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ABSTRACT

Voluminous flux of a hydrous component from subducting oceanic lithosphere into the forearc mantle and its contribution to arc magmas have long been recognised but the transfer of solid-phase materials has received less consideration. Although xenocrystic zircons are known from some arc magmas and ophiolitic chromitites their origins remain enigmatic. How and when such materials are transferred into the overlying wedge of mantle lithosphere and the length of their residency therein are unclear. Using zircons and rutiles recovered from ophiolitic rocks in New Caledonia, we demonstrate unambiguous association with subducting sediments and hence evidence for inter-plate transfer. The 'fingerprints' of age spectra for both minerals can be matched to lithospheric slab components subducted during Eocene time. Their occurrence in forearc harzburgite suggests that they were incorporated into their mantle wedge host at subduction depths beyond the onset of serpentinisation at ca. 300 °C but before the ca. 600 °C destabilisation temperature of the rutile U-Pb system. Relocation from slab to forearc mantle is therefore likely to have occurred at ca. 50-60 km depth within the subduction channel. Fluid-assisted conveyance of high field strength elements within solid-state accessory mineral phases into supra-subduction mantle wedges may represent a little-recognised but significant phenomenon that is both predictable and pervasive at convergent margins globally.

1. Introduction

Recycling of volatiles from dehydrating subducting oceanic lithosphere into the overriding forearc mantle wedge has long been recognised (Arculus and Powell, 1986; Codillo et al., 2018; Miyashiro, 1973). This is a well-studied, globally significant phenomenon that strongly perturbs numerous geochemical cycles, but less consideration has been paid to transfer of solid-phase xenocrystic materials. Although inherited minerals have been reported from arc magmas (Rojas-Agramonte et al., 2016 and references therein) and ophiolite-hosted chromitites (Yang et al., 2014 and references therein), their origins remain enigmatic due to complex paleotectonic settings and processes.

Crustal-level ophiolite lithologies commonly can be dated using zircon occurring in evolved rock types such as oceanic plagiogranites and gabbros (Grimes et al., 2013 and references therein). Zircons from these rock types typically yield single-aged populations that are interpreted to represent magmatic ages. The occurrence of zircon and rutile xenocrysts in mantle-level samples (harzburgite and chromitite) of the Eocene-age New Caledonian ophiolite that exhibit similar broad-ranging age spectra is therefore highly noteworthy. They provide an opportunity to consider what role xenocrystic solid-phase materials might play in the inter-plate transfer of high field strength elements (Spandler and Pirard, 2013 and references therein).

The relatively simple tectonic configuration of New Caledonia during Eocene time (Aitchison et al., 1995; Cluzel et al., 2001; Maurizot et al., 2020a) facilitates detailed consideration of the origins and significance of these xenocrysts. The extensive New Caledonia ophiolite or Peridotite Nappe (Avias, 1967) originally covered much of the 450 km long island of Grand Terre in the SW Pacific (Fig. 1). During latest Eocene time this slice of mantle, interpreted as part of the proto-Loyalty forearc (Cluzel et al., 2016), was thrust south-westward over a basement formed of pre-Late Cretaceous amalgamated arc-related terranes (Aitchison et al., 1995; Cluzel et al., 2001) and unconformable Late Cretaceous-

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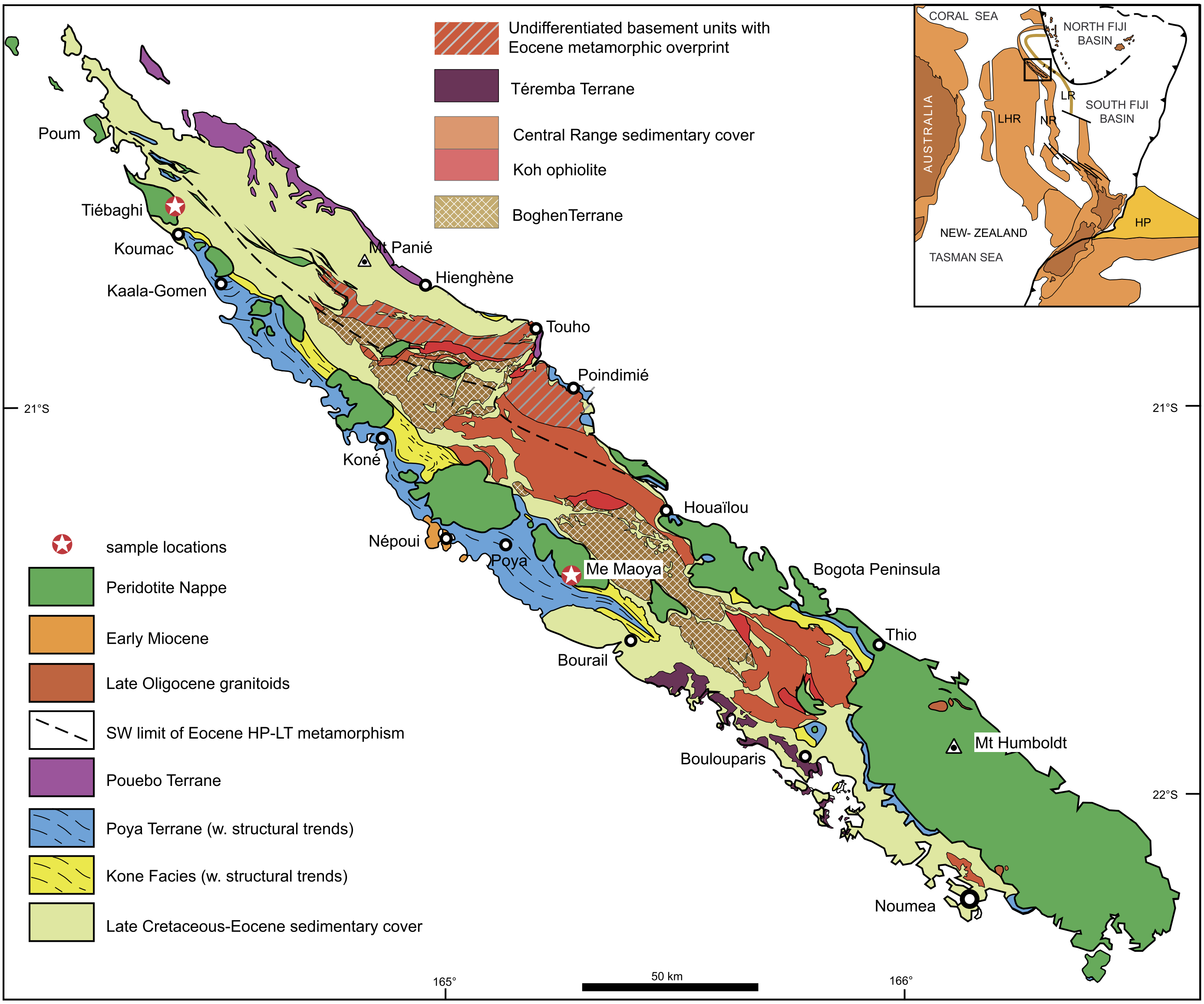

Fig. 1. Geological map of New Caledonia showing the distribution of key tectonic units discussed together with the Peridotite Nappe locations from which bulk samples were collected are shown. Abbreviations in inserted SW Pacific map; LHR: Lord Howe Rise, NR: Norfolk Ridge, LR: Loyalty Ridge, HO: Hikurangi Plateau. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

Eocene sedimentary cover that comprised an extension of the Norfolk Ridge at the north-easternmost margin of Zealandia. Some of the pre-Late Cretaceous terranes developed in a forearc setting associated with intra-oceanic subduction outboard the continental margin of eastern Gondwana; others represent a coeval subduction complex (Cluzel et al., 2012b). The Late Cretaceous-Paleocene Poya Terrane tectonically overlies this basement and sits immediately beneath the Peridotite Nappe (Cluzel et al., 2018).

Subduction, culminating in nappe obduction started at ca. 56 Ma as indicated by granulite-facies amphibolites in a metamorphic sole (U-Pb dating on zircon and Ar/Ar dating on amphibole) (Cluzel et al., 2012a; Soret et al., 2016). Zircon U-Pb ages from dykes intruding mantle peridotites provide the best age constraint for the New Caledonia ophiolite of 53.3 ± 0.73 Ma ($N = 19$) (Cluzel et al., 2006; Maurizot et al., 2020a). Felsic dykes from Tiébaghi yield U-Pb ages of 54.3 ± 0.9 Ma (zircon) and 49.2 ± 3.6 Ma (sphene) [Supplementary material]. 55-53 Ma U-Pb ages are reported for zircons from similar felsic blocks in metamorphosed serpentinite mélange of the Eocene high-P metamorphic belt (Cluzel, 2020; Spandler et al., 2005). Ar/Ar apparent ages of island-arc tholeiitic dolerites (50-47 Ma) and clinoenstatite-bearing boninite (47 Ma) from the ophiolite sole at Népoui (Cluzel et al., 2016) provide cooling ages for the youngest ophiolitic magmatic events. Thus, fore-arc magmatism was short-lived, starting *ca* 55 Ma and ending between 50-47 Ma.

In addition to slab melts injected into the fractured fore-arc, material transfer from the subduction zone into the supra-subduction mantle through melt/fluid circulation was recorded by high-temperature peridotite metasomatism (Secchiari et al., 2020) and fluid-induced mantle wedge melting (Cluzel et al., 2016). At lower temperatures, upwards-decreasing pervasive serpentinisation (lizardite ± chrysotile, magnetite) of the nappe (Ulrich et al., 2020) and tremolite-antigorite-chlorite crack seals (Cluzel et al., 2020), provide geochemical and isotopic evidence of slab-derived fluids. However, despite strong suspicion this material originated from the Eocene subduction zone, the precise timing and nature of material involved remain relatively unconstrained.

This study records discovery of refractory accessory minerals (zircon, rutile) in New Caledonian peridotites and associated podiform chromitites. Age similarities amongst Phanerozoic grains (e.g.

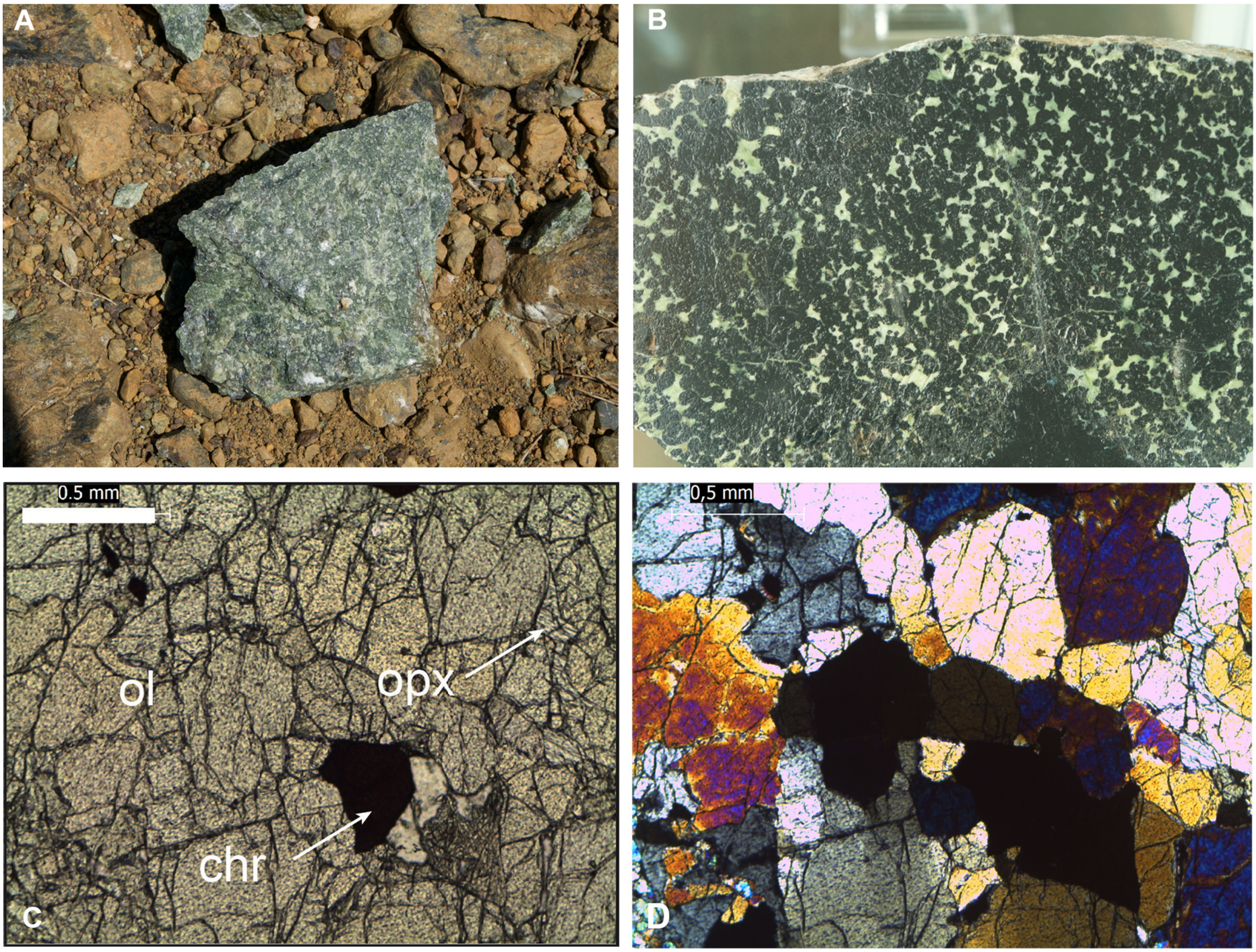

Fig. 2. A: Fragment of unserpentinised harzburgite from Me Maoya freshly broken from massive (<2 m^3) boulder littering the bed of Baraoua River draining the southern flanks of Me Maoya massif NE of Bourail. B: Example of the podiform chromitite ore from collections of the Tiébaghi Historical Society in the museum at the former Tiébaghi mine village. C: Photomicrograph of unserpentinized harzburgite from the Me Maoya Massif collected from the Baraoua River (plain polarised light) ol = olivine, opx = orthopyroxene, chr = chromite). D: Photomicrograph of unserpentinized harzburgite from the Me Maoya Massif collected from the Baraoua River (cross-polarised light).

Silurian zircons and Late Jurassic rutiles) suggest that at least some of the xenocryst populations may share common sources. Features of xenocryst populations (U-Pb ages, REE content, Hf and O isotope geochemistry) can be matched to likely sources on the subducting slab and highlight fluid-assisted transfer of solid material during forearc metasomatism.

2. Host rocks

New Caledonia harzburgites are highly depleted, resulting from multiple superimposed melting episodes and re-enrichments (Cluzel et al., 2012b; Pirard et al., 2013; Soret et al., 2016). Although detailed geochemical documentation is beyond the scope of this article, we note that the extremely low incompatible element contents specifically Zr, make direct crystallisation of zircon unlikely and otherwise it must be xenocrystic. Rather than a strictly mantle signature, isotopic features of the harzburgites reveal their modification by different fluid and melt inputs (Secchiari et al., 2020). Nd isotopic ratios range from $-0.8 \leq \varepsilon Nd_i \leq +13.32$ and negatively correlate with Sr isotopes ($0.7025 < {}^{87}Sr/{}^{86}Sr < 0.7077$). Pb isotopes trend from depleted MORB mantle (DMM) towards crustal-derived fluids/melts. Samples collected from Me Maoya are remarkably fresh and have escaped pervasive serpentinisation (Fig. 2).

The harzburgites (olivine + orthopyroxene + spinel) are ultramafic tectonites displaying two generations of high-temperature minerals (Pirard et al., 2013). An early Mg-rich olivine and orthopyroxene association is preserved as porphyroclasts, while secondary olivine and orthopyroxene neoblasts are aligned within the foliation. Cores of orthopyroxene porphyroclasts yield Ca-in-orthopyroxene temperatures of 950-1150 °C. Core-to rim compositional variations locally reflect cooling of ca. 50-100 °C. Ca-in-olivine and olivine-spinel geothermometers testify to significant cooling (T(Ca in Ol) = 800-850 °C; T (Ol-Sp) = 840-965 °C). For neoblastic orthopyroxene and olivine, calculated equilibrium temperatures are slightly lower (T(Ca in Ol) = 730-790 °C; T(BK) = 940-1065 °C) as are secondary orthopyroxene films (T=810-850 °C) (Secchiari et al., 2020). Temperatures estimated using Ca-Mg exchange between secondary clino- and orthopyroxene vary between 916-932 °C and 924-966 °C (Secchiari et al., 2020). These geothermometers attest to the pristine nature of these rocks with only high-temperature processing recorded and absence of any low-temperature overprint.

Tiébaghi Massif represents <2% of the total peridotite cover and was once one of the world's largest and richest Cr mines.

The Cr content in ore is exceptionally high (>40% wt% Cr_2O_3) and >3.27 Mt of ore mined represents >87% of New Caledonia's total Cr production (Maurizot et al., 2020b). It consists of steeply SW-dipping foliated peridotites, with, from east to west, harzburgite and dunite, overlain by diopside harzburgite and spinel lherzolite locally equilibrated in the plagioclase lherzolite facies (Moutte, 1982) with all peridotites exhibiting tectonite textures (Page et al., 1982).

3. Sample collection and processing

Two >450 kg bulk samples of unserpentinised harzburgite and chromitite were collected from Me Maoya and Tiébaghi massifs respectively (Fig. 1). Difficulty of access and clean, unweathered exposure led to one sample being collected from massive boulders littering the bed of Baraoua River draining the southern flanks of Me Maoya massif NE of Bourail. They represent some of the freshest harzburgites and are typical of such rocks found nearby at Kopeto and Poya (Secchiari et al., 2020). The other sample was collected from fresh chromite ore stockpiles at Tiébaghi Cr mine wash-plant.

After field collection, all samples were cleaned before shipping from New Caledonia and dried using sunlight on clean plastic sheets. They were put in clean cloth bags and placed into several food grade HDPE plastic barrels that were tightly sealed. Samples were shipped from Noumea (New Caledonia) to Xingang, Tianjin (China) via Brisbane where all samples remained onboard during transit. Importantly, at no stage have any samples come into contact with any part of the Australian continent.

Mineral separation was undertaken at the Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences (CAGS), Zhengzhou, where a well-tested workflow of mineral separation for ultramafic rocks that is designed to avoid any possibility of sample contamination has been developed over the last two decades. In order to obtain heavy mineral concentrations, each sample underwent a process involving numerous steps of separation with density, magnetism, and electrostatics (see Supplementary Materials and Fig. 6 in Xu et al., 2009 for a flowchart outlining steps in processing workflow).

4. Analytical methods

U-Pb and oxygen isotopic compositions as well as REE abundances we determined by Sensitive High Resolution Ion Microprobe (SHRIMP) instruments at Australian National University (ANU) Research School of Earth Sciences (RSES). U-Pb isotopic compositions were determined on SHRIMP II following standard operating procedures (Ireland and Williams, 2003) with U-Pb data normalised to Temora 2 at 417 Ma. Rutile U-Pb analysis followed similar protocols to zircon with the reference material being the R632 rutile (Axelsson et al., 2018). REE abundances in zircon were determined on SHRIMP RG operating with high mass resolution (5000 $M/\Delta M_{10\%}$) and energy filtering based on the reduction of the $^{30}Si^{+}$ intensity by half relative to no energy offset. This has been found to yield an energy offset of ca. 15 eV (Ireland et al., 2018), which is sufficient to effectively discriminate against all significant polyatomic species with more than three atoms. It also tends to ameliorate matrix effects. Data were normalised relative to the NIST610 standard in conjunction with the SL1 zircon reference material. This combined normalisation was used to allow normalisation with zircon sensitivity factors calculated relative to $^{96}Zr^{+}$ and NIST610 to $^{30}Si^{+}$. Oxygen isotopic compositions of zircon were determined on SHRIMP SI with data referenced to Temora 2 at $\delta^{18}O$ of +8.2‰ (Ávila et al., 2020 and references therein).

A Laser ablation Multicollector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) was used for zircon Hf isotope analysis undertaken at the Centre for Geoanalytical Mass Spectrometry, School of Earth and Environmental Sciences, University of Queensland with standard operating procedures (Zhou et al., 2020) being followed. Equipment included an ASI RESOlution 193 ArF nm excimer laser system and a Nu Plasma II MC-ICP-MS. The laser was run with a 50 μm diameter round spot at 10 Hz, with a measured instrument laser-fluence (laser pulse energy per unit area) of 3 J/cm^2. Only zircon grains that had previously been dated with SHRIMP II at RSES, ANU were analysed (see above). For each spot, 10 s of blank was collected, followed by 20 s of ablation and 15 s of wash out. Prior to data acquisition, MC-ICP-MS signals were optimized during tuning with standard glass and Mud Tank zircon. We collected masses 171-181 simultaneously. Initial reduction of raw data was accomplished using the program *Iolite* (Paton et al., 2011). $\varepsilon Hf_{(t)}$ values were calculated using U-Pb ages, and measured $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ ratios. Established parameters including: $^{176}Lu/^{177}Hf_{CHUR}$, $^{176}Hf/^{177}Hf_{CHUR}$, $^{176}Lu/^{177}Hf_{DM}$, $^{176}Hf/^{177}Hf_{DM}$, $^{176}Lu/^{177}Hf_{Crust}$, and $\lambda^{176}Lu$, were used (Blichert-Toft, 2008 and references therein). Zircon 91500, which has a $^{176}Hf/^{177}Hf$ value of 0.282308 ± 0.000006, was used as the primary reference material. One primary reference zircon was analysed for every five unknown grains (including our own samples and secondary reference zircon). Temora 2 zircon, which has a $^{176}Hf/^{177}Hf$ value of 0.282686 ± 0.000008 and Plešovice zircon, which has a $^{176}Hf/^{177}Hf$ value of 0.282482 ± 0.000013 (Sláma et al., 2008 and references therein) were used as secondary reference materials. Sessions yielded results within 2 $\varepsilon Hf_{(t)}$ units for secondary reference material.

5. Zircon

Rare zircons (<100) were recovered from each 450 kg sample. Forty zircons from Me Maoya and 25 from Tiébaghi were mounted in epoxy and polished to midsection for analysis. Both samples yielded Eocene to Precambrian age distributions (Fig. 3; Supplementary material). The youngest population is identified through eight zircons at circa 48.2 Ma and is unique to Tiébaghi chromitite. Recovered zircons are euhedral or subhedral with one or more terminations. They are relatively large ranging in length from 150 to 200 μm with aspect ratios around 0.25-0.5. Both samples contain older zircons with most being Phanerozoic including clusters of Triassic to Cretaceous and Silurian ages. Ages >1 Ga are seen from Me Maoya, which includes grains as old as Neoarchean (2693 ± 14 Ma).

Most of the xenocrystic population yields low to negative $\varepsilon Hf_{(t)}$ values well below that of the depleted mantle and in the case of some Late Paleozoic to Mesozoic grains strongly negative values indicating prolonged crustal residence of their source rocks (Hoskin and Ireland, 2000). The youngest (48.2 Ma) zircon population is distinct in having highly positive $\varepsilon Hf_{(t)}$ values (13.6-21.2) consistent with derivation from a magma of primitive composition (Fig. 3a, b).

The youngest age population from Tiébaghi lies within or close to primitive mantle VSMOW-normalised $\delta^{18}O$ compositions of 5.3 ± 0.6 (2s Valley et al., 2005) whereas many older grains plot well above this value indicating likely crustal processing (Fig. 3c, d). Low to negative $\delta^{18}O$ values concentrated amongst older zircons from Tiébaghi may reflect degrees of earlier unrelated hydrothermal alteration amongst the xenocrystic population (Grimes et al., 2013). Given that zircons from this sample that are considered likely to be magmatic have $\delta^{18}O$ values close to that of depleted mantle this alteration is unlikely to be related to chromite ore forming processes. When compared to zircons from Eocene-age dikes that intrude the Peridotite Nappe near Népoui in the Kopeto massif (Xu et al., 2021) and near Coulée in the massif du Sud ages

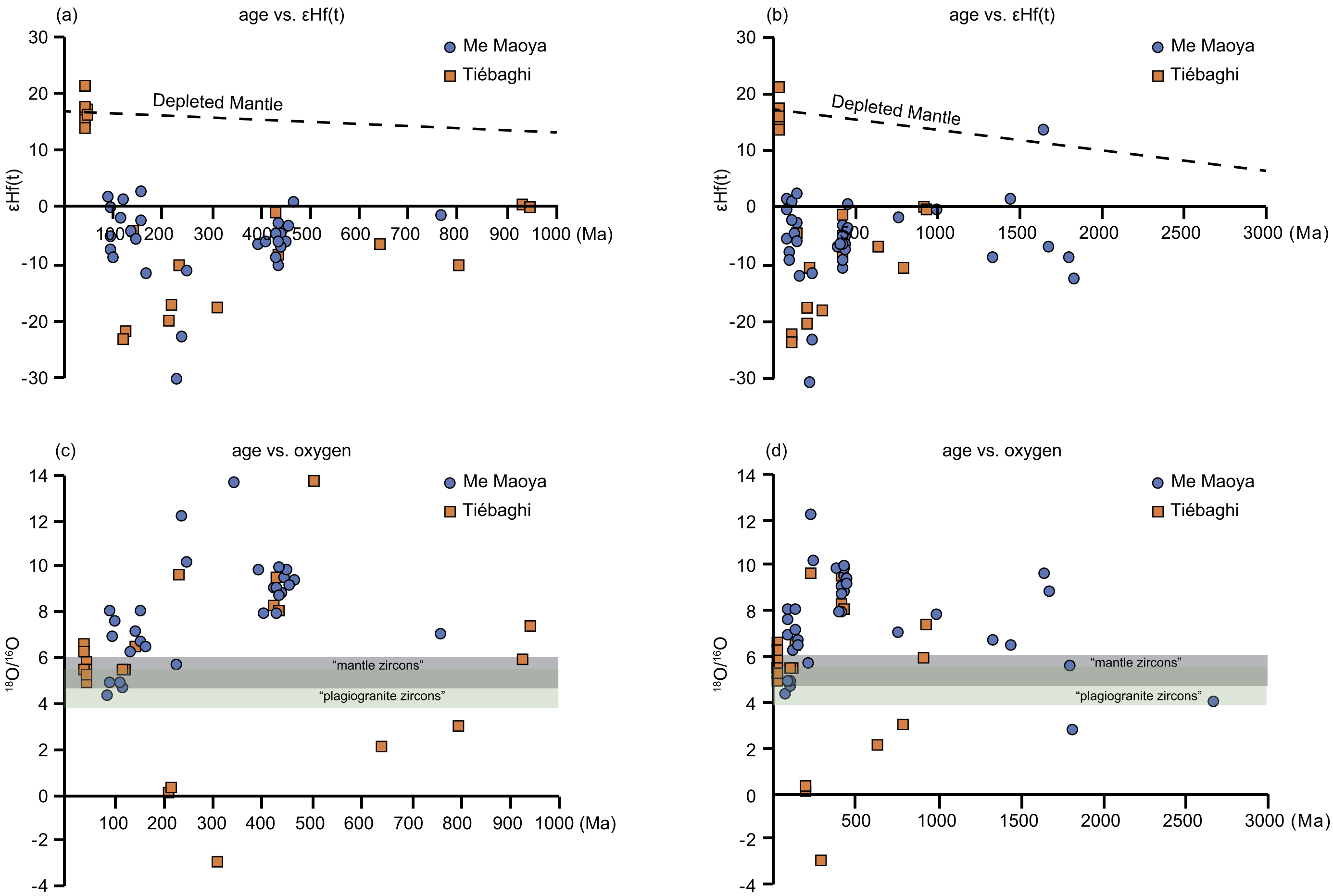

Fig. 3. Plots of U-Pb ages vs. $\varepsilon Hf_{(t)}$ (a: 0-1 Ga), (b: 0-3 Ga) and VSMOW-normalised $\delta^{18}O$ isotope data (c: 0-1 Ga), (d: 0-3 Ga) for zircons from mantle samples collected from the Tiébaghi chromitite and Me Maoya harzburgite. Highly positive $\varepsilon Hf_{(t)}$ values (13.6-21.2) amongst the youngest (48.2 Ma) zircon population from Tiébaghi suggest derivation from primitive magmatic compositions.

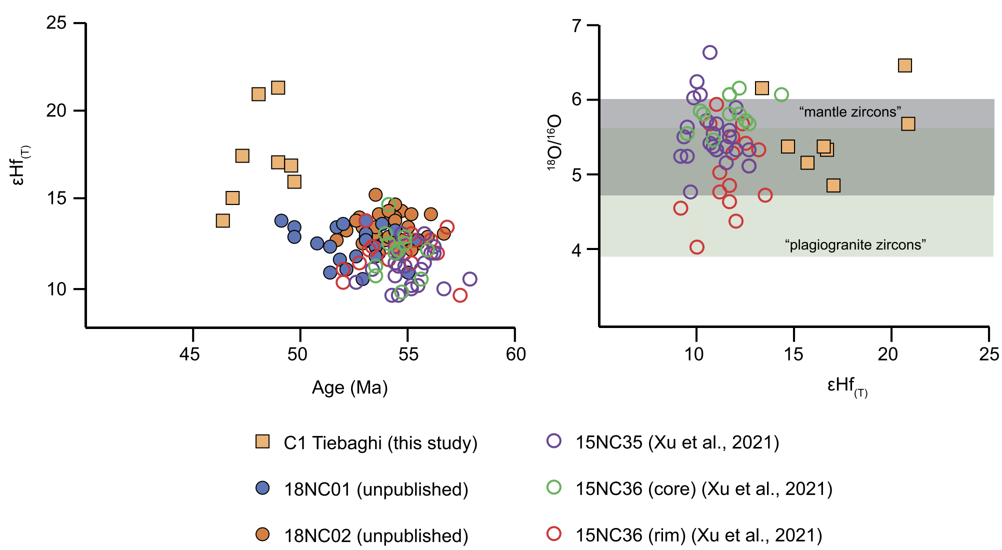

Fig. 4. Plots of $\varepsilon Hf_{(t)}$ vs. age and VSMOW-normalised $\delta^{18}O$ vs. $\varepsilon Hf_{(t)}$ for the youngest, potentially magmatic zircon population in the C1 Tiébaghi sample allowing comparison with zircons from Eocene dykes that intrude the Peridotite Nappe elsewhere. Zircons from samples 15NC35 and 15NC36 were collectednear Népoui in the Kopeto massif (Xu et al., 2021) and samples 18NC01 and 18NC02 are unpublished data of J.C.A., D.C. and R.J.Z. from Eocene-age zircons in dykes from near Coulée in the massif du Sud.

for the Tiébaghi zircons are slightly younger and although $\delta^{18}O$ compositions are similar $\varepsilon Hf_{(t)}$ values range higher (Fig. 4).

Chondrite-normalised rare earth element (REE) patterns for zircons from both samples plot predominantly within the normal range for zircons of igneous origin (Hoskin and Ireland, 2000) (Fig. 5). Early Eocene (48 Ma) zircons from Tiébaghi chromitite are of interest because they are likely magmatic and possibly linked to ore-forming processes. Their bulk REE content is consistent with a magmatic origin, however, REE patterns are more fractionated ($[La/Yb]n = 1.7 \times 10^{-6}$) with less LREE and more HREE than av-

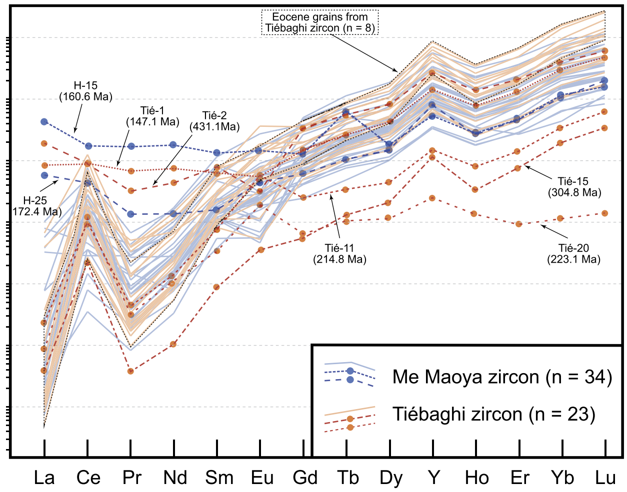

Fig. 5. Plot of C1 chondrite-normalised (Sun and McDonough, 1989) REE abundance patterns for zircons from the Tiébaghi chromitite and Me Maoya harzburgite.

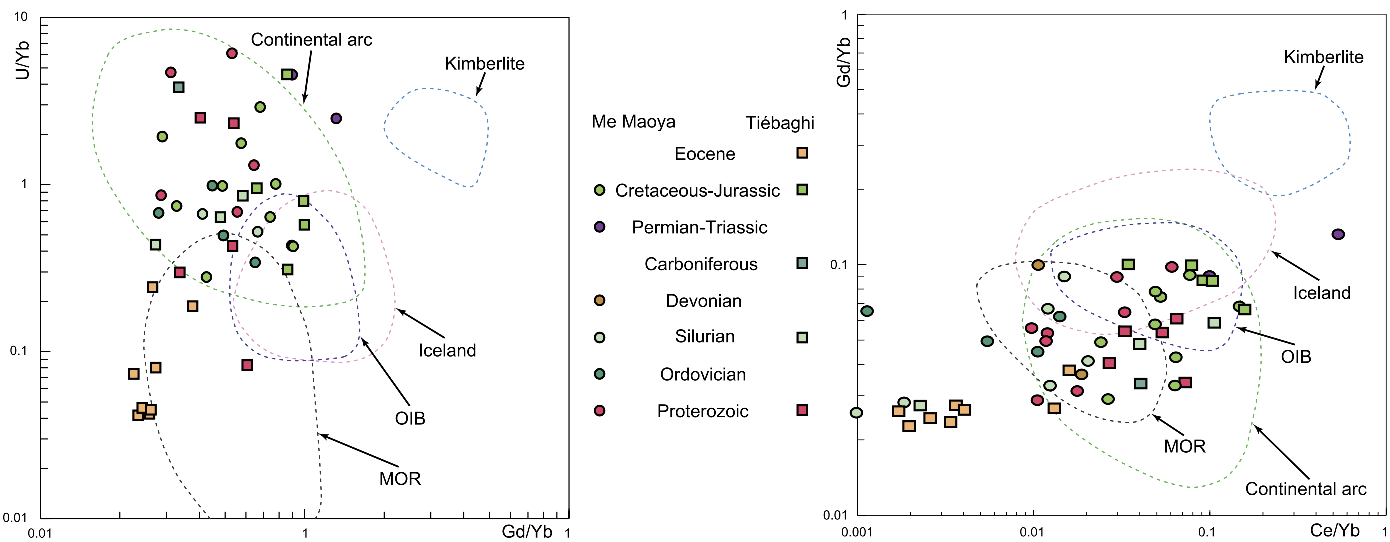

Fig. 6. Plots of a) U/Yb vs. Gd/Yb and b) Gd/Yb vs. Ce/Yb showing distribution by age populations for sampled zircons. Fields outlined are drawn as if around distributions of data from zircons of known tectonic origin (Grimes et al., 2015).

erage magmatic zircons (Hoskin and Ireland, 2000), except the youngest (46.3 Ma) zircon C1-22-1 ($[La/Yb]n = 4.3 \times 10^{-5}$), which however has a very high Zr content and thus is not a single zircon crystal but possibly a mixture of zircon and baddeleyite. When the behaviour of Gd/Yb and Ce/Yb are considered many older Mesozoic and Paleozoic xenocrysts plot in a continental arc field (Grimes et al., 2015) (Fig. 6), consistent with possible derivation from eastern Gondwana. Early Eocene zircons from Tiébaghi exhibit REE patterns similar to those of MOR zircons and on discriminant plots lie outside continental arc, ocean island and kimberlite fields and within or near MOR fields similar to supra-subduction zone ophiolite zircons (Grimes et al., 2015). The histories of zircons that exhibit anomalous REE patterns (Tié-1, Tié-2, Tié-11, Tié-15 Tié-20, H15 and H25) all of which are members of the xenocrystic population remain indeterminable but likely represent multiple metamorphic overprints.

6. Rutile

Well-preserved but rare rutiles were also recovered from both samples. The first ever U-Pb ages determined from rutiles in harzburgite include 12 from Me Maoya and 16 from Tiébaghi (Fig. 7). Ages ranging from latest Triassic to Cretaceous were determined from the former with a similar range from Tiébaghi. Notably, Tiébaghi rutiles show a similar pattern to zircons yielding two early Eocene age grains and a solitary late Eocene outlier at 37.3 Ma.

The combination of zircons and rutiles with similar age characteristics is important. Such a coincidence mitigates against any possibility of laboratory contamination as a source for these xenocrysts. It also indicates that these accessory minerals are endemic to both harzburgite and chromitite.

7. Discussion

Podiform chromitites develop in supra-subduction zone ophiolites in response to interactions between ultra-depleted melts and mantle wedge peridotites (González-Jiménez et al., 2014). Incongruent melting of orthopyroxene and replacement by olivine leaves residual dunite associated with sheared and recrystallised high-Cr chromite bodies. Chromite is locally/lately associated with poikiloblastic crystals of Cr-rich amphibole and Na-rich phlogopite (Leblanc, 1978), an observation implicating hydrous fluids (González-Jiménez et al., 2014; Johan et al., 2017 and references therein). The regional-scale Belep-Poum shear zone, closely associated with the Tiébaghi deposit (Leblanc, 1978) likely provided

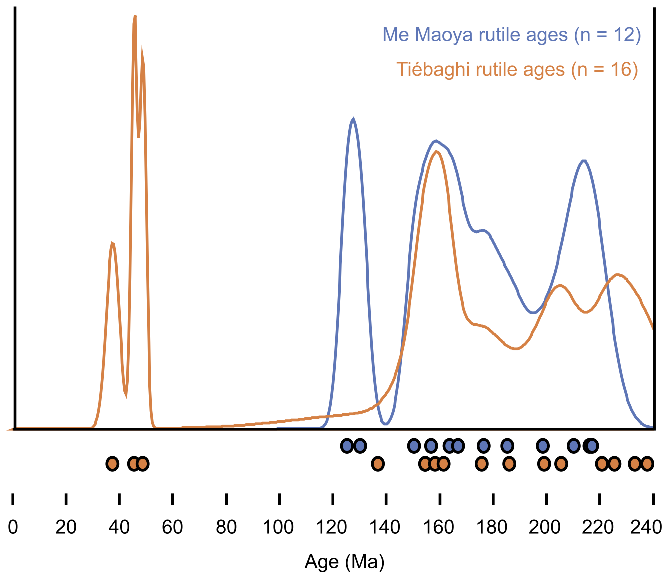

Fig. 7. Histogram of U-Pb ages obtained for rutiles collected from the Tiébaghi chromitite and Me Maoya harzburgite.

a steeply SW-dipping channel for melt and fluid circulation. The youngest zircon population from Tiébaghi is interpreted as magmatic and as might be expected in a depleted forearc mantle correlates with juvenile or radiogenic mantle-derived $\varepsilon Hf_{(t)}$ values. Cross-cutting relationships between chromite bodies and early Eocene dykes imply that the latter are slightly younger (Maurizot et al., 2020a) although our U-Pb zircon ages suggest to the contrary (Cluzel et al., 2006; Supplementary material). This first direct dating of podiform chromite at 48 Ma using co-occurring magmatic zircons constrains the timing of ore formation by supra-subduction melt-rock interaction.

The chromitite and harzburgite from which the zircons and rutiles were extracted are elements of the Peridotite Nappe, the former upper plate in the Paleogene subduction system of New Caledonia. This nappe is dominated by rocks of intra-oceanic lithospheric mantle affinities and no continental basement rocks are known from it (Maurizot et al., 2020a). Unless the zircons and rutiles were somehow intrinsic to these mantle rocks we must regard them as xenocrysts. The only known continental basement rocks in this system are those associated with the down-going slab; these are potentially an extension of the Norfolk Ridge and the northeasternmost margin of Zealandia (Maurizot et al., 2020a). It is therefore useful to interpret the age spectra of both minerals and compare them with potential sources amongst elements of the regional geology.

Albian (113.2-100.5 Ma) zircons in the harzburgite suggest indirect derivation from Late Cretaceous terrigenous sediments. They are widespread in correlative sediments in the SW Pacific and in New Caledonia are predominant (>50%) in the Formation à charbon, Diahot terrane metasediments and Poya terrane turbidites (Koné facies) (Adams et al., 2009; Cluzel et al., 2011). Notably, the Coniacian (89.39-85.7 Ma) Koné facies systematically contains a prominent (>20%) coeval zircon population (*ca* 88 Ma) associated with rift magmatism (Cluzel et al., 2018), which is absent from our samples and therefore can be excluded as a source. Thus, Formation à charbon and Diahot terrane or subducted equivalents are the most likely sources for the majority of zircon xenocrysts. Many of the late Mesozoic zircons have ages indistinguishable from those in pre-Late Cretaceous Teremba, Central or Boghen terranes (Adams et al., 2009; Aitchison et al., 1998; Campbell et al., 2018). The Late Jurassic - Early Cretaceous rutile age spectrum is also consistent with derivation from metamorphic rocks of the Boghen terrane (Cluzel and Meffre, 2002).

The 312 Ma age of a single Carboniferous zircon lies within error of ages for Koh terrane ophiolite (Aitchison et al., 1998). No Devonian or Carboniferous xenocrysts were recorded, which is notable given many tectonic reconstructions place New Caledonia immediately outboard of the Gondwana continental margin where such ages are common amongst arc and accretionary complex terranes (Korsch et al., 2009). Zircons of this age are also absent in Late Cretaceous sediments of New Caledonia, suggesting that in contrast to western New Zealand, proto-New Caledonia may have already been isolated from Gondwana (Cluzel et al., 2011).

Silurian zircons are interesting given that few have been reported from elsewhere in New Caledonia (Adams et al., 2009; Campbell et al., 2018). They have both (negative) $\varepsilon Hf_{(t)}$ values ranging from −3.4 to −10.6 for Me Maoya and −1.7 to −9.2 for Tiébaghi and elevated $\delta^{18}O$ values ranging from 7.78 to 10.81 for Me Maoya and 7.94 to 9.43 for Tiébaghi, They bear close similarity to $\varepsilon Hf_{(t)}$ and $\delta^{18}O$ values −7.79 to −9.86 and 8.36 to 9.47 respectively for zircons from S-type granites of similar ages reported from the Lachlan orogen (Kemp et al., 2009). Notably $\varepsilon Hf_{(t)}$ values are positive for Macquarie arc zircons that lie in the same age range. Subordinate older Proterozoic to Neoarchean grains occur as might be expected amongst sediment sourced from eastern Gondwana.

Based on the above, any direct 'first-cycle' origin of detrital zircons from eastern Australia may be considered unlikely due to isolation of New Caledonia since the Permian (Campbell et al., 2018; Cluzel et al., 2011). Instead, an origin from Late Cretaceous sediments through reworking of pre-Late Cretaceous basement terranes can be considered. Such sediments are known to form part of the Eocene HP-LT metamorphic belt and zircon transit from the subduction zone is thus possible.

Aside from Eocene zircons and rutiles in the Tiébaghi chromitite, which are absent from harzburgite and may be related to specific Cr-ore forming processes, xenocrysts must have been introduced into their host rocks by some physical process. Most of zircon grains are concordant and do not display metamorphic overgrowths or metamict textures. Their U-Pb systems are undisturbed denoting temperatures below 900 °C (Cherniak and Watson, 2001). Importantly, co-existing undisturbed Cretaceous rutile grains cannot have not been heated above the U-Pb closure temperature of their system (620 ± 20 °C) (Kooijman et al., 2010). Therefore, xenocrystic contributions transited from the subduction zone before host rocks reached critical recrystallization temperatures. Accordingly, pre-Eocene xenocrysts in the chromitite and harzburgite were likely introduced into the lithospheric mantle wedge at temperatures well below equilibrium temperatures computed from ultramafic mineral assemblages. This is consistent with the relatively minimal age difference between the youngest sediments and their incorporation into the harzburgite.

Transfer of solid material from subducting to over-riding plates at convergent margins via off-scraping at the front of the subduction wedge or lithospheric underplating is extensively documented. In extant intra-oceanic systems such as the Izu-Bonin-Marianas (IBM), forearc regions are studded with serpentinite mud volcanoes. These features tap the subduction channel at depths of 10-25 km and provide unambiguous evidence for the return of subducted material (e.g. coralline blocks and blueschists) to the surface of the forearc region (Fryer et al., 2020 and references therein). However, there is no evidence of xenoliths amongst the material we have sampled from New Caledonia and subduction depths of 50 km lie further inboard of the trench than IBM serpentinite volcanoes.

Although the interface between the New Caledonia ophiolite and Poya terrane on upper and lower plates respectively is marked by a zone of serpentinite-matrix mélange both Me Maoya and

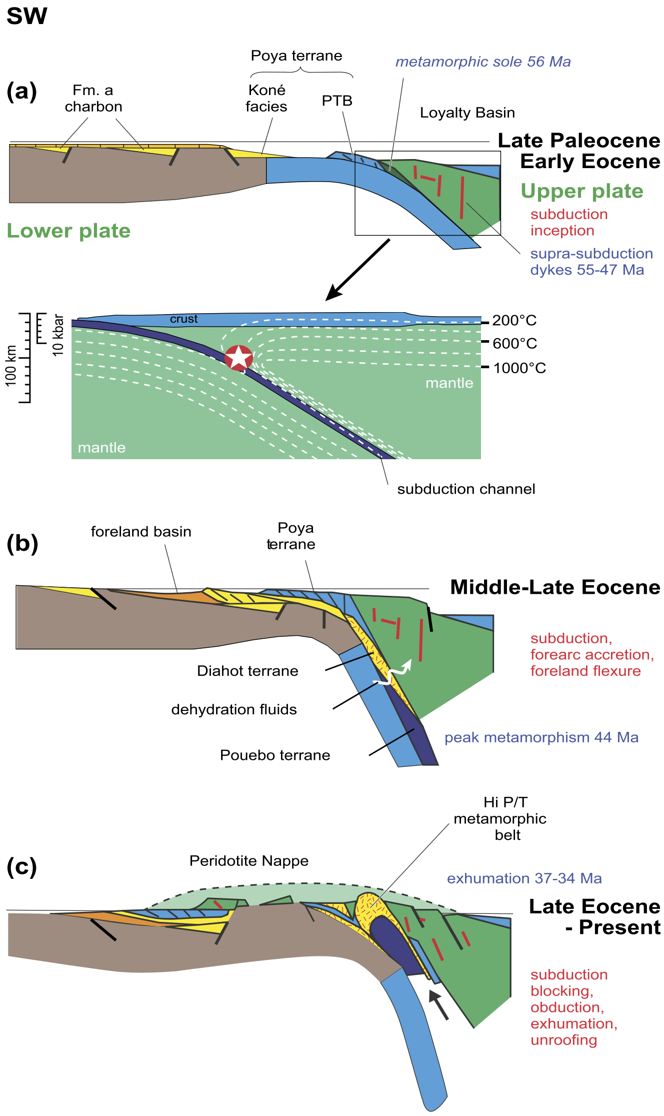

Fig. 8. Evolutionary model for Eocene New Caledonia depicting the crust/mantle section and postulated location of isotherms in the subduction channel (Peacock and Wang, 1999). The approximate location of the zone in which zircons and rutiles were transferred from terranes on the down-going (subducting) slab into the forearc mantle is indicated.

Tiébaghi localities lie well above this zone and do not appear to be associated with any subduction channel mélange or underplating (Bebout, 2007).

What occurs at deeper levels beneath the forearc mantle wedge is uncertain. As the down-going slab experiences higher pressures and temperatures dewatering and release of volatiles accompanying mineralogical phase changes results in a significant fluid flux that hydrates the over-riding mantle wedge as evidenced by low mantle velocities (Cai et al., 2018). Based on compositions and age spectra, the majority of the refractory minerals contained in chromite and harzburgite from the New Caledonian Peridotite Nappe probably come from Late Cretaceous sediments carried on the subducting Australian Plate and/or trench-fill sediments derived therefrom. The occurrence of xenocrystic zircons and rutiles in unserpentinised harzburgite implies that they were already present in their forearc mantle wedge host before the onset of supra-subduction serpentinisation at ca. 300 °C. Therefore the zircon and rutile transit from the slab into the suprasubduction zone mantle likely occurred in the subduction channel at temperatures between ca 300 °C and 600 °C (Fig. 8), and maybe coincident with the peak zone of devolatilization and transfer of aqueous fluid at 525-550 °C and 1.5-2.0 GPa (Cai et al., 2018; Manning and Frezzotti, 2020; Stewart and Ague, 2020). Following this reasoning, we infer the transferring medium cannot be slab melt if indeed it exists. Instead, aqueous fluids released during subduction metamorphism may not only be associated with metasomatism of suprasubduction mantle peridotites they may act to winnow sediment near the top of the subducting slab concentrating dense refractory accessory minerals such as zircon and rutile. We suggest that these solid xenocrystic particles maybe small enough to circulate in open fractures and be inserted into intergranular voids.

Discovery of this xenocrystic material provides a hitherto unconsidered yet plausible explanation for a mechanism by which forearc regions and associated magmas can become enriched in HFSE and HREE. As Eocene magmatic zircons amongst our samples are restricted to the Tiébaghi chromitite, we suggest that it implicates a supra-subduction ore-forming process for this podiform chromite body. The short-lived nature and polarity of the New Caledonian subduction system from its inception to ophiolite emplacement together with transfer of solid-state material between plates has implications for understanding of ancient analogues globally.

8. Conclusions

- Rare zircon and rutile mineral grains have been recovered from 450 kg samples of harzburgite and chromitite of the New Caledonia Peridotite Nappe.
- The chemical, isotopic, and age spectra of these minerals can be related directly to an origin associated with the subducting slab.
- Zircon and rutile have been transferred from the subducting slab to the overlying wedge at depths of less than 60 km.
- Incorporation of xenocrystic mineral grains is therefore a feature of subduction with transfer of material not just limited to fluids.

CRediT authorship contribution statement

Jonathan C. Aitchison: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Dominique Cluzel:** Conceptualization, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Trevor R. Ireland:** Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Renjie Zhou:** Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Dongyang Lian:** Investigation, Resources. **Daniel Patias:** Investigation, Writing – review & editing. **Zhen Yan:** Investigation, Writing – review & editing. **Jingsui Yang:** Conceptualization, Methodology, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2021.117251. These data include the Google maps of the most important areas described in this article.

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