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The importance of talc and chlorite “hybrid” rocks for volatile recycling through subduction zones; evidence from the high-pressure subduction mélange of New Caledonia

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Abstract The transfer of fluid and trace elements from the slab to the mantle wedge cannot be adequately explained by simple models of slab devolatilization. The eclogite-facies mélange belt of northern New Caledonia represents previously subducted oceanic crust and contains a significant proportion of talc and chlorite schists associated with serpentinite. These rocks host large quantities of H₂O and CO₂ and may transport volatiles to deep levels in subduction zones. The bulk-rock and stable isotope compositions of talc and chlorite schist and serpentinite indicate that the serpentinite was formed by seawater alteration of oceanic lithosphere prior to subduction, whereas the talc and chlorite schists were formed by fluid-induced metasomatism of a mélange of mafic, ultramafic and meta-sedimentary rocks during subduction. In subduction zones,

dehydration of talc and chlorite schists should occur at sub-arc depths and at significantly higher temperatures (~ 800°C) than other lithologies (400–650°C). Fluids released under these conditions could carry high trace-element contents and may trigger partial melting of adjacent pelitic and mafic rocks, and hence may be vital for transferring volatile and trace elements to the source regions of arc magmas. In contrast, these hybrid rocks are unlikely to undergo significant decarbonation during subduction and so may be important for recycling carbon into the deep mantle.

Introduction

A comprehensive understanding of the metamorphic and geochemical evolution of oceanic crust and lithosphere during its descent into the mantle at subduction zones is fundamental to many first-order geological processes, such as the production of arc magmas and continental crust, the recycling of volatiles (e.g., CO₂ and H₂O) and trace elements through the Earth, and the geochemical evolution of the mantle. Most models of arc magma-genesis require an input into the mantle wedge of H₂O-rich fluid sourced from the subducting slab. In most cases, arc magmatism in the over-riding plate occurs between 90 and 150 km above the top of the subducting slab (Tatsumi and Eggins 1995). Therefore, it is expected that a flux of fluid from the slab to mantle wedge also occurs at these depths in subduction zones.

The lithological inputs at subduction zones are lithospheric mantle peridotite (~100 km thick), basaltic to gabbroic oceanic crust (5–8 km) and a thin (>1 km) layer of pelitic to calcareous sediment (Plank and Langmuir

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1998; Poli and Schmidt 2002). Many experimental studies over the last decade have focused on establishing the phase relations of these lithologies over a range of pressure (P) and temperature (T) conditions (e.g. Schmidt and Poli 1998; Ulmer and Trommsdorff 1999; Hermann and Green 2001; Forneris and Holloway 2003). Combining these phase relations with thermal models for subduction zones, predictions of volatile release from the subducting slab can be made (Schmidt and Poli 1998; Peacock 2001). Inherent in these predictions is the assumption that each rock-type retains its geochemical character during subduction.

There is a large body of evidence to show that mafic and sedimentary rocks of subducting slabs provide the majority of key lithophile trace elements to arc magmas (e.g. Hawkesworth et al. 1993; Plank and Langmuir 1998). Subducting mafic rocks also have the potential to host significant quantities of volatiles in minerals such as amphibole, lawsonite, phengite, chlorite and epidote (Peacock 1993). However, with the exception of very cold subducting slabs, most of these volatiles are likely to be expelled before the slab reaches sub-arc depths of 90–150 km (Poli and Schmidt 2002; Forneris and Holloway 2003). Sedimentary rocks lose pore fluids at very shallow depths (~ 0 –20 km), but retain most of their mineral-bound H_2O in phengite to depths well beyond the sub-arc region (Hermann and Green 2001; Hyndman and Peacock 2003; Schmidt et al. 2004). Serpentinized ultramafic rocks contain volatiles that may be released during dehydration below the volcanic front (Ulmer and Trommsdorff 1999). Therefore, serpentinites are regarded as important potential sources of H_2O for arc magmatism, yet these fluids are released at relatively low temperatures ($\sim 650^\circ C$) from rocks that are unlikely to provide many of the key elements required to explain arc magmas compositions (Tenthorey and Hermann 2004).

Overall, subducted mafic and sedimentary rocks can provide the slab-derived trace elements for arc magmas, but probably are not the only direct sources of the fluid necessary to transport these elements into the magma source region. Conversely, serpentinites may release large volumes of fluid at sub-arc depths, but these fluids are likely to contain relatively low trace-element contents (Tenthorey and Hermann 2004). Given the unambiguous component of slab-derived volatiles and trace elements in arc magmas, deep subduction-zone processes and structures must be significantly more complex than is currently envisaged.

Recent research has focused on high- P metamorphic terranes that represent exhumed fragments of subducted slabs in order to study the petrological and geochemical evolution of subduction zones (Sorensen and Grossman 1993; Scambelluri et al. 2001; Bebout and Barton 2002; Zack et al. 2002; King et al. 2003, 2006; Spandler et al.

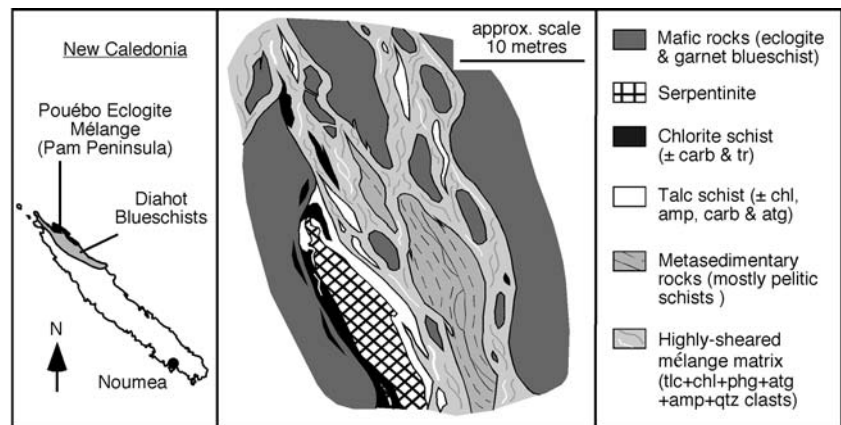
2003, 2004a; Marschall et al. 2006). Invariably, these studies reveal that the structural and petrological complexity of subducting slabs is much greater than is generally considered in models of fluid and element fluxing from the slab to mantle wedge. In particular, many high- P terranes comprise highly chaotic *mélange* and include rock-types that do not represent metamorphic equivalents of rocks normally found in crustal sequences (Sorensen and Grossman 1989, 1993; Bebout and Barton 2002; King et al. 2003). These rock-types are interpreted to have formed either through tectonic mixing of sheet silicate and amphibole-rich metamorphic rocks such as serpentinite, mica schist or amphibolite, or through metasomatic interaction between mafic, ultramafic and metasedimentary rocks during metamorphism (Bebout and Barton 2002).

The blueschist to eclogite facies belt of northern New Caledonia is a classic example of an exhumed slab that was previously subducted to depths of up to 70 km. In this paper, we outline the petrology, geochemistry, and stable-isotopic composition of talc- and chlorite-rich rocks from this high- P belt. These rocks are examples of so-called blackwall alteration zones that are also found associated with ultramafic rocks from subduction complexes and a range of other geological settings (e.g. Read 1934; Bebout and Barton 2002; King et al. 2003; Bach et al. 2004; Boschi et al. 2006). They do not represent the metamorphosed equivalents of any “standard” lithology of oceanic crust but have the potential to transport significant amounts of H_2O to greater depths than serpentinite. Deep devolatilization of these rocks will produce reactive fluids that may be capable of stripping elements or partially melting parts of the slab. Therefore, these rocks may have important consequences for the recycling of volatiles and trace elements in subduction zones.

Geological setting

The northeastern portion of New Caledonia consists of a ~ 2200 km² high- P , low- T metamorphic belt of lawsonite blueschist- to eclogite-facies rocks (Fig. 1). Peak metamorphic conditions have been constrained as 1.6–1.9 GPa and 550–600°C (Carson et al. 1999; Fitzherbert et al. 2003). The belt represents an exhumed package of Cretaceous to Paleocene oceanic crust and continental sediments that was subducted during the middle Eocene (Cluzel et al. 2001; Spandler et al. 2005). The metamorphic grade progressively increases from the south and west to the northeast (Black 1977), although the increase in metamorphic grade is largely due to effects of normal faulting (Clarke et al. 1997; Rawling and Lister 2002). The blueschist-facies rocks in the south and west of the belt are a thick sequence of metamorphosed sedimentary rocks with minor

Fig. 1 Schematic cartoon of a typical mélangé zone from the Pouébo Eclogite Mélangé. The mélangé zones have been observed at outcrop scale (cm to 10's of m), but may exist on kilometre scales. Also shown is the location of the Pouébo Eclogite Mélangé and Diahot Blueschist belt in New Caledonia. See Tables 1 and 2 for mineral abbreviations



intercalated basaltic to rhyolitic dykes and flows (Black 1977; Fitzherbert et al. 2003). In the northeast of the belt (Pam Peninsula; Fig. 1) are eclogite-facies rocks that have previously been interpreted in several ways. Maurizot et al. (1989) proposed that this region consists of a complex mélangé containing mafic, ultramafic and sedimentary rocks. Detailed mapping was considered impossible due to the heterogeneous and chaotic nature of these rocks. In contrast, Clarke et al. (1997) and Carson et al. (1999, 2000) suggested that the same area consists predominately of massive units of mafic eclogite and garnet glaucophanite that are genetically unrelated to the blueschist-facies rocks to the south and west. These authors classified the blueschist and eclogite facies rocks as separate tectonostratigraphic terranes, respectively, known as the Diahot and Pouébo Terranes. On the basis of detailed structural mapping, Rawling and Lister (2002) proposed that the eclogite-facies rocks comprise a coherent sheet that structurally overlies the lower grade rocks. Rawling and Lister (2002) also mapped a number of large-scale shear zones along the Pam Peninsula, which contain a mélangé of serpentinite, mica-schist and mafic rocks of varying metamorphic grade.

Recent work by Fitzherbert et al. (2003, 2004) includes recognition of high-grade sedimentary and ultramafic rocks on the Pam Peninsula, but retains the distinction between the Diahot and Pouébo Terranes. In contrast, Rawling and Lister (2002) question the definition of the two terranes on structural evidence and Spandler et al. (2003) have found common rock-types throughout the high-P belt. Moreover, geochronological data indicate that the blueschist- and eclogite-facies rocks have similar origins and underwent metamorphism and cooling as a coherent unit (Ghent et al. 1994; Spandler et al. 2005). In this paper, we refer to the blueschist-facies rock to the south and west (Diahot Terrane of Clarke et al. 1997) as the Diahot Blueschists. The eclogite facies rocks of the Pam Peninsula and northeastern coastline (former Pouébo Terrane) are described below and are designated the Pouébo Eclogite Mélangé (PEM; Fig. 1).

Our interpretations of the geology of the eclogite-facies rocks of the Pam Peninsula and northeastern coastline closely compare with the description of Maurizot et al. (1989). Mafic rocks are the dominant lithologies and include eclogite, garnet blueschist and garnet amphibolite. However, metamorphosed ultramafic and sedimentary rocks are also widespread and abundant. Serpentinite is the dominant ultramafic rock, but it is typically associated with varying amounts of talc- and chlorite-(± carbonate and amphibole) rich blackwall rocks (Fig. 2). Metasedimentary rocks are predominantly foliated quartz-garnet-mica schists of pelitic composition although locally these rocks may contain high chlorite or glaucophane contents. At the outcrop scale (sub-metre to 10's of metres) all of these rock-types are associated in mélangé zones (Fig. 1). We have observed such zones throughout the high-P belt, which indicates that a significant proportion (>50%) of the belt consists of mélangé. Mafic rocks form competent units adjacent to mélangé zones or boudins of varying size (mm to 10's of metres) within the mélangé zones. Many mafic boudins have rinds, up to several cm in thickness, enriched in phengite and/or glaucophane compared to the boudin cores. Some ultramafic and metasedimentary rocks occur as massive units, but more commonly are sheared together and hence comprise much of the deformed mélangé matrix. The mélangé matrix consists largely of phyllosilicate-rich minerals (talc, chlorite, phengite) but also includes quartz clasts derived from metasedimentary rocks and stringers or clots of coarse-grained amphibole. These mélangé zones have been retrogressed to greenschist-facies assemblages in some places (Carson et al. 2000), but in general the rock of the mélangé, including the mélangé matrix, preserve mineral assemblages and structures that formed during eclogite-facies conditions (Rawling and Lister 2002). This indicates that the mélangé formed prior to or during peak metamorphism.

The PEM is an excellent analogue of a slab that was subducted to depths of up to 70 km. The mafic and

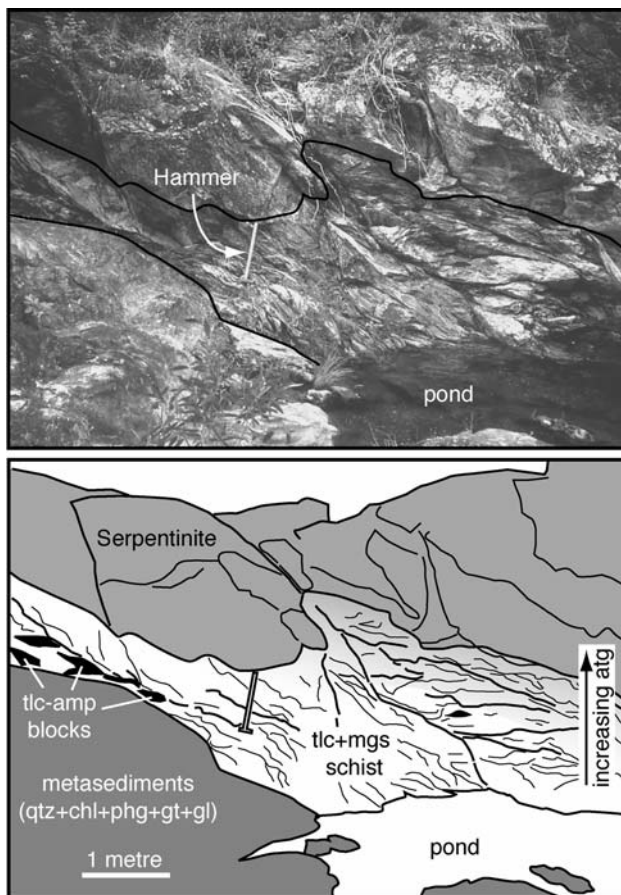


Fig. 2 Outcrop photo and geological sketch of a serpentinite-metasedimentary rock contact with talc schist developed along the contact. The outcrop is located at is 20° 15' 49" S, 164° 23' 23" E, and is from where samples 1012–1015 were taken. *gt* garnet, *gl* glaucophane. See Table 1 and Fig. 1 for other mineral abbreviations. Note the progressive increase in antigorite away from the contact and the talc-amphibole blocks within the talc schist

metasedimentary rocks represent metamorphosed equivalents of oceanic crust and ocean floor sediments, respectively (Cluzel et al. 2001; Spandler et al. 2003, 2004a). The serpentinites represent hydrated mantle rocks that likely are a major component of subducting slabs (Ulmer and Trommsdorff 1999). In contrast, very few studies have pointed out that talc and chlorite schists found associated with serpentinites may also be important in subduction zones (Sorensen and Grossman 1993; Bebout and Barton 2002; King et al. 2003, 2006). In the PEM, these rocks do not form large individual units (<3 m in width), but are widespread and therefore may comprise significant proportions of subducting slabs. Field relations and the structural setting of these rocks have been described by Fitzherbert et al. (2004). In this paper, we investigate the petrology and geochemistry of a number of serpentinite and talc and chlorite schist samples in detail.

Sampling and analytical techniques

Sampling procedure

Samples examined in this study were taken from across the PEM (Table 1); in most cases from outcrops where clear relations between rock-types could be observed (e.g., Fig. 2). No samples of the intermixed mélangé matrix were taken due to the inhomogenous nature of these rocks. For most of the sampling we utilised a range of hammers and chisels to reduce 3–5 kg blocks of visually homogenous rock down to 1–2 kg samples, taking special care to remove the weathered surfaces. The samples were then labelled and packed in plastic for transport to the Australian National University (ANU). Sample processing at the ANU involved further removal of weathered or contaminated surfaces with a rock saw, followed by rock crushing using a tungsten carbide jaw splitter and tungsten carbide plate crusher. Final chip sizes of the samples were 5 mm or less.

Bulk-rock and mineral chemistry

Approximately 300 g of each of the crushed samples were milled to a fine powder in a tungsten carbide ring mill. Powdered whole-rock samples fused with Li borate flux were analysed for major elements using a PW2400 wavelength-dispersive X-ray fluorescence (XRF) spectrometer housed at the Department of Earth and Marine Sciences, ANU. All trace element concentrations were determined from multiple analyses of Li-borate fused discs (flux-sample ratio 2:1) by laser ablation, inductively-coupled plasma mass spectrometry (LA ICP-MS) at the Research School of Earth Sciences, ANU. The LA ICP-MS employs an ArF (193 nm) EXCIMER laser and a Hewlett Packard Agilent 7500 ICP-MS. For analyses a spot size of 100 µm was used and the counting time was 30 s for the background and 70 s for sample analysis. Instrument calibration was against NIST 612 glass using the reference values of Spandler et al. (2003). ⁴³Ca was employed as the internal standard isotope, based on CaO concentrations previously measured by XRF. H₂O and CO₂ concentrations were determined by step-heating 0.1 g of powdered rock up to 1,100°C over 13 min, using a Leco RC-412 multiphase carbon/hydrogen determinator, at the Department of Earth and Marine Sciences, ANU. Calcium oxalate and pure CaCO₃ were used for hydrogen and carbon standards, respectively.

Major-element compositions for minerals were determined on polished sections of the samples using an energy-dispersive spectrometer equipped, JEOL 6400 scanning electron microscope (SEM), housed at the Electron Microscope Unit, ANU. Accelerating voltage, beam

Table 1 Location and mineralogy of investigated samples

Sample	Rock-type	Location	Latitude (S)	Longitude (E)	Prograde mineralogy	Retrograde mins
3010	Serpentinite	W of Col D'Amos	20° 18' 01''	164° 26' 06''	atg, chl	–
3104	Serpentinite	Pwac Pue Creek	20° 14' 39''	164° 18' 28''	atg, Cr-mag	–
2813	Serpentinite	Abwala Stream	20° 15' 58''	164° 23' 18''	atg, tlc, mgs	–
03J42	Serpentinite	W of Abwala Stream	20° 15' 38''	164° 23' 39''	atg, mgs, tlc, chl, Cr-mag	tlc
1012	Talc-atg schist	Abwala Stream	20° 15' 49''	164° 23' 23''	tlc, atg, mag	–
3103	Talc-atg schist	Pwac Pue Creek	20° 14' 39''	164° 18' 28''	tlc, atg, mag	–
1013	Talc schist	Abwala Stream	20° 15' 49''	164° 23' 23''	tlc, atg, chl, Ti-mag, ap	mag
2814	Talc schist	Abwala Stream	20° 15' 58''	164° 23' 18''	tlc, dol, atg, Ti-mag, ap, zrn	–
2815	Talc schist	Abwala Stream	20° 15' 58''	164° 23' 18''	tlc, mgs, Cr-mag, chl	tlc
1014	Talc schist	Abwala Stream	20° 15' 49''	164° 23' 23''	atg, mgs, Cr-mag	mag
TC01	Talc schist	W of Col D'Amos	20° 17' 44''	164° 25' 28''	tlc, chl	tlc
802	Talc-amp schist	Yambe	20° 27' 36''	164° 39' 11''	tlc, wnc, chr, chl, ap	act
1015	Talc-amp schist	Abwala Stream	20° 15' 49''	164° 23' 23''	tlc, tr, chl, rt, zrn	chl, tnt, qtz, act
2816	Chlorite schist	Abwala Stream	20° 15' 54''	164° 23' 20''	chl, dol, tr, rt, ap, zrn	cc, tnt, tr

Notes: Mineral abbreviations: *atg* antigorite, *tlc* talc, *amp* amphibole, *chl* chlorite, *tr* tremolite, *wnc* winchite, *act* actinolite, *mgs* magnesite, *dol* dolomite, *Ti-mag* titanomagnetite, *Cr-mag* Cr magnetite, *mag* magnetite, *chr* chromite, *ap* apatite, *rt* rutile, *tnt* titanite, *zrn* zircon, *qtz* quartz, *cc* calcite

current and counting time were set at 15 kV, 1 nA and 100 s, respectively. Element concentrations were standardized against known mineral standards produced by Astimex Scientific Limited. Trace element analyses of selected minerals was also conducted using the LA ICP-MS system described above. A 70 µm spot size was used for all analyses. The internal standard isotopes used to quantify the analyses were ^{43}Ca for carbonates and apatite, ^{49}Ti for magnetite, and ^{27}Al for chlorite. Grains were chosen to avoid foreign mineral inclusions during analysis. However, interference from inclusions was detected in some analyses, and in all cases these interferences were removed during data reduction.

Stable isotope analysis

Oxygen was extracted from whole-rock samples by conventional method (Clayton and Mayeda 1963) and talc and magnetite by CO_2 -laser (Sharp 1990) using BrF_5 as the oxidising agent. In the conventional method, the samples (powders crushed by pestle and mortar) were outgassed under vacuum at 200°C for at least 4 h and pre-treated with BrF_5 at room temperature for 15 min prior to extraction of oxygen at 550°C. For the CO_2 -laser method, mineral grains in a sample chamber were evacuated for approximately 2 h and left overnight in a BrF_5 atmosphere. Blank runs were done until oxygen yields were less than 0.1 µmol. After extraction, oxygen yields were recorded and CO_2 gas analysed on a Geo20–20 mass spectrometer. Values are reported in the familiar $\delta^{18}\text{O}$ notation, relative to VSMOW. Whole-rock and talc samples were normalized to the

international quartz standard NBS-28 using a value of +9.6 per mil (‰) and the magnetite to the garnet standard UWG-2 using a value of 5.8‰ (Valley et al. 1995). Values for ten NBS-28 and six UWG-2 standards analysed with the samples had replicate values that varied by less than 0.15 and 0.1‰, respectively. Oxygen yields for the talc and magnetite samples varied between 95 and 102%.

Carbonates were analysed for their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values by crushing samples to a fine-powder and reacting with phosphoric acid at 80°C for 2 h in an automated GEO-CAPS system. Oxygen isotope values were corrected using the appropriate phosphoric acid— CO_2 fractionation factors (McCrea 1950; Rosenbaum and Sheppard 1986). All carbonate measurements are normalised to VPDB ($\delta^{13}\text{C} = 1.95\text{‰}$) and VSMOW ($\delta^{18}\text{O} = 28.6\text{‰}$) using NBS-19 and checked for accuracy by also analysing an internal standard (GNS Marble). Replicates of carbonate standards were better than 0.05 and 0.1‰ for carbon and oxygen values, respectively.

Ultramafic and hybrid rocks of the Pouébo Eclogite Mélange

Serpentinite

Serpentinites comprise roughly 15% of the PEM. They occur as distinct blocks up to 100 m in width within the mélange (Fig. 1), or as part of the sheared mélange matrix. They are fine- to medium-grained rocks that may be strongly foliated or unfoliated. Most samples examined consist almost entirely of fibrous antigorite, but in some

cases antigorite pseudomorphs of original olivine or pyroxene grains are preserved (Table 1). Olivine was not observed, but has been reported in similar rocks by Fitzherbert et al. (2004). Chlorite is present in some samples, but perhaps because the antigorite contains Al_2O_3 (1.5–3 wt%; eTable 1), the amount of chlorite is very low. Porphyroblasts of chromian magnetite (eTable 1) are found in some samples. Close to contacts with the talc schists, the serpentinites commonly contain coarse euhedral magnesite crystals, which are associated with minor amounts of talc.

Talc schist

Talc-rich rocks are ubiquitously associated with the serpentinite blocks and mélangé matrix. These rocks form seams up to 3 m thick and are best developed on contacts between serpentinite and metasedimentary rocks, as can be seen in Fig. 2. Contacts between metasedimentary and talc rocks are typically sheared, but gradational contacts of up to a metre are commonly observed between serpentinite and talc schist. Most talc-schist samples are strongly foliated and comprise between 90 and 100% fine-grained talc that contains minor amounts of FeO (eTable 1). In some cases, coarse talc veins cut the fine-grained talc matrix (Fig. 3a), indicating that there are at least two talc generations. Antigorite is typically an accessory phase, although the proportion of antigorite increases dramatically towards contacts with serpentinite (Fig. 2). Close to the serpentinite contacts are talc-antigorite rocks that are often weakly foliated and may preserve olivine and/or pyroxene pseudomorphs. Other minor phases in the talc schists include

chlorite and coarse porphyroblasts of magnesite (or weathered pseudomorphs after magnesite) and Cr magnetite (eTable 1). Two samples (1013 and 2814) contain minor amounts of titanomagnetite (Table 1) and apatite that contain inclusions of talc and chlorite. Sample 2814 also contains dolomite porphyroblasts up to 10 mm in size, and accessory zircon. Magnetite grains from most talc schist samples are coarse (3 to 10 mm), perfect octahedra that contain small inclusions of antigorite, talc and chlorite.

Randomly distributed throughout the seams of talc schist are rare blocks that consist of talc and very coarse (up to 10 cm in length) aggregates of bladed amphibole. These blocks are typically less than 50 cm in size, have variable proportions of talc and amphibole, and may contain accessory chromite, apatite, chlorite, quartz, rutile, titanite and zircon. Most of the amphibole laths are tremolite to winchite in compositions with relatively high Na, Al and Cr contents (eTable 1). The laths typically have distinct, albeit thin, rims composed of Na-poor tremolite or actinolite (eTable 1). These rim zones are interpreted to have formed during retrograde metamorphism.

Chlorite schist

Some chlorite schist is interleaved with talc schist, but most bodies form discontinuous lenses at contacts between mafic rock and serpentinite. These rocks consist almost completely of fine-grained foliated chlorite, although dolomite porphyroblasts are commonly present (Fig. 3b). As with the talc schists, talc-amphibole blocks are also found in the chlorite schist units (Fig. 3c). We have only

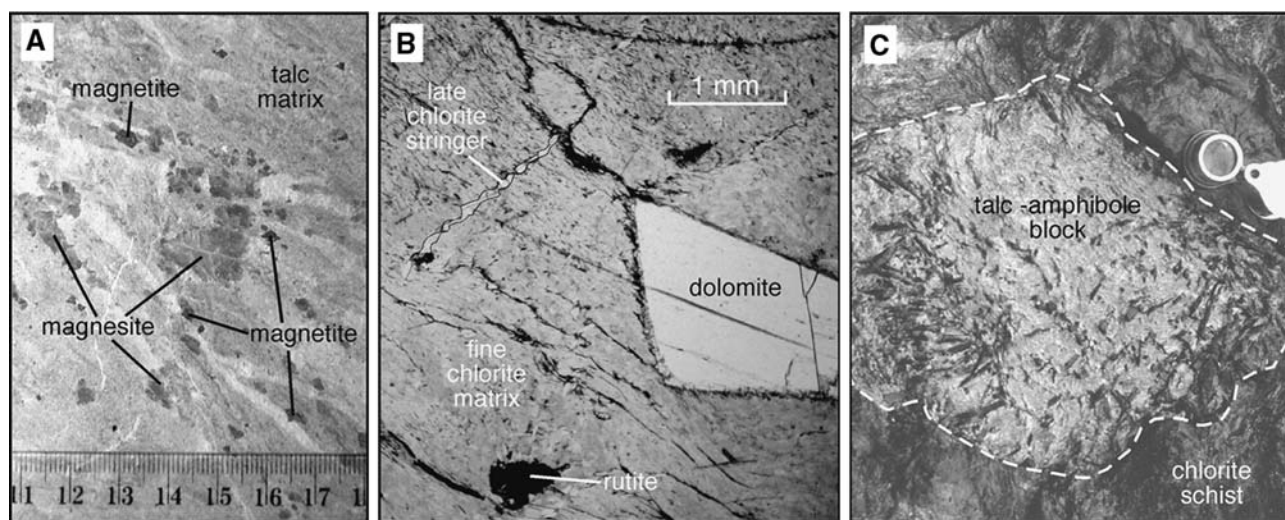


Fig. 3 **a** Polished slab photograph of a talc schist containing magnesite and magnetite. Note the lighter-coloured late-stage talc veins. Scale bar is in cm. **b** Thin section photo-micrograph of a

chlorite schist with coarse dolomite porphyroblasts, rutile grains and late-stage chlorite stringers. **c** Outcrop photograph of a talc-amphibole block in a chlorite-schist host

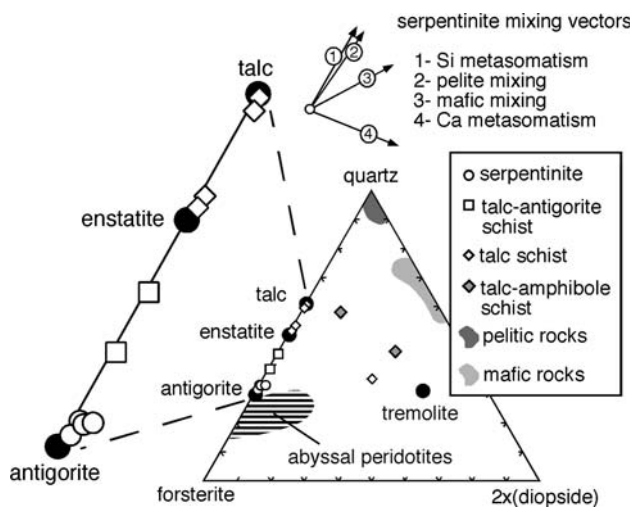


Fig. 4 Compositions of serpentinite, talc (\pm amphibole) schist, pelitic rocks and mafic rocks from the Pouébo Eclogite Mélange and pure end-member minerals projected onto the quartz-forsterite-diopside ternary diagram. The field of abyssal peridotites is plotted using the data of Niu (2004)

examined one chlorite schist sample in detail (2816). It consists of foliated clinocllore ($\sim 90\%$), coarse dolomite, minor tremolite, and rutile mantled by titanite. Apatite and zircon are accessory phases. The dolomite porphyroblasts contain inclusions of rutile, titanite, zircon and chlorite, and rutile contains chlorite inclusions. Thin veinlets of calcite and chlorite that cut the foliation throughout the rock (Fig. 3c) are interpreted to have formed during limited retrograde metamorphism.

Bulk rock compositions

Serpentinite

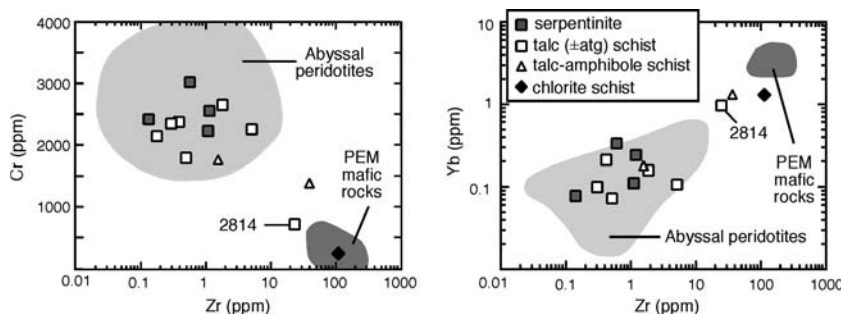
Major, minor, and trace-element abundances of 14 ultramafic and hybrid rock samples from the PEM are presented in eTable 2 and Figs. 4–6. The major-element composition of the serpentinites is close to pure antigorite (Fig. 4), but also contains 1.4–3.2 wt% Al_2O_3 , and 6.8–8.1 wt% Fe_2O_3 .

All serpentinite samples plot close to antigorite indicating that there is a small increase in the SiO_2/MgO with respect to typical harzburgite, which plot between antigorite and olivine (Fig. 4). All samples analysed have similar compositions including high Cr, Ni and H_2O , and low TiO_2 , CaO, K_2O and Na_2O contents. Other than the compatible transition metals and As, the serpentinites are poor in trace-elements (eTable 2). Compatible trace element characteristics are typical of abyssal peridotites (Fig. 5). REE are generally below chondritic values and have flat to slightly heavy-REE-enriched patterns with a prominent negative Eu anomaly and elevated La contents (Fig. 6). Sample 3010 has a pronounced negative Ce anomaly, whereas sample 03J42 features a positive Y anomaly.

Talc schist

The relative proportions of talc and antigorite strongly influence the SiO_2 and MgO contents of the analysed talc schist samples, with the most talc-rich samples containing the highest SiO_2 (Fig. 4) and the lowest H_2O contents (~ 5 wt%). Talc schist is considerably richer in SiO_2 than serpentinite and therefore does not represent an isochemically metamorphosed equivalent of the serpentinite. Nonetheless, with the exception of SiO_2 and volatiles, much of the talc schist and serpentinite have similar major and trace-element compositions (eTable 2, Figs. 5 and 6). In particular, most talc schist has Cr and Ni contents that testify it is derived from an ultramafic protolith. Talc schist samples TC01 and 2815 are strongly depleted in REE, although sample 2815 retains positive La and Y anomalies. In contrast, sample 2814 has high TiO_2 , CaO and MnO contents, is relatively enriched in REE, P, Sr, Zr, Hf, Nb and Y, and depleted in Cr and Ni (eTable 2; Figs. 4–6). Sample 1013 is also relatively enriched in Nb, P and TiO_2 , and slightly depleted in Cr. The enriched elements in these samples are hosted by titanomagnetite (TiO_2 , Nb), apatite (CaO, Sr, P, Y, REE), dolomite (MnO, Sr, REE) and zircon (Zr, Hf) (eTable 3). Despite these differences, most of the talc schist samples have REE patterns with negative Eu and

Fig. 5 Zr versus Cr, and Zr versus Yb plots of serpentinite, talc (\pm amphibole) and chlorite schists and mafic rocks from the Pouébo Eclogite Mélange. Fields for abyssal peridotite are from data from Melcher et al. (2002) and Niu (2004). PEM Pouébo Eclogite Mélange



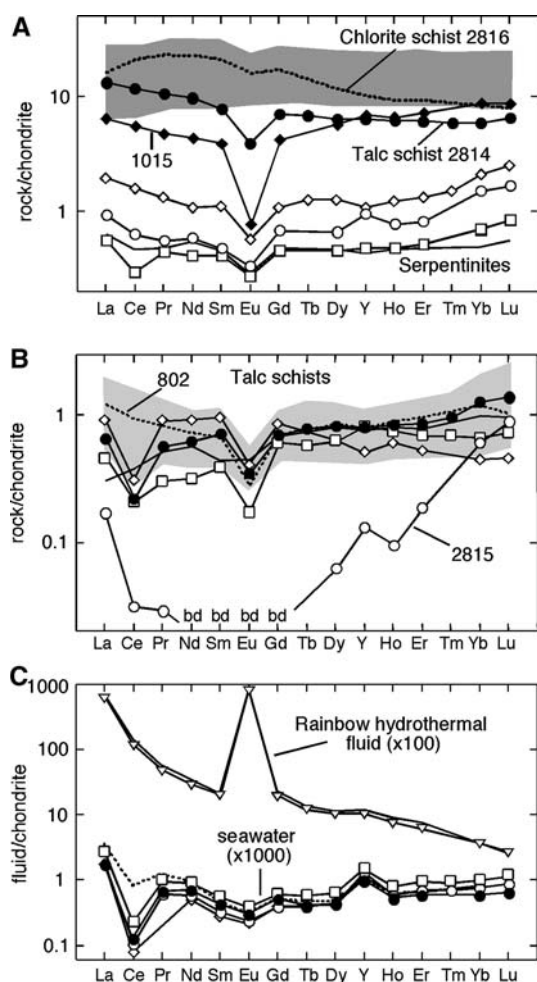


Fig. 6 Chondrite-normalised rare-earth element + Y plots for rocks of the Pouébo Eclogite Mélange and representative ocean-floor fluids. **a** PEM serpentinite samples (*open symbols*), talc schist sample 2814, talc-amphibole schist sample 1015 and chlorite schist sample 2816. The field for PEM mafic rocks is shown as the *dark grey* field (data from Spandler et al. 2004a). **b** PEM talc schist samples. The field of the PEM serpentinite is shown in *grey*. **c** Average open-ocean and continental margin seawater (>1,500 m depth) compositions (data from Bau et al. 1995; Zhang and Nozaki 1996, 1998; Douville et al. 2002) and Rainbow Vent hydrothermal fluid compositions (from Douville et al. 2002). Note, for graphically purposes the seawater and Rainbow Vent fluids compositions have been multiplied by 1,000 and 100 times, respectively. Chondrite normalising values used are from McDonough and Sun (1995)

Ce anomalies that are similar to those observed in the serpentinite (Fig. 6).

The talc-amphibole blocks have compositions that are transitional between typical talc schist and mafic rocks of the PEM (Figs. 4–6). Blocks with only minor amphibole (e.g., sample 802) have compositions similar to the talc schist, albeit with elevated CaO, Na₂O, P and Sr contents. Blocks rich in amphibole (e.g., 1015) are considerably richer CaO, Na₂O, TiO₂ and poorer in MgO and have trace element contents that are intermediate between mafic and ultramafic rocks.

Chlorite schist

The chlorite schist sample 2816 has low SiO₂, and high MgO, FeO and Al₂O₃, which directly reflects the dominance of chlorite in the rock. All other major-element concentrations are very low except for TiO₂ and CaO, which are hosted by rutile and dolomite, respectively. Most trace-element concentrations are similar to those of the mafic rocks of the PEM (Figs. 5 and 6; Spandler et al. 2004a), except for low Ba, Sr and Sc abundances. Dolomite, apatite, rutile and zircon are likely to be the major trace element hosts, whereas chlorite has relatively low trace element contents (eTable 3). The REE pattern for the chlorite schist is relatively heavy-REE depleted with a slight negative Eu anomaly and slight La depletion (Fig. 6).

Stable isotopes

We present new bulk-rock and mineral isotopic data for a range of rock-types from the PEM in Table 2 and Fig. 7. Two eclogite-facies pelitic rocks have oxygen isotopic compositions of 12.2 and 12.3‰, while a pelitic blueschist (923) has a value of 8.5‰. Samples of mafic eclogite and garnet blueschists have compositions of between 8.2 and 8.9‰. These values for the mafic rocks are heavier than mantle values (Fig. 7), but are typical of shallow-level hydrothermally-altered oceanic crust (Gregory and Taylor 1981). Samples of weakly foliated serpentinite have $\delta^{18}\text{O}$ values of 8.6 and 7.5‰, whereas serpentinite that contains carbonate and talc has heavier $\delta^{18}\text{O}$ values of 13.3 and 11.8‰. The bulk oxygen isotope composition of the talc schist samples spans a restricted range from 9.5 to 10.2‰, and analysis of a chlorite schist returned a $\delta^{18}\text{O}$ value of 10.6‰.

Carbonate minerals from two talc schists, one serpentinite, and a chlorite schist were analysed for O and C isotopes (Table 2). Carbonates from all samples have relatively high $\delta^{18}\text{O}$ values. Magnesite samples from the talc schist and serpentinite samples yield similar $\delta^{13}\text{C}$ values (−7.4 and −6.3‰, respectively), but contrasting $\delta^{18}\text{O}$ values of 9.8 and 18.2‰, respectively. Dolomite from talc schist sample 2814 has $\delta^{13}\text{C}$ of −5.2‰ and $\delta^{18}\text{O}$ of 12.4‰. The dolomite from the chlorite schist has a much lower $\delta^{13}\text{C}$ value (−12.7‰) and a $\delta^{18}\text{O}$ value of 14.2‰. Despite the variation in isotopic values, the overall range is comparable to that of calcite from metasedimentary rocks across the high-P belt of New Caledonia (Black 1974).

The large oxygen-isotope fractionation factors between co-existing magnetite or carbonate and most common silicate minerals enables temperature calculations to be made provided isotope equilibrium between magnetite–silicate or

Table 2 Oxygen and carbon isotope composition of rocks and minerals from the Pouébo Eclogite Mélange

Sample no.	Rock-type	$\delta^{18}\text{O}_{\text{wr}}$	$\delta^{18}\text{O}_{\text{carb}}$	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{tlc}}$	$\delta^{18}\text{O}_{\text{mag}}$	Calc. T ($^{\circ}\text{C}$)	$\delta^{18}\text{O}$ fluid at T (tlc and mag)	$\delta^{18}\text{O}$ fluid at T (carb)
3010	Serpentinite	8.6							
3104	Serpentinite	7.5							
2813	Serpentinite	13.3							
03J42	Serpentinite	11.8	18.2	-6.3			~200		~8.1
1012	Talc-atg. schist	9.6							
1013	Talc schist	9.6–10.2*			10.3	3.2	510	10.3	
2814	Talc schist		12.4	-5.2	10.3	3.0	490	10.2	9.8
2815	Talc schist	9.7	9.8	-7.4	9.8	3.3	560	10.0	7.7
1014	Talc schist	9.5–10.1*			10.3	3.4	530	10.4	
2816	Chlorite schist	10.6	14.2	-12.7			~500		~11.5
923	Pelitic blueschist	8.5							
1008**	Pelitic schist	12.3							
72819	Pelitic schist	12.2							
1003**	Mafic blueschist	8.9							
705**	Mafic eclogite	8.9							
2903**	Mafic eclogite	8.2							
Other data for the PEM	Source						Calc. T ($^{\circ}\text{C}$)	$\delta^{18}\text{O}$ fluid at T (qtz and phg)	$\delta^{18}\text{O}$ fluid at T (Garlick index)
Silicious metasediment	Black (1974)—7 samples						470–580	11–15	
Mafic blueschist	Black (1974)—1 sample						475	8.2	
Pelitic schist	Spandler and Hermann (2006)—2 samples						600		~12
Mafic eclogite	Spandler and Hermann (2006)—3 samples						600		~10

Notes: $\delta^{18}\text{O}$ values are ‰ relative to standard mean ocean water (VSMOW). $\delta^{13}\text{C}$ values are ‰ relative to pee dee belemnite (VPDB). *wr* whole rock, *carb* carbonate, *phg* phengite. Other mineral abbreviations are given in Table 1. Fluid compositions and temperatures were calculated using isotope fractionation factors of Zheng (1991, 1993a, b, 1999). * whole rock isotope compositions of 1013 and 1014 were calculated from mineral compositions and modes. ** petrographic description and geochemistry of these samples is outlined in Spandler et al. (2003, 2004a) and Spandler and Hermann (2006)

carbonate–silicate mineral pairs is attained (e.g. Chacko et al. 2001). Magnetite is present in the talc schist as coarse euhedral octahedra; a texture not observed in the serpentinite samples. Therefore, the magnetites in the talc schist are not regarded as relict grains, but are interpreted to have crystallised together with talc during metasomatism. In this case, the oxygen isotopic compositions of coexisting talc and magnetite permit calculation of the temperature of formation of the talc schists. Talc and magnetite separates from four talc-schist samples analysed for oxygen isotopes returned $\delta^{18}\text{O}$ values from 9.8 to 10.3‰ for talc and 3.0 to 3.4‰ for magnetite. Using the mineral fractionation factors of Zheng (1991, 1993a), these results indicate metamorphic temperatures of between 490 and 560°C (Fig. 8). Calculated $\delta^{18}\text{O}$ values of water in equilibrium with these minerals at these temperatures ranges from 10.0 to 10.4‰ (Fig. 8, Table 2). Using carbonate fractionation factors of Zheng (1999), a similar $\delta^{18}\text{O}_{\text{water}}$ value of 9.8‰ was calculated for dolomite in talc schist sample 2814, but magnesite from sample 2815 has a $\delta^{18}\text{O}_{\text{water}}$ value of

7.7‰. The lower $\delta^{18}\text{O}$ value calculated from magnesite in 2815 suggests that magnesite may not be in isotopic equilibrium with talc and magnetite in this rock. Carbonate minerals are known to undergo oxygen isotopic diffusion and exchange more readily than silicate minerals (Cole 2000; Zheng et al. 2004), so it is expected that the $\delta^{18}\text{O}$ of magnesite from 2815 may have been altered during retrograde metamorphism. Unlike oxygen, the carbon isotope signature of the carbonates is unlikely to be significantly altered during retrogression, as neither retrograde fluids (Carson et al. 2000) nor neighbouring minerals are likely to have contained significant amounts of carbon.

Isotope equilibrium temperatures cannot be calculated for chlorite schist sample 2816 or the serpentinite, because coexisting mineral pairs were not analysed. However, these rocks largely consist of chlorite and antigorite, respectively. Because bulk-rock and carbonate isotope values for sample 2816 and serpentinite sample 03J42 have been measured, calculations of approximate chlorite $\delta^{18}\text{O}$ values for 2816, and antigorite $\delta^{18}\text{O}$ values for 03J42, can be

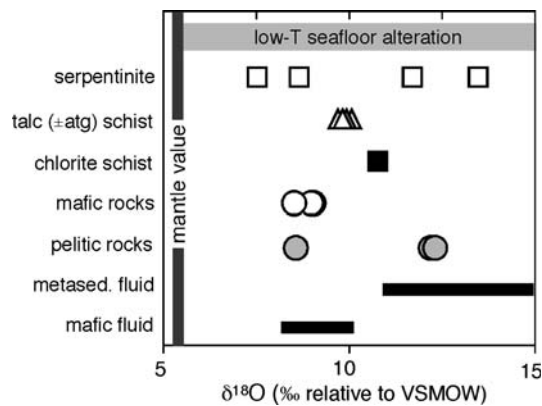


Fig. 7 Bulk oxygen isotope data (‰, VSMOW) for various rock types and fluids from the Pouébo Eclogite Mélange. The range of fluid values for metasedimentary and mafic rocks ($T = 470\text{--}600\text{ }^{\circ}\text{C}$) were calculated on the basis of isotopic data reported by Black (1974) and Spandler and Hermann (2006) (see Table 2). The low- T seafloor alteration of oceanic crust range is adapted from Gregory and Taylor (1981), Putlitz et al. (2000) and Früh Green et al. (2001)

made by mass balance. If there was isotopic equilibrium between dolomite and chlorite in sample 2816 and between magnesite and antigorite in sample O3J42, temperatures for these samples were calculated to be ~ 500 and $\sim 200^{\circ}\text{C}$, respectively. Equilibrium fluids at these temperatures have $\delta^{18}\text{O}$ values of 11.5‰ for the chlorite schist and 8.1‰ for serpentinite sample O3J42. However, these results must be regarded with caution because isotopic equilibrium between the carbonates and other minerals cannot be verified. If the carbonates in these samples had suffered isotopic modification during retrogression, then the above temperature estimates are likely to be maximum values.

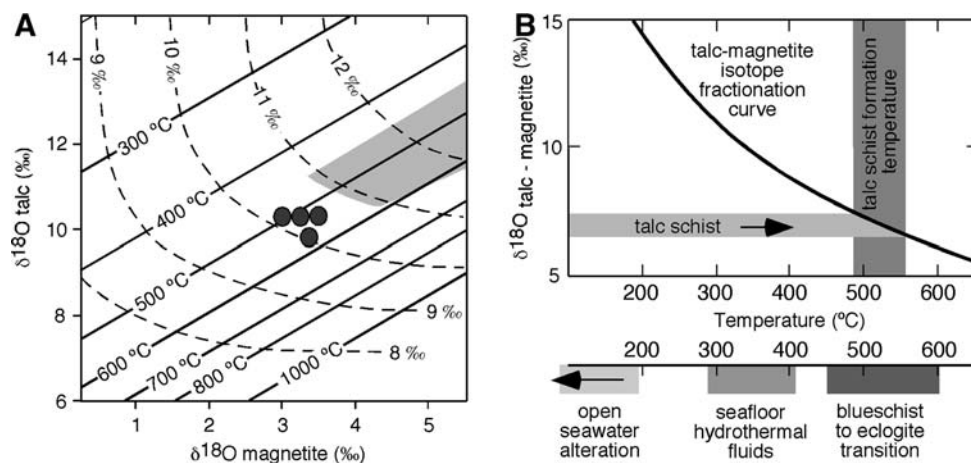


Fig. 8 **a** Coexisting $\delta^{18}\text{O}$ of magnetite versus $\delta^{18}\text{O}$ of talc from talc schist samples from the Pouébo Eclogite Mélange (dark grey dots). Solid lines represent isopleths of temperature and dashed lines are isopleths of $\delta^{18}\text{O}_{\text{water}}$ composition. The grey field represents the field of metasedimentary-derived fluids (Table 2). **b** $\delta^{18}\text{O}_{\text{talc-magnetite}}$ versus temperature. The solid black line represents the isotope fractionation

Discussion

Origin of the serpentinite

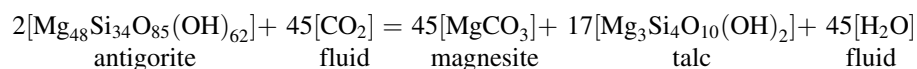
Samples of serpentinite from the PEM have similar geochemical compositions and are interpreted to have had a common origin. Compatible element contents (e.g., Cr, Ni, Yb, Zr) are typical of ocean floor peridotites (Fig. 5; Niu 2004). Structural evidence confirms that these rocks were part of the high- P belt prior to peak metamorphism (Rawling and Lister 2002; Fitzherbert et al. 2004). Therefore, the serpentinites are likely to be either; (1) the lithosphere of the subducting plate that was serpentinized during seafloor hydrothermal alteration prior to subduction or; (2) mantle wedge peridotite that was first hydrated by slab-derived fluids, then incorporated into the high- P belt during subduction. Fitzherbert et al. (2004) and Rawling and Lister (2002) favour the second origin for the serpentinite units and suggested that they might be part of the New Caledonia Ultramafic Nappe, which was thrust over the island in the Late Eocene (Cluzel et al. 2001). However, age constraints on the high- P metamorphism suggests that emplacement of the ultramafic nappe occurred at least 10 million years later than eclogite-facies metamorphism (Spandler et al. 2005). Therefore, the serpentinite and the hybrid rocks must derive from a different protolith than the New Caledonia Ultramafic Nappe.

The low CaO contents of the serpentinite relative to Al_2O_3 indicate Ca loss during serpentinization (Coleman and Keith 1971); a fractionation typically observed during open-system alteration of the oceanic lithosphere. Also, the serpentinites have a higher SiO_2/MgO than normal

curve for talc-magnetite pairs. Talc schist samples have $\delta^{18}\text{O}_{\text{talc-magnetite}}$ of 6.5–7.3, corresponding to temperatures of 490–560°C (see Table 2). For comparison, temperature ranges of seafloor alteration processes and the blueschist/eclogite transition in the Pouébo Eclogite Mélange are shown. The isopleths and the fractionation curve were calculated from mineral fractionation factors of Zheng (1991, 1993a)

harzburgite in agreement with open system alteration (Fig. 4). Serpentinite REE patterns feature negative Eu anomalies and La enrichments, one sample has a negative Ce anomaly and another a positive Y anomaly (Fig. 6a). These features cannot be explained by any simple magmatic process, but reflect the unique characteristics of seawater, as shown in Fig. 6c (see also Enderfield and Greaves 1982). Seawater has very low REE contents, so for serpentinite to inherit seawater REE characteristics requires open-system water–rock interaction, which is most likely to occur close to the seafloor at relatively low T (<200°C). Abyssal serpentinite may also form by reaction of peridotite with hot (300–400°C) fluids in abyssal hydrothermal fields (e.g., Paulick et al. 2006). However, these hydrothermal fluids have relatively high REE contents, positive Eu anomalies and lack Ce or Y anomalies (Fig. 6c). Serpentinite formed in such environments tend to inherit these features (e.g. Paulick et al. 2006), so this origin is unlikely for the PEM serpentinite.

Oxygen isotope studies of relatively undeformed high-P metamorphic rocks suggest that the isotope values of seafloor alteration may be preserved during metamorphism (e.g., Barnicoat and Cartwright 1995; Putlitz et al. 2000; Früh-Green et al. 2001). In this case, the heavy $\delta^{18}\text{O}$ values of serpentinite relative to mantle (Gregory and Taylor 1981) indicates that serpentinization took place at temperatures below 200°C (Wenner and Taylor 1973), which is consistent with the temperature of $\sim 200^\circ\text{C}$ calculated for sample O3J42 (Table 2). Serpentinite samples that contain magnesite and talc have a similar chemical composition to other serpentinite samples but have heavier $\delta^{18}\text{O}$ values (Fig. 7). The formation of talc and magnesite in serpentinite by CO_2 input can be achieved by the reaction:



If we assume the isotopic composition of serpentinizing fluids is constant, the relatively heavy bulk-rock $\delta^{18}\text{O}$ values (11.8–13.3‰) of this type of serpentinite can be explained by the presence of magnesite and talc, both of which have heavier $\delta^{18}\text{O}$ values than serpentine at low temperature (Zheng 1993a, 1999).

The major- and trace-element and isotopic characteristics of serpentinite indicate that these rocks formed prior to subduction on, or close to, the seafloor by seawater-dominated alteration at low temperature. The serpentine mineral formed at these conditions was probably lizardite, but this would have converted to antigorite under

greenschist-facies metamorphism during subduction (Ulmer and Trommsdorff 1999). Prograde metamorphic olivine that forms from the reaction of antigorite with brucite is often observed in subducted serpentinites (e.g., Scambelluri et al. 2001; Fitzherbert et al. 2004). The elevated SiO_2/MgO ratio of the investigated serpentinites prevents the formation of brucite and hence no prograde olivine is present. Analogous rocks have been recovered from drilling the seafloor of the Iberian abyssal plain (Agrinier et al. 1996). Geochemical, petrographic and oxygen isotope evidence also demonstrates some of the associated mafic rocks of PEM underwent low-temperature hydrothermal alteration on the seafloor prior to subduction (Fig. 7; Spandler et al. 2004a, b).

Origin of the talc and chlorite schists

The talc–chlorite–amphibole-bearing schists described above are examples of blackwall alteration assemblages, as first documented by Read (1934). Blackwall rocks have since been described from contacts between ultramafic rocks and mafic or sedimentary rocks in many locations worldwide. Nearly pure talc and/or chlorite rocks have also been recovered during drilling and dredging of ocean floor spreading centres and hydrothermal vents (Lonsdale et al. 1980; Hannington et al. 2001; Bach et al. 2004; D’Orazio et al. 2004; Boschi et al. 2006). Blackwall rocks also occur in many high-P metamorphic terranes [e.g., Cyclades, Greece (Katzir et al. 2000; Marschall et al. 2006); Sanbagawa Belt, Japan (Maekawa et al. 2004); Central Alps (Widmer 1996; Pfiffner and Trommsdorff 1998); Maksyotov Complex, Russia (Beane and Liou 2005); Catalina Schist, California (Sorensen and Grossman 1989; Bebout

1991; Bebout and Barton 2002; King et al. 2006); Franciscan Complex, California (King et al. 2003); and the Shuksan Suite, Washington (Brown et al. 1982; Sorensen and Grossman 1993)], but these rocks are rarely subject to detailed scientific study. Exceptions include the high-P terranes of Washington, California and Japan by Sorensen and Grossman (1989, 1993), Bebout and Barton (2002), King et al. (2003, 2006) and Maekawa et al. (2004).

The present study, together with the work of Fitzherbert et al. (2004), documents the occurrence of metasomatic blackwall rocks from the blueschist- to eclogite-facies belt of northern New Caledonia. Based on structural and

petrographic evidence, Fitzherbert et al. (2004) suggested that the talc and chlorite-rich rocks formed at, or prior to, peak metamorphic conditions. These rocks contain mineral assemblages that are not diagnostic of a particular metamorphic facies, hence the conditions of metamorphic formation are difficult to determine. Field relations and geochemistry indicate that the talc schist has a genetic relationship with the serpentinite. Talc schist typically has gradational contacts with serpentinite (Fig. 2) and has Cr, Ni and REE abundances similar to the serpentinite. The REE patterns of both talc schist and serpentinite have Ce, Eu and Y anomalies that suggest the former presence of seawater (Fig. 6). However, talc-rich rocks found in oceanic environments are enriched in REE compared to the serpentinite and/or have positive Eu anomalies (Escartin et al. 2003; D’Orazio et al. 2004; Boschi et al. 2006; Paulick et al. 2006). These talc rocks are interpreted to form during alteration of peridotite or gabbro by hot (300–400°C) hydrothermal fluids. The characteristics of ocean floor talc rocks are not shared by the PEM talc schist, indicating that seafloor hydrothermal processes did not form the latter rocks.

Temperatures for PEM talc schist estimated from oxygen isotope compositions of coexisting talc and magnetite are 490–560°C (Fig. 8), while temperature estimates for the chlorite schist are around 500°C (Table 2). These temperatures, which are significantly greater than those of seafloor hydrothermal fluids, resemble estimates for the blueschist to eclogite facies transition in the PEM (450–600°C; Clarke et al. 1997; Fitzherbert et al. 2003). The presence of rutile in the chlorite schist, and rutile and Na- and Al-rich amphibole in the talc-amphibole rocks is also consistent with formation under high-P conditions. The blueschist to eclogite transition in the PEM is expected to have liberated significant volumes of aqueous fluid from mafic and pelitic rocks (Peacock 1993; Spandler et al. 2003), so the talc and chlorite schists are interpreted to have formed during prograde metamorphism of the PEM via metasomatism by fluids produced during the blueschist/eclogite-facies transition (Fig. 8). An episode of retrograde greenschist-facies metamorphism is well documented in the PEM (Carson et al. 2000). We suggest that this phase of retrogression is manifest as late-stage talc veins in the talc schists (Fig. 3a), the late chlorite veins and titanite mantling of rutile in the chlorite schists (Fig. 3b), and the formation of Na-poor amphibole and titanite in the talc-amphibole schists.

The REE and other trace-element characteristics of most of the talc schist were likely inherited from precursor serpentinite protoliths. However, some samples have significantly different geochemical characteristics, despite similar isotopic compositions and calculated formation temperatures. Samples TC01 and 2815 are

strongly depleted in REE. These are unlikely to be metasomatised samples of more depleted mantle, because other elements (e.g., Al, Cr, Ni, Ba) are not depleted. These samples probably lost REE during conversion to talc schist. Talc schist sample 2814 and the talc-amphibole samples also are geochemically and mineralogically distinct from other talc schist samples. The former have compositions that are intermediate between serpentinite or talc schist and mafic rocks (Figs. 4–6). The presence of talc and chlorite inclusions in the trace-element-rich minor phases such as dolomite, apatite and Ti-magnetite indicates that these minerals grew during metasomatism. We suggest that these rocks are metasomatised mafic rocks or peridotite-mafic rock hybrids. Talc schist sample 1013 also has high Ti, P and Nb contents and is slightly depleted in Cr and Ni relative to the serpentinite, indicating it may also contain a small mafic component.

Chlorite schist typically occurs between serpentinite and high-P mafic rock. The major-element composition of the chlorite schist is primarily controlled by the proportion of chlorite, which is the major phase that formed by metasomatism. Moreover, textural relations and mineral inclusion assemblages indicate that at least tremolite, dolomite and rutile are cogenetic with chlorite. The trace-element and isotopic compositions of the chlorite schist are either like those of PEM mafic rocks, or are intermediate between PEM mafic rocks and serpentinite (eTable 2; Table 2; Figs. 5, 6). Evidently, the chlorite schist is also a product of metasomatic reaction between mafic and ultramafic rocks.

Constraints on the origin and composition of the fluid

Hybrid rocks of the PEM include rocks of the *mélange* matrix and the talc and chlorite schists found along contacts of ultramafic, mafic and metasedimentary units (Fig. 1). Although not specifically investigated in this study, it is likely that the *mélange* matrix formed from intershearing and tectonic mixing of mafic, metasedimentary and ultramafic rocks, as has been described in other exhumed subduction complexes (Sorensen and Grossman 1993; Bebout and Barton 2002). Based on the field evidence, and isotopic and geochemical data presented above, we conclude that the talc and chlorite schists from ultramafic-crustal rock contacts in the PEM formed during subduction by metasomatic interaction between peridotite and crustal rocks in a high-P *mélange* zone. However, the sources of fluid required to drive this metasomatism are uncertain. Serpentinite is unlikely to have undergone significant dehydration during prograde metamorphism (Ulmer and Trommsdorff 1999), and hence is not considered as a major fluid source. In contrast, both the mafic and

metasedimentary rocks of the PEM underwent metamorphic dehydration during conversion from blueschist to eclogite facies assemblages (Clarke et al. 1997; Spandler et al. 2003). These rocks could have provided fluid for metasomatism, as they are intimately associated with the talc and chlorite schists in the PEM. The oxygen isotope composition of fluids derived from PEM metasedimentary rocks at temperatures from 470–600°C range from 11 to 15‰, based on isotopic data of Black (1974) and Spandler and Hermann (2006), and the isotopic fractionation factors of Zheng (1993a, b) (see Table 2; Fig. 5). Isotopic values of fluids from PEM mafic rocks are sparse (Table 2), but imply fluid $\delta^{18}\text{O}$ values somewhat lower (8.2–10‰) than those of the metasedimentary rocks.

The oxygen isotope compositions of the fluids that formed the talc (10.0–10.4‰) and chlorite (~11.5‰) schists are intermediate between the mafic and metasedimentary sourced fluids (Table 2). In contrast, carbon isotopic values for the talc and chlorite schists (–5.2 to –12.7‰) coincide with PEM metasedimentary rocks (–5.8 to –10.4‰; Black 1974). These results imply that either the mafic or metasedimentary rocks, or both, could have been fluid sources for metasomatism; a premise supported by the similar temperature of fluid release from mafic and metasedimentary rocks during metamorphism and temperature of formation of the talc and chlorite schists (Fig. 8).

The blueschist to eclogite facies transformation yields aqueous fluids with low X_{CO_2} (Molina and Poli 2000; Kerrick and Connolly 2001) and low solute loads, with the notable exception of up to 5 wt% dissolved silica (Manning 1995, 2004; Hermann et al. 2006; Spandler et al. 2007). Petrogenetic calculations of ultramafic rock metasomatism at high P (Connolly and Trommsdorff 1991; Ogasawara et al. 1995) show that interaction between ultramafic rock and fluid of low X_{CO_2} (<0.01) could form carbonate (dolomite or magnesite) with antigorite and talc during subduction. Therefore, influx of serpentinite with such fluids can cause the silica and CO_2 enrichment required to form the talc schist (\pm carbonates), without significant addition of other chemical components. Conversion of serpentinite (~12 wt% H_2O) to talc schist (~5 wt% H_2O) is a fluid-producing reaction (King et al. 2003) that could strip other elements from the serpentinite during metasomatism. This may explain the REE depletion of talc schist samples 2815 and TCO1 and the lower As and Sb contents of the talc schist compared to the serpentinites (eTable2). Formation of the chlorite schist is difficult to explain in detail. We suggest that this rock formed from mafic rock that underwent extensive loss of Si and gain of H_2O (and CO_2) during metasomatism, as has been proposed for formation of similar rocks from the Catalina Schist (Bebout and Barton 2002).

Formation of hybrid rocks in subduction mélanges

Mélange is present in high-P terranes worldwide (e.g., Katzir et al. 2000; Engi et al. 2001; Bebout and Barton 2002; Beane and Liou 2005) and in some cases can be demonstrated to have formed during prograde metamorphism (e.g., Bebout and Barton 2002; this study). Geodynamic modelling of subduction zones also indicates that mélange zones several km in thickness form at the top of a subducting plate (Cloos and Shreve 1988; Beaumont et al. 1999; Geyra et al. 2002). In the PEM, the serpentinite units probably formed by seawater alteration of oceanic lithosphere prior to subduction. Nonetheless, in many subduction zones large volumes of serpentinite formed by hydration of the mantle wedge may become incorporated in the subducting mélanges (Geyra et al. 2002) allowing for metasomatic formation of hybrid rocks during subduction.

The origin of talc and chlorite schists of the PEM is likely similar to hybrid rock formation in the subduction melange zones of the Catalina Schist (Bebout 1991; Bebout and Barton 2002) and the Franciscan Complex (King et al. 2003), and is consistent with predictions of peridotite metasomatism in subducted slabs (Peacock and Hyndman 1999). In particular, the comprehensive studies of the Catalina Schist by Gray Bebout and co-workers (e.g., Bebout 1991; Bebout and Barton 2002; King et al. 2006) have documented talc and chlorite schist formation during subduction by metasomatic and mechanical mixing in a mélange zone that developed at the slab-mantle wedge interface. The significance for subduction-zone processes of mélange and hybrid rock formation in the Catalina Schist has been questioned, given that estimated metamorphic conditions are of greater T/P than that expected for subducting slabs (King et al. 2006). The hybrid rock-types of the PEM are likely to have formed from similar processes to those described from the Catalina Schist, but the P–T conditions of the PEM are expected to be typical of subduction (Clarke et al. 1997; Spandler et al. 2003). This information, together with the common occurrence of talc- and chlorite-rich rocks in other high-P terranes that represent exhumed subducted slab (e.g. Brown et al. 1982; Sorensen and Grossman 1993; Widmer 1996; Pfiffner and Trommsdorff 1998; Katzir et al. 2000; Maekawa et al. 2004; Beane and Liou 2005; Marschall et al. 2006) supports the suggestion of King et al. (2006) that mélange and hybrid rock formation commonly occurs in subduction zones. Moreover, nearly pure talc and chlorite schists formed during seafloor hydrothermal processes (e.g., Bach et al. 2004; Boschi et al. 2006) will also end up as components of subducting slabs.

Regardless of whether the talc and chlorite-rich rocks formed on the ocean floor or by metasomatism in mélange zones during subduction, subducting slabs are likely to

contain significant amounts of these rock-types. Based on the field relations in the PEM and other high-P terranes, we expect that the upper portions of the slab may contain in excess of 5% hybrid rock-types at sub-arc depths (90–150 km). Therefore, these hybrid rocks should be considered together with mafic rock, metasediment, and serpentinite as an important volatile-bearing components of subducting slabs, and hence may have a significant influence on volatile and trace element fluxing from the slab to the mantle wedge.

Implications for fluid and element transfer in subduction zones

Subducting mafic and sedimentary rocks are rich in incompatible trace elements, but are expected to release most of their H₂O at fore-arc depths (e.g., Poli and Schmidt 2002). These rocks are thus unlikely to be direct sources of H₂O for arc magmatism. In contrast, serpentinite in subducting slabs is regarded to be an important source of water for arc magmas because it contains ~12 wt% water and is predicted to dehydrate at sub-arc depths (Ulmer and Trommsdorff 1999). Serpentinite-derived fluids may transfer some elements from the slab to the mantle wedge. However, in general the trace-element content of fluids released by serpentinite dehydration are expected to be low due to the relatively low temperatures (~650°C; Figs. 9, 10) of fluid release and low trace-element content of the host serpentinite (Tenthorey and Hermann 2004).

Collectively, these properties of subducted materials indicate that simple models of metamorphic dehydration and subsequent fluid migration cannot adequately account for the flux of slab-derived volatiles and trace elements (e.g., LILE, Sr, U and LREE) into the source regions of arc magmas (see also, Spandler et al. 2004a; Hermann et al. 2006; King et al. 2006). However, components derived from different rock-types in the slab may interact to produce the necessary fluid and trace-element flux from the slab. Fluids released by antigorite breakdown may flow upwards into zones of higher temperature, such as the slab-mantle wedge interface. In these zones, the fluid may interact with mafic and pelitic rocks to produce melts or trace element-rich fluids that then ascend into the mantle wedge to contribute to arc magma-genesis (Hermann et al. 2006). Field and isotopic evidence from PEM and other high-P terranes (e.g., Barnicoat and Cartwright 1995; Scambelluri and Philippot 2001; Ague 2006) suggest that large-scale fluid flow in subduction zones is highly channelized. The interaction between fluids derived from lower-slab serpentinite and upper-slab mafic and pelitic rocks may therefore be somewhat limited.

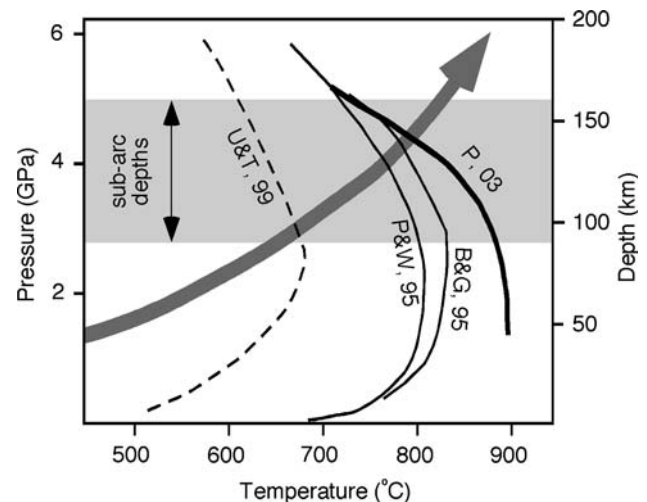


Fig. 9 Pressure versus temperature plot showing the maximum stability limits for antigorite (dashed line), talc (solid black lines) and chlorite (thick black line). The grey field represents sub-arc depths and the arrowed thick-grey line represents a typical intermediate P–T path of a subducting slab (after Kincaid and Griffiths 2004). The antigorite stability curve is taken from Ulmer and Trommsdorff (1999). The talc and chlorite stability curves are taken from Pawley and Wood (1995), Bose and Ganguly (1995), and Pawley (2003), respectively

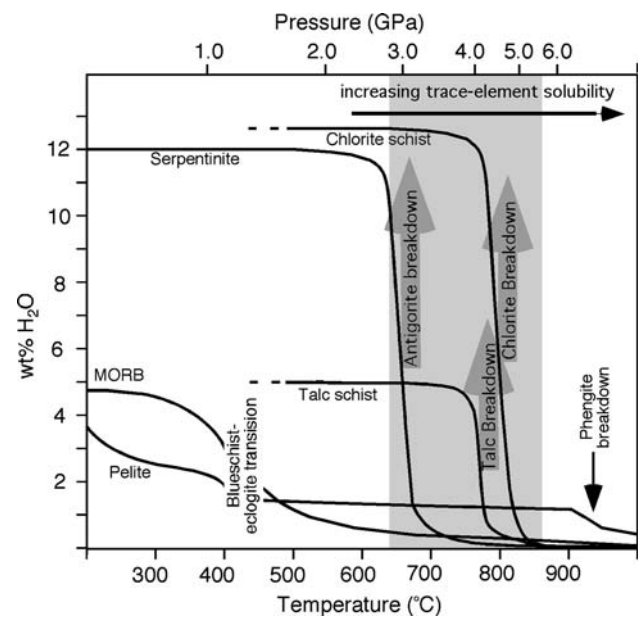


Fig. 10 Variation in calculated H₂O content of rock-types with prograde metamorphism following an intermediate P–T subduction path as shown in Fig. 7. The light grey field represents sub-arc depths and the thick grey arrows represent major fluid release events at sub-arc depths. Calculated water content curves for respective rock-types; pelite and MORB—Schmidt and Poli (1998) and Hyndman and Peacock (2003); serpentinite—Ulmer and Trommsdorff (1999); talc schist—Pawley and Wood (1995) and Bose and Ganguly (1995); chlorite schist—Pawley (2003)

Hybrid rocks in subducting *mélange* zones may provide an alternate mechanism for transferring fluid and trace elements from the slab to arc magma source regions. Bebout (1991) and Bebout and Barton (2002) show that subduction-generated hybrid rocks could carry volatiles to deep levels of subduction zones. Near monomineralic talc and chlorite schists will only undergo extensive metamorphic dehydration once they reach the conditions of maximum stability for talc and chlorite, respectively. Combining a subduction P-T path that is consistent with recent geodynamic modelling (van Keken et al. 2002; Kincaid and Griffiths 2004) and experimentally-determined stability limits for talc and chlorite (Bose and Ganguly 1995; Pawley and Wood 1995; Pawley 2003; Fumagalli and Poli 2005), predictions of talc and chlorite schist dehydration and fluid release in subduction zones can be made (Figs. 9, 10). For the modelled subduction path, the talc and chlorite schists will undergo almost complete dehydration at 4.0–4.5 GPa and 750–800°C, releasing ~5 and ~13 wt% H₂O, respectively (Fig. 10). Like serpentinite, the talc and chlorite schists dehydrate at sub-arc levels and have relatively low trace-element contents (eTable 2). However, the elevated temperatures of dehydration of the talc and chlorite schists allow for greater solubility of trace elements in the exsolved fluids. In the PEM and other subduction *mélanges* (e.g., Catalina Schist—Bebout and Barton 2002; Cyclades—Ague 2006) fluid flow is likely to be channelled along lithological boundaries or through the *mélange* matrix. In this case, trace elements may be stripped from juxtaposed pelitic and mafic rocks in the subduction *mélange*. Furthermore, the presence of free fluid may promote partial melting of the metasedimentary rocks and produce hydrous granitic melts (Sorensen and Barton 1987; Hermann and Green 2001; Schmidt et al. 2004; Hermann et al. 2006). Migration of such melts or trace element-rich fluids into the mantle wedge may be crucial to the recycling of volatiles and trace elements through subduction zones and the evolution of arc magmas.

Implications for carbon recycling into the deep mantle

Mg-rich carbonate minerals (dolomite or magnesite) are a common component of serpentinite and the hybrid rocks from the PEM. Formation of these carbonate minerals may be related to seafloor alteration prior to subduction or may result from metasomatism during subduction, even if the fluids have $X_{\text{CO}_2} < 0.01$ (Connolly and Trommsdorff 1991; Ogasawara et al. 1995). Therefore, ultramafic rocks within the slab or overlying mantle wedge may be highly efficient at sequestering even small amounts of CO₂ from fluids sourced from subducting mafic or metasedimentary rocks. Deeper burial of these rocks, either as part of the

slab or by corner-induced mantle flow, could transport carbon to sub-arc regions and deeper. As we have shown, significant volumes of hydrous fluid are produced during dehydration of serpentinite and hybrid rock-types at sub-arc depths. These fluids may partially dissolve some of the carbonates from these rocks, and hence may be a source of CO₂ for arc magmas. However, mass balance calculations indicate that a significant proportion of subducted carbon is not returned to the surface at volcanic arcs, but rather is recycled into the deep mantle (Kerrick and Connolly 2001). Mafic, metasedimentary, and ultramafic rocks are all considered able to transport carbonates beyond the sub-arc level (Kerrick and Connolly 1998, 2001; Molina and Poli 2000), but only magnesite is expected to be the stable carbonate form at lower mantle depths (Biellmann et al. 1993; Isshiki et al. 2004). Magnesite is most stable in high-Mg rocks such as peridotites and hybrid rock-types.

The carbon isotopic composition of carbonate minerals from the PEM serpentinite, hybrid rocks and metasedimentary rocks is between -5.2 and -12.7‰ (Table 2; Black 1974). By contrast, unmetamorphosed equivalent sedimentary rocks from New Caledonia have $\delta^{13}\text{C}$ carbonate values around 0‰ (Black 1974), which are typical of marine carbonate. The carbon isotopic composition of rocks of the PEM were evidently shifted to lower values during subduction, but prior to blueschist metamorphism of ~250°C (Black 1974). Similar isotopic shifts with metamorphism have been reported from the Franciscan Complex and Western Baja Terrane by Sadofsky and Bebout (2001) who attributed the shift to both mixing of organic carbon ($\delta^{13}\text{C} \sim -25\%$) with sedimentary carbonate, and isotopic fractionation during low-temperature decarbonation. Low-temperature decarbonation of subducted material at shallow levels of subduction zones is predicted from thermodynamic and experimental studies (Molina and Poli 2000; Kerrick and Connolly 2001) and is supported by the presence of extensive carbonate veining in accretionary wedges and ocean-floor carbonate chimneys in fore-arc regions (Fisher 1996; Fryer et al. 1999). We speculate that fractionation of subducted carbonate to negative $\delta^{13}\text{C}$ values may commonly occur in subduction zones.

The $\delta^{13}\text{C}$ value of most carbon-bearing mantle materials (e.g., carbonatites, kimberlites, diamonds) is around -5‰, whereas subducted carbon has an average $\delta^{13}\text{C}$ value of around -1‰ (Coltice et al. 2004). This difference of isotopic composition is cited as evidence that deep mantle carbon such as diamond is not derived from subducted carbonates (e.g. Deines 2002). However, the Mg-rich carbonates in subducted peridotites and hybrid rock-types have “mantle like” $\delta^{13}\text{C}$ values, may be transported to well beyond the sub-arc level, and thus are a potential source of carbon for diamond formation.

Conclusions

We have investigated the petrology and geochemistry of a suite of serpentinite and hybrid rock-types from the eclogite-facies mélange zone of northern New Caledonia. The serpentinite represents oceanic lithosphere that was partly hydrated on the ocean floor prior to subduction, whereas associated talc and chlorite schists probably formed during subduction by metasomatism and mixing among mafic, metasedimentary and ultramafic rocks. These hybrid rocks host large quantities of H₂O and CO₂ and may be important for transferring volatiles to great depths in the subduction zones. Dehydration of these rocks will occur at sub-arc depths, producing ~800°C fluids that may be capable of dissolving high trace-element loads or partially melting adjacent pelitic or mafic rocks in the subduction mélange. These fluids or melts may subsequently migrate into the mantle wedge and contribute to arc magma-genesis. In contrast, carbonate in the hybrid rocks and serpentinite are unlikely to undergo significant breakdown and may transfer carbon to the lower mantle. These results indicate that hybrid rocks that form in subduction mélanges may play a vital role in the recycling of volatile and trace elements through the Earth.

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