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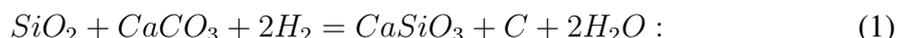
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Low-temperature wollastonite formed by carbonate reduction : a marker of serpentinite redox conditions

Benjamin Malvoisin^{1,2}, Christian Chopin¹, Fabrice Brunet^{1,2}, Matthieu Galvez³
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Abstract

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 \pm perovskite on the serpentinite side, followed towards the marble by a 1-5 cm thick zone of massive wollastonite (\pm grossular), followed by a 5-20 cm thick dark zone (the halo) consisting of wollastonite + quartz + graphitic material (\pm grossular \pm 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. A clue to its origin is the abundance of graphitic matter with the wollastonite within a few decimetres of the serpentinite body. We interpret this observation as evidence for local reduction of Ca-carbonate to form elemental carbon and wollastonite according to the reaction



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 ($-6 < \Delta FMQ < -1$), 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 serpentinization 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 \pm 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.

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0.0.1 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 serpentinite (serpentinization) 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 (Rüpke 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.

0.0.2 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 and 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 and 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 gabbro, basalt, peridotite and subordinate sedimentary material including radiolarite and calcschist. Other intercalated units comprise material of more continental derivation

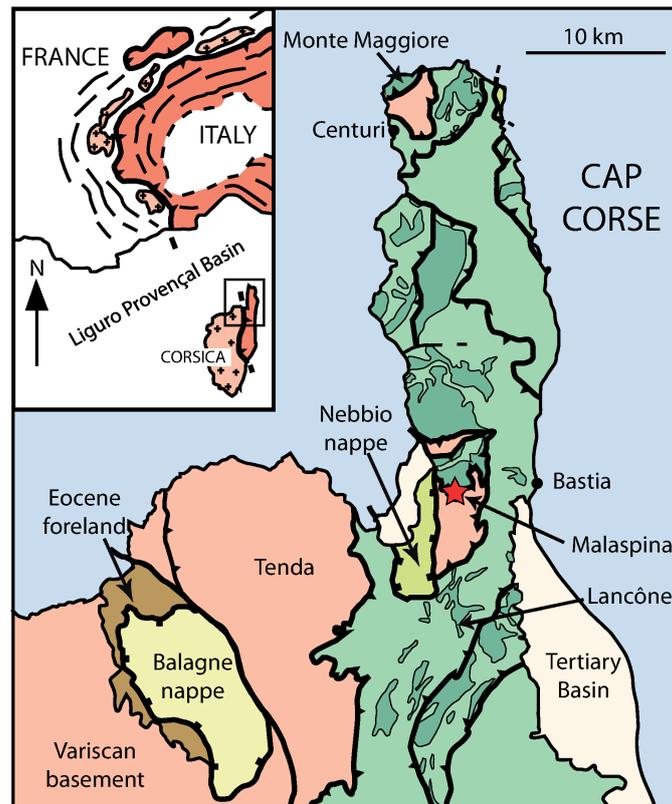


Figure 1 – Geological sketch map of the Cap Corse area, NE Corsica, after Malavieille et al. (1998) and Chopin et al. (2008). Flesh colour refers to continental units (Variscan basement) with parautochthonous cover (brown), green refers to the metamorphic oceanic units with a darker shade for serpentinite 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).

(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, $T(\text{grt-cpx inclusion}) \sim 430 - 520$ °C, $T(\text{grt-cpx in matrix}) \sim 500 - 600$ °C, revised to $P > 1.5$ GPa, $T \sim 450 - 490$ °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 Lancône Pass, a structurally deeper unit about 10 km further south, are 1.9 - 2.6 GPa, 340 - 415 °C (Ravna et al., 2010), revised to 2.3 ± 0.1 GPa and 520 ± 20 °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 °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 Lancône Pass ; Fig. 1). The largest sliver, less than 100m 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 480m 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.

0.0.3 The serpentinite - marble interface

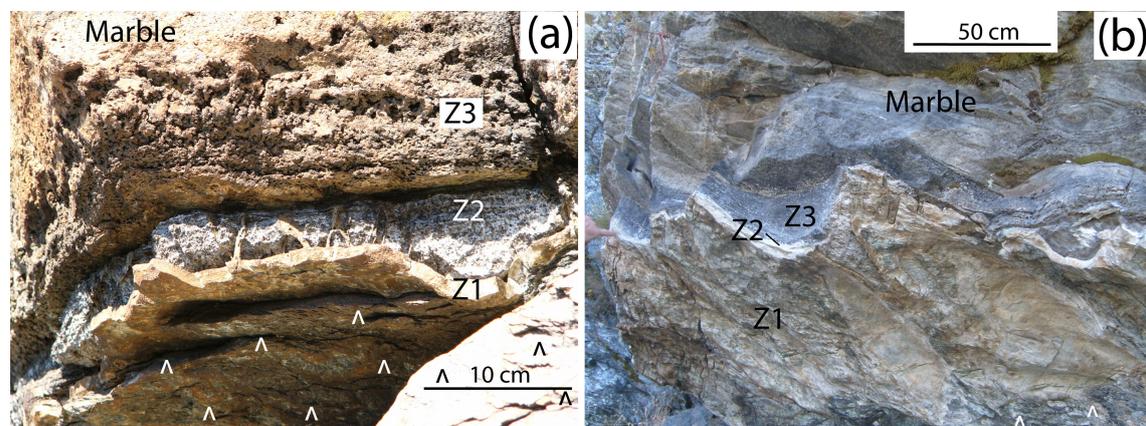


Figure 2 – Field photographs of the reaction zone between serpentinite (Λ) and marble. (a) On the weathered outcrop, alteration reveals the layered structure of the reaction zone with, from deformed serpentinite to marble, a very tough, protruding yellowish zone (Z1), a more alterable grey zone (Z2), and a zone similar in texture to the overlying marble but displaying weathering pits (Z3). Photograph courtesy of O. Beyssac. (b) Fresh cut of the gently folded reaction zone showing the same zonation as in (a). The Z1 and Z2 layers, each about 1cm thick, form an overhang above the serpentinite; the darker colour of the Z3 layer should be noted.

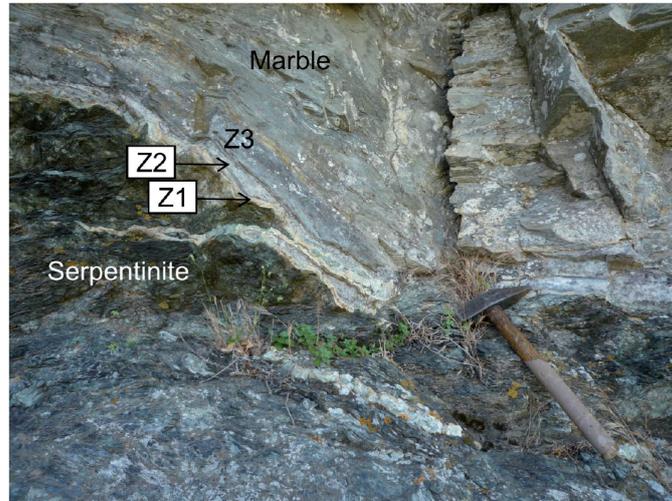


Figure 3 – Field photograph taken along the north side of Malaspina ridge, showing the reaction zone between serpentinite (bottom) and siliceous marble (top) in an area of intense recumbent folding. The near constant thickness of the nephritic rim along the folded contact is taken as evidence for the syn- to late formation of the rim with respect to folding. The tight recumbent fold is cored by the Z2 zone.

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 100m), regardless of the folded nature of the contact (Fig. 3), 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.

0.0.4 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 - SigmaTM) equipped with a 50mm² EDS detector (X-MaxTM, Oxford Instruments) at the Ecole normale supérieure (ENS, Paris). The EDS detector can quantify concentrations of more than 1mol % with an accuracy of 5 % and qualitatively detects elements reaching concentrations of more than 0.1mol %. 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 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 $\sim 1\text{cm}^3$ samples drilled from the reaction zone, by combustion under oxygen at 1400 °C with a Carbon - Nitrogen LECO SC 144DRPC analyser at the Service d'Analyse des Roches et des Minéraux (CRPG, Vandoeuvre-lès-Nancy).

Petrography and mineral chemistry

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

Serpentine occurs as platy crystals. It displays three Raman peaks at 1045, 3665 and 3697 cm^{-1} , which are attributed to the antigorite polymorph (Lemaire et al., 1999 ; Auzende et al., 2004). Serpentine composition (Tab. 2) shows significant Al_2O_3 content variations at the thin-section scale, between 1.5 and 6.5 wt % (i.e. variable amesite component) and $\text{Mg}/(\text{Fe}+\text{Mg}+\text{Mn})$ varying from 0.90 to 0.97. Serpentine of similar composition (Tab. 2) is also found in thin veinlets penetrating the contact zone until zone Z2 but with a more prismatic morphology, which is probably related to a later generation. Small anhedral clinopyroxene crystals (5 - 20 μm across) are concentrated in planes parallel to the schistosity. Clinopyroxenes have high CaO contents (22.7 - 26.1wt %) and low Al_2O_3 (0 - 3.5 wt %) and FeO_{tot} contents (0.7 - 2.7 wt %) corresponding to $\text{Mg}/(\text{Mg}+\text{Fe})$ ratios of 0.92 - 0.98 (Tab. 1). The analysis of SEM images (about 1mm²) reveals that magnetite occupies between 0.1 and 11 % of the image surface. Garnet (up to 100 μm in size, 55

Garnet Sample Zone	Garnet							Clinopyroxene						
	09-10 Serp	09-10 Serp	09-04 Z1	09-05 Z1	09-04 Z1/Z2	09-04 Z2	09-04 Z3	10-10 Serp	10-10 Serp	09-11 Serp	09-04 Z1	09-05 Z1	09-05 Z2	
SiO ₂	34.93	35.34	35.78	36.57	37.43	37.53	39.27	52.83	54.05	54.94	55.89	55.01	54.34	
TiO ₂	0.75	0.67	0.03	0.02	0.56	0.07	0.40	0.23	0.14	0.03	0.02	0.00	0.00	
Al ₂ O ₃	0.39	1.37	1.32	2.30	9.81	8.25	21.38	3.45	1.33	0.05	0.00	0.03	0.33	
Cr ₂ O ₃	18.09	14.20	0.01	0.00	0.02	0.00	0.00	0.75	0.20	0.00	0.00	0.00	0.00	
Fe ₂ O ₃	12.14	13.78	28.86	27.15	17.04	19.08	1.24	2.62	2.09	0.68	0.51	1.03	3.69	
MnO	0.00	0.00	0.12	0.09	0.23	0.12	0.48	0.06	0.12	0.11	0.12	1.30	2.16	
MgO	0.06	0.11	0.00	0.00	0.00	0.00	0.00	16.69	17.78	18.56	17.69	16.98	14.23	
CaO	33.44	34.08	33.44	33.62	35.10	34.98	36.77	22.70	23.54	25.40	26.23	25.84	25.43	
Na ₂ O	0.04	0.02	0.00	0.01	0.04	0.08	0.00	0.53	0.27	0.04	0.02	0.00	0.07	
NiO	0.00	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	
Total	99.85	100.02	99.60	99.83	100.36	100.25	100.03	99.93	99.56	99.88	100.59	100.56	100.28	
Structural formula based on 8 cations								Structural formula based on 4 cations						
Si	2.929	2.950	3.011	3.052	2.990	3.019	2.976	Si	1.919	1.966	1.986	2.015	2.000	2.008
Ti	0.047	0.042	0.002	0.001	0.033	0.004	0.023	Ti	0.006	0.004	0.001	0.000	0.000	0.000
Al	0.039	0.135	0.131	0.226	0.923	0.782	1.910	Al	0.148	0.057	0.002	0.000	0.001	0.014
Cr	1.199	0.937	0.000	0.000	0.001	0.000	0.000	Cr	0.022	0.006	0.000	0.000	0.000	0.000
Fe ³⁺	0.767	0.867	1.830	1.707	1.026	1.156	0.071	Fe	0.080	0.064	0.020	0.015	0.031	0.114
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	Mn	0.002	0.004	0.003	0.004	0.040	0.067
Mn	0.000	0.000	0.008	0.007	0.016	0.008	0.031	Mg	0.904	0.964	1.000	0.951	0.920	0.784
Mg	0.007	0.013	0.000	0.000	0.000	0.000	0.000	Ca	0.883	0.917	0.984	1.013	1.007	1.007
Ca	3.004	3.048	3.016	3.006	3.004	3.015	2.986	Na	0.037	0.019	0.003	0.001	0.000	0.005
Na	0.006	0.004	0.000	0.001	0.007	0.013	0.000	Ni	0.000	0.000	0.000	0.000	0.001	0.000
Ni	0.000	0.004	0.001	0.000	0.000	0.000	0.000	Mg#	0.92	0.94	0.98	0.98	0.97	0.87
Almandine %	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Andradite %	39.01	45.90	93.30	88.30	52.87	59.67	3.62							
Grossular %	0.00	4.46	6.65	11.66	46.76	40.19	95.37							
Pyrope %	0.00	0.02	0.00	0.00	0.00	0.00	0.00							
Spessartine %	0.00	0.00	0.03	0.04	0.31	0.14	1.01							
Uvarovite %	60.99	49.62	0.02	0.00	0.05	0.00	0.00							

TABLE 1 – Garnet and clinopyroxene composition in serpentine and the reaction zones

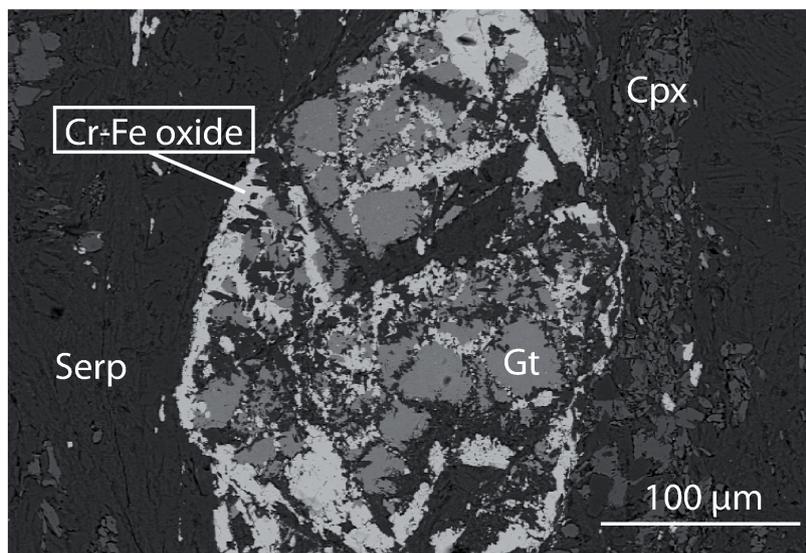


Figure 4 – Back-scattered electron (BSE) image of serpentinite showing a garnet ± Cr-Fe oxide + chlorite aggregate and clinopyroxene in the serpentine foliation (sample 10-10), suggesting garnet formation from former chromite and clinopyroxene.

mol % uvarovite - 45 mol % andradite, Tab. 1), associated with Cr-bearing magnetite (up to 23 wt % Cr₂O₃) and some chlorite (up to 10 wt % Cr₂O₃, Tab. 2), forms small

Serpentine Sample Zone	09-11 Serp	10-10 Serp	09-10 Serp	09-04 Serp/Z1	Chlorite 09-10 Serp	'Balangeroite' MAL Serp	Wollastonite 09-04 Z3	Carbonate 09-04 Marble	Mica Sample Zone	09-04 Marble	09-05 Marble	Talc/Sépiolite ? 09-04 Marble
SiO ₂	41.16	42.94	41.33	39.16	31.87	19.83	51.62	0.02	SiO ₂	53.43	52.33	51.65
TiO ₂	0.01	0.01	0.00	0.03	0.06	0.02	0.02	0.04	TiO ₂	0.13	0.02	0.03
Al ₂ O ₃	2.97	1.60	2.20	3.35	6.98	0.34	0.01	0.01	Al ₂ O ₃	19.57	24.50	0.64
FeO	2.91	2.62	2.41	3.50	3.76	47.68	0.02	0.00	FeO	3.02	3.11	0.42
MnO	0.08	0.24	0.12	0.30	0.00	0.00	0.00	0.00	MnO	0.30	0.04	0.27
MgO	38.38	39.06	39.21	39.05	34.36	3.28	0.00	0.00	MgO	4.85	3.20	27.19
CaO	0.04	0.07	0.04	0.15	0.08	0.57	47.82	58.70	CaO	0.37	0.02	0.29
Cr ₂ O ₃	0.22	0.42	0.20	0.02	10.06	0.05	0.07	0.00	Na ₂ O	0.00	0.01	0.04
NiO	0.24	0.14	0.38	0.06	0.00	13.39	0.00	0.12	K ₂ O	10.67	10.61	0.30
Total	86.00	87.19	86.04	86.02	87.18	85.26	99.76	59.00	Cr ₂ O ₃	0.02	0.05	0.00
									NiO	0.25	0.14	0.07
									Total	92.98	94.34	81.18

Structural formula based on:	7 (O)	14(O)	58 cations	2 cations	1 cation	11(O)	11(O)
Si	1.949	2.003	1.958	1.879	3.140	15.019	1.002
Ti	0.000	0.000	0.000	0.001	0.002	0.010	0.000
Al	0.166	0.088	0.123	0.189	0.800	0.299	0.000
Fe	0.115	0.102	0.095	0.141	0.300	30.198	0.000
Mn	0.003	0.009	0.005	0.012	0.000	0.000	0.000
Mg	2.710	2.716	2.770	2.793	5.040	3.700	0.000
Ca	0.002	0.003	0.002	0.008	0.004	0.466	0.995
Cr	0.008	0.015	0.007	0.001	0.780	0.032	0.001
Ni	0.009	0.005	0.015	0.002	0.000	8.159	0.000
Mg#	0.96	0.96	0.97	0.95	0.94		
							0.000 Si
							3.694
							0.007
							0.001
							0.000 Ti
							0.007
							0.000 Al
							1.595
							0.000 Al
							1.957
							0.000 Fe
							0.175
							0.176
							0.000 Fe
							0.017
							0.003
							0.017
							0.000 Mn
							0.017
							0.000 Mn
							0.003
							0.500
							0.323
							0.000 Mg
							0.500
							0.000 Mg
							0.323
							0.997 Ca
							0.028
							0.001
							0.023
							0.000 Na
							0.000
							0.001
							0.006
							0.002 K
							0.941
							0.917
							0.029
							Cr
							0.001
							0.003
							0.001
							0.003
							Ni
							0.001
							0.003
							Celadonite%
							66.18
							46.94
							Muscovite%
							27.47
							43.77
							Paragonite%
							0.00
							0.12
							Pyrophyllite%
							5.24
							8.02

TABLE 2 – Serpentine, chlorite, balangeroite, wollastonite, carbonate, mica and talc composition in serpentinite and the reaction zones

aggregates in the serpentinite (Fig. 4), 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 serpentine, with high FeO_{tot} (47.7 - 51.1 wt %) and NiO (4.3 - 13.4 wt %) contents and a low SiO_2 content of 15.2 - 19.8 wt % (Tab. 2). Its stoichiometry matches that of balangeroite, $\text{Mg}_{42}\text{Si}_{16}\text{O}_{54}(\text{OH})_{40}$ (Compagnoni et al., 1983) with Fe and Ni substituting for Mg. Similar Fe- and Ni-rich balangeroite was recently described by Evans and 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 Co_9S_8 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. 5a, bottom ; Fig. 6d). 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 (Tab. 1). Accessory phases are garnet, apatite, titanite and iron sulphide. A sample from which aragonite - garnet intergrowths have been described was found in an equivalent position (Chopin et al., 2008).

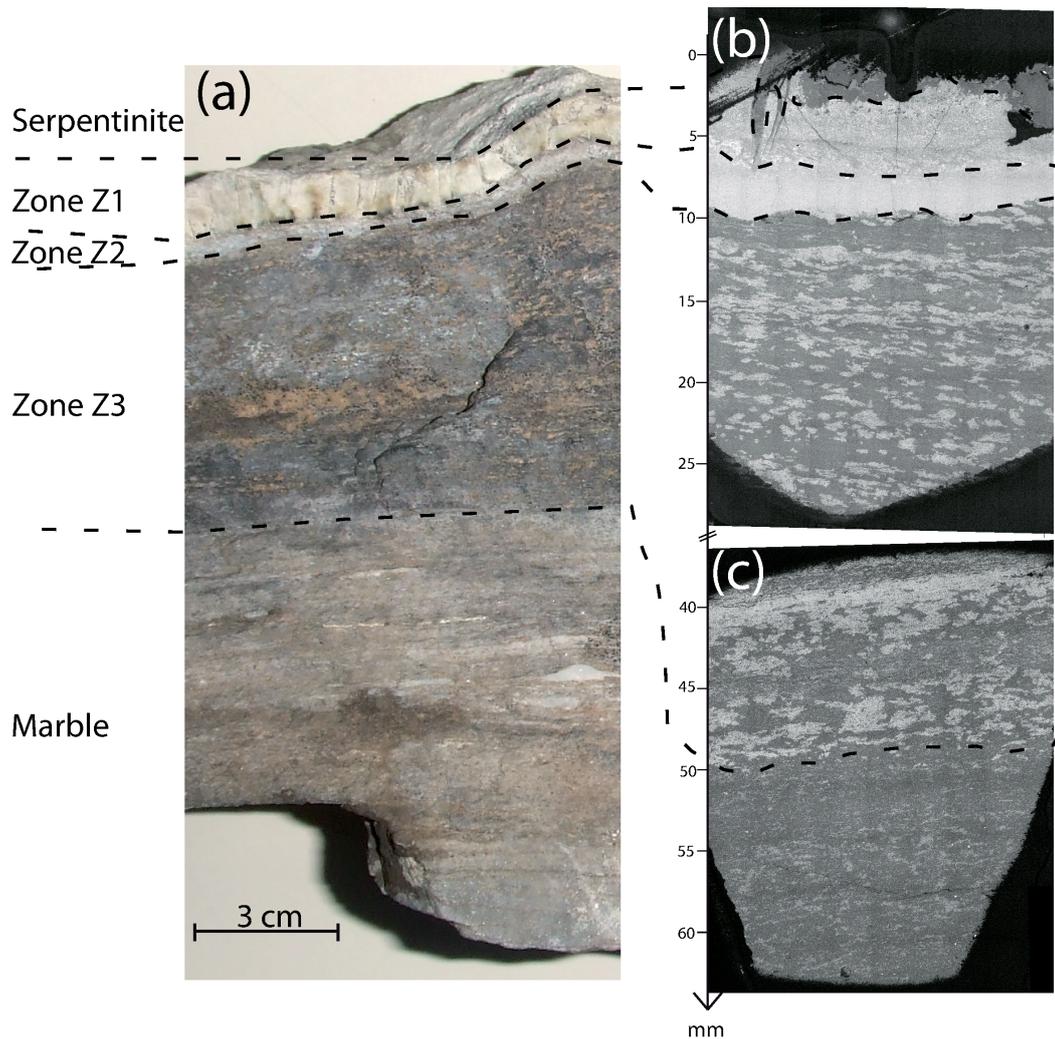


Figure 5 – A section through the reaction zone between serpentinite and marble. (a) Photograph of sample 09-04; the reaction zone is divided into layers (Z1-Z3) as described in Fig. 2 and the text. The darker colour of zone Z3, the lighter colour of zone Z2 and the jade-like, 'nephritic' aspect of zone Z1 should be noted. (b, c) BSE images of whole thin sections prepared from a slice cut through sample 09-04 [perpendicular to the plane of (a)], the top of (b) being in contact with serpentinite, and the bottom of (c) in contact with marble. [Note the difference in scale between (a) and (b, c), as well as the difference in colour and texture from one zone to another, reflecting changes in chemistry and mineral content as indicated in Figs 6 and 8.]

Zone Z1 Zone Z1 is composed of extremely fine-grained clinopyroxene and garnet (Fig. 6a), hence its toughness, with accessory perovskite (CaTiO_3). The composition of garnet (typically 10 - 20 μm , up to 50 μm in size) lies on the andradite - grossular join (Tab. 1). The XFe^{3+} ratio in the garnet octahedral site, defined as $\text{XFe}^{3+} = \text{Fe}^{3+} / (\text{Al}^{3+} +$

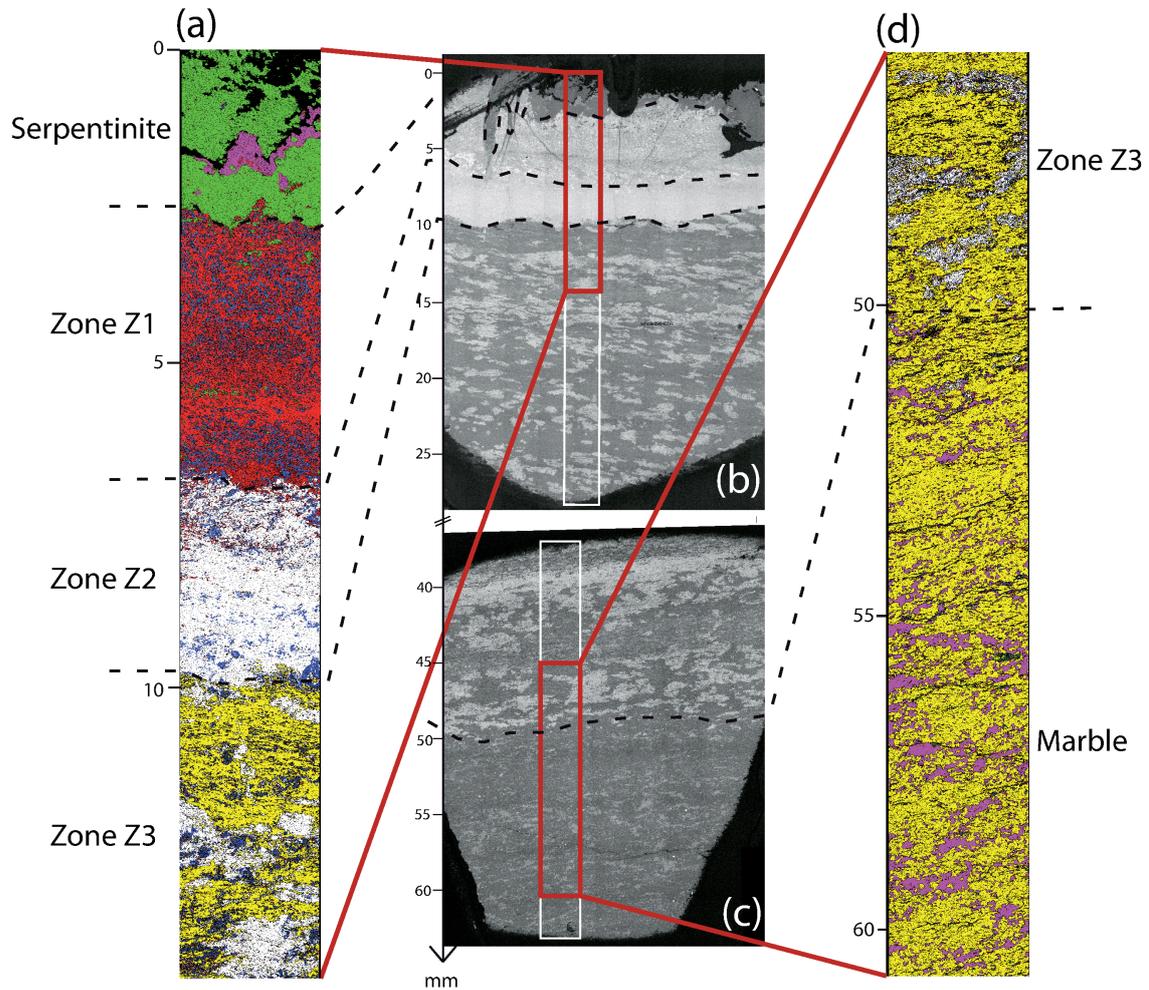


Figure 6 – (a to d) Anatomy of the reaction zone between serpentinite and marble. (b, c) BSE images of two thin sections from sample 09-04 (as indicated in Fig. 5b and c). (a, d) Selected parts [red rectangles in (b) and (c)] of profiles obtained from EDS mapping and BSE images show the variations in mineral content across the reaction zone. Green refers to serpentine, violet to calcite, red to clinopyroxene, blue to garnet, white to wollastonite, yellow to quartz, and dark green to mica.

Fe^{3+}), 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 XFe^{3+} than rims. Clinopyroxene is close to the diopside end-member : $\text{Ca}(\text{Mg}_{1-x}, \text{Fe}_x)\text{Si}_2\text{O}_6$ 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

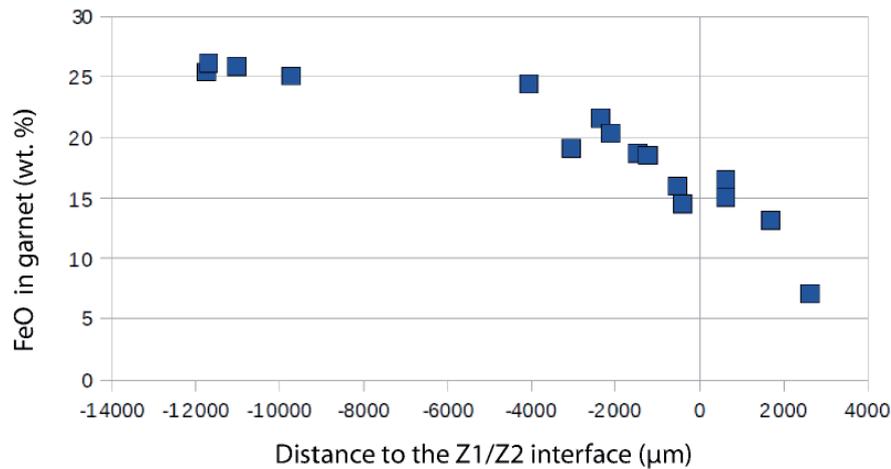


Figure 7 – Profile of FeO content (wt. %) in garnet across Z1 and a part of Z2. The x axis is positive when progressing towards the marble and negative when progressing towards the serpentinite (Z1 is on the left of the diagram and Z2 on the right). Note the increase of andradite end-member into garnet when progressing towards the serpentinite.

on the Z1 side (Fig. 6a). Crystals (up to 100 μm across) are short prismatic, with little or no preferred orientation. Garnet composition varies within the zone from *c.* $\text{Adr}_{55} - \text{Grs}_{45}$ on the Z1 side to nearly pure grossular in the middle of the zone, and then remains unchanged to Z3 (Tab. 1 ; Fig. 7). 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 serpentine-filled cracks, which therefore postdate the contact zone formation.

Zone Z3 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 5 and 6a, d). Small amounts of elongated grossular garnet (Tab. 1) and rare pectolite, $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$, 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

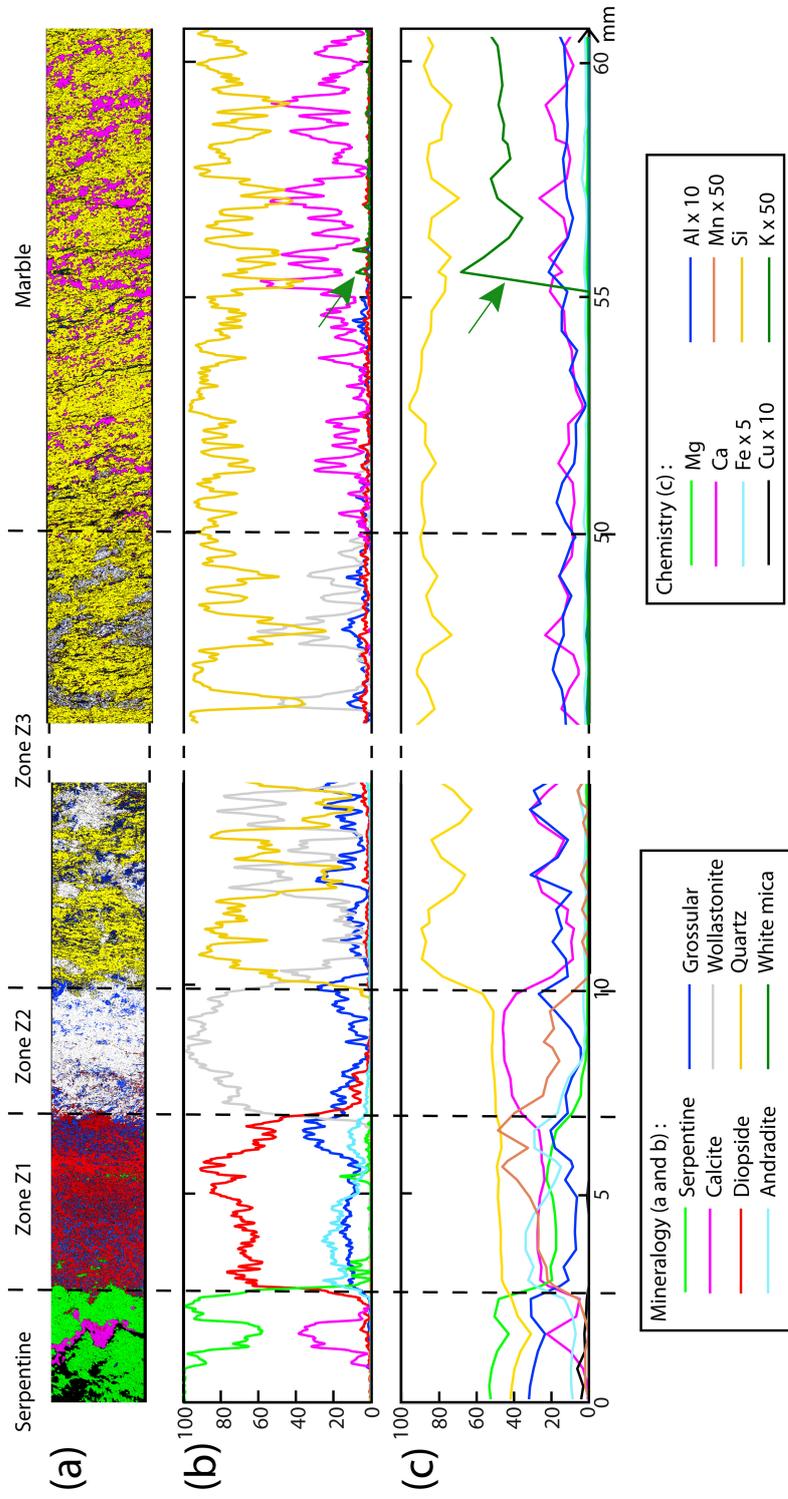


Figure 8 – Profiles through the reaction zone (sample 09-04). (a) Mineralogical mapping across selected boundary areas (reproduced from Fig. 6a and d for reference). (b) Mineral and garnet end-member modes across the reaction zone. The changes associated with each zone boundary and the presence of white mica only in the marble should be noted. Calcite in the serpentinite is a late cross-cutting vein. (c) Chemistry as determined by integration (on 3 μm stripes) of the EDS maps across the profile. Values are in molar proportions of the cations. The high concentrations in Mn, Fe and Mg in zone Z1, and the presence of K (in phengite - green arrows) only in the distal part of the marble (with respect to serpentinite) should be noted.

The bulk-chemistry of the various zones was determined by averaging the results of EDS mapping (3 μm pixels) on a mesh of 3mm 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 0.0.4). 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. 8 and in Tab. 3.

	Serpentinite	Zone Z1	Zone Z2	Zone Z3	Marble
SiO ₂	47.8	50.6	53.1	80.6	84.0
Al ₂ O ₃	2.2	d.	d.	1.3	1.1
FeO _{tot}	6.2	7.8	d.	d.	d.
MnO	n.d.	d.	d.	n.d.	n.d.
MgO	41.9	13.4	0.8	d.	d.
CaO	1.6	26.5	43.8	16.8	13.1
Na ₂ O	n.d.	n.d.	n.d.	d.	n.d.
Cr ₂ O ₃	d.	d.	d.	d.	n.d.
K ₂ O	n.d.	n.d.	n.d.	n.d.	d.
Total	100.0	100.0	100.0	100.0	100.0

n.d.: not detected

d.: detected (<1 mol.%)

TABLE 3 – Composition in wt.% of the rocks of the reaction zone from EDS analyses

From the serpentinite contact towards the marble, Mg and Al molar concentrations are both reduced by a factor of *c.* 2.5 (Fig. 8c). In contrast, Ca and Fe show a marked concentration increase. The decoupling between Mg and Fe at the serpentinite - 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. 8). Beyond Z1, the aluminium concentration is relatively constant (*c.* 1.3mol %); 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 (*c.* 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. 8b).

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

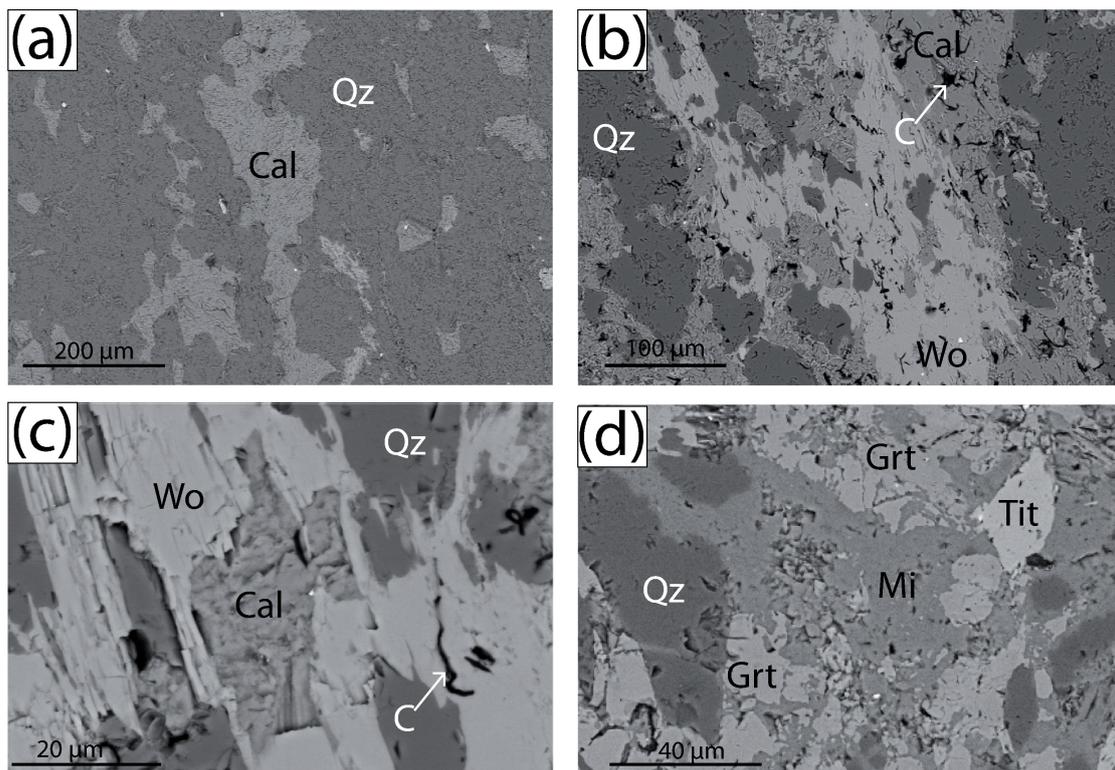
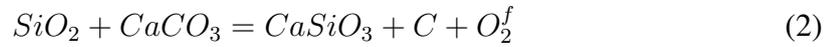


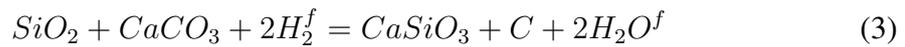
Figure 9 – BSE images illustrating the occurrence of wollastonite and garnet within the marble exclusively at the serpentinite-marble interface. (a-c) Wollastonite (+ graphitic matter) appearance (sample 09-04) : comparison of texture in 'unreacted' siliceous marble (a) and in the boundary zone (b) where wollastonite appears within marble (i.e. at the marble-Z3 interface). The abundance of a black phase interpreted as carbon in (b) compared with (a) should be noted. (c) Close-up showing calcite 'armoured' by wollastonite in a wollastonite + quartz groundmass in the narrow (c. 1.5 mm) transition zone where calcite, quartz, wollastonite and carbon coexist (sample 09-04). (d) Garnet in siliceous marble (sample 09-05) close to the marble-Z3 boundary. The concomitant presence of white mica (Mi), quartz and garnet is proposed as evidence for reaction (4). (See also Fig. 10.)

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 *c.* 1.5mm thick. Fig. 9 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. 9b and c) and their crystallization is accompanied by GM formation (Fig. 9c). The size of the wollastonite grains increases towards Z2 concomitantly with GM content (Fig. 9b). 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 :



which may also be written, considering water dissociation,



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 5.2 to 2.88 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 (2) 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. 8c), is hosted by white mica in the original marble. At the zone Z3 - marble contact, white mica is surrounded by garnet (Fig. 9d) 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. 10). The combination of

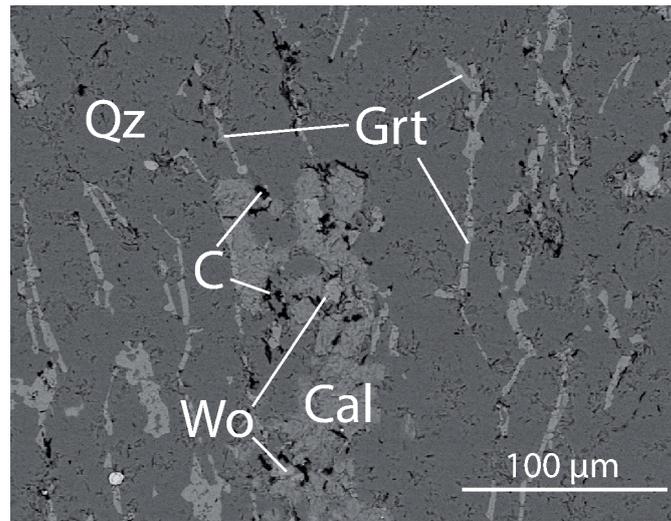
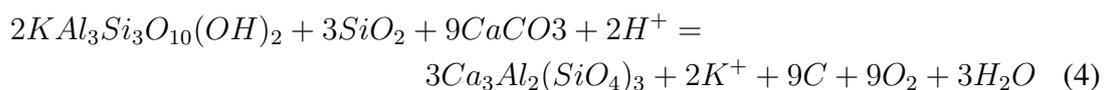


Figure 10 – BSE image showing the texture of the boundary zone between marble and Z3. The presence of wollastonite and carbon and the lamellar growth of garnet, mimicking the habit of mica in the marble, should be noted. Garnet occurs with the same lamellar shape within zone Z3 but is difficult to observe in BSE images because of its similarity to wollastonite in backscattering power.

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 :



which is pH and f_{O_2} dependent and also produces elemental carbon.

Formation of zones Z2 and Z1 ; locating the former interface The Si content decreases by a factor of two from Z3 (and marble) to Z2 (and Z1) as indicated by the disappearance of quartz. In Z2, the Ca/Si molar ratio reaches that of wollastonite, the main Z2 mineral that contains both Ca and Si cations. Consequently, Z2 is, to the first order, equivalent to zone Z3 that has entirely lost its quartz component. Therefore in the framework of a reaction process between two contrasted lithologies (serpentinite and siliceous marble), Z2 would be of marble affinity. In comparison, Z1 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 Z1).

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 \pm chlorite (Fig. 5). Interestingly, this type of reaction is accompanied by the oxidation of the Fe²⁺ present in Fe - Cr oxides into Fe³⁺ in the andradite component, which represents 45 mol % of the garnet. Assuming that this garnet formed during subduction metamorphism, its formation contributed to fuelling the redox potential of the serpentinite during metamorphism.

0.0.5 Quantification of the RedOx conditions during serpentinite - marble interaction

In the previous section, a series of zones with contrasting mineralogy and chemistry were described, which occur at the contact between a serpentinite and a marble unit and formed under blueschist-facies conditions. The presence of wollastonite in such a low-temperature terrane, in association with GM, is interpreted as resulting from calcite reduction in the presence of quartz and a reducing fluid. In the following sections, thermochemical modelling is used to constrain the oxygen fugacity that prevailed during serpentinite - marble interaction and that, apparently, reached a low enough value to trigger carbonate reduction.

Databases and modelling methods

Equilibrium constants of reaction were calculated for various P and T from reaction Gibbs free energy calculated with the database of Holland and Powell (1998 ; 2002 update). Equilibrium constants involving aqueous species and gas fugacities [e.g. reaction (2)] were determined with SUPCRT92 (Johnson et al., 1992) with the limitation that the Gibbs free energy of aqueous species cannot be calculated for pressures above 0.5GPa with this software. Consequently, this computational limitation does not allow us to model equilibrium at the conditions experienced here ; however, the effect of pressure on equilibrium constants was found to be negligible compared with the impact of temperature and uncertainty on them.

Stable mineral and fluid - mineral associations for a given bulk composition (in a given P - T range) were calculated using Perple_X (Connolly, 1990, 2005 ; Connolly and Petrini, 2002). The modelled system was assumed to be graphite-saturated. The mixed equations of state for O₂, H₂O and CO₂ from Connolly and Cesare (1993) were used. The amount of H and O atoms in the modelled system was not fixed but taken as a variable through the X_O parameter ; that is, the number of oxygen atoms in the fluid divided by the number of oxygen plus hydrogen atoms in the fluid, at graphite saturation (Connolly, 1995). Therefore X_O is a purely compositional variable in the C - O - H system, with no bearing on speciation. Even though the Gibbs free energy minimization performed by Perple_X fails to retrieve oxygen fugacity (oxygen contents being far too low), the oxygen fugacity (and fluid composition) in a carbon-saturated system can be

recalculated for a given X_O value using appropriate equilibrium constants (Connolly, 1995). The solid-solution model for clinopyroxene is taken from Holland and 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 ΔFMQ .

Modelling results

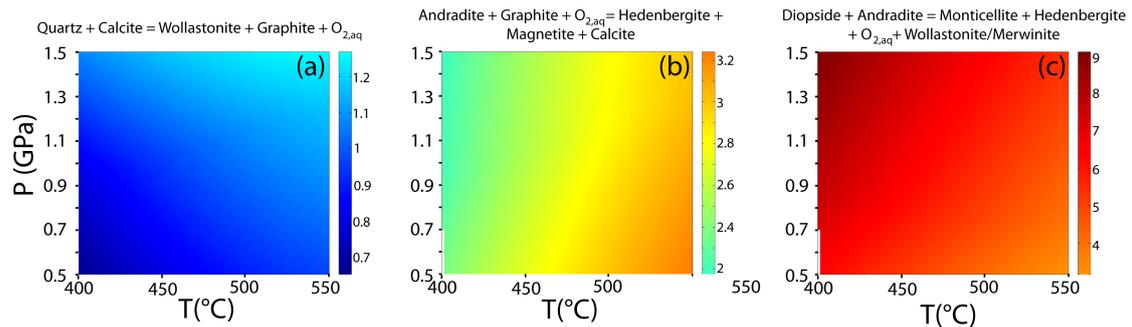


Figure 11 – Calculations of oxygen fugacity [scale in the colour codes is in $-\Delta FMQ \log(f_{O_2})$] for relevant buffer reactions in P-T space. (a) Reaction (2) pertaining to the boundary layer between marble and zone Z3. This provides the f_{O_2} value at a given P and T. (b) Reaction (5) relevant to zone Z1 (andradite + diopsidic pyroxene), providing an upper bound on f_{O_2} . (c) Reaction (6) [or (7), depending on P], relevant to zone Z1, which provides a lower bound on f_{O_2} . The solid-solution model by Holland and Powell (1996) was used for clinopyroxene assuming 3 mol % hedenbergite in diopside as estimated from electron microprobe analyses (Tab. 1).

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 (2) ($K_{E,1}$). As a result, for relevant conditions of pressure and temperature (e.g. 400 - 450 °C at 1.5GPa), maximum f_{O_2} conditions of $\sim \Delta FMQ - 1$ are required to achieve calcite reduction (Fig. 11a).

The stability in $f_{O_2} - T - P$ 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 and Cesare, 1993 ; Connolly, 1995) although GM is no longer observed in Z1 (see 0.0.6). Both Al and Mn (respectively 0.8 and 0.5mol %) 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 Perple_X modelling was therefore SiO₂ 50.69, FeO 7.90, MgO 13.57, CaO 27.84 wt %. Fig. 12a shows the result of a simulation performed at 1.5GPa 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 corresponding to $c. \Delta FMQ - 3$ (Fig. 12b). For $X_O > 0.32$ (in the presence of GM), the alternative assem-

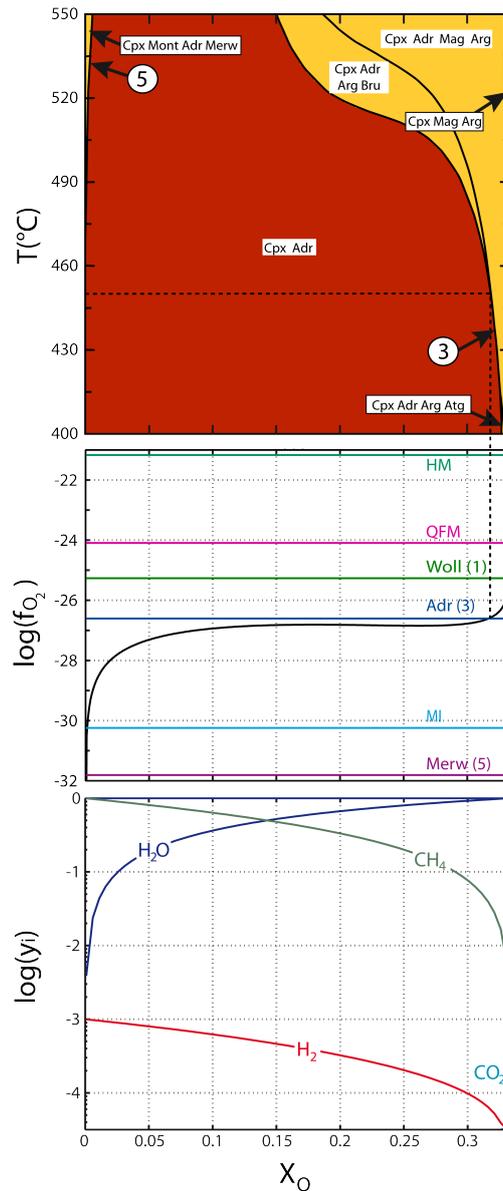
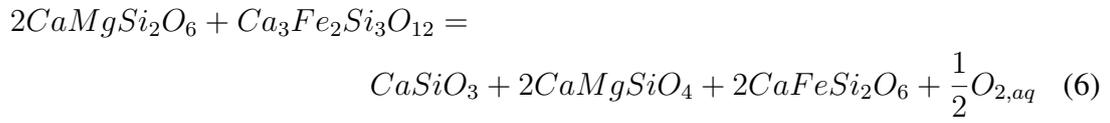


Figure 12 – Thermochemical isobaric modelling for the simplified bulk composition of zone Z1 (andradite + diopsidic pyroxene), as a function of X_O at carbon saturation, where X_O is the molar ratio $O/(O + H)$ in the fluid [$P = 1.5$ GPa; $X_{Fe^{2+}}(\text{cpx}) = 0.03$]. (a) Stable assemblages as 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 (5)] and a lower [reaction (7)] 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 $\log(f_{O_2})$ 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; Woll, reaction (2); Adr, reaction (5); MI, magnetite-iron; Merw, reaction (7). (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 *Perple_X*. For $X_O = 0.2$, $\log(CO_2) = -4.76$ and $\log(CO) = -7.62$.

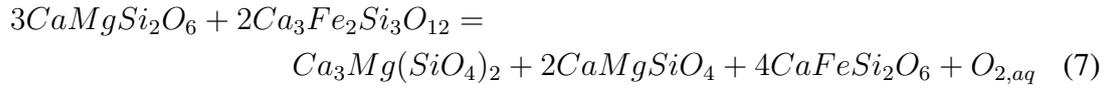
blage clinopyroxene + andradite + magnetite + Ca-carbonate is more stable according to the limiting reaction



whereas, for $X_O < 0.001$ and depending on pressure, the association clinopyroxene + andradite + monticellite + wollastonite/merwinite is more stable as inferred from the limiting reaction



below 0.7GPa, or



above 0.7GPa.

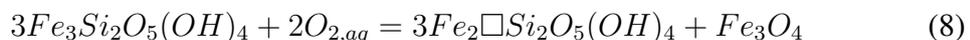
Equilibrium constants for these reactions were determined over a wide range of pressures and temperatures, to scan the whole spectrum of compatible f_{O_2} conditions (Fig. 11). A maximum oxygen fugacity of $c. \Delta FMQ - 2.6 (\pm 0.6)$ is implied by the stability of andradite vs hedenbergite + magnetite + calcite (Fig. 11b). On the other side, reactions (6) and (7) provide a lower bound on f_{O_2} , the stability of andradite + diopside vs hedenbergite + monticellite + wollastonite/merwinite implying redox conditions above $\Delta FMQ - 7 (\pm 2, \text{ depending on P and T})$ (Fig. 11c).

If saturation of the aqueous fluid phase with respect to GM is postulated, then the fluid-mediated interaction between serpentinite 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 CH_4 and H_2 (Fig. 12c).

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 serpentine - 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 serpentinitized 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 and 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 serpentinitized 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 :



The equilibrium constant of (8) 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 Fe³⁺/Fe²⁺ ratio in serpentine and oxygen fugacity ($K_{E6} = 10^{57.5}$). Through this reaction, the oxidation of serpentine from $\Delta FMQ - 4$ (i.e. oxygen fugacity of a natural serpentinite ; Frost, 1985 ; Frost and Beard, 2007 ; Evans, 2008) to $\Delta FMQ - 1$ [i.e. maximum f_{O_2} at which carbonate is no longer reduced according to reaction (2)] results in the formation of magnetite with an O₂ uptake of 0.008 mole of O₂ per mole of serpentine. Assuming that this O₂ entirely comes from the reduction of CaCO₃ in the neighbouring marble, then 1g of CaCO₃ can be reduced by 350 g of a serpentine initially equilibrated at $\Delta FMQ - 4$. This simple mass-balance calculation supports the field evidence that a fully serpentinitized peridotite entrained in a subduction zone has still the potential to reduce carbonates in the nearby sedimentary formations.

0.0.6 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 - 2GPa at

450 - 500 °C (Lahondère, 1996 ; Chopin et al., 2008). The presence of high-Si phengite in marble imposes minimum pressures of about 1.5GPa (Massonne and Schreyer, 1987 ; Coggon and 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 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 $\Delta FMQ - 1$. 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 (4), 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 :

$$K_{E2}(P, T) = \frac{a_{K^+}^2 \cdot a_{O_2}^9 \cdot a_{H_2O}^3}{a_{H^+}^2} \quad (9)$$

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 ($\Delta FMQ - 1$ 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^{-5} litres of H₂O per kg rock at 0.5 GPa, 450 °C, $\Delta FMQ - 2$ and pH 6) is sufficient to entirely dissolve the potassium of white mica (0.85 mol % of the rock) under these conditions. However, this calculation is also strongly temperature dependent (10^5 litres of H₂O 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 H₂, O₂, CH₄, SiO₂, CaO, 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 f_{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 and 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 (CO₂-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 Western Alps (Dal Piaz, 1969), rodingites also occur in the Franciscan Complex of California and Oregon (e.g. Coleman, 1967). In serpentinites at Cape San Martin and Leech Lake Mountain, CA, both in greywacke countryrock, fibrous masses and veins of wollastonite were found, respectively, by Gresens (1966) and in a sample collected by S. O. Agrell and included in Wenk's (1969) crystallographic study. This sample, which we re-examined on loan from the Harker Collection, Cambridge Univer-

sity, UK, shows anastomosing millimetre-size veins of wollastonite with sparse grains ($> 100 \mu\text{m}$) of andraditic grossular, cross-cutting a matrix of transformed greywacke made of diopside and grossular (*c.* $10 \mu\text{m}$ 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 and Niida, 1983), and the JM Asbestos mine, Québec, where fluid inclusions contain CH_4 (probably deriving from a serpentinization fluid; Normand and Williams-Jones, 2007). Xonotlite, $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$, a low-temperature hydrated equivalent of wollastonite, was also found in rodingites from New Zealand (O'Brien and 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 f_{O_2} 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 serpentinite had lost its reducing potential. Interestingly, late calcite veinlets cross-cutting the Malaspina reaction zone (Fig. 8) 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, CO_2 -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 H_2 resulting from the reduction of H_2O (Berndt et al., 1996; Charlou, 2002; Seyfried et al., 2007; Klein and 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 and Newman, 1994), geochemistry and fluid inclusion studies in mantle xenoliths (Parkinson and Arculus, 1999; Andersen and Neumann, 2001), iron distribution in garnet from orogenic peridotites (Malaspina et al., 2009), and study of the Fe^{3+}/Fe ratio in basaltic glasses and melt inclusions (Kelley and Cottrell, 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 $\Delta FMQ - 1$). Moreover, the thermochemical modelling presented here indicates that in situ serpenti-

nization 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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