Low-temperature Wollastonite Formed by Carbonate Reduction: a Marker of Serpentinite Redox Conditions

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In the Alpine blueschist- to eclogite-facies meta-ophiolitic units of northern Corsica, the contact between a serpentinite body and an immediately overlying siliceous marble is remarkable for the occurrence of wollastonite and, on the marble side, a dark halo around the serpentinite. The refolded, continuous contact is a rodingite-type reaction zone with a centimetre-thick nephritic selvage of diopside + andradite/grossular + perovskite on the serpentinite side, followed towards the marble by a 1–5 cm thick zone of massive wollastonite + quartz + graphitic material + diopside, with no carbonate. The transition to the overlying wollastonite-free, calcite + quartz-bearing layers is sharp. Considering the stability of calcite + quartz everywhere else in the regional metamorphic series, this low-temperature occurrence of wollastonite (c. 400–450°C) requires unusual conditions. We interpret this observation as evidence for local reduction of Ca-carbonate to form elemental carbon and wollastonite according to the reaction

\[ SiO_2 + CaCO_3 + 2 H_2 \rightarrow CaSiO_3 + C + 2 H_2O. \]

A similar carbonate + mica reduction reaction is responsible for the disappearance of phengite and the appearance of grossular + carbon within a narrow zone in the marble above the wollastonite–quartz zone. Textural and solubility considerations suggest that the development of the zonal sequence is an essentially diffusive process. Thermochemical modelling of mineral stability in the successive reaction zones suggests a positive oxygen-fugacity gradient from the serpentinite to the marble (c. 6 < ΔFMQ < 1), mediated through a CH4- and H2-bearing aqueous intergranular fluid. In line with the field evidence, it is calculated that a serpentinite body equilibrated at ΔFMQ = 4 after oceanic serpentinitization can still impose, through Fe2+–bearing serpentine oxidation, highly reducing conditions while entrained at depth in a subduction wedge and channel. This may contribute to the presence of H2 + CH4 in the fluid and cause the destabilization of calcite in favour of graphite. In addition to the consequences for wollastonite and elemental carbon formation at low temperature, this finding has direct implications for redox conditions in subduction zones.

KEY WORDS: wollastonite; redox; serpentinite; carbonate reduction; H2 and CH4 fluids; rodingite; blueschist; Corsica

INTRODUCTION

Hydrothermal interaction between seawater and oceanic peridotite leads to the formation of hydrous phases dominated by serpentine-group minerals. The progressive transformation of nominally anhydrous peridotite to

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serpentinite (serpentization) not only affects the bulk water content of the rock system but it also strongly modifies its redox potential. Peridotite–seawater interaction results in the oxidation of Fe in the original ultramafic rock and in the corresponding reduction of the aqueous fluid that may, ultimately, dissociate to form H₂ (Moody, 1976; Charlou, 2002; Kelley et al., 2005). Hydrated peridotites are incorporated into subduction zones (Ripke et al., 2004; Iyer et al., 2010) where they can interact chemically with the mantle wedge, in particular when they start dehydrating (Deschamps et al., 2010). Obviously, the redox potential of this released fluid will depend on the oxidation state of the parent serpentinite. As an insight into the redox conditions associated with serpentinite environments, we report here petrological evidence for the development of a reduced halo in marble in contact with a serpentinite body that experienced blueschist- to eclogite-facies metamorphic conditions as part of an Alpine ophiolite complex in Corsica. We show that serpentinite may preserve and locally impose some of its initial redox conditions throughout the vagaries of subduction and exhumation.

The incentive for this study was the discovery of wollastonite, nominally a high-temperature mineral, in low-temperature, blueschist- to eclogite-facies rocks from Corsica. This paradoxical occurrence is strictly bound to a zone of graphitic matter enrichment along a serpentinite–marble interface. It is completely at odds with the classical regional- or contact-metamorphic origin of wollastonite through high-temperature devolatilization of a calcite–quartz assemblage (e.g. Trommsdorff, 1968; Ferry et al., 2001). The stability of calcite + quartz throughout the Alpine low-T metamorphic pile in Corsica calls for another origin for the wollastonite. We show that its occurrence in Corsica along with graphitic matter is the result of the reduction of carbonate around the serpentinite body during metamorphism. This provides evidence for the maintenance of the reducing potential of serpentinites during subduction and accretionary-wedge evolution.

**GEOLOGICAL SETTING**

The northeastern part of Corsica belongs to the Alpine orogen (Fig. 1, inset) and consists mainly of Mesozoic formations of oceanic derivation, some of them possibly transitional between a continental margin (to the west) and more typical ophiolitic units (e.g. Faure & Malavieille, 1981; Jolivet et al., 1990; Malavieille et al., 1998; Vitale Brovarone et al., 2011a, for more details). Most units were buried and metamorphosed under high-pressure and low-temperature conditions during the Alpine orogeny; some reached the lawsonite-eclogite facies (Caron & Péquignot, 1986; Ravna et al., 2010; Vitale Brovarone et al., 2011b). At Cap Corse, the northern tip of the island (Fig. 1), the metamorphic pile comprises several ophiolitic units, mostly serpentinite with some gabbrö, basalt, peridotite and subordinate sedimentary material including radiolarite and calcschist. Other intercalated units comprise material of more continental derivation (e.g. the Farinole and Serra di Pigno gneisses). The metamorphic grade may not be uniform throughout the pile. The Farinole series contains jadeite-bearing metagranite and lawsonite-eclogite, for which early estimates by Lahondère (1988) were $P > 1$ GPa, $T$ (grt–cpx matrix) $\sim 430$–520$^\circ$C, $T$ (grt–cpx in matrix) $\sim 500$–600$^\circ$C, revised to $P > 15$ GPa, $T \sim 450$–490$^\circ$C if one combines Lahondère’s (1996) new estimates for orthogneiss and metabasite [mineral names are abbreviated after Kretz (1983), capitalized for end-members; e.g. Aeg for aegirine]. More recent estimates for lawsonite-eclogite in meta-pillow-basalts of the Lanco”ne Pass, a structurally deeper unit about 10 km further south, are 19–26 GPa, 340–415$^\circ$C (Ravna et al., 2010), revised to 2.3 ± 0.1 GPa and 520 ± 20$^\circ$C by Vitale Brovarone et al. (2011b). In the structurally higher, blueschist-facies ophiolitic units exposed along the Cap Corse ridge, temperatures did not exceed 350–430$^\circ$C as indicated by relics of Fe–Mg-carpholite and thermometry based on Raman spectroscopy of carbonaceous material (RSCM thermometry, Vitale Brovarone et al., in preparation). The following description pertains to one of them.

Above the village of Patrimonio, the Malaspina ridge, which leads to the Serra di Pigno, exposes slivers of a metasedimentary series within a large serpentinite body (which overlies the Farinole–Serra di Pigno gneisses, which themselves lie structurally above meta-ophiolitic units of the Lanco”ne Pass; Fig. 1). The largest sliver, less than 100 m across strike, consists of massive beds of siliceous marble with carbonate-bearing quartzite at its base, grading upwards into more pelitic layers with a few mafic intercalations. The series rests in direct contact with the serpentinite and was refolded with it, as shown by metre-scale recumbent and sheath folds affecting the contact that are well exposed on the ridge and on its northern side at about 480 m elevation. The marble–serpentinite contact is generally concordant with the sedimentary bedding, as far as one can judge from lithological heterogeneities. This sedimentary series may represent the stratigraphic cover of a tectonized ocean floor (but see Vitale Brovarone et al., 2011a).

Minerals found in the first few metres of the series above the serpentinite (i.e. in the more carbonate-rich layers) are calcite, quartz, clinozoisite, titanite, apatite, graphitic material, rare phengite, albite, and locally prehnite. Aragonite (Chopin et al., 2008) occurs exclusively as oriented fibres in garnet crystals within a black calcite marble layer that immediately overlies the serpentinite (see below), and to which garnet is restricted, along with minor diopside. Glaucophane (‘crossite’) and phengite occur in the more pelitic layers, higher in the series.
Fig. 1. Geological sketch map of the Cap Corse area, NE Corsica, after Malavieille et al. (1998) and Chopin et al. (2008). Flesh colour refers to continental units (Variscan basement) with paraautochthonous cover (brown), green refers to the metamorphic oceanic units with a darker shade for serpentinite bodies, greenish yellow to the uppermost, nearly non-metamorphic nappes. The star indicates the location of the Cima di Malaspina outcrop. Inset: Alpine chain with internal units (reddish brown) and external crystalline massifs (flesh colour).
THE SERPENTINITE–MARBLE INTERFACE

At the Malaspina outcrop, the serpentinite–marble contact (Fig. 2) is marked by a centimetre-thick, weathering-resistant rim of calc-silicate rock, which is remarkable for its continuity throughout the outcrop (i.e. over about 100 m), regardless of the folded nature of the contact (see Fig. S1 in the Supplementary Material, which is available for downloading at http://www.petrology.oxfordjournals.org), suggesting a syn- to post-folding formation. As such this kind of contact is a classical geological feature, long recognized as a reaction zone between serpentinite and country-rock [= ‘skarn’, ‘rodingite’ or ‘nephrite’; see Coleman (1967) and Harlow et al. (2007) for a review]. However, this contact shows two unusual features: one is the occurrence of wollastonite, and the other is the presence of a conspicuous dark halo, typically one to a few decimetres thick, in the marble directly overlying the contact (Fig. 2). The dark colour is due to the presence of graphitic matter, which is locally so abundant as to stain the fingers.

Differential weathering outlines the fine structure of the reaction zone (Fig. 2a) and reveals, from the serpentinite to the marble, three layers of distinctive colour: a protruding, very resistant, whitish nephritic layer, 0.5–3 cm thick (zone Z1); a massive but less resistant pale greyish zone ranging from 0.5 to 5 cm in thickness (zone Z2); and a darker, 5–25 cm thick zone that preserves the appearance and original texture of the marble except for numerous weathering pits (zone Z3, Fig. 2a). A fresher cut across this contact (Fig. 2b) and detailed observation of samples confirm the three sharp zones and highlight the darkness of zone Z3.

ANALYSIS OF THE REACTION ZONE

Analytical methods

The mineral content of the various contact zones has been characterized from a series of thin sections using optical microscopy. Mineral compositions were obtained by electron microprobe analyses (SX100 Cameca instrument at Camparis, UPMC, Paris, in wavelength-dispersive mode, 15 kV, 15 nA, with mineral standards and PAP correction). Further chemical (elemental X-ray mapping) and textural data [back-scattered electron (BSE) images] were obtained using an FE-SEM (Zeiss®/Sigma®) equipped with a 50 mm² EDS detector (X-Max®, Oxford Instruments) at the Ecole normale superieure (ENS, Paris). The EDS detector can quantify concentrations of more than 1 mol % with an accuracy of 5% and qualitatively detects elements reaching concentrations of more than 0.1 mol %. Raman microspectrometry was used to determine the mineralogy of serpentine using a Renishaw inVia spectrometer at ENS with a 514.5 nm argon laser focused through a DMLM Leica optical microscope. The mineral modes in the reaction zone were determined from both BSE images and X-ray maps. The composition (point analysis) and the associated colour range were first determined for each mineral. Then, mineral identification was performed automatically by correlating the BSE images and X-ray maps. The composition (point analysis) and the associated colour range were first determined for each mineral. Then, mineral identification was performed automatically by correlating the BSE images and X-ray maps for each pixel of 3 μm. Finally, the surface area of each mineral (interpreted as the mineral mode) across the reaction zone was determined in the form of a reconstituted profile with 30 images pasted together. Total organic content (TOC) measurements were performed on ~1 cm³ samples drilled from the reaction zone, by combustion under oxygen at 1400°C with a

Petrography and mineral chemistry

Serpentinite

The serpentinite shows a pronounced schistosity (Fig. 2a). Samples collected within 1 m of the contact are mainly composed of serpentine, Cr–Fe oxides, clinopyroxene and uvarovite-rich garnet (Tables 1 and 2), as are those collected further away. Neither orthopyroxene, olivine, brucite, a humite-group mineral, nor Fe–Ni alloys were found here.

Table 1: Garnet and clinopyroxene composition in serpentine and the reaction zones

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Garnet</th>
<th>Clinopyroxene</th>
</tr>
</thead>
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<tr>
<td></td>
<td>09:10</td>
<td>09:10</td>
</tr>
<tr>
<td>Zone:</td>
<td>Serp</td>
<td>Z1</td>
</tr>
<tr>
<td></td>
<td>09:04</td>
<td>09:04</td>
</tr>
<tr>
<td></td>
<td>Z1/2</td>
<td>Z2</td>
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<tr>
<td></td>
<td>09:06</td>
<td>Z3</td>
</tr>
<tr>
<td>SiO₂</td>
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<td>0.35</td>
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<td>TiO₂</td>
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<td>0.03</td>
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<td>0.18</td>
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<tr>
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<tr>
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<td>MnO</td>
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<td>0.00</td>
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<tr>
<td>MgO</td>
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</tr>
<tr>
<td>Na₂O</td>
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<td>0.00</td>
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<tr>
<td>NiO</td>
<td>0.00</td>
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<td>Total</td>
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</tbody>
</table>

Table 2 shows significant Al₂O₃ content variations at the thin-section scale, between 1.5 and 6.5 wt % (i.e. variable amsite component) and Mg/(Fe + Mg + Mn) varying from 0.90 to 0.97. Serpentine of similar composition (Table 2) is also found in thin veinlets penetrating the
Table 2: Serpentine, chlorite, balangeroite, wollastonite, carbonate, mica and talc composition in serpentinite and the reaction zones

<table>
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<tr>
<th></th>
<th>Serpentine</th>
<th>Chlorite</th>
<th>‘Balangeroite’</th>
<th>Wollastonite</th>
<th>Carbonate</th>
<th>Phengite</th>
<th>Talc</th>
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<td>Serp</td>
<td>Serp/Z1</td>
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<td>Z3</td>
<td>Marble</td>
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<td>SiO₂</td>
<td>41.16</td>
<td>42.94</td>
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<td>31.87</td>
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<td>TiO₂</td>
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<td>0.01</td>
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<td>0.06</td>
<td>0.02</td>
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<td>Al₂O₃</td>
<td>2.97</td>
<td>2.60</td>
<td>2.20</td>
<td>3.35</td>
<td>6.88</td>
<td>0.24</td>
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<tr>
<td>FeO</td>
<td>2.91</td>
<td>2.62</td>
<td>2.41</td>
<td>3.50</td>
<td>3.76</td>
<td>47.68</td>
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<td>MnO</td>
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<td>MgO</td>
<td>38.38</td>
<td>39.06</td>
<td>38.21</td>
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<td>CaO</td>
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<td>0.07</td>
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<td>0.15</td>
<td>0.08</td>
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<td>0.42</td>
<td>0.20</td>
<td>0.02</td>
<td>10.06</td>
<td>0.05</td>
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<td>NiO</td>
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<td>0.14</td>
<td>0.38</td>
<td>0.06</td>
<td>0.00</td>
<td>13.39</td>
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<tr>
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<td>87.19</td>
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<td>87.18</td>
<td>85.26</td>
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Structural formula

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<td>0.010</td>
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<td>Fe</td>
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<td>0.095</td>
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<tr>
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<tr>
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<td>2.770</td>
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<td>Mg²⁺</td>
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</table>

(about 1mm²) reveals that magnetite occupies between 0.1% and 1.1% of the image surface. Garnet (up to 100 μm in size, 55 mol % uvarovite–45 mol % andradite, Table 1), associated with Cr-bearing magnetite (up to 23 wt % Cr₂O₃) and some chlorite (up to 10 wt % Cr₂O₃, Table 2), forms small aggregates in the serpentinite (Fig. 3), most probably on the site of former Cr-rich spinel. In two samples, a reddish and elongated silicate mineral (aggregates
of up to 100 μm across) was found intercalated with serpentinite, with high FeOtot (47.7–51.1 wt %) and NiO (4.3–13.4 wt %) contents and a low SiO2 content of 15.2–19.8 wt % (Table 2). Its stoichiometry matches that of balangeroite, Mg42Si16O54(OH)40 (Compagnoni et al., 1983) with Fe and Ni substituting for Mg. Similar Fe- and Ni-rich balangeroite was recently described by Evans & Kuehner (2011) in a serpentinite from Japan. A few small grains (less than 5 μm in size) of both ilmenite and pentlandite with up to 3 mol % of Co9S8 were also found. A few grains of native copper were observed in the serpentinite immediately underlying zone Z1.

Marble
The marble bed overlying the serpentinite is composed of varying proportions of calcite and quartz (c. 100 μm grain size), reflecting the original sedimentary compositional layering (Fig. 4a, bottom; Fig. 5d). It contains minor amounts of sheet-silicates, oriented parallel to the layering and the contact; these are a highly silicic phengitic mica with 3.5–3.7 Si per formula unit, sometimes interleaved or associated with a magnesian phase. This phase has a talc stoichiometry but low analytical totals suggestive of sepiolite (Table 1). Accessory phases are garnet, apatite, titanite and iron sulphide. A sample from which aragonite–garnet intergrowths have been observed was found in an equivalent position (Chopin et al., 2008).

Zone Z1
Zone Z1 is composed of extremely fine-grained clinopyroxene and garnet (Fig. 5a), hence its toughness, with accessory perovskite (CaTiO3). The composition of garnet (typically 10–20 μm, up to 50 μm in size) lies on the andradite–gроссular join (Table 1). The XFe3+ ratio in the garnet octahedral site, defined as XFe3+ = Fe3+/Fe3+ + Fe3+, decreases from 0.98 in crystals close to the contact with the serpentinite to 0.4 in the vicinity of the next zone (Z2). BSE images show that the garnet is zoned, particularly close to zone Z2, with cores having lower XFe3+ than rims. Clinopyroxene is close to the diopside end-member: Ca(Mg1−x,Fex)Si2O6 with x between 0.02 and 0.07. Late calcite veins locally cross-cut the serpentinite and zone Z1. Isolated tiny grains of native copper also occur in this zone.

Zone Z2
This zone is made almost completely of wollastonite, which is responsible for its easier weathering (Fig. 2), with subordinate garnet throughout and some diopside on the Z1 side (Fig. 5a). Crystals (up to 100 μm across) are short prismatic, with little or no preferred orientation. Garnet composition varies within the zone from c. Aδr35–Gr345 on the Z1 side to nearly pure grossular in the middle of the zone, and then remains unchanged to Z3 (Table 1; Supplementary Material, Fig. S2). Locally, short en échelon veinlets have opened in zone Z2 and are filled with white fibres of monomineralic wollastonite. Single-crystal diffraction data point to the simultaneous presence of the two main polytypes of wollastonite, the triclinic 1A (with its twin-related counterpart) prevailing over the monoclinic 2M (S. Merlino, personal communication, 2009). Zones Z1 and Z2 are both cross-cut by narrow serpentinite-filled cracks, which therefore postdate the contact zone formation.
The texture of zone Z3 is similar to that of the marble but the rock is made of c. 70% quartz and 30% prismatic wollastonite oriented in the marble layering (Figs 4 and 5a, d). Small amounts of elongated grossular garnet (Table 1) and rare pectolite, NaCa$_2$Si$_3$O$_8$(OH), are also observed. As mentioned above, zone Z3 is remarkable for its dark colour. Optical microscopy as well as SEM secondary-electron images and micro-Raman spectroscopy (Galvez et al., in preparation) show that graphitic matter is responsible for the darkness of this zone.

Modal and chemical changes across the reaction zone

The bulk-chemistry of the various zones was determined by averaging the results of EDS mapping (3 μm pixels) on a mesh of 3 mm length parallel to the profile and 3 cm width perpendicular to the profile; mineral modes were derived from elemental X-ray mapping coupled with image analysis (see Analytical methods). Bulk composition data are given normalized to the mole percentage of the cations (i.e. the molar percentages of all the analyzed cations sum to 100%). The corresponding results are displayed in Fig. 6 and in the Supplementary Material (Table S1).

From the serpentine contact towards the marble, Mg and Al molar concentrations are both reduced by a factor of c. 2.5 (Fig. 6c). In contrast, Ca and Fe show a marked concentration increase. The decoupling between Mg and Fe at the serpentine–Z1 interface can be explained by the presence of andradite in Z1, which hosts trivalent iron and no magnesium, magnesium being mostly concentrated in diopside in this zone (Fig 6). Beyond Z1, the aluminium concentration is relatively constant (c. 1.3 mol %); small
Al variations are correlated with changes in the Ca/Si ratio, which may therefore represent initial heterogeneity in the former carbonate sediment. The Mg, Fe and Mn concentrations are below the EDS detection limit beyond Z2. The Si and Ca concentrations are roughly constant through zones Z1 and Z2 (ca. 45 and 35 mol %, respectively) whereas at the contact between zones Z2 and Z3 Si strongly increases whereas Ca, like most elements, strongly decreases. Beyond that contact, Ca and Si concentrations display inverse trends owing to the fact that Ca and Si are held by the two most abundant minerals, either wollastonite and quartz or calcite and quartz in the marble. For example, in zone Z3, the wollastonite ‘mode’ (surface area) is between 5 and 80% and is complementary to that of quartz (Fig. 6b).

Variations in the relative proportions of calcite and quartz in the marble are probably related to compositional heterogeneities of sedimentary origin. Similar Ca/Si variations in Z3 may have the same origin and therefore be a first hint that wollastonite replaced calcite in that zone. This assumption is supported by the chemical continuity, at first order, between the dark zone Z3 and the marble.

Upon closer examination, the transition between zone Z3 and marble is marked by a drop in potassium concentration. This drop coincides with the appearance of garnet, thereby defining a cryptic subzone in the marble, next to zone Z3, characterized by the presence of garnet and the near-absence of mica. The aragonite-grossular-bearing sample studied by Chopin et al. (2008) is a lateral equivalent of this subzone.

**Identifying the main reactions**

**Formation of wollastonite in the reaction zone**

One of the most striking observations in the contact zone is the abrupt disappearance of calcite coupled with the appearance of graphitic matter (GM) and wollastonite to form a marked dark reaction zone (Z3). The reaction front is ca. 15 mm thick. Figure 7 shows the textural relationship between quartz, calcite, wollastonite and GM at the marble/Z3 contact. Lath-shaped crystals of wollastonite seem to replace calcite (Fig. 7b and c) and their crystallization is accompanied by GM formation (Fig. 7c).
The size of the wollastonite grains increases towards Z2 concomitantly with GM content (Fig. 7b). Moreover, the texture of the wollastonite + quartz assemblage in zone Z3 is very similar to the texture of the calcite + quartz zone in the marble. We take all these observations, in particular the coincidence of carbon enrichment (the dark halo) with wollastonite appearance and calcite disappearance, as compelling evidence that zone Z3 arose from the progression of the following decarbonation reaction into the original marble, by which carbonate is reduced directly to produce elemental carbon:

$$\text{SiO}_2 + \text{CaCO}_3 = \text{CaSiO}_3 + \text{C} + \text{O}_2^f$$  \hspace{1cm} (1)

which may also be written, considering water dissociation,

$$\text{SiO}_2 + \text{CaCO}_3 + 2\text{H}_2^f = \text{CaSiO}_3 + \text{C} + 2\text{H}_2\text{O}_f$$  \hspace{1cm} (1b)

Given the stability of calcite + quartz everywhere else in the series and the metamorphic pile, the progress of this reduction reaction must imply the presence of an unusually reducing fluid.

The TOC (total ‘organic’ content) in marble sample 09-04 ranges from 0.22 to 0.34 wt % with the higher value close to Z3. In contrast, TOC in Z3 from the same sample ranges from 0.2 to 0.88 wt % with the lower value close to Z2. The amount of elemental carbon that could be produced by decomposition of calcite in Z3 following reaction (1) is 3.0 wt %. This value is consistent with the 3.7 wt % average difference between the TOC content in each zone, thus supporting the idea that marble calcite can be the main carbon source for GM enrichment in zone Z3 (i.e. the dark halo). A detailed chemical and isotopic study coupled with micro-Raman characterization (Galvez et al., in preparation) confirms this point and thoroughly addresses the effectiveness and the mechanisms of this uncommon formation of elemental carbon.

**A garnet-forming reaction in the marble**

The chemical profile from marble to serpentinite provides an answer to the question left pending by Chopin *et al.* (2008), namely that of the garnet-forming reaction in the marble, and its localization to the immediate vicinity of the serpentinite (higher in the series, the marble is free of garnet). Potassium, which is absent from the reaction zone (Fig. 6c), is hosted by white mica in the original marble. At the zone Z3–marble contact, white mica is surrounded by garnet (Fig. 7d) and is no longer observed in the Z1–Z3 reaction zone, but it may have been initially present in the parts that represent former marble; that is, Z3 (as shown above) and most probably Z2 (see below). Actually, in zones Z2 and Z3 where white mica is now absent, garnet displays lamellar morphologies mimicking a mica habit (Fig. 8). The combination of textural and chemical information with respect to potassium therefore...
suggests that the disappearance of white mica is coupled to potassium leaching and garnet growth, and to the unusual conditions prevailing near the contact with the serpentinite. On this basis and taking Ca-carbonate reduction into account, a tentative dissolution reaction can be proposed as follows:

\[
2\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 3\text{SiO}_2 + 9\text{CaCO}_3 + 2\text{H}^+ = 3\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3 + 2\text{K}^+ + 9\text{C} + 9\text{O}_2 + 3\text{H}_2\text{O}
\] (2)

which is pH and \(\phi\text{O}_2\) dependent and also produces elemental carbon.

Formation of zones \(\mathcal{Z}_2\) and \(\mathcal{Z}_1\); locating the former interface

The Si content decreases by a factor of two from \(Z_3\) (and marble) to \(Z_2\) (and \(Z_1\)) as indicated by the disappearance of quartz. In \(Z_2\), the Ca/Si molar ratio reaches that of wollastonite, the main \(Z_2\) mineral that contains both Ca and Si cations. Consequently, \(Z_2\) is, to the first order, equivalent to zone \(Z_3\) that has entirely lost its quartz component. Therefore in the framework of a reaction process between two contrasted lithologies (serpentinite and siliceous marble), \(Z_2\) would be of marble affinity. In comparison, \(Z_1\) appears as totally different with higher Si/Ca, Fe/Ca and Mg/Ca ratios, more consistent with a serpentinite affinity. The original interface between serpentinite and marble has been overprinted; it must, however, have been located between the serpentine and the wollastonite fronts (i.e. within the present zone \(Z_1\)).

Formation of uvarovite–andradite garnet in the serpentinite

In serpentinite, subordinate garnet is uvarovite–andradite in composition; this occurs in aggregates along with Fe–Cr oxides and Cr-rich chlorite in the presence of clinopyroxene. This textural relationship suggests that the aggregates replace a former Fe–Cr–Al spinel, which reacted with clinopyroxene to form Cr-rich garnet ± chlorite (Fig. 4). Interestingly, this type of reaction is accompanied by the oxidation of the \(\text{Fe}^{3+}\) present in Fe–Cr oxides into \(\text{Fe}^{3+}\) in the andradite component, which represents...
Equilibrium constants of reaction were calculated for various pressure and temperature ranges assuming equilibrium with a reducing fluid at graphite saturation. The solid-solution model for clinopyroxene is taken from Holland & Powell (1996). For thermochemical computation, the graphitic material is considered here to be graphite (see Galvez et al., in preparation). All oxygen fugacities are given relative to the fayalite–magnetite–quartz buffer (FMQ) as $\Delta$FMQ.

**Modelling results**

*Across the reaction zone*

The association wollastonite + quartz + GM, in the absence of calcite, sets an upper value to oxygen fugacity, which can be determined from the equilibrium constant of reaction (1) ($K_{O_2}$). As a result, for relevant conditions of pressure and temperature (e.g., 400–450°C at 1.5 GPa), maximum $f_{O_2}$ conditions of $\Delta$FMQ=−1 are required to achieve calcite reduction (Fig. 9a).

The stability in $f_{O_2}$ vs. $T$ vs. $P$ space of the mineral assemblage andradite + diopside found in zone Z1 has also been investigated assuming equilibrium with a reducing fluid at graphite saturation (Connolly & Cesare, 1993; Connolly, 1995) although GM is no longer observed in Z1 (see Discussion). Both Al and Mn (respectively 0.8 and 0.5 mol %) were omitted from the bulk composition of zone Z1 determined by EDS, to limit the number of phases in the pseudosection (e.g., no grossular or chlorite); the bulk composition used for PerpleX modelling was therefore SiO$_2$ 50.69, FeO 7.90, MgO 13.57, CaO 27.84 wt %.

Figure 10a shows the result of a simulation performed at 1.5 GPa between 400 and 550°C (the geologically plausible range), as a function of fluid composition with $X_O$ ranging from zero to 0.33. The andradite–diopside paragenesis (zone Z1) is found to be stable for $X_O$ ranging from 0.001 to 0.32; that is, for redox conditions

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**Figure 8.** BSE image showing the texture of the boundary zone between marble and Z3. The presence of wollastonite and carbon and the lamellar growth of garnet, mimicking the habit of mica in the marble, should be noted. Garnet occurs with the same lamellar shape within zone Z3 but is difficult to observe in BSE images because of its similarity to wollastonite in backscattering power.
corresponding to \( c. \Delta \text{FMQ} = -3 \) (Fig. 10b). For \( X_{O_2} > 0.32 \) (in the presence of GM), the alternative assemblage clinopyroxene + andradite + magnetite + Ca-carbonate is more stable according to the limiting reaction

\[
12 \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 18 \text{C} + 13 \text{O}_2, \text{aq} = 18 \text{CaFeSi}_2\text{O}_6 + 2 \text{Fe}_3\text{O}_4 + 18 \text{CaCO}_4
\]

whereas, for \( X_{O_2} < 0.001 \) and depending on pressure, the assemblage clinopyroxene + andradite + monticellite + wollastonite/merwinite is more stable as inferred from the limiting reaction

\[
2 \text{Ca}_3\text{MgSi}_2\text{O}_6 + \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} = \\text{CaSiO}_3 + 2 \text{CaMgSi}_2\text{O}_4 + 2 \text{CaFeSi}_2\text{O}_6 + \frac{1}{2} \text{O}_2, \text{aq}
\]

below 0.7 GPa, or

\[
3 \text{CaMgSi}_2\text{O}_6 + 2 \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} = \text{Ca}_3\text{Mg}(-\text{Si}_4\text{O})_2 + 2 \text{CaMgSi}_2\text{O}_4 + 4 \text{CaFeSi}_2\text{O}_6 + \text{O}_2, \text{aq}
\]

above 0.7 GPa.

Equilibrium constants for these reactions were determined over a wide range of pressures and temperatures, to scan the whole spectrum of compatible \( f_{O_2} \) conditions (Fig. 9). A maximum oxygen fugacity of \( c. \Delta \text{FMQ} = 2.6 (\pm 0.6) \) is implied by the stability of andradite vs hedenbergite + magnetite + calcite (Fig. 9b). On the other side, reactions (4) and (5) provide a lower bound on \( f_{O_2} \), the stability of andradite + diopside vs hedenbergite + monticellite + wollastonite/merwinite implying redox conditions above \( \Delta \text{FMQ} = 7 (\pm 2, \text{depending on } P \text{ and } T) \) (Fig. 9c).

If saturation of the aqueous fluid phase with respect to GM is postulated, then the fluid-mediated interaction between serpentine and marble under reducing conditions, already inferred from calcite reduction (Z3), is confirmed by the mineral assemblage of Z1. It should be noted that under the redox conditions calculated with Perple_X at graphite saturation for zone Z3, the equilibrium fluid is indeed reducing and is characterized by large proportions of CH4 and H2 (Fig. 10c).

Important issues with respect to determination of the redox conditions that prevailed during the growth of the reaction zones are the evolution of the carbon distribution (either as carbonate or as GM) and the saturation of the fluid with respect to GM. Carbon is present in the form of carbonate (along with some GM) in the pristine marble whereas it occurs solely as GM in Z3. The location of the original serpentinite–marble interface within Z1 suggests that carbon was initially present also in Z2 and in part of zone Z1, where it is no longer observed. By what process has carbon been removed? Under the reducing conditions calculated above for the contact zone, a likely means for carbon removal is the formation of CH4 molecules, which are definitely more mobile than solid GM. Consequently, the fluid that reduced zones Z1 and Z2 and stripped away any GM must have had a higher H2 content than zone Z3 fluid, pointing again to a redox gradient (or reduction front) across the contact zone, with the most reducing conditions prevailing on the serpentinite side.

**Redox potential of a fully serpentinized peridotite**

The redox conditions modelled here and the areal distribution of the wollastonite–GM halo point to the reducing effect of the serpentinite body during metamorphism. In the serpentinite the coexistence of Co-bearing pentlandite and magnetite is the only constraining assemblage with respect to oxygen fugacity. Klein & Bach (2009) have shown that, considering the whole range of H2S fugacities, the field of coexistence of these phases at 400°C and 500 bars is only limited towards high oxygen fugacity by the hematite–magnetite equilibrium. Consequently, in the absence of Fe–Ni alloys, the ambient oxygen fugacity of the
serpentinite is difficult to constrain. It is now well established that peridotites have a strong reducing potential (Berndt et al., 1996; Charlou, 2002; Seyfried et al., 2007; Evans, 2010; Marcaillou et al., 2011). However, the reducing effect of a fully serpentinized body that could further interact with aqueous fluids (i.e. post-serpentinization interaction) has not been investigated so far. In addition to uvarovite–andradite garnet formation, for which thermodynamic data are lacking, a reaction that can account for the reducing potential of the serpentinite is the following serpentine–magnetite equilibrium:

$$3\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{O}_{2,\text{aq}} = 3\text{Fe}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Fe}_3\text{O}_4.$$  

(6)

The equilibrium constant of (6) at 450°C and 0.5 GPa ($K_{E6}$) was calculated with the thermodynamic database of Klein et al. (2009) and the SUPCRT92 software (Johnson et al., 1992) to relate the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in serpentine and oxygen fugacity ($K_{E6} = 10^{57.5}$). Through this reaction, the oxidation of serpentine from /C1 FMQ^4 (i.e. oxygen fugacity of a natural serpentinite; Frost, 1985; Frost & Beard, 2007; Evans, 2008) to /C1 FMQ^1 [i.e. maximum $f_O$ at which carbonate is no longer reduced according to reaction (1)] results in the formation of magnetite with an $O_2$ uptake of 0.008 mole of $O_2$ per mole of serpentine. Assuming that this $O_2$ entirely comes from the reduction of CaCO$_3$ in the neighbouring marble, then 1 g of CaCO$_3$ can be reduced by 350 g of a serpentine initially equilibrated at /C1 FMQ^4. This simple mass-balance calculation supports the field evidence that a fully serpentinized peridotite entrained in a subduction zone has still the potential to reduce carbonates in the nearby sedimentary formations.

**DISCUSSION**

**Conditions and processes of formation of the reaction zone**

The reaction zone studied here between serpentinite and marble is located in metamorphic units that experienced pressures and temperatures of the order of 1–2 GPa at 450–500°C (Lahondere, 1996; Chopin et al., 2008). The presence of high-Si phengite in marble imposes minimum pressures of about 1.5 GPa (Massonne & Schreyer, 1987; Coggon & Holland, 2002); continuing RSCM thermometry studies in the area indicate temperatures closer to 425°C (Vitale-Brovarone et al., in preparation; Galvez et al., in preparation). Garnet formed during the interaction between serpentinite and marble has trapped aragonite inclusions (Chopin et al., 2008); therefore, the reaction zone must have formed at metamorphic, high-pressure and low-temperature conditions. The thickness of the reaction zone implies transport of species over several centimetres (or even tens of centimetres). This transport must have

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**Fig. 10.** Thermochemical isobaric modelling for the simplified bulk composition of zone Z1 (andradite + diopсид pyroxene), as a function of $X_O$ at carbon saturation, where $X_O$ is the molar ratio $O/(O+H)$ in the fluid [$P=1.5$ GPa; $X_{Fe^{2+}}$(cpx) = 0.03]. (a) Stable assemblages as a function of $T$ and $X_O$. The assemblage observed in Z1 (andradite–clinopyroxene) is shown in red, bounded by three other parageneses. Considering the limits of this field at a given $T$ provides an upper [reaction (3)] and a lower [reaction (5)] bound on oxygen fugacity at the base of zone Z1 (i.e. on the serpentinite side, where garnet is near-end-member andradite). (b) $X_O$ vs log($f_O$) diagram calculated at 450°C and 1.5 GPa showing (black line) the oxygen fugacity of the equilibrium COH fluid at carbon saturation, and the oxygen fugacities imposed by a variety of buffer reactions under the same $P$–$T$ conditions (labelled lines): HM, hematite–magnetite; QFM, quartz–fayalite–magnetite; Wall, reaction (1); Adr, reaction (3); MI, magnetite–iron; Merw, reaction (5). (c) Chemical concentration of the main species in the fluid phase at carbon saturation as a function of $X_O$ at 450°C and 1.5 GPa, calculated with PerpleX. For $X_O = 0.2$, log(CO$_2$) = −176 and log(CO) = −7.62.
been promoted by the presence of a fluid that, in the context of high-P, low-T metamorphism of serpentinite, is likely to have been mostly aqueous. In addition, the reduction of Ca-carbonate (either calcite or aragonite) in the presence of quartz to form wollastonite + GM indicates that this aqueous fluid was reducing and imposed redox conditions below ΔFMQ = 1.

The assumption of a reaction process dominated by diffuse transport rather than fluid advection underlies this study; it is apparently challenged by the potassium profile, which could suggest potassium leaching in the marble by aqueous fluid flow. Potassium dissolution can be accounted for by reaction (2), the equilibrium constant \( K_{E2} \) of which depends on the potassium, water and oxygen activities as well as the pH of the aqueous fluid, in addition to \( P \) and \( T \), as follows:

\[
K_{E2}(P, T) = \left( a_{\text{K}}^{2} * a_{\text{H}^2\text{O}} \right) / \left( a_{\text{H}^4\text{O}} \right).
\]

Potassium concentration in the marble can be used to constrain the minimum fluid/rock ratio needed to dissolve all the potassium out of the rock. This fluid/rock ratio is highly dependent on oxygen fugacity as its exponent is nine in this equation. Using the low oxygen fugacity determined previously (ΔFMQ = 1 to 3) and the \( K_{E2} \) (0.5 GPa, 450°C) value calculated with SUPCRT92 (Johnson et al., 1992), it turns out that a very small water/rock ratio (of the order of 10⁻³ litres of \( \text{H}_2\text{O} \) per kg rock at 0.5 GPa, 450°C, ΔFMQ = 2 and pH 6) is sufficient to entirely dissolve the potassium of white mica (0.83 mol % of the rock) under these conditions. However, this calculation is also strongly temperature dependent (10³ litres of \( \text{H}_2\text{O} \) per kg rock are required at 400°C) and extrapolation to higher pressures is fraught with uncertainty. Consequently, the calculation only shows that repeated renewal of the pore fluid or constant fluid flow is not necessarily required to account for most of the reaction features of the contact zone, as decreasing the oxygen fugacity strongly increases potassium solubility. This is in line with the unusual lamellar texture of garnet (replacing mica) in zone Z3, suggesting very limited mass transfer. Therefore, the view of Fickian diffusion in an almost stagnant fluid medium may be retained here for simplicity. There is indeed no clear evidence that deformation-triggered advection took place in these rocks under the near-climax metamorphic conditions during which the reaction zone developed. On this basis, we can tentatively interpret the formation of the reaction zone as the result of chemical potential gradients between serpentinite and marble in the presence of an intergranular fluid, which enhances species diffusion (Rubie, 1986; Baxter, 2003). The division of the contact zone into three reaction zones (Z1, Z2 and Z3) results in the decoupling of the species transport kinetics through contrasted apparent diffusion coefficients for \( \text{H}_2\text{O} \), \( \text{O}_2 \), \( \text{CH}_4 \), \( \text{SiO}_2 \), \( \text{CaO} \), \( \text{MgO} \), etc. The steep concentration gradient observed at the interface between each of the reaction zones reveals an overall diffusion-controlled process where precipitation, crystallization and reaction kinetics are not limiting factors. Among the obvious chemical potential gradients that have driven the formation of the reaction zones, the one imposed by contrasted oxygen fugacity between serpentinite and marble is remarkable, as it led to the reduction of calcite and to the low-temperature formation of wollastonite and elemental carbon, three rare features in metamorphic environments. Another major boundary condition is the gradient in silica activity between silica-undersaturated serpentinite (with perovskite) and siliceous marble; silica diffusion between them, across the quartz-free wollastonite zone (Z2), may be a limiting factor for the growth of the rodingite rim (Z1).

It is also worth noting that redox gradients, here, are not independent of the chemical potential gradient of other components. For example, part of the ferrous iron from the serpentinite is transferred to Z1 and part of Z2 as ferric iron in andradite. Consequently, andradite formation contributes to maintaining a low \( \text{O}_2 \) on the serpentinite side. Mass-balance calculations are now required to determine whether the oxygen fugacity gradient across the contact zone could be self-sustained, at least in a transient way, by the coupled formation of andradite in Z1 after having been only sparked off by the reducing conditions of the serpentinite.

Another feature of the reaction zone is the high Ca content in Z1 and Z2, which is classical for rodingite. In other rodingites, this enrichment has been linked to serpentinization and chloritization of the primary clinopyroxene of the peridotite and to fluid transport in fracture zones (Austrheim & Prestvik, 2008). In the Malaspina serpentinite, even though clinopyroxene is concentrated in foliation planes, there is no evidence of Ca release associated with rodingitization. In this case, however, the country-rock marble at the contact is the most obvious Ca reservoir and source.

**Low-temperature wollastonite: a marker for reducing fluids? Review of other occurrences**

This study shows that wollastonite and elemental carbon can form through calcite or aragonite decarbonation at low temperature if sufficiently reducing (\( \text{CO}_2 \)-free) conditions are achieved. Reports of wollastonite in low-grade terranes are, with one exception (Markl, 1999), all linked to serpentinites. In the Western Alps, Amstutz (1962) and Di Colbertado et al. (1967) mentioned wollastonite in marbles at the contact with the Cogne serpentinite body. However, there is no mention of abundant graphite and these early reports are now questioned (Piccoli et al., 2007; R. Compagnoni, personal communication, 2010). As in the
oxidizing, CO2-rich, externally derived fluids (e.g. open-system behaviour and to pervasive flow of more zones (compare listvenite) points to a much more bodies, the development of carbonate-rich alteration tectono-metamorphic evolution. In other serpentinite reducing conditions during the latest stages of the zone (Fig. 6) did not react with quartz, suggesting less late calcite veinlets cross-cutting the Malaspina reaction pentinite had lost its reducing potential. Interestingly, happened, either for kinetic reasons or because the ser- reaction zones (e.g. Malaspina or Leech Lake Mountain) may reflect the difference between serpentinite contacts in the Alps or Corsica do not show a ratio.

associated with diffusion of a fluid with a low water/rock reduction in and around the serpentinite in this study is indicated with sparse grains (e.g. 10 μm grain size for both). This sample can be safely ascribed to the reaction zone described along the serpentinite–country-rock contact (see the photograph of Chesterman, 1960), by analogy with the profiles studied by Coleman (1967) on the margin of other Franciscan ultramafic bodies. Similar occurrences of wollastonite in rodingite are known from the Kamiukotan belt, Hokkaido (Katoh & Nitta, 1983), and the JM Asbestos mine, Québec, where fluid inclusions contain CH4 (probably deriving from a serpentinization fluid; Normand & Williams-Jones, 2007). Xonotlite, Ca8Si6O17(OH)2, a low-temperature hydrated equivalent of wollastonite, was also found in rodingites from New Zealand (O’Brien & Rodgers, 1973) and in the Ronda massif, Spain, where carbonaceous material is also observed (Esteban et al., 2003).

Therefore, wollastonite does occur at low temperatures, but almost exclusively in reaction zones in and around serpentinites. In the Franciscan, Kamiukotan, New Zealand and Québec examples, the absence of carbonates in the country-rock does not allow one to use the maximum fO2 indicator offered by their stability versus elemental carbon+wollastonite. On the other hand, some carbonate-serpentinite contacts in the Alps or Corsica do not show a reaction zone. This may reflect the difference between relatively early contacts with continuously traceable reaction zones (e.g. Malaspina or Leech Lake Mountain) and late tectonic contacts where no such reaction happened, either for kinetic reasons or because the serpentine had lost its reducing potential. Interestingly, late calcite veinlets cross-cutting the Malaspina reaction zone (Fig. 6) did not react with quartz, suggesting less reducing conditions during the latest stages of the tectono-metamorphic evolution. In other serpentinite bodies, the development of carbonate-rich alteration zones (compare listvenite) points to a much more open-system behaviour and to pervasive flow of more oxidizing, CO2-rich, externally derived fluids (e.g. Tsikouras et al., 2006; Beinlich et al., 2010). In contrast, the reduction in and around the serpentinite in this study is associated with diffusion of a fluid with a low water/rock ratio.

Serpentinite as a reducing environment: implication for redox conditions in subduction zones

It is well established that serpentinization of oceanic peridotites near slow-spreading centres produces highly reducing fluids containing dissolved H2 resulting from the reduction of H2O (Berndt et al., 1996; Charlou, 2002; Seyfried et al., 2007; Klein & Bach, 2009; Klein et al., 2009; Marcaillou et al., 2011). In contrast, there is no consensus on the redox conditions in subduction zones. Arc lavas studies (Arculus, 1994; Stolper & Newman, 1994), geochemistry and fluid inclusion studies in mantle xenoliths (Parkinson & Arculus, 1999; Andersen & Neumann, 2001), iron distribution in garnet from orogenic peridotites (Malaspina et al., 2009), and study of the Fe3+/Fe ratio in basaltic glasses and melt inclusions (Kelley & Cotrell, 2009) tend to show that these zones are oxidized, whereas Zn/Fe ratios (Lee et al., 2010) and other fluid inclusion data (Song et al., 2009) suggest that they are reduced. Our study shows that subducting serpentinites can impose reducing conditions (oxygen fugacities below ΔFMQ=1). Moreover, the thermochemical modelling presented here indicates that in situ serpentinization of anhydrous peridotite during subduction-zone metamorphism is not required to generate reducing conditions. Both during oceanic hydrothermal alteration and later in the subduction zone, reducing conditions far below ΔFMQ can be reached during metamorphism in and around pre-serpentinized ultramafic bodies, as revealed by the occurrences of low-T wollastonite and graphitic material, which imply the presence of H2- and possibly CH4-bearing aqueous fluids.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at Journal of Petrology online.


