

# **Slab-derived origin of tremolite-antigorite veins in a supra-subduction ophiolite; the Peridotite Nappe (New Caledonia) as a case study.**

Dominique Cluzel, Philippe Boulvais, Marion Iseppi, Didier Lahondère, Stephane Lesimple, Pierre Maurizot, Jean-Louis Paquette, Alexandre Tarantola, Marc Ulrich

### **To cite this version:**

Dominique Cluzel, Philippe Boulvais, Marion Iseppi, Didier Lahondère, Stephane Lesimple, et al.. Slab-derived origin of tremolite-antigorite veins in a supra-subduction ophiolite; the Peridotite Nappe (New Caledonia) as a case study.. International Journal of Earth Sciences, 2020, 109 (1), pp.171-196.  $10.1007/s00531-019-01796-6$ . insu-02369790

# **HAL Id: insu-02369790 <https://insu.hal.science/insu-02369790v1>**

Submitted on 28 Nov 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

#### [Click here to view linked References](https://www.editorialmanager.com/ijes/viewRCResults.aspx?pdf=1&docID=5657&rev=3&fileID=226065&msid=bd83d2a8-f389-4f0b-989d-4098c08f762d)

 $\stackrel{\bullet}{=}$ 

- 1 **Slab-derived origin of tremolite-antigorite veins in a supra-subduction ophiolite; the Peridotite**
- 2 **Nappe (New Caledonia) as a case study.**
- 3
- 4 Cluzel Dominique<sup>1</sup>, Boulvais Philippe<sup>2</sup>, Iseppi Marion<sup>1-3-4</sup>, Lahondère Didier<sup>3</sup>, Lesimple Stéphane<sup>4</sup>,
- 5 Maurizot Pierre<sup>4</sup>, Paquette Jean-Louis<sup>5</sup>, Tarantola Alexandre<sup>6</sup>, Ulrich Marc<sup>7</sup>.
- 6
- <sup>1</sup> 7 University of New Caledonia, Institut des Sciences Exactes et Appliquées, BP R4 Nouméa, New
- 8 Caledonia ; [dominique.cluzel@unc.nc](mailto:dominique.cluzel@unc.nc)
- <sup>2</sup> 9 University of Rennes 1, CNRS UMR 6118, Geosciences Rennes, France
- 10 <sup>3</sup> Bureau de Recherches Géologiques et Minières, Orléans, France
- 11 4 New Caledonia Geological Survey, DIMENC, Noumea, New Caledonia
- <sup>5</sup> 12 University Clermont-Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000
- 13 Clermont-Ferrand, France
- <sup>6</sup> 14 University of Lorraine, CNRS, GeoRessources, Faculté des Sciences et Technologies, F-54506
- 15 Vandoeuvre-lès-Nancy, France
- 16 <sup>7</sup> University of Strasbourg, IPGS-EOST, CNRS UMR 7516, Strasbourg, France

#### **Abstract**

 Hydration of mantle peridotites provides information on the exhumation history and on the fluid regime accompanying exhumation of these rocks (reservoirs involved, fluid/rock ratios, temperature of interaction). Highly depleted harzburgites and dunites of the Peridotite Nappe of New Caledonia are crosscut by fractures, which have been pervasively serpentinized, producing lizardite, brucite, 22 magnetite and minor chrysotile in a near-static environment, probably by sea water circulating in 23 cooling joints. This event is generally referred to as "primary serpentinization". In a next step, already serpentinized joints were re-opened to produce tension and shear cracks sealed by higher-25 temperature synkinematic fibrous minerals. Locally, tremolite-bearing veins and pockets, which do 26 not display evidence for void infill, were generated by metasomatic replacement of the wall rock 27 peridotite. Most veins only contain fibrous antigorite but some display tremolite-antigorite 28 intergrowths or even pure tremolite. The latter rocks yield high contents of Ca and incompatible 29 elements, which contrast with the overall depletion of the peridotite host rock and suggest 30 contribution of an external source. Whole-rock geochemical and isotopic features (Sr/ $86$ Sr,  $\delta^{18}$ O and  $\delta$ H) suggest that antigorite veins, which bear highly radiogenic Sr isotope signatures, were strongly 32 influenced by fluids emitted by the subducted slab and associated sediments. In contrast, the geochemical and isotopic signatures of tremolite-bearing rocks suggest a genetic link with Early Eocene supra-subduction dykes and fluids that leached them. Calcium, strontium and REE-bearing oxidized fluids reacted with already serpentinized fracture wall rock as shown by fibre nucleation, chromite alteration and high Cr contents in tremolite. The bulk of syn-tectonic fluid-rock interaction associated with shear and tensile fracture development probably occurred at the onset of Eocene intra-oceanic subduction, when the buoyant lower plate (the South Loyalty Basin) obliquely forced its way beneath the nascent Loyalty fore-arc. Mobile elements extracted from supra-subduction dykes temporarily enriched the circulating fluids and generated tremolite, antigorite, Mg-chlorite and magnetite instead of antigorite and magnetite solely. Tremolite crystallization probably ceased due to the exhaustion of Ca-rich fluids in a globally cooling fore-arc environment. Keywords

- Ophiolite, tremolite, antigorite, veins, metasomatism, supra-subduction, dykes
- 

#### **1. Introduction**

 Most ultramafic ophiolites are interpreted to represent supra-subduction mantle (Pearce et al. 1984) having recorded multiple events related to oceanic accretion, cooling, basin inversion and fore- arc evolution. Fluid and melt release through dehydration, decarbonation and partial slab melting within subduction zones is responsible for profound modifications of the supra-subduction mantle, 52 which are overprinted on previous metasomatic events. Hydration of supra-subduction mantle peridotites (Wang et al. 2009; Mothersole et al. 2017) results in the occurrence of hydrous silicates of the serpentine and amphibole groups, which are difficult to distinguish from those formed near the ridge during the cooling of the ocean lithosphere (Mével 2003; Morishita et al. 2009). In contrast, melts appearing during the early stages of arc formation (fore-arc melts) display diagnostic features that may be a clue for identifying supra-subduction events.

 The ultramafic allochthon of New Caledonia, termed Peridotite Nappe (Avias 1967; Fig. 1), is formed of partly or totally serpentinized peridotites, which have evolved from a back-arc basin ridge into a fore-arc setting, before being obducted (Cluzel et al. 2012). The Peridotite Nappe is crosscut by a spaced vein network, which contains fibrous minerals that mainly belong to the serpentine group (antigorite, chrysotile) and more rarely to the amphibole group (anthophyllite, tremolite). Most antigorite and tremolite occurrences correspond to synkinematic fibrous seals associated with the opening of tension cracks, or motion along micro-faults. However, some tremolite occurrences appear in irregular streaks and pockets without obvious link to faults, and partly correspond to metasomatized peridotites, which contain remains of their protolith such as chromite streaks (Lahondère et al. 2012).

 In weakly serpentinized lherzolites of the Peridotite Nappe, calcium content is relatively high (1.5 wt% to 2.2 wt% CaO) (Secchiari et al. 2016). It is lower in unserpentinized harzburgites (0.3 wt% to 0.6 wt% CaO) (Secchiari et al. 2019). However, occurrence of such fresh rocks is extremely rare and the bulk of the Peridotite Nappe underwent 40% to 100% serpentinization (lizardite mesh) and contain less than 0.1 wt% CaO (0.01%-0.1%), a general feature of serpentinized peridotites (Kodolànyi et al. 2000). In spite of this, tremolite, a Ca-rich amphibole, is not unusual in serpentinized ultramafic rocks and occurs in tectonic melanges, unroofed abyssal peridotites, transform fault zones and fore-arcs (e.g., Kodolànyi et al. 2000). Tremolite occurrences and hence Ca input have been attributed to mobilization from the peridotite itself or, alternatively, external sources. As far as an external source is needed, tremolite crystallization may result from the interaction of serpentinite with Ca-rich metasediments in mélanges (i.e., nephrite jade; Adams et al. 2007) or with mafic rocks in subduction zones (Marocchi et al. 2010), from the recrystallization of dykes crosscutting serpentinites (e.g., rodingites; Bach and Klein 2009; Harlow and Sorrensen 2005; Koutsovitis et al. 2013; Sivell and Waterhouse 1986), from mobilization of Ca from pyroxenes during serpentinization 82 (Python et al. 2011), or "hydrothermal" remobilisation of Ca from calcite veins coming from sea

water at shallow depth (Agrinier et al. 1996). In New Caledonia, in addition to crosscutting veins,

84 tremolite locally appears in the lower crustal section of the Peridotite Nappe in greenschist-facies

mylonitic gabbronorite cumulates (Ouen Island "jade"; Maurizot and Lesimple 2012). However, in

86 these rocks tremolite displays strong preferred orientation but never shows asbestiform texture. In

contrast, tremolite occurrences dealt with in this article are always located in serpentinized

88 peridotite, away from any mafic crustal rock.

89 In a general fashion, fibrous crack seals are nucleated on wall rock and the nature of minerals that

fill the progressively opening spaces depends strongly on the composition of the host rock. There is a

consensus on the fact that synkinematic minerals, which form the crack seals, come from pressure-

92 or shear-solution and are in equilibrium with pore fluids. Thus, synkinematic mineral growth is at

least partly fed by dissolved elements that are not carried over large distances (e.g., Baghat and

Marshak 1990; Beach 1974, 1977; Bons and Jessel 1997; Durney 1972, 1976; Pollard and Segall 1987;

Rutter 1983). Accordingly, only serpentine minerals (antigorite, lizardite, chrysotile, polygonal

serpentine, depending upon P-T conditions) are expected to be in equilibrium with the more or less

deeply serpentinized peridotite wall rock. This assertion has been confirmed by recent studies

(Andreani et al. 2007; Kurat et al. 2011); therefore, owing to the very low Ca content of depleted

peridotite, the occurrence of faults and cracks filled with tremolite in the Peridotite Nappe raises the

100 question of the composition and the origin of the associated fluids.

 No associated sediments are known in the Peridotite Nappe that could be a source for Ca. Scarce carbonate veins are documented in the Peridotite Nappe (e.g. Lahondère et al. 2012; Mothersole et 103 al. 2017) and clearly post-date the bulk of serpentinization. Generally these veins are composed of magnesite or hydromagnesite, and although aragonite has been observed locally (Lahondère et al.

2012) it is related to late (post-obduction ?) joints infill of supergene origin.

Therefore, there are three internal and external possible sources:

i. Calcium may come directly from fluids emitted by the subduction zone.

 ii. Although harzburgites and dunites of the Peridotite Nappe are strongly depleted (even unserpentinized rocks -a very rare occurrence though- yield very low Ca contents), they could be a source of Ca for tremolite, provided the leaching of large amounts of rock.

111 iii. Early Eocene felsic dykes (up to 17 wt% CaO; Cluzel et al. et al. 2006) emplaced in already fractured and serpentinized rocks commonly display disequilibrium features related to syn- and post- magmatic tectonics (Rodgers, 1973a, b, 1974; Cluzel et al. 2006; see below), which suggest easy fluid circulation through the fracture network and a possible source for Ca.

 Tracking the origin of the tremolite-crystallizing fluids has been attempted using four methods: i) geological characterization of the geometry and kinematics of the veins; ii) major elements, trace

elements, and REE geochemistry of tremolite-bearing veins; iii) Sr isotopes (tracer of Ca origin); and

119 iv) oxygen ( $18O/16O$ ) and hydrogen (D/H) isotope ratios. As far as possible, tremolite features have 120 been compared with that of fibrous minerals of the serpentine group (antigorite), which are 121 commonly associated with tremolite in peridotite massifs.

#### **2. Geological setting**

 The geology of New Caledonia is characterized by: i) a pre-Late Cretaceous basement formed of amalgamated arc-derived terranes (Meffre 1995), which relate to the Southeast Gondwana margin; 126 ii) a Late Cretaceous to Late Eocene sedimentary cover; iii) a Eocene high-pressure metamorphic belt, 127 exposed in the northern part of the island; and, iv) two large allochthonous terranes emplaced during 128 the Eocene, the Poya Terrane and the Peridotite Nappe, which together represent almost one half of the island's surface (Fig. 1) (Cluzel et al. 2012; Maurizot et al. in press a).

 The Peridotite Nappe of New Caledonia (Avias 1967), results from obduction of the Loyalty Basin lithosphere over the continental Norfolk/New Caledonia Ridge (Collot et al. 1987). It originally 132 covered most of the island; however, several phases of erosion isolated tectonic klippes spread along the west coast and a larger unit termed "Massif du Sud" in the south of the island. A highly sheared serpentinite sole, 20-200 m thick, indicates top-to-the-southwest emplacement kinematics (Quesnel et al. 2013, 2016), while thrust-related deformation rapidly decreases upward.

 The Peridotite Nappe is dominantly composed of harzburgite (>80%), dunite and minor lherzolite (in northern massifs only) that represent a prominently depleted supra-subduction mantle lithosphere (Marchesi et al. 2009; Pirard et al. 2013). Owing to their depletion in incompatible 140 elements compared to primitive mantle composition, residual harzburgites probably underwent about 20%-25% partial melting (Prinzhoffer 1981; Secchiari et al. 2019). They are overlain by dunite, pyroxenite, websterite and gabbronorite cumulates (Prinzhoffer 1981). Cumulate websterite and gabbronorite probably crystallized in equilibrium with depleted melts intermediate between boninite and island-arc tholeiite (Marchesi et al. 2009; Pirard et al. 2013; Cluzel et al. 2016; Secchiari et al. 145 2018), which at present are not preserved. Whole rock and mineral chemical constraints on 146 lherzolites allow a polyphase evolution to be drawn, from re-enrichment by circulating melts during oceanic accretion to mantle metasomatism during subduction (Marchesi et al. 2009; Secchiari et al. 2016; Spandler and Pirard 2013; Ulrich et al. 2010).

 The inception of intra-oceanic subduction that eventually led to obduction is time-constrained by the granulite-facies "metamorphic sole", dated at 56 Ma (Cluzel et al. 2012a). Afterwards, the Peridotite Nappe was crosscut by a series of dykes and sills emplaced at ca. 55-50 Ma (Early Eocene; Cluzel et al. 2006), which are not present in the underlying Poya Terrane. These intrusive rocks comprise minor dolerite dykes, and a variety of medium to coarse grain rocks (sills and dykes), the compositions of which vary from ultramafic (pyroxenite and hornblendite) to felsic (diorite,

 leucodiorite and granite). Dolerite dykes crosscut all the levels of the Peridotite Nappe, including 156 gabbro cumulates, while felsic and intermediate dykes and sills are apparently restricted to the ultramafic part of the allochthon. Dolerites display supra-subduction affinities (island-arc tholeiites), and likely represent the product of partial melting of "normal" supra-subduction mantle. In contrast, the majority of felsic or intermediate dykes come from slab melts formed by partial melting of diverse mafic oceanic crust rocks including gabbro cumulates; some others, however, may be referred to as boninite-series generated by hydrous melting of highly depleted mantle wedge peridotites enriched by slab melts and fluids (Cluzel et al. 2006, 2016; Secchiari et al. 2018). Thin tremolite coatings around high-temperature minerals (olivine/orthopyroxene) and crosscutting tremolite needles, which have been rarely found in unserpentinized harzburgites (Secchiari 2016; Secchiari et al. 2019), signal early Ca input by circulating fluids or melts. Rocks of the Peridotite Nappe are serpentinized at various degrees (0% to 100%) and this early tremolite

 crystallization did not survive the development of lizardite-brucite (± chrysotile) mesh and tremolite now only appears in syntectonic or replacement veins in serpentinized peridotites.

 The development of serpentinization at large scale is crucial for Ni ore-forming processes during tropical weathering (e.g. Orloff 1968; Pelletier 1996; Butt and Cluzel 2013; Maurizot et al. in press b) because Ni substitutes Mg to form Mg-Ni silicates (the garnieritic ore) and has been systematically described by mining geologists. Since the work of Orloff (1968) in New Caledonia, there has been a 173 consensus about the timing and origin of serpentinization, which was considered to be primarily 174 related to Eocene obduction and decreasing in intensity from the serpentinite sole upwards. However, this view, which fits well with serpentinization at a large scale, is challenged by the local observations of unserpentinized peridotites in which incipient serpentinization develops downwards 177 independently of the distance to the tectonic sole.

 Thus, three main episodes of serpentinization may be defined: i) primary (intra-oceanic) serpentinization is thought to have formed during cooling and hydration of mantle lithosphere; ii) secondary, upward decreasing serpentinization was likely due to the subduction/obduction process; 181 iii) finally, continuing (minor?) serpentinization accounts for the local occurrence of hyper-alkaline springs (Monin et al. 2014), somewhat similar to the Lost City oceanic geothermal field (Rivizzigno et al. 2001). The products of present serpentinization are unknown and could only be reached by drilling.

185 Serpentines formed by "primary" serpentinization and that due to subduction/obduction are dominated by lizardite and somewhat difficult to discriminate where they overprint each other. The 187 only difference holds in the large amount of chrysotile, which is apparently a feature of the tectonic sole.

 With the exception of the tectonic sole, the Peridotite Nappe is weakly deformed and displays m-to dm-spaced joints with only scarce evidence for shearing motion. Most of these joints have

 serpentinized boundaries mm- to dm-thick, composed of sheeted seams of dark cryptocrystalline 192 lizardite and brucite crosscut by minor chrysotile veins. From the serpentinized fractures outwards, lizardite seams are connected to the intra-crystalline serpentine mesh of olivine, which forms 40% to 100% of the bulk rock volume. In extremely scarce locations, peridotites have escaped pervasive serpentinization and allow the observation of its progressive development. These weakly serpentinized areas display upward, downward and laterally increasing amount of serpentinization without strong associated deformation. Fresh olivine grains are crosscut by closed micro-cracks (Fig. 2a), which probably resulted from cooling-related differential shrinkage. Interconnection of these micro-cracks with lizardite-bearing well-organized fractures (Fig. 2b) suggests that these structures have been controlled by larger-scale joint development (Fig. 2c & 2d). Serpentinization progressed 201 from the fracture walls outward without significant relative motion and the occurrence of almost 202 undeformed mineral grains such as pyroxene (bastite) or chromite forming bridges across the 203 serpentinized fractures show that the latter were not significantly open and serpentinization was 204 dominantly static. The process of serpentinization may have varied through time and from place to 205 place and secondary minerals show some compositional variation due to protolith, fluid 206 composition, temperature and variation of the fluid/rock ratio (for a review, see Agrinier et al. 1996; Frost et al. 2013 and references therein). It is worth noting that "primary" serpentinization (i.e. lizardite-forming) left chromite grains unaltered; in contrast, chromite grains in antigorite-tremolite veins frequently display chromian magnetite pseudomorphs (see below). 210 In contrast with static (or primary) serpentinization, which never gave birth to Ca-bearing silicates, 211 the crystallization of fibrous antigorite (and minor chrysotile) and tremolite occurred when serpentinized fractures were reactivated by opening perpendicular or oblique to fracture walls filled with synkinematic fibrous minerals (Fig. 3). Antigorite-bearing veins are widespread in the Peridotite Nappe (e.g., Lahondère et al. 2012; Quesnel et al. 2016). They commonly reach several metres in length and bear fibrous crack seals several mm to dm long. The angle between fibres and vein walls is generally acute (45-25°) and denote oblique opening. Vein boundaries are generally composed of 217 dark lizardite, on which antigorite fibres are nucleated (Fig. 3b); but in some other localities, the vein boundaries are made of porcelain-like whitish serpentine seams, which may result from the leaching 219 or recrystallization of lizardite vein walls. Antigorite-tremolite and pure tremolite veins display the same characteristics; however, tremolite fibres are shorter and commonly perpendicular or strongly oblique to vein walls (Fig. 3c & 3d). In all

- 222 cases the development of antigorite and tremolite post-dated the lizardite-bearing "primary"
- serpentinization.
- 
- **3. Analytical procedures**

 Because it may have fibrous, asbestiform habits (Dorling and Zussman 1987), and frequently 227 shows intergrowth with antigorite (this study), tremolite was sometimes overlooked in the field. Therefore, lab analysis (i.e., polarized light microscopy, XRD, IRS, Raman spectrometry) was often necessary to distinguish the various asbestiform minerals.

230 Raman data were acquired with a Renishaw inVia spectrometer of the Geology Lab. of Ecole 231 Normale Supérieure de Paris. The spectrometer is fitted with a Physics Argon laser delivering 232 monochromatic coherent light beam of 20mW at 514.5 nm (green laser). The laser beam is focused 233 through a Leica DMLM microscope fitted with 4 short focus lenses (x5, x20, x50 (Numerical 234 aperture=0.75), x100 (NA=0.90)) and 2 long focus lenses (x50 and x100). In the most effective 235 configuration, the resolution was in the order of 1 $\mu$ m for 1mW power at the sample surface so that 236 any irradiation damage may be avoided. The Rayleigh diffusion (< 100 cm<sup>-1</sup>) was eliminated by 237 dielectrical filters. The Raman signal was then spread with a network of 1800 lines mm<sup>-1</sup> (or 3000 238 lines mm<sup>-1</sup>) and measured with a CCD RENCAM detector of 400 x 576 pixels cooled by Peltier effect. 239 The microspectometer is fitted with a motorized Prior Scientific stage, which allowed moving across 240 the sample

241 Geochemical whole-rock analyses were performed at Service d'Analyse des Roches et Minéraux 242 (CNRS-CRPG, Vandoeuvre, France). Major elements were analysed by ICP-AES, trace and Rare Earth 243 elements by ICP-MS (a description of analytical procedures and detection limits may be obtained on 244 the SARM web site[: http://helium.crpg.cnrs-nancy.fr/SARM/\)](http://helium.crpg.cnrs-nancy.fr/SARM/).

245 Single minerals major elements concentrations have been determined on polished thin sections 246 with a Cameca SX five electron microprobe (W beam source) of the analytical platform of University 247 of Orleans/CNRS/BRGM.

248 Strontium isotope analyses have been carried out at Clermont-Ferrand isotope laboratory of 249 Laboratoire Magmas et Volcans (UMR 6524 CNRS-Université de Clermont-Ferrand, France) by TIMS 250 using a Thermo Fischer Triton instrument, corrected for mass fractionation by normalisation to  $251$   $86$ Sr/ $88$ Sr = 0.1194. Strontium sample decomposition and chemical separation followed the procedure 252 developed by Pin and Santos Zalduegui (1997). Strontium isotope ratios were corrected for in-situ 253 decay at 53 Ma, based upon the average U-Pb zircon age of dykes (Cluzel et al. 2006). Concentrations

254 of Sr are given in  $\mu$ g.g<sup>-1</sup>. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio measured for the NIST SRM 987 standard during the

255 period of analyses gave a mean value of 0.710238  $\pm$  9 (2 $\sigma$ , n = 30).

256 Oxygen isotope compositions were measured on dried silicates reacted using BrF5, following the 257 method of Clayton and Mayeda (1963). Isotopic compositions were measured on  $CO<sub>2</sub>$  with a VG 258 Optima triple collector mass spectrometer. Measured isotopic compositions were normalized to NBS 259 28 standard (9.6 ‰). The reproducibility is 0.25‰.

260 Hydrogen isotope compositions were analyzed at the CRPG UMR 7358 CNRS-UL (Nancy, France) 261 using an Eurovector Elemental Analyzer (EA) coupled to a VG Isoprime Isotope Ratio Mass

 Spectrometer (IRMS), following the procedure described in Lupker et al. (2012), Bell and Ihinger (2000) and Bigeleisen et al. (1952). Powdered samples were loaded into tin capsules and degassed at 264 120 °C under vacuum for 48 h in a degassing canister to remove adsorbed water. After dehydration, 265 samples were transferred under a  $N_2$  dry atmosphere in a customized, sealed, automatic sampler 266 pre-flushed with He in order to avoid any contact with atmospheric moisture. This sampler was then 267 connected to the EA-IRMS system. Samples were combusted at 1450 °C on an EA glassy Carbon 268 reaction tube, filled with glassy carbon chips, leading to the reduction of hydroxyl groups to H<sub>2</sub>. After 269 chromatographic separation, the recovered  $H_2$  was introduced in the IRMS source and analyzed for hydrogen isotopic composition. Three different internal standards (Muscovite: MuscD65, Phlogopite: Mica-Mg and a fine grained marine sediment from the Bay of Bengal: SO188) were included during 272 the sample analyses. Values of  $\delta D$  are reported in standard per mil (‰) notation relative to SMOW (Standard Mean Ocean Water). The overall, long term, 1σ, reproducibility of the method on silicate powders is given at 2‰ for δD.

 Mineral abbreviations used in figures of this article follow recommendations by the IUGS Subcommission on the Systematics of Metamorphic Rocks: Web version 01.02.07 according to Kretz (1983) completed by Siivola and Schmid (2007).

- 
- **4. Veins and dykes petrography and structure**

### **4.1. Tremolite-antigorite veins**

281 In addition to widespread lizardite mesh and lizardite-coated joints formed in relatively static 282 conditions, which can be referred to "primary serpentinization" (see above), peridotites of the Peridotite Nappe are crosscut by tension and shear cracks filled with fibrous serpentine and amphibole. They appear independently of their location in the Peridotite Nappe and especially have 285 no relation to the tectonic sole. Acicular/fibrous crack seals composed of antigorite (± chrysotile), tremolite, or both, are nucleated on lizardite seams (Fig. 3c, 3d, 4d, 5) and thus post-date them. Fibrous amphiboles (anthophyllite and tremolite) are mainly present in Poro, Thio and Tiebaghi areas, but also appear in many other sites (Fig 1). In the Poro area (east coast) crack seals are filled with tremolite often associated with antigorite (Fig. 6), whereas in the Tiebaghi area vein infills are dominated by anthophyllite (Lahondère et al. 2012). In most cases, Raman analysis only allowed the determination of intimately intergrown tremolite and antigorite (Fig. 6 and 7). In the Massif du Sud crack infills comprised tremolite, anthophyllite and Mg-chlorite. Anthophyllite reaction rims generally 293 appear at the margin of some felsic dykes and around peridotite enclaves within the same dykes. Crack seals with Mg-rich amphiboles appear closely related to felsic dykes in the Thio area (east coast). Microfaults with synkinematic fibrous tremolite and anthophyllite coatings crosscut dykes related to the lower Eocene dyke complex (Thio, Bogota Peninsula) (Lahondère and Maurizot 2009 ; Lahondère et al. 2011, 2012). Thus, field evidence and radiochronologic data from felsic dykes

suggest that amphibole-bearing veins, which are more or less associated with felsic magmatic dykes

formed after 55 Ma.

- Most synkinematic fibrous or acicular antigorite and tremolite crystals that appear in cm- to dm-thick open cracks and dikelets are:
- either strongly oblique or perpendicular to fissure walls and thus resemble tension cracks (Fig. 3c)
- 304 or, slightly oblique to fissure walls and very much resemble to pull-apart crack seals associated with micro-faulting (oblique slip) (Fig. 3d)
- These well-known tectonic features of brittle and semi-brittle rocks, which are extensively used for structural analysis, are generally filled with quartz, calcite and other minerals, depending on the composition of host rock (quartzite, limestone, etc.), which dominantly come from pressure/shear solution. Therefore, analogous process is postulated in serpentinized peridotites in which serpentine minerals are formed at medium to low temperature in the presence of water. In any case, these open tension or shear cracks are dilatational features, which likely record low lithostatic, or
- alternatively, relatively high fluid pressure.
- In many places, tensile and shear fractures are closely associated and their fibres are aligned in the same direction, which represents the direction of maximum finite stretch ("X" axis of the local strain ellipsoid). When the vein thickness is larger than 5-10 cm, tremolite fibres are frequently organised in radiate or sheaf-like aggregates (Fig. 3a), which likely record fracture opening faster than synkinematic crystal growth. In some occurrences, first phase synkinematic fibrous crystals are micro-folded or crenulated during a second tectonic phase with different kinematic axes. It is worth noting that in this case, the second tectonic event generated antigorite only. Tremolite also appears 320 in poly-mineral associations with antigorite, Mg-chlorite and magnetite in heaps and reaction structures.
- 

#### **4.2. Lower Eocene dykes**

 Lower Eocene supra-subduction magmas intruded the pre-existing fracture network as shown by the zig-zag geometry of some dykes (Cluzel et al. 2006); therefore, a relationship with serpentinization may be suspected (e.g., Python et al. 2011). However, not all dykes display lizardite walls and some of a zigzag geometry, display serpentinized and unserpentinized walls, depending upon fracture orientation. The only (scarce) occurrences of reaction rims around Eocene dykes are composed of relatively coarse-grain anthophyllite or Mg-chlorite. Therefore, lizardite "black walls" formed before dyke intrusion and cannot be related to peridotite-magma interaction. In a few locations (Poro, Kopeto) dm- to m-thick "dykes" are composed of whitish massive

- material dominated by tremolite. Samples from these localities display high Ti and Al contents (eg.
- sample POR1b, see below) and are probably deeply altered HFSE-depleted felsic dykes (Cluzel et al.

334 2012), which contain no zircons that could be dated. Remarkably, the two tremolite types,

335 synkinematic and reaction-type coexist on these outcrops, a fact that suggests a genetic relationship. 

#### **4.3. Structural analysis of lower Eocene dykes and tremolite-antigorite veins**

 Crosscutting dykes are found at all levels of the ophiolite, except in gabbronorite cumulates, which are crosscut by IAT dolerites only. Strongly fragmented dykes are also present in the 340 porphyroclastic serpentinite sole, whereas they are well preserved in the rest of the Peridotite Nappe. It is worth noting that in contrast with Late Oligocene granitoids (Cluzel et al. 2005; Paquette 342 and Cluzel 2007) Eocene dykes never crosscut the parautochthonous or autochtonous basement of the ophiolite, a feature consistent with their pre-obduction character. Most dykes trend NW-SE (av. N140°E) and NNE-SSW (av. N30°E), and some sills intruded parallel to the peridotite foliation. Their orientations are roughly consistent with the main structural trends of the Peridotite Nappe and locally, sub-parallel to antigorite and tremolite-bearing veins, but they rarely coexist. Most ultramafic, mafic and felsic intrusive rocks are medium to coarse grained and locally display pegmatite texture; in contrast, dolerites are fine-grained and often display chilled margins. Thin medium-temperature reaction rims with anthophyllite, talc, and chlorite, develop around most coarse-grained felsic dykes. In contrast, chilled margins of the younger dolerite dykes unambiguously show that they were emplaced at lower host rock temperatures. Locally (Massif du Sud, Ouen Isl.), coarse-grained diorite and hornblendite dykes are severely deformed and display ductile strain features including high-temperature foliation marked by amphibole preferred orientation, boudinage and stretching, plagioclase-hornblende banding and locally isoclinal folding (Ouen Isl.), evolving internally toward lower-temperature mylonite and cataclastic mylonite. Shallow dipping stretching lineation and/or hornblende preferred orientation suggest strike-slip or oblique slip tectonics; i.e., sinistral-reverse motion along N150°E trending dykes (Soret et al. 2016). U-Pb dating of zircon gave 358 magmatic ages at ~55-52 Ma (Cluzel et al. 2006) close to <sup>40</sup>Ar/<sup>39</sup>Ar hornblende cooling ages at ~55 Ma (Soret et al. 2016). The occurrence of internal ductile textures suggests synkinematic intrusion in a transcurrent tectonic regime. This event is thus slightly younger than amphibolites of the metamorphic sole, which record subduction initiation at ca. 57-56 Ma (Cluzel et al. 2012; Soret et al. 2016). It is worth noting that IAT dolerite dykes, which occur at about the same level of the Peridotite Nappe never display such tectonic features and thus post-date this event at ca. 50 Ma (Cluzel et al. ; Cluzel and Jourdan unpubl.  $40Ar/39Ar$  data). These data also suggest significant unroofing of the Peridotite Nappe during the 55-50 Ma interval. Most dykes apparently escaped the mineral transformations that commonly affect the host

peridotite and have well preserved magmatic mineralogy; however, some display secondary

- development of epidote, albite and green amphibole (Rodgers 1973a, 1973b; Rodgers and Bevan
- 1974; Maurizot and Lesimple 2012) depending upon local thermal anomalies and/or fluid-rock ratio.

Therefore, the elemental mobility associated with greenschist alteration is likely to have occurred

during or soon after dyke emplacement.

 The oblique arrangement of the kinematic axes deduced from antigorite and tremolite-antigorite shear veins (Iseppi 2018) is consistent with the development of the oblique subduction postulated on the basis of paleogeographic and tectonic evidence (Cluzel et al. 2001; Maurizot and Cluzel 2014). Meanwhile, the development of "extensional" strain (i.e. shallow dipping stretching axis) in the upper plate of the subduction/obduction system is consistent with stress orientation in the upper plate in shallow subduction settings (Chemenda et al. 2000; Espurt et al. 2008; Gutscher et al. 2000; McCaffrey et al. 2000; McNulty and Farber 2002). Overall, it is consistent with the tectonic features that may develop at subduction inception (Fig. 15).

 At island scale, the fracture network of the Peridotite Nappe shows a N130°E dominant trend, associated with subordinate N090°E, N045°E and N000°E directions (Leguéré 1976; Moutte and Paris 1977) that control most geomorphological features. At outcrop scale and near the base of the nappe, peridotites are affected by dense and complex fracture sets, which are probably due to several superimposed tectonic events during obduction and exhumation to shallow depth. Brittle failure at low lithostatic pressure accounts for changing stress ellipsoids and complex joint patterns. In contrast, antigorite and tremolite-antigorite veins, which characteristically have several meters to several tens of meters spacing and have been filled at relatively high temperature, display consistent structural orientations and likely originated from the same tectonic events independently of obduction.

 Tremolite and antigorite appear in tension cracks, strike-slip, normal or reverse faults related to the frictional reactivation of pre-existing fractures. Inversion of fracture data from the Massif du Sud 392 yields a sub-horizontal stretching axis of the strain ellipsoid with a roughly N-S ( $\pm$  20°) orientation. In contrast, in the klippes of the northwest coast (Koniambo and Tiebaghi), the stretching axis is oriented WNW-ESE (Iseppi 2018). In general, the shortening axis, although variably oriented, is steeply dipping. The strain ellipsoid denotes transtensional setting in the upper plate of the subduction consistent with inception of oblique subduction (Gurnis et al. 2004; Gutscher et al. 2000). 

**5. Analytical results** 

**5.1. Whole-rock geochemistry**

 Sampling has been undertaken in several nickel open pit mines throughout New Caledonia and ten samples from the Poro mine (east coast) judged representative, have been selected for chemical 402 analysis (Table 2). Seven of these samples had been identified in the field as tremolite and three as antigorite taken for comparison. It appeared thereafter that most samples were not pure mineral phases but actually a mix of tremolite and other minerals (talc-chlorite, antigorite). By comparison

 with theorical tremolite, only two samples are close to the pure end-member with only a limited amount of Fe/Mg substitution, which accounts for the pale green colour of some prismatic crystals. In a general fashion, trace elements contents in serpentinized harzburgite and dunite are very 408 low; similarly, REE contents of most antigorite samples are extremely low and below the detection 409 limit of routine analysis. However, the tremolite-bearing samples have contents higher than serpentines; specifically, REE could have been analysed with a good accuracy by ICP-MS analysis. The specific behaviour of Eu is worth noting; REE patterns of tremolite-bearing veins display positive Eu anomalies (Fig. 8), which contrast with the negative anomaly of most felsic dykes due to feldspar fractionation.

#### **5.2. Mineral chemistry**

 Microprobe analyses of syntectonic tremolite needles/fibres on polished thin sections show some 417 variability without clear connection with location or textural features. On the Fe/(Mg+Fe<sup>2+</sup>) vs. total Si binary diagram (Leake 1968, Leake et al. 1997; Hawthorne et al. 2012), the analysed amphiboles (Table 3) dominantly plot in the domain of tremolite and alternatively in the tremolite-hornblende 420 domain (Fig. 9) with a strong negative correlation between Mg# and total Si. Chromium content also 421 displays a close negative correlation with Si content (Fig. 10a) and a positive correlation with  $X_{FeA}$  (Fig. 422 10b), which both are indicative of increasing T° of crystallization. High-Mg chlorites associated with 423 tremolite in some veins (0.29 < Fe<sub>tot</sub> < 0.34; 9.67 < Mg < 9.92) may be termed penninites according to Hey's classification (Hey, 1954); they are referred herein to as Mg-chlorites.

#### **5.3. Strontium isotopes**

 The <sup>87</sup>Sr/<sup>86</sup>Sr ratio is a possible marker of the origin of Ca in tremolite because Ca and Sr display 428 similar geochemical behaviour. The very low Ca and Sr content of antigorites makes the analysis 429 difficult as Sr contents are often below the detection limit of routine analysis (0.1 ppm). Therefore, more analyses have been performed on purified minerals to get more accurate data to build the Sr 431 vs. 87Sr/86Sr diagram. On the Sr and Ca vs. 87Sr/86Sr diagrams (Fig. 11; Table 4), tremolite-bearing veins 432 plot in a narrow array with a negative slope (Fig. 11). The  ${}^{87}Sr/{}^{86}Sr$  ratios of almost pure tremolite (CaO= 9-12 wt%; Sr= 4-9 ppm) are in the range of 0.7042-0.7045. In contrast, antigorites, which have very low Ca (0.002 wt%-0.01 wt% CaO) and Sr contents (0.03 ppm-1.4 ppm) display a wider range of 435 highly radiogenic 87Sr/86 Sr ratios (0.7062-0.7116) without clear correlation with Ca or Sr contents. 

#### **5.4. Oxygen and hydrogen isotopes**

 Tremolite and serpentine minerals likely were in isotopic equilibrium with circulating/pore water during their crystallization; therefore, isotopic compositions of minerals reflect that of water (Méheut et al. 2010). Fresh tremolite and antigorite were carefully selected by hand picking and

 analysed for oxygen and hydrogen isotopes, compared to weathered specimens and data from Ni-442 rich and Ni-poor supergene silicates: "garnierite" (an informal mixture of Ni-rich serpentine, talc and smectite) of New Caledonia (Amisse et al. 2010); and deweylite (Wenner and Taylor 1974) (Table 5). 444 Isotopic ratios were plotted on the δD vs.  $\delta^{18}$ O diagram (Fig. 12). Fresh tremolites (av.  $\delta^{18}$ O = 6.8‰;  $\delta$ D = -54.8‰) and antigorites (av.  $\delta^{18}$ O = 6.4‰;  $\delta$ D =-46.0‰) from this study plot in a narrow field similar to that of "continental antigorites" of Wenner and Taylor (1974); in contrast, tremolite and 447 antigorite from the weathering profile of the same sites, have lower  $\delta D$  (-60‰ to -110‰) at 448 somewhat constant δ<sup>18</sup>O. Fresh tremolite and antigorite have higher δ<sup>18</sup>O and lower δD than supergene silicates (Amisse et al. 2010).

 Serpentinites of the tectonic sole characteristically display supergene isotopic signatures (Ulrich 2010), which may due to infiltration of meteoric waters during obduction (Quesnel et al. 2013, 2016) or alternatively, post-obduction (i.e. post-kinematic) rock-water interaction. In any case, field evidence shows that tremolite-bearing veins predate and have no genetic relationship to the brittle shearing and fracture development related to obduction. Therefore, fresh tremolite and antigorite veins have been most likely formed in endogenous conditions and did not interact with meteoric water.

#### **6. Discussion**

 Tremolite- and antigorite-bearing veins from the Peridotite Nappe of New Caledonia display geochemical and isotopic features that drastically contrast with their host rocks. Prominent enrichment of tremolite-bearing veins in some major and trace elements compared to serpentinized 462 peridotites, and the synkinematic character of fracture infill suggest that they likely formed at depth through a metasomatic process in connection with minor tectonic events. Their geochemical and isotopic composition thus results from the interaction of several potential solid and fluid sources, the role of which may vary through time. Solid sources are represented by the variably serpentinized peridotite host rocks and the lower Eocene dykes which crosscut them, while fluid sources may be 467 the fluids that circulated in the supra-subduction mantle; i.e., mostly aqueous fluids released by slab dehydration.

#### **6.1. Textural features, relative chronology and temperature constraints**

 Much attention has been paid to ultramafic terranes having undergone HP-LT metamorphism in 472 subduction/collision zones. For example, the stability fields of serpentine minerals have been mainly defined at high pressure (e.g., Debret et al. 2013; Deschamps et al. 2013; Schwartz et al. 2013; Padrón-Navarta et al. 2010, 2013). In contrast, data from low-pressure ultramafic terranes are 475 scarce, except those retrieved by ocean drilling programs, which generally correspond to serpentinite 476 bodies exhumed at magma-poor extensional systems or at transform faults. The Peridotite Nappe of

477 New Caledonia is a supra-subduction ophiolite (see geological setting above and Fig. 15) and

478 although there are no precise P-T constraints available, its evolution lacked high pressure conditions and is probably similar to "oceanic" terranes at least during the first steps.

 Syntectonic antigorite and tremolite-antigorite bearing veins crosscut and frequently reactivate (re-open) lizardite veins formed during "primary" pervasive serpentinization. Instead of static pseudomorphic replacement of the high-temperature parageneses (olivine + Opx) by relatively low- temperature lizardite and brucite, they record shearing deformation due to a low-strain tectonic event. Some tremolite-bearing veins display final crystallization of antigorite. Thus, a rough 485 chronology may be established as follows: 1) early tremolite (mostly erased); 2) static lizardite ( $\pm$  chrysotile); 3) synkinematic antigorite or antigorite + tremolite, 4) synkinematic antigorite solely, 5) supergene minerals.

 In spite of some uncertainty on boundaries, this mineral sequence allows some constraints on the evolution in temperature to be proposed. The upper stability limit of lizardite (± chrysotile) at low pressure (< 0.4 GPa) is established to about 300-320°C (Evans, 2004), while antigorite stability starts at about 320°C and persists up to 500-550°C (Wenner and Taylor, 1971). At low to medium pressure 492 (0.1-0.5 GPa) tremolite appears at 350-550°C and disappears at 400-650°C depending on the CO<sub>2</sub> partial pressure (Jenkins 1983; Chernosky et al. 1998; Evans 2004; Evans et al. 2000, 2013). 494 Therefore, the relative chronology above records: 1) a net increase in temperature after primary serpentinization, during the formation of tremolite-antigorite-bearing veins; 2) a gentle temperature decrease at the end of tremolite crystallization; and 3) a final temperature decrease down to supergene conditions (ca. 50-35°C).

 The total thickness of the Peridotite Nappe does not exceed 2 km; therefore, a depth-dependent variation of temperature is unlikely and with the exception of chrysotile, which seems to be more concentrated near the tectonic sole, there is no specific location for tremolite- or antigorite-bearing veins.

#### **6.2. Selective input of incompatible trace-elements record of tremolite-bearing veins**

 Tremolite-bearing veins are generally enriched by about 10 to 100 times in REE and incompatible elements compared to peridotite host rock and commonly display positive Eu (Fig. 8) and negative Zr-Hf anomalies (Fig. 13).

 Positive Eu anomalies have been described in peridotite-hosted hydrothermal fluids (Allen and Seyfrid 2003, 2005; Schmidt et al. 2007) and in serpentines of mid-oceanic ridges (German et al. 1999; Douville et al. 2002; Paulick et al. 2006, Ningthoujam et al. 2012) and thus, early hydrothermal circulations could be a source for REE. However, Eu anomalies do not appear in serpentinized dunites and harzburgites of the Peridotite Nappe and only secondarily silicified and carbonated rocks 512 of the serpentinite sole display bulk REE enrichment (~10 times) especially in LREE (Ulrich 2010; Fig.

7). Rare Earths Elements patterns of moderately silicified and carbonated serpentines

 characteristically display Ce negative anomalies. This feature is diagnostic of REE enrichment of supergene origin because Ce<sup>4+</sup> is residual during oxidizing alteration and accumulates with hematite on top of the weathering profile (Braun et al. 1990); therefore, supergene fluids circulating from the weathering profile were probably Ce-depleted. Thus, high REE content of tremolite-bearing veins is likely unrelated to supergene alteration and of probable hydrothermal origin, the hydrothermal fluids having interacted with feldspar in order to acquire a positive Eu anomaly. Owing to the relative chronology established above, REE enrichment most likely appeared after primary serpentinization, during subsequent water-wall rock interaction.

522 Although tremolite-bearing veins have obviously not been generated by magmatic processes, the 523 contrasting behaviour of Eu compared to other REE is possibly a key for REE provenance. The REE patterns of tremolite-bearing veins analysed in this study, display a positive Eu anomaly, which has 525 the same order of magnitude regardless of the bulk REE content. Eu anomalies in tremolite-bearing veins may have been caused by precipitation of tremolite from solutions which had already 527 developed Eu anomalies. Therefore, a positive Eu anomaly in tremolite may possibly come from reaction with fluids having altered a plagioclase-rich rock such as a gabbro cumulate or a felsic dyke. Assessing the enrichment of tremolite veins in some trace-elements compared to

 peridotites/serpentinites is not always possible because some trace-element abundances in the 531 latter are below the standard detection limit (Secchiari et al. 2019; table 2). When measurable, this 532 enrichment is not uniform and prominent depletion appears in HFSE (Nb, Ta, Zr and Hf), some of which are below the detection limit of standard ICPMS whole rock analysis (Table 2). HFSE depletion is a common feature of subduction zone magmatism, and generally interpreted to result from the occurrence of HFSE-retaining residual minerals in the subducting slab (e.g. Garrido et al. 2005; Holm et al. 2016; Munker et al. 2004 ; Rubatto et al. 2003; Woodhead et al. 2011); consequently, HFSE- depleted fluids are transferred toward the mantle wedge. Therefore, fluids directly emitted by the subduction could have circulated in the supra-subduction mantle (Fig. 14b) and generated tremolite- antigorite veins with a similarly HFSE-depleted signature. However, strontium, oxygen and hydrogen isotopic features of tremolite are not consistent with direct slab derivation and point to a "magmatic" signature (see 6.4 and 6.6 below).

 In contrast to most subduction zone magmatic rocks, Eocene supra-subduction dykes of the 543 Peridotite Nappe dominantly display strong positive Zr and Hf anomalies ( $\sim$ 10 times) and contain abundant magmatic zircons (Cluzel et al. 2006). Hydrothermal fluids circulating in fractures hosting Eocene dykes may be relatively depleted in certain elements contained in refractory minerals and 546 this is possibly the case for Hf and Zr captured by zircon and other Hf- and Zr-retaining minerals. At moderate temperature within the tremolite stability domain (<600°C), Ca and other mobile elements may have been leached from dykes, while magmatic zircons remained unaffected, thus resulting in

 Zr-Hf depletion in circulating fluids. In contrast, leaching of peridotites or felsic cumulates (gabbronorites), which do not contain zircon would not result in such a feature and thus can be discarded. Preferential Ca leaching may also be expected by autometamorphism of some dykes. By 552 the end of crystallization, supercritical hydrous fluids originally contained in the magma (2% to 10% depending upon magma composition) are ejected at sub-solidus temperatures. This process was likely responsible for the appearance of secondary amphibolite to greenschist facies parageneses in some dykes and favoured the development of ductile tectonic features (banding, preferred orientation, isoclinal folding, mylonitization) within some dykes, which did not appear in the peridotite host

- 
- 

#### **6.3. Origin of antigorite veins, constraints from Sr isotopes.**

 The <sup>87</sup>Sr/<sup>86</sup>Sr ratio in harzburgites and lherzolites of the Peridotite Nappe, which are the most common wall rocks of antigorite and tremolite-bearing veins, covers a relatively large range (0.7049- 0.7077) (Secchiari 2016; Secchiari et al. 2019) and a certain role of "primary" serpentinization may be suspected. However, there is no correlation between the LOI, which could represent the degree of 564 primary serpentinization and Sr isotope ratio of unserpentinized (LOI= 0%-0.7%;  $\binom{87}{5}$ r/ $\binom{86}{1}$ = 0.7077-565 0.7054) and moderately serpentinized lherzolites and harzburgites (LOI= 6.0%-10.7%;  $(^{87}Sr)^{86}Sr$ )<sub>i</sub> = 0.7075-0.7049) (Seccchiari et al. 2016; 2019). Thus, a moderate amount of primary serpentinization does not significantly change the Sr isotope ratio of peridotites. Therefore, serpentinization cannot 568 be directly responsible for the radiogenic character and variability of the  $87$ Sr/ $86$ Sr ratio of New Caledonia's peridotites, which are thus likely due to slab-derived magma input (Secchiari et al. 2019). As far as shear- or pressure-solution origin is considered for antigorite veins, the Sr isotope composition of antigorite is expected to reflect the variability of peridotite wall rock, pending some 572 influence of circulating fluids. However, the Sr/ $86$ Sr of antigorite veins is much higher than that of peridotites (up to 0.7117), close to the present ocean water composition and even much higher than that of lower Eocene waters (Murthy and Beiser 1968; Elderfield 1986; Veizer 1989; McArthur et al. 2012). These values are slightly lower than that of hemi-pelagic terrigenous sediments (e.g. McLennan et al. 1990; Hemming et al. 2007) and infer sediment-water mixing/leaching. Thus, the 577 highly radiogenic 87Sr/86 Sr ratios from antigorite veins (Fig. 11) may reflect some influence of subducted sediments on the fluids emitted by the subduction zone, which infiltrated the supra- subduction mantle and were involved in antigorite crystallization. The nature of involved sediments remains unknown; however, Late Cretaceous sediments similar to those included in the Poya Terrane; abyssal argillites associated with basalts and hemipelagic turbidites of the Kone Facies, are 582 good candidates for the source of high Sr/ $86$ Sr fluids. At that stage, there are no constraints on the mechanisms and P-T conditions of fluid release from the slab.

#### **6.4. Origin of Ca in tremolite-bearing veins, constraints from Sr isotopes.**

586 Tremolites from veins and pockets plot in a narrow field with low Sr/ $86$ Sr (0.7042-0.7045), that clearly differ from the isotopic signatures of lherzolites and harzburgites; thus, a direct origin of Ca by leaching of peridotites is unlikely. Alternatively, tremolite seems to have been in equilibrium with 589 "magmatic" fluids (Fig. 11); a feature consistent with  $\delta^{18}$ O and  $\delta$ H values (see below), even though a certain influence of ocean-like water cannot be excluded. The "sedimentary" signature of antigorite veins, possibly derived from subduction-related fluids (see 6.3 above), was probably diluted in tremolite-bearing veins, which contain 100 to 1000 times more Sr than antigorite.

 A comparison with exhumed serpentinites of the Atlantis Massif (Boschi et al. 2008) shows that similar trends may exist in oceanic ridge environments; variable Ca-Sr contents at high and constant Sr/ $86$ Sr ratio record metasomatism from oceanic water/sediments, while additional Ca-Sr 596 enrichment with decreasing Sr/ $86$ Sr signals some influence of (crustal ?) magmatic rocks (Fig. 11). It is unlikely that tremolite formed by direct reaction of felsic magma with serpentinized wall rock, because in all observed reaction rims around dykes, anthophyllite and/or Mg-chlorite are formed instead of tremolite. In the frequent absence of direct contact between felsic dykes and tremolite veins or pockets, it may be suggested that tremolite merely formed by reaction between hydrous fluids released by the subduction zone and having leached the still hot felsic dykes and the serpentinized wall rocks of active shears or tension cracks. This may account for the compositional variability, REE contents 10 times lower than that of dykes and the presence of large amounts of compatible elements taken from fracture walls. Thus, three end-members are likely involved in the formation of tremolite: 1) an aqueous fluid emitted from the subduction zone and somewhat influenced by sediments; 2) a REE-poor and compatible elements-rich ultramafic end-member that displays variable Sr isotope signature; and 3) a REE-rich magmatic end-member with a mantle-like isotopic signature, which very much resembles Lower Eocene dykes, or fluids evolved from these dykes.

- 
- 

#### **6.5. High Cr contents and wall rock involvement**

 An important geochemical feature of New Caledonia tremolites is the high content of compatible trace elements such as Cr (Fig. 9). Cr is relatively immobile in hydrothermal and supergene systems and should appear in tremolite with moderate contents only. Whole-rock analysis of tremolite- bearing veins revealed high Cr contents (2,800 – 3,300 ppm), which may be due to Cr contained in newly crystallized (syn-kinematic) minerals, or alternatively, to residual chromite. However, 617 microprobe analyses of tremolites display up to 2.6 wt%  $Cr_2O_3$  (Table 3). Cr content correlates negatively with total Si (Fig. 10a) and positively with Fe content (XFeA = 100(Fe+Mn)/(Fe+Mn+Mg) (Fig. 10b), a feature that suggests increasing Cr incorporation with higher temperature. The

polymineralic tremolite-bearing veins and pockets coming from the replacement of peridotite along

 fractures contain residual streaks of chromite, which display evidence for Cr mobility. Altered chromites are generally composed of a residual chromite core rimmed by a microcrystalline association of chromite and Cr-rich magnetite (Fig. 13). Fe-Cr substitution giving birth to Cr-rich magnetite may be responsible for Cr mobility and its incorporation into tremolite. Therefore, high Cr contents in tremolite may be explained by an intervening Cr-rich end-member during water rock interaction, which is most likely the peridotite wall rock.

627 The mobility of Cr in hydrous fluids strongly depends on its oxidation state; whereas  $Cr^{3+}$  species 628 are relatively immobile,  $Cr^{6+}$  are highly mobile (e.g. James, 2003). Thus chromite dissolution and formation of Cr-rich magnetite rims around inherited chromite grains needs oxidizing fluids consistent with the preferential leaching of Eu from felsic dykes and occurrence of positive Eu anomalies in tremolite. Oxidized character is a feature of fluids emitted by subduction zones that involve highly serpentinized upper mantle rocks (Evans et al. 2017). Nothing is known about the degree of primary serpentinization of the lower plate of the subduction/obduction system of New Caledonia, which has totally disappeared in the subduction zone, whereas its partial preservation in the exhumed eclogitic melange (Pouebo Terrane) is problematical. However, considering that the degree of serpentinization of the upper and lower plates might have been identical prior to subduction inception, it may be postulated that an important part of the serpentinization of the Peridotite Nappe was acquired prior to subduction and is unrelated to obduction.

#### **6.6. Origin of the tremolite- and antigorite-precipitating fluids**

641 The  $\delta^{18}$ O and  $\delta$ D of hydrous minerals result from complex balance of several parameters: the 642 isotopic composition of the wall rock, the water/rock ratio, mineral-water fractionation coefficients, isotope ratios of circulating water, and temperature. In this study, a probable temperature of tremolite-antigorite formation can be estimated in the range 300-450°C (end of section 6.2). Under 645 these temperatures, tremolite and serpentine minerals should display comparable  $\delta^{18}$ O values as an 646 equilibrium isotopic fractionation of about  $\delta^{18}$ O <sub>Trem-Serp</sub> = -0.3‰ is expected (Zheng, 1993). The mean  $8^{18}$ O values depicted above (6.8‰ and 6.4‰ for tremolite and antigorite, respectively, 648 corresponding to  $\delta^{18}O_{\text{Term-Serp}} = +0.4\%$ ) are somewhat at variance with the theoretical equilibrium. In fact, in the crystallizing sequence (end of section 6.2), we argue for a slight temperature decrease at the end of tremolite crystallization. All other things equal, this should imply a small increase of the 651 isotopic fractionation between tremolite and water, and thus an increase in the  $\delta^{18}$ O value of 652 tremolite. The fact that tremolite is actually slightly enriched ( $\delta^{18}$ O = 6.8‰) in <sup>18</sup>O relative to 653 antigorite ( $\delta^{18}$ O = 6.4‰) is consistent with a small temperature decrease. It remains that, at first order, both minerals likely crystallized in equilibrium with a unique aqueous reservoir. Assuming then that fluid was in excess at the time of vein formation (i. e., the

656 fluid/rock ratio is isotopically infinite, which was very likely in the case of the studied veins), the  $\delta^{18}$ O

 value of the invading fluid can be estimated between 6.5‰ and 8.5‰ (using the fractionation factors between H2O and serpentine and antigorite between 300 and 450°C from Zheng, 1993). These values are consistently expected for the fluids involved in supra-subduction contexts, like the one prevailing for the formation of the studied veins. Indeed, these fluids, originally derived from seawater, underwent significant isotopic exchange with crustal and mantle rocks, as shown by the Sr 662 isotope and REE systematics of vein minerals, which results in increasing their initial, low  $\delta^{18}$ O value. 663 A magmatic contribution to the fluid budget that would add a high- $\delta^{18}$ O component (about 7‰) to the fluid is permitted by the data.

 From the observations presented above, it appears that lizardite formed during the primary serpentinization did not significantly recrystallize when the rock went into the antigorite stability field. It should be kept in mind that lizardite and antigorite may coexist at low pressure depending upon serpentine composition (e.g., Caruso and Chernosky 1979; O'Hanley et al. 1989; Schwartz et al. 2013). However, antigorite fibres in the study are nucleated on lizardite "black walls" and partly originated from the destabilization of lizardite as shown by the accumulation of iron oxide at the lizardite-antigorite interface (Fig. 4c & 4d). However, the pervasive replacement of "primary" lizardite by antigorite would require an unlikely large water/rock ratio given the relative impermeability of lizardite coatings and restriction of fluid circulation along open fractures. It is worth noting that some serpentine samples from open pit mines did not escape tropical weathering and yield strongly negative δD ratios similar to that of supergene silicates. In order to evaluate the effect of weathering, four samples of the same steep antigorite vein were taken across the weathering profile of Vulcain mine. Upward decreasing δD values (-38.7‰ > δD > -107.2‰; Table 5) unambiguously show that only unweathered antigorites taken in the bedrock retain their original isotopic signature. In addition, rocks of the serpentinite sole display strongly negative δD (- 80‰<δD<-105‰) (Fig. 12; Ulrich 2012); thus, these otherwise unweathered rocks have been

- profoundly modified by fluids of supergene origin as also shown by their negative Ce anomaly.
- 

#### **7. Conclusion**

 The formation of tremolite- and antigorite-bearing veins recorded an elevation of temperature compared to the initial oceanic (primary) serpentinization of peridotites, which was marked by the formation of lizardite and minor chrysotile; therefore, a heat source is needed as well as a source for Ca. This event was associated with shear/tensile reactivation of pre-existing joints already coated by lizardite.

689 The widespread antigorite-bearing low-Ca veins bear highly radiogenic Sr $/86$ Sr signatures, which record some influence of subducted sediments. In contrast, this "sedimentary" signature is diluted in high-Ca tremolite, which probably comes from Ca input of direct or indirect magmatic origin. The Sr 692 isotope signature of tremolite, the REE abundance, the  $\delta^{18}$ O and  $\delta$ D values, all suggest that the Ca

 source was the supra-subduction Early Eocene felsic dyke system and thus indirectly, the subducted slab. Europium positive anomaly and paradoxically high contents of some compatible elements (Cr) suggests that Ca was carried by oxidized hydrothermal fluids that leached the dykes and interacted with Cr-rich wall rock (serpentinized peridotite). These features provide a constraint on the timing of tremolite crystallization, because supra-subduction dykes intruded peridotites within a narrow span of time at ca. 55-50 Ma (U-Pb zircon; Cluzel et al. 2006). Since these dykes are mostly slab melts and boninite-series magmas that formed shortly after subduction inception (Cluzel et al. 2012, 2016), already existing fractures were reactivated in an oblique-extensional regime under relatively high fluid pressure and gave way to magma and laterally/upward to Ca-bearing fluids when the young and 702 buoyant slab had to force its way beneath the nascent fore-arc lithosphere (Fig. 14). The heat source needed for crystallizing tremolite and antigorite after lizardite was likely provided by the injection of supra-subduction slab melts. The coexistence of tremolite and antigorite in the same fracture fillings, and thereafter crystallization of antigorite solely, could signal the exhaustion of magmatic fluids, while synkinematic crystallization associated with small-scale fault motion and tension cracks was continuing. It also signals that tremolite and antigorite veins were related to the same tectonic event, whereas only fluid composition differed through time.

 Therefore, independent of decreasing-upward serpentinization due to the obduction of the Peridotite Nappe, the development of tremolite-antigorite veins may be related to a three-step evolution: i) the "oceanic" period (Late Cretaceous-Paleocene), during which static serpentinization developed along cooling joints (Fig. 14a); ii) at subduction inception (latest Paleocene), when the injection of slab-derived supra-subduction magmas and fluids, together with semi-brittle shearing due to tectonic deformation of the upper plate of the system generated the tremolite-antigorite vein system (Fig. 14b); finally, iii) the fluid-assisted melting of the supra-subduction mantle generated strongly depleted melts, the fractionation of which resulted in gabbronorite cumulates (Fig. 14c) that now represent the only remnants of fore-arc crust.

#### **Acknowledgements**

 This study is a contribution of CNRT Nickel et son Environnement research programs « Amiante- serpentinisation et fibrogenèse dans les massifs de péridotite de Nouvelle-Calédonie » and « Ophiostruct-Connaissance de l'ophiolite, structure et géophysique aéroportée ». T. Rigaudier (CRPG, Vandœuvre-lès-Nancy, France) is warmly thanked for assistance in isotope analyses. We acknowledge Professor Katy Evans and an anonymous reviewer for their constructive reviews. 

- 
- 



Beach A (1977) Vein arrays, hydraulic fractures and pressure-solution structures in a deformed

flysch sequence S.W. England. Tectonophysics 40: 201-225 https://doi.org/10.1016/0040-

1951(77)90066-X

Bell DR and Ihinger PhD (2000) The isotopic composition of hydrogen in nominally anhydrous

mantle minerals. Geochimica et Cosmochimica Acta 64: 2109–2118 https://doi.org/10.1016/S0016-

7037(99)00440-8

- Bigeleisen J, Perlman ML and Posser HC (1952) Conversion of hydrogenic materials to hydrogen
- for isotopic analyses Analytical Chemistry 24: 1356–1357 https://doi.org/10.1021/ac60068a025
- Bons P and Jessell M (1997) Experimental simulation of the formation of fibrous veins by
- localised dissolution–precipitation creep Mineralogical Magazine 61: 53–63
- Boschi C, Dini A, Früh-Green GL and Kelley DS (2008) Isotopic and element exchange during
- serpentinization and metasomatism at the Atlantis Massif (MAR 30°N): Insights from B and Sr isotope

data. Geochimica et Cosmochimica Acta 72: 1801-182[3 https://doi,org/10,1016/j,gca,2008,01,013](https://doi,org/10,1016/j,gca,2008,01,013)

- Braun JJ, Pagel M, Muller JP, Billong P, Michard A and Guillet B (1990) Cerium anomalies in
- lateritic profiles. Geochimica et Cosmochimica Acta 54: 781-795 https://doi.org/10.1016/0016-
- 7037(90)90373-S
- Butt CW and Cluzel D (2013) Laterite Nickel ore deposits: weatherered serpentinites. Special
- Issue "serpentines" Elements 9: 123-128 https://doi.org/10.2113/gselements.9.2.123
- 781 Caruso LJ and Chernosky JV Jr. (1979) The stability of lizardite. Canadian Mineralogist 17: 757-
- 769.
- Chemenda A, Lallemand S and Bokun A (2000) Strain partitioning and interplate friction in
- oblique subduction zones: Constraints provided by experimental modelling. Journal of Geophysical
- Research 105: 5567–5581 https://doi.org/10.1029/1999JB900332
- Chernosky JV, Berman RG and Jenkins DM (1998) The stability of tremolite: new experimental
- data and a thermodynamic assessment. American Mineralogist 83: 726-739
- https://doi.org/10.2138/am-1998-7-805
- Clayton RN and Mayeda TK (1963) The use of bromine pentafluoride in the extraction of oxygen
- from oxides and silicates for isotopic analysis. Geochimica et Cosmochimica Acta 27: 43-52
- [https://doi.org/10.1016/0016-7037\(63\)90071-1](https://doi.org/10.1016/0016-7037(63)90071-1)
- Cluzel D, Bosch D, Paquette JL, Lemennicier Y, Montjoie Ph and Ménot RP (2005) Late Oligocene
- post-obduction granitoids of New Caledonia: a case for reactivated subduction and slab break-off.
- The Island Arc 14: 254-271 https://doi.org/10.1111/j.1440-1738.2005.00470.x
- Cluzel D, Meffre S, Maurizot P and Crawford AJ (2006) Earliest Eocene (53 Ma) convergence in
- the Southwest Pacific; evidence from pre-obduction dikes in the ophiolite of New Caledonia. Terra
- Nova 18: 395-402 <https://doi.org/10.1111/j.1365-3121.2006.00704.x>
- Cluzel D, Jourdan F, Meffre S, Maurizot P and Lesimple S (2012) The metamorphic sole of New
- 799 Caledonia ophiolite;  $^{40}$ Ar/ $^{39}$ Ar, U-Pb, and geochemical evidence for subduction inception at a
- spreading ridge. Tectonics 31, 3 https://doi.org/10.1029/2011TC003085
- 801 Cluzel D, Ulrich M, Jourdan F, Paquette JL, Audet MA, Secchiari A and Maurizot P (2016) Early
- 802 Eocene clinoenstatite boninite and boninite-series dikes of the ophiolite of New Caledonia; a witness
- of slab-melt enrichment of the mantle wedge in a nascent volcanic arc. Lithos 260: 429-442
- <https://doi.org/10.1016/j.lithos.2016.04.031>
- 805 Cluzel D, Whitten M, Meffre S, Aitchison JC and Maurizot P (2017) A reappraisal of the Poya
- Terrane (New Caledonia). Accreted Late Cretaceous marginal basin upper crust, passive margin
- sediments and Eocene E-MORB sill complex. Tectonics 37: 48-70
- <https://doi.org/10.1002/2017TC004579>
- Collot JY, Malahof A, Recy J, Latham G and Missegue F (1987) Overthrust emplacement of New
- Caledonia ophiolite: geophysical evidence. Tectonics 6: 215-232
- <https://doi.org/10.1029/TC006i003p00215>
- Craig H (1961) Isotopic variations in meteoric waters. Science 133: 1702-1703
- <https://doi.org/10.1126/science.133.3465.1702>
- Debret B, Andreani M, Godard M, Nicollet C, Schwartz S and Lafay R (2013) Trace element
- behavior during serpentinization/de-serpentinization of an eclogitized oceanic lithosphere: A LA-
- 816 ICPMS study of the Lanzo ultramafic massif (Western Alps). Chemical Geology 357: 117-133
- <https://doi.org/10.1016/j.chemgeo.2013.08.025>
- Deschamps F, Godard M, Guillot S and Hattori K (2013) Geochemistry of subduction zone
- serpentinites: A review. Lithos 178: 96–127.<http://dx.doi.org/10.1016/j.lithos.2013.05.019>
- 820 Dorling M and Zussman J (1987) Characteristics of asbestiform and non-asbestiform calcic
- amphiboles. Lithos 20: 469-489 [https://doi.org/10.1016/0024-4937\(87\)90030-2](https://doi.org/10.1016/0024-4937(87)90030-2)
- Douville E, Charlou JL, Oelkers EH, Bienvenu P, Jove Colon CF, Donval JP, Fouquet Y, Prieur D and
- Appriou P (2002) The rainbow vent fluids (26°14'N, MAR): the influence of ultramafic rocks and
- 824 phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids. Chemical
- Geology 184: 37–48 [https://doi.org/10.1016/S0009-2541\(01\)00351-5](https://doi.org/10.1016/S0009-2541(01)00351-5)
- Durney DW (1972) Solution-transfer, an important geological deformation mechanism. Nature
- 235: 315-317 <https://doi.org/10.1038/235315a0DO>
- Durney DW (1976) Pressure-solution and crystallization deformation. Philosophical Transactions
- of the Royal Society of London. Series A, Mathematical and Physical Sciences 283, 1312, A Discussion
- 830 on Natural Strain and Geological Structure, 229-240.
- Elderfield H (1986) Strontium isotope stratigraphy. Palaeogeography, Palaeoclimatology,
- Palaeoecology 57: 71-90 [https://doi.org/10.1016/0031-0182\(86\)90007-6](https://doi.org/10.1016/0031-0182(86)90007-6)
- Espurt N, Funiciello F, Martinod J, Guillaume B, Regard V, Faccenna C and Brusset S (2008) Flat
- 834 subduction dynamics and deformation of the South American plate: Insights from analog modeling.
- Tectonics 27: TC3011 [https://doi.org/10 .1029 /2007TC002175](https://doi.org/10%20.1029%20/2007TC002175)
- Evans BW (2004) The serpentinite multisystem revisited: chrysotile is metastable, International
- Geology Review 46: 479-50[6 http://dx.doi.org/10.2747/0020-6814.46.6.479](http://dx.doi.org/10.2747/0020-6814.46.6.479)
- Evans BW, Ghiorso MS and Kuehner SM (2000) Thermodynamic properties of tremolite: A
- correction and some comments. American Mineralogist 85: 466-472 [https://doi.org/10.2138/am-](https://doi.org/10.2138/am-2000-0407)
- [2000-0407](https://doi.org/10.2138/am-2000-0407)
- Evans BW, Hattori K and Baronnet A (2013) Serpentinite: What, Why, Where? Elements 9:99-106
- <https://doi.org/10.2113/gselements.9.2.99>
- Evans KA, Reddy SM, Tomkins AG, Crossley RJ and Frost BR (2017) Effects of geodynamic setting
- 844 on the redox state of fluids released by subducted mantle lithosphere. Lithos 278: 26-42.
- <https://doi.org/10.1016/j.lithos.2016.12.023>
- Evensen NM, Hamilton P J and O'Nions RK (1978) Rare earth abundance in chondritic meteorites.
- Geochimica et Cosmochimica Acta 42: 1199–212 [https://doi.org/10.1016/0016-7037\(78\)90114-X](https://doi.org/10.1016/0016-7037(78)90114-X)
- Frost BR, Evans KA, Swapp SM, Beard JS and Mothersole FE (2013) The process of
- serpentinization in dunite from New Caledonia. Lithos 178: 24-39
- <http://dx.doi.org/10.1016/j.lithos.2013.02.002>
- German CR, Hergt J, Palmer MR and Edmond JM (1999) Geochemistry of a hydrothermal
- 852 sediment core from the OBS vent-field, 21° N East Pacific Rise. Chemical Geology 155: 65-75
- [https://doi.org/10.1016/S0009-2541\(98\)00141-7](https://doi.org/10.1016/S0009-2541(98)00141-7)
- Gurnis M, Hall C and Lavier L (2006) Evolving force balance during incipient subduction.
- Geochemistry Geophysics Geosystems 5, 7<https://doi.org/10.1029/2003GC000681>
- Gutscher MA, Spakman W, Bijwaard H and Engdahl ER (2000) Geodynamics of flat subduction:
- Seismicity and tomographic constraints from the Andean margin. Tectonics 19: 814–833
- [https://doi.org/10 .1029 /1999TC001152](https://doi.org/10%20.1029%20/1999TC001152)
- Hawthorne FC, Oberti R, Harlow GE, Maresch WV, Martin RF, Schumacher JC and Welch MD
- (2012) Nomenclature of the amphibole supergroup. American Mineralogist 97: 2031–2048
- <http://dx.doi.org/10.2138/am.2012.4276>
- Harlow GE and Sorensen SS (2005) Jade (Nephrite and Jadeitite) and Serpentinite: Metasomatic
- Connections. International Geology Review 47: 113-146 <https://doi.org/10.2747/0020-6814.47.2.113>
- Hemming SR, Van de Flierdt T, Goldstein SL, Franzese AM, Roy M, Gastineau G and Landrot G
- (2007) Strontium isotope tracing of terrigenous sediment dispersal in the Antarctic Circumpolar
- Current: Implications for constraining frontal positions. Geochemistry, Geophysics, Geosystems, 8 (6)
- <http://doi.org/10.1029/2006GC001441>
- Hey MH (1954) A new review of the chlorites. Mineralogical Magazine 30: 277-92
- Holm PM, Søager N, Alfastsen M and Bertotto GW (2016) Subduction zone mantle enrichment
- 870 by fluids and Zr-Hf-depleted crustal melts as indicated by backarc basalts of the Southern Volcanic
- Zone, Argentina. Lithos 262: 135–152 <http://dx.doi.org/10.1016/j.lithos.2016.06.029>
- **Iseppi M (2018) Polyphase brittle tectonics and structural controls of supergene nickel ore**
- deposits of New Caledonia. New exploration methods and ore deposit models. PhD Thesis University
- of New Caledonia, Noumea New Caledonia.
- Jenkins DM (1983) Stability and composition relations of calcic amphiboles in ultramafic rocks.
- Contributions to Mineralogy and Petrology 83: 375-38[4 https://doi.org/10.1007/BF00371206](https://doi.org/10.1007/BF00371206)
- Kodolányi J, Pettke T, Spandler C, Kamber BS and Gméling K (2012) Geochemistry of ocean floor
- 878 and fore-arc serpentinites: constraints on the ultramafic input to subduction zones. Journal of
- Petrology 53: 235-270<https://doi.org/10.1093/petrology/egr058>
- Koutsovitis P, Magganas A, Pomonis P and Ntaflos T (2013) Subduction-related rodingites from
- East Othris, Greece: Mineral reactions and physicochemical conditions of formation. Lithos 172-173:
- 139-157<http://dx.doi.org/10.1016/j.lithos.2013.04.009>
- Kretz R (1983) Symbols for rock-forming minerals. American Mineralogist 68: 277 279
- Kurat, G, Palme H, Embey-Isztin A, Touret J, Ntaflos T, Spettel B, Brandstätten F, Palme C, Dreibus
- G and Prinz M (1993) Petrology and geochemistry of peridotites and associated vein rocks of
- Zabargad Island, Red Sea, Egypt. Earth and Environmental Science, Mineralogy and Petrology 48:
- 309-341<https://doi.org/10.1007/BF01163106>
- Lahondère D and Maurizot P (2009) Typologie et protocole d'échantillonnage des occurrences naturelles d'amiante en Nouvelle-Calédonie. Rapport BRGM/RP-57334-FR, 164 p.
- Lahondère D, Cagnard F, Lahfid A, Wille G, Maurizot P (2011) L'amiante dans les massifs de
- péridotite de Nouvelle-calédonie. Rapport BRGM/RP-59252-FR, Rapport final, 302 p.
- Lahondère D, Lesimple S, Cagnard F, Lahfid A, Wille G and Maurizot P (2012) Serpentinisation et
- fibrogenèse dans les massifs de péridotite de Nouvelle-Calédonie. Rapport BRGM/RP-60192-FR,
- CNRT Nickel et son environnement ; Amiante program, final report, 458 p.
- Leake BE (1968) A catalog of analyzed calciferous and subcalciferous amphiboles together with
- their nomenclature and associated minerals. Geological Society of America Special Paper 98.
- Leake BE, Woolley AR, Arps CES, Birch WD, Gilbert MC, Grice JD, Hawthorne,FC, Kato A, Kisch HJ,
- Krivovichev VG, Linthout K, Laird J, Mandarino JA, Maresch WV, Nickel EH, Rock NMS, Schumacher
- JC, Smith DC, Stephenson NVN, Ungaretti L, Whittaker EJW and Youzhi G (1997) Nomenclature of
- amphiboles. American Mineralogist 82: 1019-1037
- Leguéré J (1976) Des corrélations entre la tectonique cassante et l'altération supergène des
- péridotites de Nouvelle Calédonie. PhD thesis, Université de Montpellier, France, 161 p.
- Lupker M, France-Lanord C, Galy V, Lave J, Gaillardet J, Gajurel AP, Guilmette C, Rahman M, Singh
- KS and Sinha R (2012) Predominant floodplain over mountain weathering of Himalayan sediments

(Ganga basin). Geochimica et Cosmochimica Acta 84: 410-432

<https://doi.org/10.1016/j.gca.2012.02.001>

- Marchesi C, Garrido CJ, Godard M, Belley F and Ferré E (2009) Migration and accumulation of
- ultra-depleted subduction-related melts in the Massif du Sud ophiolite (New Caledonia). Chemical
- Geology 266: 171-18[6 https://doi.org/10.1016/j.chemgeo.2009.06.004](https://doi.org/10.1016/j.chemgeo.2009.06.004)
- Marocchi M, Hermann J, Tropper P, Bargossi GM and Mair V (2010) Amphibole and phlogopite in
- "hybrid" metasomatic bands monitor trace element transfer at the interface between felsic and
- ultramafic rocks (Eastern Alps, Italy). Lithos 117: 135–148
- <https://doi.org/10.1016/j.lithos.2010.02.011>
- Maurizot P and Cluzel D (2014) Pre-obduction records of Eocene foreland basins in central New
- Caledonia (Southwest Pacific); an appraisal from surface geology and Cadart 1 borehole data. New
- Zealand Journal of Geology and Geophysics 57: 307-311
- <https://doi.org/10.1080/00288306.2014.885065>
- Maurizot P and Lesimple S (2012) Le jade de Nouvelle-Calédonie. Aspects géologiques,
- gemmologiques et archéologiques. Geological Survey of New Caledonia internal report, 24 p.
- Maurizot P, Cluzel D, Patriat M, Collot J, Iseppi M, Lesimple S, Secchiari A, Bosch D, Montanini A,
- 921 Macera P and Davies HL (in press a) The Eocene Subduction-Obduction Complex. In: Mortimer, N.
- (ed) New Caledonia: Geology, Geodynamic Evolution and Mineral Resources. Geological Society,
- London, Memoir, chapter 5
- Maurizot P, Sevin B, Lesimple S, Bailly L, Iseppi M and Robineau B (in press b) Mineral resources
- 925 and prospectivity of the ultramafic rocks of New-Caledonia. In: Mortimer, N. (ed) New Caledonia:
- Geology, Geodynamic Evolution and Mineral Resources. Geological Society, London, Memoir, chapter
- 10
- McArthur JM, Howarth RJ and Shields GA (2012) Strontium Isotope Stratigraphy. In: Gradstein F,
- Ogg J, Schmitz M, Ogg G The Geologic Time Scale 2012. Elsevier [https://doi.org/10.1016/B978-0-444-](https://doi.org/10.1016/B978-0-444-59425-9.00007-X) [59425-9.00007-X](https://doi.org/10.1016/B978-0-444-59425-9.00007-X)
- McCaffrey R, Zwick PC, Bock Y, Prawirodirdjo L, Genrich JF, Stevens CW, Puntodewo SSO and
- Subarya C (2000) Strain partitioning during oblique plate convergence in northern Sumatra: Geodetic
- 933 and seismologic constraints and numerical modelling. Journal of Geophysical Research 105(B12):
- 28363–2837[6 https://doi.org/10.1029/1999JB900362](https://doi.org/10.1029/1999JB900362)
- McLennan SM, Taylor SR, McCulloch MT and Maynard JB (1990) Geochemical and Nd-Sr isotopic
- composition of deep-sea turbidites: Crustal evolution and plate tectonic associations. Geochimica et
- Cosmochimica Acta 54: 2015-2050 [https://doi.org/10.1016/0016-7037\(90\)90269-Q](https://doi.org/10.1016/0016-7037(90)90269-Q)
- McNulty B and Farber D (2002) Active detachment faulting above the Peruvian flat slab: Geology
- 30: 567–570 https://doi.org/10 .1130 /0091-7613 (2002)030 <0567: ADFATP>2 .0 .CO;2
- Méheut M, Lazzeri M, Balan E and Mauri F (2010) First-principles calculation of H/D isotopic
- fractionation between hydrous minerals and water. Geochimica and Cosmochimica Acta 74: 3874–
- 388[2 https://doi.org/10.1016/j.gca.2010.04.020](https://doi.org/10.1016/j.gca.2010.04.020)
- Mével C (2003) Serpentinization of abyssal peridotites at mid-ocean ridges. Compte Rendus
- Geoscience 335: 825–852.<https://doi.org/10.1016/j.crte.2003.08.006>
- Monnin C, Chavagnac V, Boulart C, Ménez B, Gérard M, Gérard E, Pisapia C, Quéméneur M,
- Erauso G, Postec A, Guentas-Dombrowski L, Payri C and Pelletier B (2014) Fluid chemistry of the low
- temperature hyperalkaline hydrothermal system of Prony Bay (New Caledonia). Biogeosciences 11:
- 5687–5706 https://doi.org/10.5194/bg-11-5687-2014
- Morishita T, Hara K, Nakamura K, Sawaguchi T, Tamura A, Arai S, Okino K, Takai K and Kumagai H
- (2009) Igneous, alteration and exhumation processes recorded in abyssal peridotites and related
- fault rocks from an oceanic core complex along the Central Indian Ridge. Journal of Petrology 50 (7):
- 1299-132[5 https://doi.org/10.1093/petrology/egp025](https://doi.org/10.1093/petrology/egp025)
- Mothersole FE, Evans K and Frost BR (2017) Abyssal and hydrated mantle wedge serpentinised
- peridotites: a comparison of the 15°20'N fracture zone and New Caledonia serpentinites.
- Contribution to Mineralogy and Petrology 172: 69.<https://doi.org/10.1007/s00410-017-1381-x>
- Moutte J and Paris JP (1977) Observations nouvelles sur le grand massif ultramafique du sud de
- la Nouvelle-Calédonie. Bulletin du BRGM section IV, I-1977: 43-51
- Münker C, Wörner G, Yogodzinski G and Churikova T (2004) Behaviour of high field strength
- elements in subduction zones: constraints from Kamchatka-Aleutian arc lavas. Earth and Planetary
- Science Letters 224: 275-293 <https://doi.org/10.1016/j.epsl.2004.05.030>
- Murthy RV and Beiser E (1968) Strontium isotopes in ocean water and marine sediments.
- Geochimica and Cosmochimica Acta 32: 1121–1126[. https://doi.org/10.1016/0016-7037\(68\)90111-7](https://doi.org/10.1016/0016-7037(68)90111-7)
- Ningthoujam PS, Dubey CS, Guillot S, Fagion A-S and Shukla DP (2012) Origin and serpentinization
- of ultramafic rocks of Manipur Ophiolite Complex in the Indo-Myanmar subduction zone, Northeast
- India. Journal of Asian Earth Sciences 50: 128–134. <https://doi.org/10.1016/j.jseaes.2012.01.004>
- O'Hanley DS, Chernosky JV Jr. and Wicks FJ (1989) The stability of lizardite and chrysotile.
- Canadian Mineralogist 27: 483-493.
- Orloff O (1968) Etude géologique et géomorphologique des massifs d'ultrabasites compris entre Houailou et Canala (Nouvelle Calédonie). PhD Thesis, University of Montpellier (France), 80p.
- Padrón-Navarta JA, Hermann J, Garrido JC, López Sánchez-Vizcaíno V and Gómez-Pugnaire MT
- (2010) An experimental investigation of antigorite dehydration in natural silica-enriched serpentinite.
- Contributions to Mineralogy and Petrology 159: 25-42 <https://doi.org/10.1007/s00410-009-0414-5>
- Padrón-Navarta JA, López Sánchez-Vizcaíno V, Hermann J, Connolly JAD, Garrido JC, Gómez-
- Pugnaire MT and Marchesi C (2013) Tschermak's substitution in antigorite and consequences for
- 975 phase relations and water liberation in high-grade serpentinites. Lithos 178: 186-196
- <https://doi.org/10.1016/j.lithos.2013.02.001>
- Paquette JL and Cluzel D (2007) U-Pb zircon dating of post-obduction volcanic-arc granitoids and
- a granulite-facies xenolith from New Caledonia. Inference on Southwest Pacific geodynamic models.
- International Journal of Earth Sciences (Geol. Rundsch.) 96: 613–622
- <https://doi.org/10.1007/s00531-006-0127-1>
- 981 Paulick H, Bach W, Godard M, De Hoog JCM, Suhr G and Harvey J (2006) Geochemistry of abyssal
- peridotites (Mid-Atlantic Ridge, 15°20'N, ODP Leg 209): Implication for fluid/rock interaction in slow
- spreading environments. Chemical Geology 234: 179–210.
- <https://doi.org/10.1016/j.chemgeo.2006.04.011>
- Pearce JA (1982) Trace element characteristics of lavas from destructive plate margins. In Thorpe
- 986 R. S. (ed.). Andesites, John Wiley, Winchester pp. 528-548
- Pearce JA, Lippard SJ and Roberts S (1984) Characteristics and tectonic significance of supra-
- subduction zone ophiolites. Geological Society, London, Special Publications 16: 77-94
- <https://doi.org/10.1144/GSL.SP.1984.016.01.06>
- Pelletier B (1996) Serpentines in nickel silicate ore from New Caledonia. Nickel 96 Conference,
- Kalgoorlie, Western Australia. Expanded abstracts volume: 197-206
- Pirard C, Hermann J and O'Neil StC (2013) Petrology and geochemistry of the crust-mantle
- boundary in a nascent arc, Massif du Sud Ophiolite, New Caledonia, SW Pacific. Journal of Petrology
- 54: 1759-1792<https://doi.org/10.1093/petrology/egt030>
- Pollard DD and Segall P (1987) Chapter 8: Theoretical Displacements and Stresses Near Fractures
- in Rock: With Applications to Faults, Joints, Dikes, and Solution Surfaces, in Fracture Mechanics of
- Rock, B. Atkinson, ed., Academic Press, London, pp. 277-349
- Prinzhoffer A (1981) Structure et pétrologie d'un cortège ophiolitique: le Massif du Sud (Nouvelle
- Calédonie): la transition manteau-croûte en milieu océanique. PhD Thesis École Nationale Supérieure
- des Mines de Paris, France. 185 p.
- Python M, Yoshikawa M, Shibata T and Arai S (2011) Diopsidites and Rodingites: Serpentinisation
- and Ca-Metasomatism in the Oman Ophiolite Mantle. In: Dyke Swarms: Keys for Geodynamic
- Interpretation. Springer, Berlin, Heidelberg[. https://doi.org/10.1007/978-3-642-12496-9\\_23](https://doi.org/10.1007/978-3-642-12496-9_23)
- Quesnel B, Boulvais P, Gautier P, Cathelineau M, John CM, Dierick M, Agrinier P and Drouillet M
- (2016) Paired stable isotopes (O, C) and clumped isotope thermometry of magnesite and silica veins
- in the New Caledonia Peridotite Nappe. Geochimica et Cosmochimica Acta 183: 234–249
- <https://doi.org/10.1016/j.gca.2016.03.021>
- Quesnel B, Gautier P, Boulvais Ph, Cathelineau M, Maurizot P, Cluzel D, Ulrich M, Guillot S,
- Lesimple S and Couteau C (2013) Syn-tectonic, meteorite water-derived carbonation of the New
- Caledonia peridotite nappe. Geology 41: 1063–1066 <https://doi.org/10.1130/G34531.1>
- Quesnel B, Gautier P, Cathelineau M, Boulvais P, Couteau C and Drouillet M (2016) The internal
- 1012 deformation of the Peridotite Nappe of New Caledonia: A structural study of serpentine-bearing
- faults and shear zones in the Koniambo Massif. Journal of Structural Geology 85: 51–67

<https://doi.org/10.1016/j.jsg.2016.02.006>

- Rivizzigno P, Lebon GT, Roe KK, Schrenk MO, Olson EJ, Lilley MD, Butterfield DA, Früh-Green GL
- and Blackman DK (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30° N.
- Nature 412: 145-149 <https://doi.org/10.1038/35084000>
- Rodgers KA (1973a) Uralites and uralitization in the ultramafic belt of southern New Caledonia.
- Geological Magazine, G.B., 110: 125-131
- Rodgers KA (1973b) Felsic plutonic rocks from the southern portion of the New Caledonian
- ultramafic belt. Geological Magazine, G.B. 110: 431-446
- Rodgers KA and Bevan JC (1974) Hornblendites from the southern portion of the New Caledonian
- ultramafic belt. Mineralogical Magazine G.B., 39: 890-893.
- Rubatto D and Hermann J (2003) Zircon formation during fluid circulation in eclogites (Monviso,
- Western Alps): implications for Zr and Hf budget in subduction zones. Geochimica et Cosmochimica
- Acta 67: 2173–2187 [https://doi.org/10.1016/S0016-7037\(02\)01321-2](https://doi.org/10.1016/S0016-7037(02)01321-2)
- Rutter EH (1983) Pressure solution in nature, theory and experiment. Journal of the Geological Society, 140: 725-740<https://doi.org/10.1144/gsjgs.140.5.0725>
- Schmidt K, Koschinsky A, Garbe-Schönberg D, de Carvalho LM and Seifert R (2007) Geochemistry
- of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15°N on the Mid-
- Atlantic Ridge: temporal and spatial investigation. Chemical Geology 242: 1–21
- <https://doi.org/10.1016/j.chemgeo.2007.01.023>
- Schwartz S, Guillot S, Reynard B, Lafay R, Debret B, Nicollet C, Lanari P and Auzende AL (2013)
- Pressure-temperature estimates of the lizardite/antigorite transition in high pressure serpentinites.
- Lithos 178: 197–210 <https://doi.org/10.1016/j.lithos.2012.11.023>
- 1036 Secchiari A (2016) Geochemical and Sr, Nd, Pb isotope investigation of the New Caledonia
- ophiolite. Co-tutored PhD Thesis, University of Parma (Italy) and University of Montpellier (France), 188 p.
- Secchiari A, Montanini A, Bosch D, Macera P and Cluzel D (2016) Melt extraction and enrichment
- processes in the New Caledonia lherzolites: evidence from geochemical and Sr-Nd isotope data.
- Lithos 260: 28-4[3 https://doi.org/10.1016/j.lithos.2016.04.030](https://doi.org/10.1016/j.lithos.2016.04.030)
- Secchiari A, Montanini A, Bosch D, Macera P and Cluzel D (2018) The contrasting geochemical
- message from the New Caledonia gabbronorites: insights on depletion and contamination processes
- of the sub-arc mantle in a nascent arc setting. Contributions to Mineralogy and Petrology 173: 66
- <https://doi.org/10.1007/s00410-018-1496-8>
- Secchiari A, Montanini A, Bosch D, Macera P and Cluzel D (2019) Sr, Nd, Pb and trace element
- systematics of the New Caledonia harzburgites: tracking source depletion and contamination
- 1048 processes in a SSZ setting. Geosciences Frontiers (special issue on Ophiolites).

<https://doi.org/10.1016/j.gsf.2019.04.004>

- Siivola J and Schmid R (2007) Recommendations by the IUGS Subcommission on the Systematics
- of Metamorphic Rocks: Web version 01.02.07 www.bgs.ac.uk/scmr/home.html
- 1052 Sivell W J and Waterhouse J B (1986) The geochemistry, origin, and tectonic significance of
- rodingites from the Dun Mountain Ultramafics, D'Urville Island, New Zealand. New Zealand Journal of
- Geology and Geophysics 29: 9-2[7 https://doi.org/10.1080/00288306.1986.10427519](https://doi.org/10.1080/00288306.1986.10427519)
- Soret M, Agard P, Dubacq B, Vitale-Brovarone A, Monié P, Chauvet A, Whitechurch H and
- Villemant B (2016) Strain localization and fluid infiltration in the mantle wedge during subduction
- initiation: Evidence from the base of the New Caledonia ophiolite. Lithos 244: 1-19
- <https://doi.org/10.1016/j.lithos.2015.11.022>
- Trotet F, Kadar M and Marini D (2015) Typology of the New Caledonian Ni-laterite deposits: from
- natural to industrial processes. The Society for Geology Applied to Mineral Deposits, 13th SGA
- meeting, August 2015, Nancy, France. Abstr. vol.
- Ulrich M (2010) Péridotites et serpentinites du complexe ophiolitique de la Nouvelle-Calédonie.
- Études pétrologiques, géochimiques et minéralogiques sur l'évolution d'une ophiolite de sa
- formation à son altération. Co-tutored PhD thesis, University of New Caledonia and University Joseph
- Fourier (Grenoble, France), 273 p.
- Ulrich M, Bureau S, Chauvel C and Picard C (2012) Accurate Measurement of Rare Earth
- Elements by ICP-MS after Ion-Exchange Separation: Application to Ultra-Depleted Samples.
- Geostandards and Geoanalytical Research, 36: 7-20 [https://doi.org/10.1111/j.1751-](https://doi.org/10.1111/j.1751-908X.2011.00116.x)
- [908X.2011.00116.x](https://doi.org/10.1111/j.1751-908X.2011.00116.x)
- Veizer J (1989) Strontium isotopes in seawater through time. Annual Review of Earth and
- Planetary Sciences 17: 141-167
- Wang X, Zeng Z and Chen J (2009) Serpentinization of peridotites from the southern Mariana
- forearc. Progress in Natural Science 19: 1287–1295.
- Wenner DB and Taylor HP Jr (1971) Temperatures of serpentinization of ultramafic rocks based
- 1075 on O<sup>18</sup>/O<sup>16</sup> fractionation between coexisting serpentine and magnetite. Contributions to Mineralogy
- and Petrology 32: 165-185 <https://doi.org/10.1007/BF00643332>
- 1077 Wenner DB and Taylor HP Jr (1974) D/H and  $O^{18}/O^{16}$  studies of serpentinization of ultramafic
- rocks. Geochimica et Cosmochimica Acta 38: 1255-1286 [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(74)901203)
- [7037\(74\)901203](https://doi.org/10.1016/0016-7037(74)901203)
- Woodhead J, Hergt J, Greig A and Edwards L (2011) Subduction zone Hf-anomalies: mantle
- messenger, melting artefact or crustal process? Earth and Planetary Science Letters 304: 231–239
- <https://doi.org/10.1016/j.epsl.2011.01.036>
- Zheng YF (1993) Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates. Earth
- and Planetary Science Letters 120: 247-263 [https://doi.org/10.1016/0012-821X\(93\)90243-3](https://doi.org/10.1016/0012-821X(93)90243-3)



 Figure 7: Raman spectra of tremolite and antigorite from sample# NC581DLA (see Fig. 6). Intensity is 1122 given in arbitrary units (a.u.).

- Figure 8: Comparison of chondrite-normalized REE patterns (Evensen et al. 1978) to show the hook shape and relatively high REE contents of tremolite veins compared to New Caledonia peridotites (Secchiari 2016), early Eocene dykes (Cluzel et al. 2006) and serpentinites of the tectonic sole (with negative Ce anomaly; Ulrich, 2010)
- 
- Figure 9: Chemical classification (Leake, 1968; Leake et al. 1997) of microprobe analyses of single minerals from tremolite-bearing veins and pockets; the data form a continuous array spanning 1131 from high-Si tremolite to tremolite hornblende.
- 
- Figure 10: Hydrothermal incorporation of Cr in tremolite. a: Cr vs. Si plot of tremolite showing the increasing Cr molecular content with decreasing total Si content at increasing temperature 1135 (from tremolite to tremolite-hornblende. b:  $Cr_2O_3$  (wt%) and  $X_{FeA}$  covariation similarly showing 1136 the positive correlation of Cr content and Fe ratio of tremolite.
- 

1138 Figure 11: a: Plot of Sr vs. <sup>87</sup>Sr/<sup>86</sup>Sr to compare Sr isotopic composition of tremolite and antigorite (this study) to unserpentinized peridotites (Secchiari et al. 2018, 2019), gabbronorites (Secchiari et al. 2016), Early Eocene dykes (Cluzel et al. 2006) from the Peridotite Nappe, and Atlantis Massif serpentinites (Boschi et al. 2008). Ocean waters compositions are from Murthy and Beiser 1968, Elderfield (1986), Veizer (1989) and McArthur et al. (2012); b: plot of Ca vs.  $\frac{87}{5}$ r/ $\frac{86}{5}$ r, same symbols as in 11a.

- 1145 Figure 12:  $\delta^{18}$ O and  $\delta$ D isotopic ratios of fibrous serpentines and tremolites of Poro site. "Oceanic" serpentinites after Agrinier et al. (1995, 1997); supergene silicates field ("garnierite") after Amisse et al. (2010) and deweylite after Wenner and Taylor (1974), serpentinite sole of the Peridotite Nappe after Ulrich (2010).
- 
- Figure 13: a: SEM image of altered chromite grain from peridotite isolated within a tremolite-
- antigorite replacive "vein". The grain is formed of a residual core of primary chromite and a
- 1152 cortex of micro-granular chromian magnetite and low-Cr chromite. b & c sketch drawing to
- 1153 show the metasomatic replacement of peridotite wall rock by a mixture of tremolite and
- antigorite with partly altered chromite
- 

Figure 14: Geodynamic model of subduction inception showing the timing of tremolite-antigorite

veins development.

- Table 1: Raman shift data from Raman spectra of two samples of tremolite-antigorite veins from 1160 Poro mine (data from Lahondere et al. 2012) uncertainty is  $\pm 2$ cm<sup>-1</sup>
- Table 2: Whole rock major and trace-elements composition of representative tremolite-antigorite veins of Poro Ni mine
- Table 3: Microprobe analyses of tremolites
- Table 4: Strontium isotopic data for tremolite-antigorite and antigorite veins from Poro Ni mine (east 1165 coast New Caledonia). Sr/ $86$ Sr normalization value = 0.710245
- Table 5: Oxygen and hydrogen isotopic compositions of fibrous veins from Poro nickel mine (east
- coast New Caledonia)

- Table 1: Raman shift data from Raman spectra of two samples of tremolite-antigorite veins from
- Poro mine (data from Lahondere et al. 2012) uncertainty is ±2cm-1
- 
- 







1176



1177

1178

# Table 3: microprobe analyses of tremolites





## 1184 Table 4 : Sr isotopic compositions of tremolite-antigorite veins

1185



1186

## 1188 Table 5: Oxygen and hydrogen isotopic compositions

1189



1190

1191





























≛

**<sup>87</sup>Sr/<sup>86</sup>Sr**







