thin 125 films of metasomatic ortho- and clinopyroxene (Fig. S1d) was interpreted as the 126 127 result of percolation by small fractions of subduction-related magmas (Secchiari et al., 2019a-b). 128

Rare sulphide grains with variable size, shape and position have been recognised in the lherzolites and were analysed for their major element chemistry in samples BA1

and POU2 (see Table S1). Small (40 to 100  $\mu$ m x 30 to 80  $\mu$ m) sulphide inclusions 131 (Fig. S2a-e), bearing polyhedral or spherical shape, have been observed within olivine 132 and pyroxene porphyroclasts. Interstitial sulphide grains occur as polyhedral blebs 133 (Fig. S2f), up to 300 x 100/150  $\mu$ m in maximum dimensions, and are generally 134 located at olivine-pyroxene grain boundaries. Sulphide composition is relatively 135 homogeneous (Table S1 and Fig. S2), with Ni-poor (Fe/Ni=1.4-2.5) monosulphide 136 solid solution (Guo et al., 1999) being the most abundant phase. Ni-rich (Fe/Ni =0.7-137 0.8) pentlandite has also been identified in the sample POU2. The sulphides frequently 138 show lamellae and rims made by Fe-oxides/hydroxides due to desulphidation 139 reactions. 140

141 3. Analytical methods

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143 3.1 HSE and chalcophile elements

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Seven lherzolites and ten harzburgites (including four duplicates) have been analysed in the geochemistry laboratory at Freie Universität for HSE, S, Se, Te mass fractions in whole rocks and <sup>187</sup>Os/<sup>188</sup>Os.

Detailed procedure descriptions have been given in previous work from this laboratory (e.g. Fischer-Gödde et al., 2011; Wang et al., 2013; Wang and Becker, 2013). The methods will only be briefly summarized below.

About 2.5 g of sample powder was weighed into 90 ml quartz glass digestion vessels and spiked with mixed <sup>191</sup>Ir-<sup>99</sup>Ru-<sup>194</sup>Pt-<sup>105</sup>Pd, <sup>77</sup>Se-<sup>125</sup>Te, <sup>185</sup>Re-<sup>190</sup>Os and <sup>34</sup>S solutions. Then, 5 ml 14 mol/L, N<sub>2</sub>-bubbled HNO<sub>3</sub> and 2.5 ml 9 mol/L HCl were added. The vessels were immediately sealed with Teflon tape and samples were digested for 16 h at 320°C and 100 bar. After digestion, osmium was extracted from the reverse aqua regia into chloroform, back extracted into HBr (Cohen and Waters, 1996), and further purified by micro distillation from a  $H_2SO_4$ -dichromate solution into 15  $\mu$ l of HBr (Birck et al., 1997)

Osmium isotopes were determined as  $OsO_3^-$  in negative mode using the Thermo 159 Finnigan Triton TIMS, using a secondary electron multiplier. Signal intensities of the 160 spike isotope <sup>190</sup>Os of samples were ~ 150,000-500,000 cps. Standard runs with 161 different amounts of Os on the filament (10 pg and 100 pg) were also run in between 162 the studied samples, yielding an average value of  $0.1139 \pm 0.0002$  (2 s. d., n = 24) 163 for 100 pg loads. Two hundreds scans were collected in each measurement for high-164 Os samples, while at least 120-140 scans were obtained for the low-Os samples. Raw 165 166 data were corrected for isobaric  $OsO_3^-$  interferences, mass fractionation using the <sup>192</sup>Os/<sup>188</sup>Os ratio of 3.08271, contributions from the Os spike solution and blank 167 contributions. <sup>187</sup>Os/<sup>188</sup>Os were finally adjusted relative to the mean of the Os 168 standard. The oxygen isotope compositions used for the oxide correction of Os oxide 169 molecules were  ${}^{18}\text{O}/{}^{16}\text{O}$  of 0.00204 and  ${}^{17}\text{O}/{}^{16}\text{O}$  of 0.00037 (Nier, 1950). 170

About 50% of the digestion solution was used for separation of the HSE fraction and 171 172 about 30% for S-Se-Te separation. Chemical separation of the HSE fraction from the matrix was performed on columns filled with 10 ml of pre-cleaned Eichrom 50W-X8 173 (100-200 mesh) cation exchange resin (Fischer-Gödde et al., 2011). During 174 separation, the HSE fraction was collected in 14 ml 0.5 mol/L HCl-40 vol.% acetone 175 mixture. After the volume of the solution has been reduced to about 2 ml it was 176 analysed for Au, Re, Ir and Pt. In order to remove interfering Cd, the remaining 177 solution was further purified in 0.2 mol/L HCl on 3 ml Eichrom 50W-X8 (100-200 178 179 mesh) resin. The collecte dsolution was evaporated to near dryness and the residue was taken up in 0.28 M HNO<sub>3</sub> for ICP-MS analysis. The analyses were carried out 180 using a single collector Element XR instrument. We used either a Scott-type spray 181

182 chamber (Re, Ir, Pt, Au) or an Aridus-I desolvator (Ir, Ru, Pt, Rh, Pd) at an oxide 183 formation rate of  $CeO^+/Ce^+ < 0.004$ .

A two-step ion exchange chromatography method was used for separation of S, Se and Te (see Wang et al., 2013). Sulphur measurements were performed on the S–Se fraction at medium mass resolution mode on the Element XR. Selenium and Te were measured using a double pass Scott type glass spray chamber at low mass resolution mode on the Element XR, combined with a hydride generation sample introduction system by reacting the sample solution with 1 g/100 g NaBH<sub>4</sub> in 0.05 mol/L NaOH (see Wang et al., 2013 for details).

For each batch of analysis, one procedural blank has been used. Procedural blanks 191 192 yielded the following mean values ( $\pm 1 \text{ s.d.}$ , n = 4-5): Re = 2.5  $\pm 2.0 \text{ pg}$ ; Os = 0.5  $\pm$ 0.3 pg with  ${}^{187}$ Os/ ${}^{188}$ Os ratios of 0.14 ± 0.03; Ir = 15 ± 5 pg; Ru = 45 ± 14 pg; Rh = 193  $24 \pm 22 \text{ pg}; \text{Pt} = 23 \pm 29 \text{ pg}; \text{Pd} = 640 \pm 330 \text{ pg}; \text{Au} = 4 \pm 2 \text{ pg}; \text{Te} = 1.1 \pm 0.8 \text{ ng};$ 194 Se = 2.3  $\pm$  0.8 ng; S = 2.8  $\pm$  0.7  $\mu$ g. Samples were corrected for total procedural 195 196 blanks using the mean values. Blank corrections for Re are negligible for most of the analysed samples ( $\leq 0.3 - 0.8$  %), but more significant for the harzburgites ( $\sim 4 - 8$ 197 198 %). Blank corrections for Pt and Pd are again negligible for the lherzolites ( $\sim 0.2 - 0.3$ %) a few percents for the harzburgites ( $\sim 0.4 - 4$  %, with the exception of KPT2, 199 KPT5 and PO3 for which the correction for Pt is  $\sim 11 - 36$  %). Blanks of Os, Ir, Ru and 200 Rh are insignificant for most of the samples ( $\leq 0.4$  %) but higher for the most 201 depleted harzburgites, i.e. KPT2, KPT5 (~ 2 – 7 % for Os, Ir, Rh) and PO3 (~ 9 % for 202 Os and Ir, 13 % for Rh,). Blank corrections for S, Se and Te in Iherzolites range 203 between 1 - 1.7 % (S - Se) and 3-6% (Te), while for harzburgites blank corrections 204 205 for these elements strongly affected the obtained results (corrections  $\sim 10 - 26$  % for 206 S and up to 40 - 80% for Se and Te), given the very low measured abundances.

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210 Iron oxidation state in studied spinel was measured using flank approach designed for 211 the JEOL JXA-8200 electron microprobe analyser at Freie Universität on a collection of natural and synthetic spinel standards characterized for their  $Fe^{3+}/\Sigma Fe$  at IPGG RAS 212 (St. Petersburg) using Mössbauer spectroscopy (Goncharov, 2018). The analytical 213 procedure was similar to experiments performed over the last decades to study 214  $Fe^{3+}/\Sigma Fe$  in mantle garnets after procedure developed by (Höfer and Brey, 2007). The 215 flank positions were calculated from the difference spectrum of almandine-andradite 216 for the spectrometer in wavelength range related to FeLa and FeLß lines. FeLa and 217 FeLß intensities were collected at a wavelength of flank lines for 300 seconds each 218 with 3 repetitions in the core and rim parts of 4-5 spinel grains within one thin 219 section. Measurement conditions were 15 kV and 60 nA using TAP crystal for 220 intensities at flank positions and with remaining 4 spectrometers were measured 221 chemical composition at the same spot simultaneously. Averaged FeLa and FeLß 222 intensities for one sample were used to calculate iron oxidation state of spinel from 223 the equation obtained after standardization, where FeL<sub>β</sub>/FeLa ration and FeO total 224 content correlate with  $Fe^{3+}/\Sigma Fe$  measured by Mössbauer spectroscopy. 225

Owing to the lack of an appropriate geobarometer for spinel peridotites, the assumed equilibrium pressure for oxygen fugacity calculations has been set at P = 1.5 GPa. Equilibrium temperatures have been calculated using coexisting minerals and the Cain-orthopyroxene geothermometer of Brey and Köhler (1990) and olivine–spinel geothermometer of Li et al. (1995).

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232 4. Results

## 4.1 HSE and chalcophile elements in spinel and plagioclase lherzolites

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HSE and chalcophile element compositions of the New Caledonia Iherzolites are 236 reported in Table 1 and displayed in Fig. 2, 3, 4. Spinel and plagioclase lherzolites are 237 relatively homogeneous in terms of HSE, Se, Te concentrations, abundance patterns 238 and Os isotopic compositions, with plagioclase-bearing samples showing 239 indistinguishable patterns from those of spinel lherzolites. The concentrations of the 240 highly siderophile and chalcophile elements are in the range of those observed for 241 modern abyssal and ophiolitic peridotites, displaying good correlation for Ir group PGE 242 (IPGE, e.g., Os vs. Ir and Ir vs. Ru) and more dispersed variations for the Pt group 243 PGE (PPGE, Fig. S3). In primitive mantle (PM) normalised concentration diagrams 244 (Fig. 3), the lherzolites exhibit flat or gently sloping patterns with similar PM-245 normalized PGE concentrations and depletions in Au (except for sample BAB2B) and 246 Re compared to the PGE (with the exception BAB2B for Au and POU1A and POU3 for 247 Re). Overall, absolute contents of the PGE are similar or slightly lower than primitive 248 mantle (PM) values (Becker et al., 2006; Fischer-Gödde et al., 2011), overlapping the 249 field of the abyssal peridotites and peridotite tectonites from continental settings 250 (e.g., Fig. 2 and Becker and Dale, 2016). Ru/Ir and Pd/Ir ratios are suprachondritic, 251 as observed for other mantle lherzolites (e.g. Lorand et al., 1999; Rehkämper et al., 252 1999; Luguet et al., 2003; Becker et al., 2006). 253

Initial <sup>187</sup>Os/<sup>188</sup>Os ratios calculated at 53 Ma (i.e. the inferred age of initial magmatism in the subduction system, e.g. Cluzel et al., 2006) vary from chondritic to slightly suprachondritic (0.1273-0.1329, Fig. 4a), corresponding to  $\gamma Os_{(53Ma)}$  of 0.5 to 4.9. These values overlap with data of abyssal peridotites and orogenic peridotites, but tend to be somewhat higher than for other mantle lherzolites bearing comparable

depletion degrees (Fig. 4a and 4b).  $^{187}$ Re/ $^{188}$ Os ranges from subchondritic to slightly suprachondritic values (0.186-0.525, see Fig. 4c).

Se and Te are positively correlated in the lherzolites (Fig. 5a) and range between 54 -91.3 ng/g and 7.3 - 13.8 ng/g, respectively. Se/Te ratios (5.9-7.1) are slightly lower than the PM value and similar to the data previously obtained on depleted lherzolites (Wang and Becker, 2013). Se and Te do not display any correlation with PGE abundances, with the exception of Te, which shows a weak correlation with Pd (Fig. 5b). S contents are high and variable (202 - 1268  $\mu$ g/g) compared to unserpentinised peridotites, leading to high S/Se ratios (2703-16289, Fig 5c).

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4.2 HSE and chalcophile elements in harzburgites

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271 On the basis of HSE behaviour and Os isotopic compositions (Fig. 2, 3 and 6, Table 1), 272 the studied harzburgites can be grouped into two different sub-types: type-A and 273 type-B.

Type-A harzburgites (TI1, TI2, PO4 and YA1) are characterised by notably lower mass 274 275 fractions of all PGE and most other chalcophile elements (Figs. 2, 4) and more 276 fractionated HSE and chalcophile element patterns (Fig. 6a) compared to the Iherzolites. Mass fractions of the PGE in these harzburgites are 1.07-2.07 ng/g for Os, 277 0.50-1.14 ng/g for Ir, 1.53-2.52 ng/g for Ru, 0.19-0.27 ng/g for Rh, 2.42-2.70 ng/g 278 for Pt and 0.49-0.57 ng/g for Pd. Among the sub-group A, sample YA1 displays 279 distinct PGE abundances, showing much lower Os, Ir, Pt, Pd contents (0.55 ppb for 280 Os, 0.30 ppb for Ir, 0.27 ppb for Pt and 0.26 ppb for Pd), with exceptions for Ru, Rh, 281 282 Au and S.

283 HSE and chalcophile element diagrams of type-A harzburgites display fractionated 284 patterns, with concentrations decreasing towards Re. Os and Ru are enriched

compared to Ir, leading to correlated suprachondritic Os/Ir and Ru/Ir ratios 285 (Os/Ir=2.9-7.9; Ru/Ir=1.8-2.1, Fig. 4). Pt and Au generally show positive spikes, 286 287 more pronounced for Au, with the exception of YA1, which displays a negative Pt 288 anomaly. Pd contents are low (< 0.1 PM values) and constant for PO4, TI1, TI2, with Pd/Ir showing subchondritic ratios for all studied samples. Positive correlations are 289 observed between IPGE (Fig. 2a-b-c) and Pt-Ir (not shown), and, somewhat 290 surprisingly, between IPGE and the fertility indicators (i.e.  $Al_2O_3$  and CaO, not shown). 291 Mass fractions of Te, Se and S are low, often close to or below the detection limit, 292 again with the exception of the harzburgite YA1. 293

For all type-A harzburgites, Re concentrations are very low (about 0.02 ng/g), leading to subchondritic <sup>187</sup>Re/<sup>188</sup>Os ratios (0.045 to 0.196, the latter value also reflecting the low Os concentrations in YA1). Os isotopic compositions are subchondritic to chondritic (0.1203-0.1266, corresponding  $-5 \le \gamma_{Osi(53 Ma)} \le -0.1$ ) and do not define any correlation with <sup>187</sup>Re/<sup>188</sup>Os or incompatible element depletion indices (i.e. Al<sub>2</sub>O<sub>3</sub>, see Fig. 4).

300

301 Type-B harzburgites comprise very fresh samples from Kopeto (KPT2, KPT3, KPT5), Poro (PO3) and Poya (PY1) massifs. Compared to type-A harzburgites, these samples 302 have much lower HSE abundances and display variable and strong fractionations 303 among PGE and more incompatible chalcophile elements (Fig. 2 and 6b). In detail, Os, 304 Ir and Pt show positive correlations (Fig. 2) and are strongly depleted compared to 305 Ru, Rh and Pd (Os= 0.003-0.071 ppb, Ir= 0.015-0.079 ppb, with Os/Ru=0.01-0.26 306 and Ru/Ir= 2.5-20). For sample PY1, Pt is enriched relative to IPGE, Rh and Pd 307 308 (Pt/Rh=7.7; Pt/Pd=5.5). Pd, Re and S-Se-Te have similarly low normalized 309 abundances, with chalcophile elements often close to or below the detection limit. Au

exhibits positive spikes for PY1, KPT3 and PO3 samples and tends to be more enriched than similar incompatible chalcophile elements (i.e. Pd and Re).

Measured <sup>187</sup>Os/<sup>188</sup>Os ratios vary from chondritic to suprachondritic (0.1273-0.1534) and are coupled with high and variable <sup>187</sup>Re/<sup>188</sup>Os (1.62-32). Initial Os isotopic compositions calculated at 53 Ma range from depleted to slightly suprachondritic values (0.1181-0.1365,  $-7 \le \gamma Os_{(53Ma)} \le 3$ ).

Replicate analyses of samples PY1, KPT2, KPT5, PO3 yield quite similar results for Ru (< 5 % relative deviation, except for sample KPT2) and Au (~ 6% for PY1 and KPT5) and acceptable results for Pt for PY1-KPT5 (11.5 - 14.0 % relative deviation). Values appear much more scattered for Os and Re (RSD> 30%) and less dispersed for Rh and Pd (7 $\leq$ RSD% $\leq$ 32). The relative deviation of chalcophile elements is more limited, mostly < 15%.

The large variations of mass fractions of HSE and chalcophile elements in duplicate samples reflects the very low mass fractions of these elements combined with the inhomogeneity in the distribution of HSE carrier phases in gram-size quantities of rock powder, an issue that has already been recognised in peridotitic rocks (e.g. Becker et al., 2006; Luguet et al., 2007).

327

328 4.3 Oxybarometry

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Geothermometric estimates and calculated oxygen fugacity values are reported in Table 2. Equilibrium temperatures calculated for porphyroclastic assemblies with the Ca-in-orthopyroxene thermometer (Brey and Köhler, 1990) range between 930-1130°C, with samples YA1 and TI2 displaying the lowest temperatures (930°C-980°C, see Table 2). Olivine-spinel geothermometry (Li et al., 1995) yields considerably lower equilibration temperatures (815-940°C).

Oxygen fugacity estimated with the Wood (1990) method yielded values close to the 336 FMQ (fayalite-magnetite-quartz) buffer for all the harzburgites ( $0.16 \le \Delta \log FMQ$ 337  $\leq$ 0.71). Similar estimates (0.18 $\leq$   $\Delta$ logFMQ  $\leq$ 0.76) are obtained using temperatures 338 calculated with the olivine-spinel geothermometer. No significant difference can be 339 observed between sub-group A and B harzburgites. Remarkably, the highest oxygen 340 fugacity values are recorded by two harzburgites belonging to sub-group A (YA1 and 341 TI2), which are characterised by lower degrees of depletion, as inferred from trace 342 element modelling (see Secchiari et al., 2019a). 343

344 By contrast, lherzolite BA1 lherzolite indicates much more reducing oxygen fugacity 345 conditions ( $\Delta \log FMQ \leq -3.73$ ).

346

347 5 Discussion

348

349 5.1 HSE and Re-Os systematics of the lherzolites

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Major element composition and lithophile trace element chemistry of spinel lherzolites 351 indicate moderately depleted compositions, inherited from low partial melting degrees 352 (8-9%) of a DMM source, whereas plagioclase lherzolites originated through reactive 353 354 melt percolation of spinel lherzolites by highly depleted, incremental melt fractions of a DMM source in the shallow lithosphere (Secchiari et al., 2016). In the following 355 sections the processes that may have affected HSE and Os isotopic signature of the 356 New Caledonia Iherzolites will be discussed: low temperature alteration, in particular 357 serpentinisation, partial melting and the role of melt infiltration and chemical 358 disequilibrium of the HSE in mantle rocks. 359

# 361 5.1.1 Effects of serpentinisation on HSE and <sup>187</sup>Os/<sup>188</sup>Os

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Serpentinisation is a widespread process of hydrothermal alteration in ultramafic 363 lithologies. However, its influence on HSE behaviour has not been investigated with 364 much detail, despite some authors have proposed it as a possible cause for <sup>187</sup>Os 365 ingrowth and Re variations in the upper mantle (Snow and Reisberg, 1995; Walker et 366 al., 1996; Standish et al., 2002). Recent experimental studies have shown that during 367 368 serpentinisation the formation of secondary sulphides, Fe-Ni alloys and native metals (Au-Cu) is promoted by reducing  $f_{02}$  conditions (Klein and Bach, 2009; Foustoukos et 369 al., 2015) and thus, with the exception of Au, HSE may be retained in the host rock. 370 Comparison of partially serpentinised and unserpentinised peridotites displaying 371 similar major element features supports the notion that at least PGE ratios are little 372 changed by moderate to strong serpentinisation (Becker and Dale, 2016). 373

The New Caledonia lherzolites underwent intermediate serpentinisation (LOI = 6.4 to 374 10.7 %, see paragraph 2.1 and Table 1), which had limited effects on the budget of 375 fluid immobile moderately incompatible lithophile trace elements in these rocks 376 (Secchiari et al., 2016). Notably, PGE contents and ratios in the lherzolites are similar 377 to other unaltered and serpentinised lherzolites from the modern oceans and ophiolitic 378 complexes (see Fig. 2 and 3 e.g.; Snow et al., 2000; Luguet et al., 2001, 2004; 379 Pearson et al., 2004; Alard et al., 2005; Becker et al., 2006; Fischer-Gödde et al., 380 2011; Becker and Dale, 2016). This observation supports the hypothesis that PGE 381 abundances are comparable in fresh and variably serpentinised ultramafic rocks 382 383 (Becker et al., 2006; Liu et al., 2009; Fischer-Gödde et al., 2011; Marchesi et al., 2013; Becker and Dale, 2016), implying that serpentinisation results in minor changes 384 in PGE ratios. 385

By contrast, the possible influence of serpentinisation on Au and Re is more difficult to 386 evaluate, as no study has systematically investigated its effect on the behaviour of the 387 aforementioned elements. In the lherzolites from New Caledonia, Au displays similar 388 389 normalized concentrations as Re and, with the exception of a few samples, both elements are depleted relative to Pd, Te and Se. Au abundances tend to be somewhat 390 lower than abundances in other lherzolites with similar major element composition 391 (Fig. 3). Although the compositions can be entirely explained by magmatic 392 fractionation processes (see subsequent chapters), minor losses of Au due to 393 hydrothermal alteration cannot be ruled out (e.g. Lorand et al., 1999). The lack of 394 395 correlation between Au and Al<sub>2</sub>O<sub>3</sub> (not shown) could be a hint that Au abundances 396 may have been affected by a combination of magmatic processes and serpentinisation (i.e. Fischer-Gödde et al., 2011). Rhenium is slightly depleted compared to the PGE 397 for most of the studied lherzolites, but displays higher concentrations than other 398 mantle lherzolites (Fig. 3). In addition, Re contents do not correlate with LOI and 399 400 Re/Os ratios cover the range generally reported for moderately depleted mantle rocks. The samples with the lowest Re contents display the highest LOI values, suggesting 401 402 that no significant quantities of Re were added during the interaction with seawater during serpentinisation. Likewise, the chondritic to slightly suprachondritic <sup>187</sup>Os/<sup>188</sup>Os 403 cannot be ascribed to serpentinisation, as unrealistically high water-rock ratios (~ 404  $10^{3}$ - $10^{4}$ ) would be required in order to perturb the whole rock  $^{187}$ Os/ $^{188}$ Os at the % 405 level or higher (e.g. Becker and Dale, 2016). The lherzolite data also shows mass 406 fractions of Se and Te and Se/Te that are similar to values in unserpentinised 407 Iherzolites (e.g., Wang and Becker, 2013). In contrast sulfur in most lherzolites from 408 New Caledonia shows much higher concentrations than typical for peridotites, which is 409 410 readily explained by contamination with seawater-derived sulfur during 411 serpentinisation.

We thus conclude that the HSE (perhaps with the exception of Au), Se, Te and Re-Os signature of the lherzolites offer no conclusive evidence that serpentinisation and associated reactions affected these elements in a noticeable way.

415

416 5.1.2 Partial melting and chemical disequilibrium of the HSE in the mantle

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Spinel and plagioclase lherzolites exhibit comparable HSE contents and patterns, similar to other lherzolites from oceanic or continental settings that underwent low to moderate degrees of melt extraction (Fig. 2 and 3).

Partial melting has often been invoked as a possible cause for HSE and <sup>187</sup>Os/<sup>188</sup>Os 421 variations in mantle rocks (e.g. Reisberg and Lorand, 1995; Meisel et al., 2001). 422 Studies of the behaviour of the HSE during mantle melting and their abundances in 423 mantle rocks have supported the hypothesis that HSE concentrations in residual 424 peridotites result from sulphide-silicate partitioning during magmatic processes (i.e. 425 Becker and Dale, 2016; Brenan et al., 2016 and references therein) and that at 426 temperatures relevant for mantle processes homogeneous sulphide liquid and, in 427 special cases, sulfide solid solutions, coexist in equilibrium with silicate melt, olivine, 428 pyroxenes and an Al-rich phase (e.g. Rehkämper et al., 1999; Mungall and Brenan, 429 2014; Brenan et al., 2016). Experimentally determined sulphide melt-silicate melt 430 partition coefficients (D<sup>sulph/sil</sup>) for PGE have been shown to be high and constant (10<sup>5</sup> 431 to 10<sup>6</sup>, e.g. Mungall and Brenan 2014; Brenan et al. 2016), while Au shows slightly 432 lower  $D^{\text{sulph/sil}}$  (~10<sup>4</sup>). Therefore, up to moderately high degrees of melting, PGE 433 434 behave as compatible elements and their inter-elemental ratios remain similar as long as sulphide is present in the mantle residue. By contrast, Re is much less chalcophile 435 (D<sup>sulph/sil</sup>~300-800, e.g. Fonseca et al., 2007; Brenan, 2008) and is expected to 436 become more quickly depleted in the residual mantle. 437

Major element compositions of sulphides in the spinel lherzolites (Table S1) are consistent with a residual origin after incongruent melting processes (e.g. Bockrath et al., 2004; Ballhaus et al., 2006). The occurrence of homogeneous monosulphides also suggests relatively high cooling rate after the melting event.

Overall, the studied lherzolites are characterised by flat to gently sloping PGE 442 patterns, with similar PM-normalized abundances, no PPGE fractionation and nearly 443 constant ratios for IPGE (i.e. Os/Ir, Ru/Ir). By contrast, Au and Re display the 444 strongest depletion. These features imply that HSE, with the exception of Au and Re, 445 exhibit a similar compatible behaviour during mantle melting, as expected for low to 446 moderate melting degrees in presence of residual sulphide melt. This observation is 447 448 consistent with the previous estimates obtained through geochemical modelling (Secchiari et al., 2016) and with the occurrence of a residual subsolidus sulphide 449 assemblage in spinel lherzolites. 450

Although the PGE patterns are nearly flat, with only slight depletion of Pd in a few samples, the depletion of Au and Re, the range of chondritic to slightly suprachondritic  $\gamma^{187}$ Os<sub>i</sub> and the higher mass fractions of Se and Te compared to Re and the other HSE suggest a multi-stage history of the lherzolites. Notably,  $\gamma^{187}$ Os<sub>i</sub> do not correlate with mass fractions of incompatible HSE such as Re, Re/Os nor with fertility indicators (Fig. 4), as was observed in some other suites of lherzolites (Becker and Dale, 2016).

The Os isotopic signature may be a pre-existing feature of the mantle source, i.e. already present before the recent melt extraction event (Secchiari et al., 2016). This is supported by the dispersed Os isotopes-fertility indicators trends, as well as by some old model ages recorded by our Iherzolite samples ( $T_{MA}(PM)$ = 0.4-0.8 Ga, see Table 1). In addition, the remarkable absence of magmatic Cu-Fe-rich sulphides (e.g. see Lorand et al., 2013) argue against a recent, post-melting sulphide addition. We thus speculate that the bulk HSE, Se, Te and Os isotope compositions of the

464 Iherzolites are the result of partial melting event which affected a mantle source 465 previously characterised by an heterogeneous sulphide population including both 466 residual and magmatic sulfides precipitated along grain boundaries by infiltrating 467 melts (Burton et al., 1999; Lorand et al., 1999; Alard et al., 2000, 2002).

468

### 469 5.2 Sulphur, Se and Te behaviour in the New Caledonia Iherzolites

Sulfur mass fractions are variable in the Iherzolites from New Caledonia and typically 470 much higher compared to estimates of the depleted MORB mantle source (DMM  $\sim$ 471 150-200 ppm, Mathez, 1976; Salters and Stracke, 2004) and mass fractions of S in 472 unaltered lherzolites (e.g., Wang and Becker, 2013). In addition, sulphur does not 473 correlate with fertility indicators (i.e. Al<sub>2</sub>O<sub>3</sub>), as commonly observed in unserpentinised 474 mantle tectonites (e.g., Lorand and Alard, 2010; Wang and Becker, 2013). The high S 475 concentrations and the lack of correlation with melting indicators suggest that S was 476 added late in the evolution of the rocks. The sulphur budget of mantle peridotites can 477 478 be strongly influenced by seawater-rock interaction, because of the high sulphate content of seawater, leading to hydrothermal sulphides and sulphate precipitation (Alt 479 and Shanks, 1998). We note that the major element chemistry indicates a residual 480 origin for the sulphide phases of the lherzolites (see paragraph 4.1 and 5.1.2). 481 Hydrothermal sulphides or sulphates could not be identified. 482

Recent geochemical works have demonstrated the role of serpentine as a sink of S under various oxidation states ( $S^{2-}$ ,  $S^-$ ,  $S^0$  and  $S^{6+}$ , Debret et al., 2017). These studies have shown that S concentrations can be anomalously high in serpentinised peridotites (up to 1 wt.%, see Alt et al., 2003), as S can be accommodated in serpentine minerals, accounting from 60 to 100% of the sulphur budget of the peridotite (Debret et al., 2017). In situ analysis of serpentine minerals have revealed that S can be hosted in nano-phases associated with serpentine or trapped either via

490 Si substitutions in the tetrahedra, or as a sulphate ion in the network of the 491 tetrahedral sheet of serpentine minerals (Debret et al., 2017).

The addition of S during serpentinization is also reflected in the high suprachondritic 492 493 S/Se ratios (up to 16500) and the excellent correlation observed between S concentrations and S/Se ratios (see Fig. 5c). Despite the strong S enrichments, Se 494 and Te display 'normal' concentrations and Se/Te ratios are in the range of other 495 Iherzolites (see Wang and Becker, 2013). These data confirm that Se-Te contents and 496 ratios were not significantly impacted by serpentinisation, as previously observed for 497 other peridotites that experienced low to moderate serpentinisation degrees (e.g. 498 499 Wang and Becker, 2013; Marchesi et al., 2013).

500 Moreover, Se-Te show a good correlation between each other (Fig. 5a), implying that they are controlled by the same mineral phases. In mantle peridotites, Se can replace 501 S as a chalcogen anion within the crystalline structure of sulphides (e.g. Bulanova et 502 al., 1996; Hattori et al., 2002; Helmy et al., 2010) or can form Se-rich micro phases, 503 504 while Tellurium, owing to its semi metal nature, tends to partition between sulphides and late exsolved micrometric tellurides (Pt, Pd, Te, As, Bi phases). The latter are 505 506 thought to crystallise at low temperatures during cooling, once sulphide melt becomes saturated with respect to Te (Luguet et al., 2004; Lorand et al., 2008; Lorand and 507 Alard, 2010). In the lherzolites, Se and Te do not correlate with melting indicators, 508 but Te displays a rough positive correlation with Pd (Fig. 5b), which suggests that the 509 sulphide melt-bulk silicate partition coefficient of Te should be between Se and Pd 510 (e.g., Figs. 3, 4, 5). 511

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513 5.3 Type-A harzburgites: highly siderophile element systematics of a residual sub-arc 514 mantle section

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The distinct HSE patterns and Os isotopic signature recorded by the New Caledonia harzburgites hint that they experienced a different history compared to the northern lherzolites.

Three of the four samples belonging to the sub-group A (TI1, TI2, PO4) show similar HSE patterns and chalcophile elements depletion, indicating that the same processes contributed to the HSE and chalcophile element budget of these rocks. The low chalcophile element concentrations, close to or below the detection limit, coupled with low Pd/Ir ratios and subchondritic <sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub>, point out that type-A harzburgites are residues of high degree of melt extraction, where sulphides melts must have been nearly completely dissolved in coexisting silicate melt.

Experimental studies have in fact predicted a compatible behaviour for all the PGE 526 during mantle melting as long as sulphide is retained in the peridotite (Mungall and 527 Brenan, 2014). Depending on the initial S content of the mantle rocks, ~12-20% of 528 melting is required for sulphide exhaustion (Lorand et al., 1999; Luguet et al., 2007; 529 530 Brenan et al., 2016). As melting proceeds, sulphides are progressively dissolved into the melt and the PGE become concentrated in the residual sulphide melt (Mungall and 531 532 Brenan, 2014). Provided that chemical equilibrium is attained, increasing degrees of partial melting should slightly increase whole rock PGE contents, but element ratios 533 should remain almost constant. At the point when sulphide is completely removed, 534 IPGE and Pt are accommodated in metallic alloys, while Re, Au and Pd mass fraction 535 should become extremely low, as these elements are not hosted in any residual 536 mantle phase (Mungall and Brenan, 2014). Hence for high melting degrees, the 537 abundances of the HSE in the residue should reflect mineral-melt partitioning and the 538 539 P-T and f<sub>02</sub>-dependent solubility of Pt and IPGE alloys in silicate melt (Fonseca et al., 540 2011, 2012; Mungall and Brenan, 2014; Brenan et al., 2016).

The IPGE-PPGE fractionation and the resolvable fractionations between specific PGE displayed by the type A harzburgites bear witness of the high melting degrees, which

resulted in the formation of a S-free mantle residue. The fractionated Os-Ir-Ru-Rh 543 segments of HSE patterns and the positive Pt anomalies in type A harzburgites are 544 likely carried by residual sulphides (i.e. laurite) and metallic alloys (Os-Ir and Pt-Ir, 545 546 see Lorand et al., 1999; Luguet et al., 2001, 2007). These latter are thought to precipitate from sulphide melt shortly before the complete exhaustion of sulphide 547 (Mungall and Brenan, 2014) or immediately after sulphide consumption, due to  $f_{S2}$ 548 lowering and diminished metal-sulphide complexation in the silicate melt (Fonseca et 549 al., 2012). The variable, but broadly systematic inter-element fractionation among the 550 IPGE (high Os/Ir and Ru/Ir), high Ru/Rh and the variable Pt anomaly relative to Rh 551 and Pd indicate the different proportions of residual Ir-Pt alloys in different samples 552 and preferred retention of Ru and Os relative to Ir in the residual PGE alloys (e.g. 553 Brenan and Andrews, 2001; Fonseca et al., 2012). 554

The HSE fractionations of type A harzburgites are different from HSE patterns of 555 modern harzburgites from MOR environments (Fig. 6a), as the latter are characterised 556 557 by flat or weekly fractionated Os-Ir-Ru triplet and they rarely display positive Pt spikes (Snow and Schmidt, 1998; Luguet et al., 2001, 2003). By contrast, HSE elemental 558 559 fractionations of type-A harzburgites are similar to patterns of some arc xenoliths (Saha et al., 2005; Liu et al., 2015; Scott et al., 2019) or ophiolitic peridotites bearing 560 a supra-subduction zone signature (see Büchl et al., 2002, 2004; O'Driscoll et al., 561 2012). Similar fractionations have been reported for some mantle xenoliths from the 562 Chatam Islands (New Zealand) and from some other areas (Pearson et al., 2004). 563

564 On the other hand, geochemical modelling based on lithophile incompatible elements 565 has shown that the extreme depletion in trace element contents displayed by the New 566 Caledonia harzburgites was achieved through a polyphase evolution, including a first 567 melting event in a mid-ocean ridge setting, followed by fluid-assisted melting 568 reaching clinopyroxene exhaustion after involvement in a subduction system (see 569 Secchiari et al., 2019a). Such high melting degrees are permissible in supra-

subduction zone environments, where hydrous conditions at relatively low pressures can produce melt fractions substantially exceeding 20% without invoking extremely high temperature (e.g. see Ulmer, 2001). Likewise, the observed LREE and FME (Sr, Ba, Pb) enrichments coupled with variable Pb isotope compositions of the Type A harzburgites may be explained by syn- and post-melting interactions with different subduction-related components, possibly aqueous fluids and melts originated in the forearc setting (Secchiari et al., 2019 a,b).

We thus conclude that the HSE and chalcophile element signature displayed by TI1, TI2 and PO4 predominantly reflect high degrees of melt extraction, presumably in a supra-subduction zone environment. The positive Pt spikes suggest that Pt-rich alloys were stable in the mantle residue and were only in part dissolved in the melt during melt extraction.

The enrichments of Au are modest (0.2-1.3 ng/g Au) and must be related to fluid overprint, either from slab-derived fluids (McInnes et al., 1999; Kepezhinskas et al., 2002) or from low-T alteration, e.g., during obduction (e.g. Snow et al., 2000).

The harzburgite YA1 shows higher S and Se concentrations (Fig. 5a), which, 585 considering the significant LOI value of 6.83%, could be related to serpentinisation 586 587 and precipitation of secondary sulphides. The strongly fractionated HSE pattern and the low concentrations of the incompatible HSE (i.e. Pd, Re) indicate that the HSE 588 budget of YA1 is also governed by melting, as for TI1, TI2 and PO4 harzburgites. The 589 low Os, Ir and Pt concentrations, are much closer to the values reported for type-B 590 harzburgites (see Table 1 and Fig. 5b). Sample YA1 can thus be seen as transitional 591 between type-A and type-B sub-group. 592

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595 5.4 Origin of type-B harzburgites – strong depletion followed by subduction zone 596 metasomatism?

Type-B harzburgites mostly occur in the central massifs, however one sample (PO3) has also been identified in the eastern zone, close to the area where one type-A harzburgite (PO4) was sampled. Type-B harzburgites display remarkably different HSE and Re/Os behaviour compared to type-A sub-group (Fig. 2 and 6), indicating that different processes need to be invoked in their genesis.

Type-B harzburgites show low abundances of incompatible chalcophile elements, i.e. Pd, S, Se and Re, with values in the range of type-A harzburgites. In principle such low concentrations could be reconciled with high melting degrees and sulphide exhaustion in the mantle source. The strong depletion of Os, Ir and Pt, (Fig. 6b) coupled with slightly subchondritic to suprachondritic <sup>187</sup>Re/<sup>188</sup>Os (0.23 to 37) and <sup>187</sup>Os/<sup>188</sup>Os (0.1239 to 0.302) are remarkable and do not occur in residual harzburgites from convecting mantle, as represented by abyssal peridotites.

The HSE in type-B harzburgites share similarities with some xenoliths from arc 610 settings such as low Os contents associated with chondritic to suprachondritic 611 <sup>187</sup>Os/<sup>188</sup>Os (Brandon et al., 1996, 1999; Saha et al., 2005; Widom, 2011). These 612 613 features have been ascribed to interactions with subduction zone fluids (i.e. fluids 614 from subducted altered oceanic crust and/or its sedimentary cover), which may have induced sulphide breakdown in the residual arc mantle, locally modifying the Os 615 isotopic signature of the mantle (Wisdom et al., 2003). Such gualitative observations 616 have also been supported by experimental works, that highlighted the critical 617 influence of oxygen fugacity ( $f_{O2}$ ) on sulphide and alloy stability (e.g. Andrews and 618 Brenan, 2002; Fonseca et al., 2011, 2012; Mungall and Brenan, 2014). 619

Moreover, the strongly fractionated, IPGE-depleted, HSE patterns displayed by type-B harzburgites closely resemble those observed in some refractory harzburgites and replacive dunites that underwent interaction with S-undersatured melts in some ophiolites (Büchl et al., 2002; Lorand et al., 2004).

As metasomatism by subduction fluids and hydrous melts has been proposed for the 624 New Caledonia harzburgites based on isotopic and incompatible element studies, we 625 have determined oxygen fugacities on a set of five harzburgites and one lherzolite, in 626 627 order to test if the different HSE signature of type-B harzburgites could reflect higher  $f_{02}$  conditions. As a whole, the harzburgites record more oxidised conditions compared 628 to the Iherzolite (see Table 2). This is consistent with the hypothesis that the 629 Iherzolites represent slightly depleted mantle rocks not directly involved in the Eocene 630 subduction system (Secchiari et al., 2016). However, the harzburgites exhibit  $f_{02}$ 631 values close to the FMQ buffer and in the range of the suboceanic mantle (e.g. 632 Bryndzia and Wood, 1990). Also, type A harzburgites tend to be slightly more oxidised 633 634 than type B harzburgites.

The relatively low oxygen fugacity values may be related to the high depletion 635 experienced by the harzburgites. A recent study of Bénard and coauthors (2018) has 636 in fact shown that increasing melt depletion at un-buffered  $f_{\rm O2}$  conditions can induce 637 oxygen fugacity variation in the sub-arc peridotites, as  $Fe^{3+}$  is more extensively 638 extracted than  $Fe^{2+}$  as melting proceeds, producing residues with lower  $Fe^{3+}/\Sigma Fe$  than 639 640 in the original mantle source. We note that the most depleted harzburgites (i.e. type-641 B PY1, KPT5 and PO3) in our dataset yield the lowest computed oxygen fugacities. Following this interpretation, we suggest that the harzburgites recorded higher  $f_{O2}$ 642 conditions compared to the lherzolites due to fluid-assisted melting and interaction 643 with an oxidising component, but increasing degrees of melt extraction from type A to 644 type B harzburgites possibly led to progressive lowering of  $f_{02}$ . 645

Alternatively, calculated oxygen fugacity values may partly reflect  $f_{02}$  conditions related to the melting conditions of the harzburgites in the suboceanic mantle (Lee et al., 2005). From this perspective, one may speculate that the oxidising capacity of slab-derived fluids or melts was not high enough to erase the memory of the original  $f_{02}$  conditions. For the New Caledonia archipelago, Eocene subduction started close to

or in correspondence of an active oceanic spreading center, where hot and young (~ 651 6-9 My old, Cluzel et al., 2016) lithosphere was forced to subduct. In such a context, 652 653 fluid fluxes from the downgoing slab must have been limited, due to the young age of 654 the subducted material and the intra-oceanic nature of the subduction (Cluzel et al., 2016). In addition, post-melting metasomatism is thought to have occurred through 655 interaction with small fractions (0.5-1%) of boninitic magmas, which may have not 656 been able to maintain their oxidising capacity during percolation through the sub-arc 657 mantle. 658

In conclusion, the effect of  $f_{O2}$  on the different HSE patterns of type A and B harzburgites is unclear, and perhaps insignificant, as their difference in  $\Delta \log f_{O2}$  is minor. Thus, most likely the stronger fractionation and depletion of some IPGE in type B harzburgites reflects the higher degrees of melting.

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664 5.5 Type-B harzburgites: a broader perspective

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Despite being similar in terms of chemistry or mineralogy, type-A and B harzburgites possess distinct HSE signatures. In addition, the HSE signatures of type-B harzbugites have not yet been identified in other mantle tectonites, either from modern oceanic lithosphere or ophiolitic complex.

However, similar compositions have been recently reported for some moderately depleted to highly refractory peridotites and mantle xenoliths from New Zealand (Scott et al., 2019). The New Zealand mantle is composed of isotopically heterogeneous mantle fragments with evolutionary histories extending over 2.75 Ga (Os model ages= 0.1-2.75 Ga, with a broad peak at 1.2 Ga), and PGE systematics decoupled from major element compositions (see Scott et al., 2019; Liu et al., 2015). These features have been explained by accretion of Zealandia lithospheric mantle

677 from amalgamation of genetically unrelated convecting mantle fragments which were 678 swept together beneath the Gondwana subduction margin, variably re-melted and 679 laterally accreted (Scott et al., 2019).

680 Among the New Zealand peridotite suites, mantle xenoliths from Lake Moana and Chatam Island show HSE patterns that are similar to our dataset (Fig. 8). Lake Moana 681 Cretaceous xenoliths include cpx-free harzburgites that experienced up to 30% 682 melting, while Eocene-aged Chatam Island harzburgites exhibit a less refractory 683 nature, as attested by the presence of primary clinopyroxene (up to 1.8% modal, 684 Scott et al., 2016). Such depletion degrees were achieved either by plume melting or 685 hydrous melting in an arc setting for the Lake Moana xenoliths, whereas Chatam 686 Island samples are thought to represent fragments of fore-arc lithophere (Scott et al., 687 2016, 2019). 688

689 Overall, HSE diagrams highlight that New Zealand mantle xenoliths reproduce with 690 good approximation both patterns observed in our harzburgites, namely type-A and 691 type-B (Fig. 7). IPGE patterns are broadly sub-parallel, with the New Caledonia 692 harzburgites falling within or at the lower range of values displayed by the New 693 Zealand samples, whereas Pt, Pd and Re exhibit much more variability.

694 For most of the New Zealand xenoliths, Ru concentrations are higher compared to the contents in the New Caledonia harzburgites. Higher Ru contents cannot be ascribed to 695 different degrees of melting, as fertility indicators (i.e. Mg#(OI), Cr#(SpI)) indicate 696 similar degrees of melt extraction for both peridotite suites (see Scott et al., 2016, 697 2019; Secchiari et al., 2019a). The increased Ru retention in the New Zealand 698 samples may be reconciled to the higher Cr-spinel content of these lithologies (up to 699 700 2.8%, see Scott et al., 2016, vs. up to 0.8% for our harzburgites). Numerous studies have in fact demonstrated that spinel can be a significant host for Ru ( $D^{\text{spinel/melt}} \sim 20$ , 701 Capobianco and Drake, 1990). In addition, increase in oxygen fugacity markedly 702 enhances Ru compatibility in Cr-rich spinel ( $D^{spinel/melt}$  up to 500 for  $f_{O2}$  of -0.5 FMQ, 703

Park et al., 2012), which can accomodate Ru within its crystal lattice (Pagé and 704 Barnes, 2016) or as laurite and/or Ru-rich alloy inclusions (Brenan and Andrews, 705 2001). Recent geochemical works have also illustrated the importance of Ru retention 706 707 in the sub-arc mantle for the HSE signature of arc lavas (Dale et al., 2012; Park et al., 2013). These studies explain the low Ru concentrations and the high Pt/Ru ratios of 708 the volcanic products as related to Ru retention in the mantle source due to the 709 presence of Cr-rich spinel or PGM (see Dale et al., 2012; Park et al., 2013). Likewise, 710 positive Ru anomalies in our type-B harzburgites may reflect the presence of small 711 laurite or Ru-rich phase inclusions, which could have escaped the high melting 712 713 degrees due to the shield effect of spinel.

Other HSE (e.g. Pd and Re) in the New Caledonia harzburgites display a wider range of values compared to the New Zealand samples, possibly related to variable proportions of traces of sulfide precipitated from silicate melt.

Enrichments of Pd have also been recognised in other sub-arc mantle sections, where 717 they have been attributed to slab-derived fluids metasomatism, due to the high 718 solubility of Pd in aqueous fluids (McInnes et al., 1999; Park et al., 2013). Likewise, 719 720 Re addition in mantle wedge peridotites may be due to Re release in slab derived 721 fluids during dehydration of the mafic portion of the subducting slab (see Dale et al., 2009). Hence, we conclude that Pd-Re (as well as Te-Se-S) re-enrichments in type-B 722 harzburgites may have been facilitated by minor sulfide precipitation from slab 723 derived fluids or melts. 724

By contrast, the widespread negative Pt anomalies may reflect destabilisation of a pre-existing Pt-alloy phase, possibly related to continued melting after alloy saturation (see Mungall and Brenan, 2016), and Pt release into the melt.

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5.6 Inferences from Re-Os systematics of the New Caledonia harzbugites

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All type-A harzburgites, including YA1, show unradiogenic <sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub> and very low Re/Os relative to the range of chondritic values (Walker et al., 2002) or primitive mantle estimates (Meisel et al., 1996). The  $\gamma_{Osi}$  overlap with data from depleted abyssal peridotites and mantle sections from some ophiolites (e.g., Becker and Dale, 2016).

In order to obtain an estimate of the time of melt depletion, we calculated Re-Os model ages ( $T_{MA}$ ) and Re-depletion model ages ( $T_{RD}$ ). The Re-depletion model ages are generally used for samples with low Re contents and Re/Os ratios. However it is important to note that this method provides minimum depletion ages, as melting is not expected to remove all of the Re on a whole-rock scale.

The Re-depletion ages for type-A harzburgites are quite homogeneous for three out 741 four samples (TI1, TI2, YA1) ranging between 0.4 and 0.7 Ga for (see Table 1), while 742 sample PO4 yields an older Re-depletion age of 1.3 Ga. The younger model ages can 743 be linked to the previous evolution of the New Caledonia mantle in relationship to the 744 745 eastern Australian margin, from which the New Caledonia archipelago was separated via marginal rifting about 90 Ma ago (Cluzel et al., 2001, 2012; Whattam, 2009). The 746 747 ancient Re depletion age of the harzburgite PO4, on the other hand, reflects a mantle domain that experienced long-term low Re/Os ratio. This age is also mirrored by Nd 748 isotopic signature, which shows a highly radiogenic value ( $\varepsilon_{Ndi}$  =+13.32, Secchiari et 749 750 al., 2019a), indicative of a mantle reservoir that underwent long-term depletion of Nd. In addition, similar depletion ages (i.e. 1.2 Ga) occur in the New Zealand mantle rocks 751 (see Scott et al., 2019). 752

These results are consistent with recent Re-Os studies on abyssal peridotites and mantle tectonites from ophiolitic sequences showing that the convecting mantle contains harzburgite domains that underwent depletion events much older than the age of peridotite processing under the ridge (e.g., Harvey et al., 2006).

In summary, the New Caledonia harzburgites show Re-Os systematics typical of depleted upper mantle showing Early Paleozoic Os isotopic equilibration and evidence for ancient depletion events (> 1.0 Ga). This multi-stage history led to the depleted nature of the harzburgites and possibly resulted in their complex HSE geochemical signatures.

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### 763 Summary and conclusions

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A Re-Os isotopes, highly siderophile and chalcophile element investigation of the New Caledonia peridotites was carried out to unravel the behaviour of the aforementioned elements in lherzolites and harzburgites from the New Caledonia ophiolite.

The Iherzolites exhibit subchondritic to slightly suprachondritic <sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub> (0.1273-768 0.1329). PM-normalised HSE abundance diagrams are characterised by gently sloping 769 patterns showing increasing depletion towards Re-Au, similar to lherzolites that 770 experienced low to moderate melt extraction. However, the lack of correlation 771 between HSE and fertility indicators, as well as the slightly suprachondritic Os isotopic 772 773 ratios, argue against a simple partial melting history. Rather, the aforementioned 774 features and the presence of included and interstitial residual monosulphides possibly indicate that melting occurred on a mantle domain that has previously experienced a 775 melt percolation event. The high S concentrations of the lherzolites (202-1268 ppm) 776 most likely result from late-stage seawater-rock reactions. 777

By contrast, the New Caledonia harzburgites record higher degrees of melt extraction, as attested by the strikingly low, often below the detection limit, concentrations of incompatible chalcophile elements. Despite their homogeneity in terms of mineralogical and major element compositions, HSE patterns and Os isotopic compositions indicate the occurrence of two distinct harzburgite sub-groups.

Type-A harzburgites are characterised by steeply plunging HSE patterns, showing IPGE-PPGE and Os-Ir-Ru fractionation, coupled with low Re/Os ratios and subchondritic <sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub>. The strongly fractionated HSE patterns and the positive Pt anomalies, coupled with the high modelled melting degrees, indicate that melting occurred under hydrous conditions in sub-arc mantle.

Type-B harzburgites display notably different HSE patterns, showing depleted Os-Ir compared to Ru, positive anomalies and Pd-Re re-enrichments (relative to IPGE), coupled with chondritic to strongly suprachondritic measured Os isotopic ratios (<sup>187</sup>Os/<sup>188</sup>Os = 0.127-0.153). These features have not been yet identified in mantle tectonites and might indicate Os-Ir-Pt release into silicate melt for higher partial melting degrees.

The HSE signature carried by the studied peridotites, as well as the puzzling similarity observed between the New Caledonia harzburgites and the New Zealand mantle xenoliths, might attest the presence of a mantle source bearing a long lasting evolution (> 1 Ga), possibly linked to the Zealandia formation.

798

799 Acknowledgements

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801 We thank M. Feth for help and support in the clean laboratory and D. Cluzel for 802 assistance during samples collection in New Caledonia.

A.G. thanks Russian Science Foundation project 17-77-10103 for supporting iron
 oxidation state investigations at Freie Universität of Berlin.

This work represents a continuation of the PhD project of A.S. on the New Caledonia ophiolite, that has been supported by DFG funding (SFB-TRR 170 Subproject B2) and Italian-PRIN prot. 2015C5LN35.

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1080 Figure captions

Fig. 1. a) Present-day structures of the Southwest Pacific region modified after Cluzel et al. (2012). Dark orange, land; light orange, continental plateau; white, oceanic basins (LHR: Lord Howe Rise, NR: Norfolk ridge, LR: Loyalty ridge, HP: Hikurangi

1084 Plateau); b) simplified geological map of New Caledonia showing distribution of the 1085 Peridotite massifs (modified after Cluzel et al., 2012).

1086

Fig. 2. Variations of Os, Ru, Rh, Pt, Pd, Au and Re vs. Ir for the New Caledonia peridotites. Abyssal peridotites (Kane fracture zone: Snow and Schmidt, 1998; Brandon et al., 2000; Luguet et al., 2001, 2003; Marchesi et al., 2013; MAR: Harvey et al., 2006; Lena trough: Lassiter et al., 2014) and ophiolitic peridotites (IL-EL: Internal and External Ligurides, Snow et al., 2000; Luguet et al., 2004; Fischer-Godde et al., 2011; Lanzo: Becker et al., 2006; Pyrenees: Becker et al., 2006; Luguet et al., 2007) are shown for comparison.

1094

Fig. 3. Primitive mantle normalised HSE and chalcogen patterns for the New Caledonia spinel and plagioclase lherzolites. Grey shaded area includes oceanic lherzolites from Mid-Atlantic and South West Indian ridges (Snow and Schmidt, 1998; Luguet et al., 2001; Luguet et al., 2003) and ophiolitic lherzolites from the Ligurian Units (Snow et al., 2000; Luguet et al., 2004; Fischer-Gödde et al. 2011). Normalising values after Becker et al. (2006), Fischer-Gödde et al. (2011) and Wang and Becker (2013).

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Fig. 4. a) Al<sub>2</sub>O<sub>3</sub> (wt.%)-<sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub> and b) Os-<sup>187</sup>Os/<sup>188</sup>Os<sub>i</sub> and c) <sup>187</sup>Re/<sup>188</sup>Os-1103 187Os/188Os diagrams showing data from New Caledonia Iherzolites and type-A 1104 harzburgites in comparison to PM compositions. PM data from Meisel et al. (1996). 1105 Data for abyssal peridotites are from Harvey et al., (2006) for Atlantic peridotites, 1106 Lassiter et al., (2014) for Lena through and Liu et al. (2015) for Gakkel ridge. See Fig. 1107 2 for ophiolitic peridotites references. 1108

Fig. 5. a) Te vs. Se, b) Te vs. Pd and c) S vs. S/Se correlation diagrams for New Caledonia spinel and plagioclase lherzolites. Also showing for comparison data for orogenic lherzolites from Wang and Becker (2013).

1112

Fig. 6. a) Primitive mantle normalised HSE and chalcogen abundances in type-A harzburgites. Light grey shaded field encompasses the area of modern MOR harzburgites (Snow and Schmidt, 1998; Luguet et al., 2001, 2003; Harvey et al., 2006; Marchesi et al., 2013); b) Primitive mantle normalised diagram showing HSE and chalcogen patterns of type-B harzburgites. Normalising values are after Becker et al. (2006), Fischer-Gödde et al. (2011) and Wang and Becker (2013).

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Fig. 7. Primitive mantle normalised HSE abundances of a) type-A and b) type-B harzburgites compared to the HSE composition displayed by New Zealand mantle xenoliths. See text for further detail.



Figure 2 Click here to download high resolution image











Figure 6 Click here to download high resolution image



Figure 7 Click here to download high resolution image

0.001

0.0001

Os

Ir



Pt

Pd

Re

Ru

k here to download high



Microphotographs of the New Caledonia peridotites: a) porphyroclastic texture marked by deformed and stretched olivine and orthopyroxene crystals in spl-lherzolite POU2; b) plagioclase-lherzolite thin section (BAB2A, parallel polars); c) strongly exsolved, primary clinopyroxene occurrence in TI2 harzburgite; d) interstitial orthopyroxene (opx2) formed at the expense of primary olivine (KPT5 harzburgite).



BSE images of sulphides in the New Caledonia Iherzolites: a) small included sulphide (BA1); b) larger intergranular sulphide in POU2 Iherzolite.

# Figure S3 Click here to download high resolution image





Pt vs. a) Pd and b) Rh variation diagrams for the New Caledonia peridotites. Abundances are in ppb.

Table 1

Concentrations of the HSE, S, Se and Te, Os isotopes, selected major elements and ratios for the New Caledonia peridotites

Sample	Rock	Al <sub>2</sub> O <sub>3</sub> wt.%	LOI %	Os (ng/g)	lr (ng/g)	Ru (ng/g)	Rh ( <i>ng/g</i> )	Pt (ng/g)	Pd (ng/g)	Au (ng/g)	Re (ng/g)	Os <sub>N</sub> /Ir <sub>N</sub>	Os <sub>N</sub> /Ru <sub>N</sub>	Pd <sub>N</sub> /Ir <sub>N</sub>	Ru <sub>N</sub> /Ir <sub>N</sub>	Pt <sub>N</sub> /Ir <sub>N</sub>	Pt <sub>N</sub> /Ru <sub>N</sub>	<sup>187</sup> Re/ <sup>188</sup> Os (2SE)	<sup>187</sup> Os/ <sup>188</sup> Os measured	2SE	<sup>187</sup> Os/ <sup>188</sup> Os <sub>i</sub>	$\gamma Os_{_{(53Ma)}}$	T <sub>MA</sub> (PM) Ga	T <sub>RD</sub> (PM) Ga	T <sub>RD2</sub> (PM) Ga	S (µg/g)	Se (ng/g)	Te ( <i>ng/g</i> )	S/Se	Se/Te
DOLLAR		0.40	7.50		0.40	5.04	4.57		0.00	0 704		4.00			4.07	4.00		0.505(4)	0.400000	0.45.00	0.400050			,	,		74.0		0700	
POUIA	PIL	2.49	7.56	2.93	2.48	5.31	1.57	5.54	6.23	0.704	0.319	1.06	0.99	1.24	1.07	1.03	0.96	0.525(1)	0.130822	9.1E-06	0.130358	2.9	0.8	Ţ	T	202	74.9	11.5	2703	6.5
POU2	SpL	1.46	8.63	3.88	3.45	6.76	1.23	6.60	6.56	1.04	0.213	1.01	0.18	0.94	5.71	0.88	0.15	0.265(1)	0.127574	6.8E-06	0.127340	0.5	0.7	Ţ	0.3	582	69.6	11.6	8364	6.0
POU2B	SpL	2.57	10.69	3.31	2.88	5.93	1.04	6.49	5.49	0.503	0.165	1.03	1.09	0.94	0.95	1.04	1.09	0.240(1)	0.128227	8.0E-06	0.128016	1.1	0.4	Ť	0.2	1268	77.8	10.8	16289	7.2
POU3	SpL	1.30	9.60	2.91	2.58	5.07	0.86	5.15	4.14	0.642	0.234	1.01	1.05	0.79	0.97	0.92	0.95	0.387(1)	0.131356	9.1E-06	0.131015	3.4	Ť	t	t	362	54.0	7.3	6691	7.4
BA1	Sp L	1.74	6.39	3.34	2.85	5.95	1.05	5.62	5.51	0.943	0.129	1.06	0.27	0.96	3.88	0.92	0.24	0.186(1)	0.131485	7.9E-06	0.131320	3.7	f	f	f	294	91.3	13.8	3218	6.6
BAB1B	PIL	2.61	6.98	2.96	2.61	5.46	0.965	6.73	5.42	0.641	0.125	1.02	0.24	1.02	4.30	1.19	0.28	0.202(1)	0.129664	8.9E-06	0.129485	2.2	f	f	0.0	327	66.2	9.5	4943	7.0
BAB2B	PIL	2.83	8.43	3.00	2.57	5.08	1.16	6.06	5.33	1.33	0.138	1.05	1.67	1.02	0.63	1.09	1.73	0.223(1)	0.133084	8.9E-06	0.132887	4.9	f	f	f	289	67.6	9.8	4278	6.9
TI1	н	0.78	9.01	1.51	0.864	2.52	0.275	2.42	0.488	1.25	0.022	1.57	1.08	0.28	1.46	1.29	0.89	0.070(25)	0.12479	1.7E-05	0.12473	-1.5	0.8	0.7	0.7	9	1.1	1.0	8188	1.0
TI2	н	1.03	6.04	2.07	1.14	3.78	0.254	2.70	0.499	0.264	0.019	1.63	0.98	0.21	1.65	1.09	0.66	0.045(18)	0.12662	1.3E-05	0.12658	-0.1	0.5	0.4	0.4	10	0.7	0.4	14053	1.7
PO4	н	0.43	0.18	1.07	0.499	1.53	0.191	2.56	0.570	0.160	0.018	1.93	1.26	0.56	1.53	2.36	1.54	0.081(35)	0.12040	2.4E-05	0.12033	-5.0	1.5	1.3	1.3	6	3.1	0.8	2084	4.1
YA1	н	0.46	6.83	0.554	0.297	2.35	0.326	0.268	0.263	1.17	0.022	1.67	0.42	0.44	3.95	0.42	0.11	0.196(68)	0.12551	4.7E-05	0.12534	-1.0	1.0	0.6	0.6	40	4.9	0.4	8117	11.4
PY1	н	0.78	0.00	0.049	0.077	0.643	0.269	2.08	0.378	0.336	0.016	0.58	0.14	2.43	4.19	2.97	2.97	1.62(8)	0.1299	5.3E-04	0.1284	1.4	0.0	0.0	0.2	6	0.9	0.9	6103	1.1
Duplicate				0.023	0.133	0.693	0.171	2.44	0.588	0.311	0.062							13.0(1)	0.127	1.0E-03	0.115	-8.9				53	0.3	1.0	196197	0.3
KPT2	н	0.70	3.03	0.004	0.022	0.323	0.057	0.078	0.431	0.107	0.018	0.18	0.02	9.50	7.22	0.22	0.22	19(1)	0.148	5.6E-03	0.131	3.6	0.1	f	f	5	1.3	0.4	4164	2.8
Duplicate				0.036	0.017	0.211	0.040	0.210	0.620	0 1 4 4	0.010							1 4(1)	0.302	1.3E-03	0.301	137.8			-	7	1.3	8.2	4947	0.2
KPT5	н	0 74	0.12	0.004	0.066	0.165	0.048	0.038	0.464	0.654	0.024	0.05	0.04	3.46	1 25	0.21	0.21	32(2)	0.147	6 2E-03	0.118	-6.6	0.0	f	f	3	3.0	0.7	1133	4.1
Dunlicate		0.7 1	0.12	0.007	0.062	0.165	0.054	0.046	0.512	0.603	0.056	0.00	0.01	0.10	1.20	0.21	0.21	37(1)	0.160	3.2E-03	0.127	0.5	0.0			å	0.7	13	4453	0.5
PO3	н	0.41	0.00	0.007	0.002	0.256	0.004	0.006	0.428	0.000	0.000	0.18	0.02	14 12	8 57	0.02	0.02	19(2)	0.153	8.4E-03	0.136	8.0	0.1	f	f	3	1.4	0.6	2120	2.2
Dunlicate		0.41	0.00	0.005	0.018	0.230	0.025	0.000	0.420	0.004	0.012	0.10	0.02	14.12	0.07	0.02	0.02	0.69(7)	0.1239	4 7E-04	0.1233	0.0	0.1	'		bdl	bdl	0.8	2123	2.2
KDT3	ц	0.67	0.67	0.072	0.070	0.240	0.172	0.249	0.250	0.299	0.0070	0.91	1 97	0.17	0.10	6.02	6.02	29(1)	0.1233	3.55-04	0.1200	-5.1	0.0	0.3	12	6	bdl	bdl	-	-
NP13	п	0.07	0.07	0.072	0.079	0.200	0.172	0.240	0.250	0.200	0.410	0.01	1.07	0.17	0.19	0.92	0.92	20(1)	0.1273	3.32-04	0.1204	-3.1	0.0	0.5	1.5	0	bul	bui	-	-

Duplicate: replicate digestion of the same sample powder

I L= plagioclase Iherzolite, Sp L= spinel Iherzolite, H= harzburgite

Values of PM <sup>187</sup>Os/<sup>88</sup>Os = 0.1296 and <sup>187</sup>Re/<sup>188</sup>Os = 0.434 used for calculation of T<sub>MA</sub> and T<sub>RD</sub> ages (Meisel et al., 2001); f= future model ages. T<sub>RD2</sub> (PM) indicates depletion ages calculated taking into account Re addition that may have occurred during peridotite evolution.

Table 2								
Equilibration Te	mperature, F	Pressure,	and Oxygen	Fugacity	Calculated for	selected p	eridotite sa	amples

Sample	Туре	T BK (°C)	P (GPa)	Wood (199	90)	T OI-Spl (°C)	Wood (1990)	)
				log f(O2)	$\Delta FMQ$		log f(O2)	$\Delta FMQ$
TI2	Type-A harz	930	1.5	-10.40	0.71	870	-11.37	0.76
YA1	Type-A harz	980	1.5	-9.83	0.50	815	-12.66	0.50
KPT5	Type-B harz	1130	1.5	-7.91	0.39	840	-12.20	0.48
PO3A	Type-B harz	1000	1.5	-9.86	0.17	940	-10.76	0.18
PY1B	Type-B harz	1050	1.5	-9.17	0.16	930	-10.90	0.20
BA1	Spl Iherz	1060	1.5	-13.1503	-3.96	880	-15.66	-3.73

T BK= Equilibration temperature calculated on Opx porphyroclasts using Brey and Köhler (1990)

T OI-Spl = Equilibration temperature calculated using Li et al. (1995) formulation

Oxygen fugacity estimates are from Wood et al. (1990) and are reported as  $\Delta \log$  fO2 from the quartz-fayalite-magnetite (FMQ) buffer using the Fe<sup>3+</sup>/ $\Sigma$ Fe values of the analysed spinels. See text for further details.

Sample Mineral Occurrence	POU2 mss Intergr	POU2 <i>m</i> ss Intergr	POU2 mss Incl	POU2 pn Incl	POU2 pn Incl	POU2 pn Incl	POU2 pn Incl	BA1 mss Incl	BA1 mss Incl	BA1 mss <i>Incl</i>	BA1 mss Incl	BA1 mss Incl
wt%	р	р	р	р	р	р	р	р	р	р	р	р
S	34.32	34.39	32.74	33.24	41.19	32.68	40.82	33.22	33.08	32.47	32.53	33.13
Fe	41.23	43.80	36.65	28.09	23.90	29.14	24.68	36.85	42.99	43.25	42.19	43.02
Со	0.64	0.59	0.78	0.46	1.93	1.91	2.26	0.46	0.50	0.55	0.80	0.58
Ni	23.28	20.44	29.19	37.55	32.99	35.74	32.23	25.77	23.44	24.72	24.54	23.27
Cu	0.52	0.57	0.64	0.66	bdl	0.53	bdl	3.70	bdl	bdl	bdl	bdl
Total	99.99	99.79	100.00	100.00	100.01	100.00	99.99	100.00	100.01	100.99	100.06	100.00
Fe/Ni	1.8	2.1	1.3	0.7	0.7	0.8	0.8	1.4	1.8	1.7	1.7	1.8

 Table S1

 Major element composition for selected sulphides from the New Caledonia Iherzolites

Pn= pentlandite; mss= monosulphide solid solution