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# Pervasive melt percolation reactions in ultra-depleted refractory harzburgites at the Mid-Atlantic Ridge, 15° 20'N: ODP Hole 1274A

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Abstract ODP Leg 209 Site 1274 mantle peridotites are highly refractory in terms of lack of residual clinopyroxene, olivine Mg# (up to 0.92) and spinel Cr# (~0.5), suggesting high degree of partial melting (>20%). Detailed studies of their microstructures show that they have extensively reacted with a pervading intergranular melt prior to cooling in the lithosphere, leading to crystallization of olivine, clinopyroxene and spinel at the expense of orthopyroxene. The least reacted harzburgites are too rich in orthopyroxene to be simple residues of low-pressure (spinel field) partial melting. Cu-rich sulfides that precipitated with the

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M. Seyler (🖂) Université Lille1, UFR Sciences de la Terre, Bât. SN5, Villeneuve d'Ascq cedex 59655, France e-mail: Monique.Seyler@univ-lille1.fr clinopyroxenes indicate that the intergranular melt was generated by no more than 12% melting of a MORB mantle or by more extensive melting of a clinopyroxene-rich lithology. Rare olivine-rich lherzolitic domains, characterized by relics of coarse clinopyroxenes intergrown with magmatic sulfides, support the second interpretation. Further, coarse and intergranular clinopyroxenes are highly depleted in REE, Zr and Ti. A two-stage partial melting/melt–rock reaction history is proposed, in which initial mantle underwent depletion and refertilization after an earlier high pressure (garnet field) melting event before upwelling and remelting beneath the present-day ridge. The ultra-depleted compositions were acquired through melt re-equilibration with residual harzburgites.

# Introduction

Abyssal peridotites are widely considered as complementary residues of mid-oceanic ridge basalts (MOR-Bs) after variable degree of adiabiatic melting resulting from decompression of the mantle beneath spreading ridges. In this view, their structure, texture and composition must provide valuable information on melting and melt extraction processes and source composition. Current models assume that melts segregate from their sources after melting for a very low percent melting and are rapidly extracted from the surrounding mantle to be transferred into high-porosity channels, where they are transported to the surface with no chemical interaction with the shallow mantle (Kelemen et al. 1997). Strongly depleted light to heavy rare earth element ratios (LREE/HREE) in residual clinopyroxene (Cpx) are indeed indisputable evidence for near-fractional melt extraction beneath spreading ridges (Johnson et al. 1990; Johnson and Dick 1992). On the other hand, it is argued that the last melt fractions produced by low-P partial melting of depleted peridotites may travel by diffuse porous flow, leading to extensive melt-rock reaction and peridotite refertilization in the shallow mantle (Kelemen et al. 1997; Asimow 1999; Dijkstra et al. 2003). Recently, it was recognized that a small proportion of Cpx in abyssal peridotites is not residual, but crystallized from melt as the partially molten mantle enters into the conductive thermal layer (Seyler et al. 2001; Hellebrand et al. 2002; Brunelli et al. 2006). This observation supports the idea of refertilization of the fractional melting residues by basaltic melt, which was first suggested by Elthon (1992). Reactive porous flow and refertilization are two important processes that are potentially able to deeply modify textures, mineral modes and chemical compositions of residual peridotites. Melt-rock interaction and refertilization were principally studied in plagioclase-bearing peridotites, in which feldspar-bearing veins and strong chemical gradients make these reactions immediately recognizable. In contrast, coarse-grained, plagioclasefree spinel peridotites show no obvious evidence of these reactions, because they theoretically cool at a greater depth. At a temperature close to the peridotite solidus and condition of low-strain deformation, residual and igneous minerals tend to textural and chemical equilibria. Serpentinization will then tend to blur or destroy any fragile evidence of reaction. As a consequence, description of reactional textures in abyssal peridotites is very few and little is known about the nature of reactions really involved in these processes. Hence, the extent of the reactions and the magnitude of the compositional changes they induce are poorly evaluated.

Ocean Drilling Program Leg 209 Site 1274 mantle peridotites appear to be most suitable to study these two aspects. They experienced a relatively low degree of serpentinization, and textures show greater extent of diffuse melt-rock reaction than commonly observed in most abyssal peridotites. In this paper we describe in detail a variety of these high-T microstructures, which are believed to result from pervasive melt-rock reaction in partially molten peridotites. Petrographic observation coupled with in situ mineral chemistry allows us to investigate the nature and conditions of melt-rock reactions and to constrain some aspects of the melting history of the peridotites. Fe-Ni-Cu sulfides of magmatic origin have been studied in addition to major minerals. These base metal sulfides are important petrogenetic indicators of partial melting degree and melt–rock interactions, because they concentrate chalcophile trace elements (S, Cu) that partition very similarly to CaO and  $Al_2O_3$  (Lorand 1988, 1991; Luguet et al. 2003).

# **Geological setting**

The region of the Mid-Atlantic Ridge (MAR) extending across the 15°20'N Fracture Zone (FZ) has been the focus of numerous geophysical, dredging and submersible surveys, and was recently drilled at eight sites during Leg 209 of the Ocean Drilling Program (Escartin and Cannat 1999; Fujiwara et al. 2003; Kelemen et al. 2004, and reviews therein). In this region, basaltic crust is thin and discontinuous, and mantle peridotites with gabbroic intrusions crop out nearly continuously on both sides of the rift valley from 14°40'N to 15°40'N. The overall quantity of gabbroic rocks is estimated to be 20-40%, a proportion that would correspond to 5 km of "normal" oceanic crust (Kelemen 2003). Two gravity lows, centered at ~14°N and ~16°N, are interpreted as centers of magmatic segments where thick igneous crust accreted. While the peridotites appear to have undergone an unusually high degree of melting (Bonatti et al. 1992; Cannat et al. 1992, 1997), the basalt compositions evolve from enriched-type MORBs in the 14°N region to normaltype MORBs in the 16°N region (Dosso et al. 1991, 1993).

ODP Leg 209, Site 1274, located 31 km north (15°65'N-46°68'W) of the NW intersection of the MAR with the 15°20'N FZ (Fig. 1), has drilled into 156 m of mantle peridotite, with 35% recovery. Cores recovered are mainly residual peridotite, with a few mscale gabbroic intrusions, and a large proportion of dunites (77% harzburgite; 20% dunite; 3% gabbros). Site 1274 peridotites contain the smallest proportion of gabbros with respect to other Leg 209 sites (Fig. 1). Thick fault gouge forms about 7% of the recovered cores, in the lower part of the hole, between ~95 and ~145 mbsf. Site 1274 peridotites are less serpentinized and weathered (up to 35% of the original mantle preserved) than Sites 1268 and 1272 peridotites (>99% serpentinization). In the three sites, the peridotite protolith is dominated by harzburgites varying in composition from orthopyroxene (Opx)-rich (28-30 vol% Opx) to Opx-poor (10 vol%) to dunites. Cpx content represents 1-2 vol% of the peridotites (visual estimation), with rare, local concentrations, up to 4 vol%. In a few places, a rough Opx layering can be observed, but in general, rocks have coarse granular textures lacking high-T foliation and lineation.



Fig. 1 Location and lithologies of ODP Leg 209 drill sites, shown on bathymetric map from Fujiwara et al. (2003)

# Sample selection and analytical methods

The studied sample set comprises 36 harzburgites, 1 Cpx-rich harzburgite and 1 dunite. Harzburgites were sampled away from dunite bands and gabbros (Table 1; Fig. 2a). Each sample consists of a  $35 \times 25$  mm billet, 0.5 to 0.75 cm thick, in which 1 to 3 standardsized thin sections have been cut. Primary modal proportions of 12 samples were reconstructed, using relict primary phases and their pseudomorphs, by point counting (steps of 1/3 mm; ~6,000 points per sample). Detailed textural observation and modes of finegrained mineral intergrowths were completed by analyzing backscattered electron images. In addition, the 25 SEY samples were investigated in reflected light microscopy to indentify base metal sulfides (BMS); their modal abundances (two polished thin sections per sample) were determined using a procedure reported in detail by Lorand and Grégoire (2006). Mineral compositions were analyzed with a CAMECA SX-100 electron microprobe at the University of Paris VI and at Woods Hole Oceanographic Institute. The accelerating voltage was 15 kV and beam current was 40 nA (15 nA for Na). A 2 µm beam size was used for all minerals, except a subset of pyroxenes, for which average compositions including exsolution lamellae were obtained with a defocused beam (10–15  $\mu$ m). Selected Cpx were analyzed for REEs, Zr, Ti and Sr by secondary ion mass spectrometry, using an upgraded

Table 1 Sample numbers and their position in Hole 1274A cores

Hole 1274A sample no.	Core	Section	Interval (cm)	Piece	
SEY01	1 <b>R</b>	1	4–5	1	
SEY02	1 <b>R</b>	1	27-31	4	
SEY03	1 <b>R</b>	1	65-66	8	
SEY04	1 <b>R</b>	1	88–90	10	
SEY05	2R	1	33-36	6	
SEY06	3R	1	44-45	6	
SEY07	3R	1	85-86	9	
SEY08	4R	1	15-18	1B	
SEY09	4R	1	44-46	2B	
SEY10	4R	2	1–3	1	
SEY11	5R	1	3–5	1	
SEY12	5R	1	45-49	7	
HJBD01	6R	1	38–48	6	
HJBD02	6R	3	40-50	1 <b>B</b>	
SEY13	7R	1	48–50	4	
HJBD03	7R	2	20-30	2A	
SEY14	8R	1	40-43	7	
HJBD04	8R	1	46–52	8	
SEY15	8R	2	9–11	1	
HJBD05	9R	1	14–16	3	
SEY16	11 <b>R</b>	1	11–13	2	
HJBD06	11 <b>R</b>	1	117–121	17	
SEY17	12R	1	2–4	1	
SEY18	12 <b>R</b>	1	65-67	10	
SEY19	12R	1	72–75	10	
SEY20	12 <b>R</b>	2	10-14	3	
HJBD07	13R	1	81-85	9	
HJBD08	14 <b>R</b>	1	102-106	12	
SEY21	18 <b>R</b>	1	13–16	3	
SEY22	18 <b>R</b>	1	112-113	19	
HJBD09	19R	1	17–22	4	
HJBD10	20R	1	18–24	4	
HJBD11	23R	1	53–57	11	
HJBD12	24R	1	90–95	5	
HJBD13	26R	1	52-56	9	
SEY23	27R	1	87–90	7	
SEY24	27R	1	112-116	8	
SEY25	27R	2	18–21	2	

Cameca IMS-4f ion microprobe at the University of Montpellier and following procedures described in Bottazzi et al. (1994).

## Analytical results

## Modal compositions

Olivine (Ol) and Opx contents in the studied harzburgites vary from 70.3 to 84.1 vol% and 13.4 to 27.2 vol%, respectively (Table 2). Cpx content is in the 0.7–2.6 vol% range in the harzburgites, and is 4.7 vol% in the Cpx-rich harzburgite; this sample, very close to lherzolite in Streckeisen's classification (1976), is referenced as lherzolite herein. Spinel (Sp) is ubiquitous and may be abundant in some samples (0.5–1.3 vol%). Fig. 2 ODP Leg 209 Hole 1274A. a Stratigraphic summary of lithologies with a graphical depiction of the recovery for each interval (TD = total depth; after Kelemen et al. 2004). b Distribution of magmatic sulfides in 25 samples. c Ranges of Na<sub>2</sub>O contents in clinopyroxenes from 36 samples



Table 2 Reconstructed primary modal compositions (vol%) of representative ODP Leg 209 Hole peridotites

	Li	Ol	Opx	Tot. Cpx	Tot. Sp	Cpx*	<b>S</b> 1
SEY02	Н	81.1	17.6	0.71	0.57	0.36	0.58
SEY03	Н	72.3	24.2	2.30	1.24	1.56	1.22
SEY04	L	77.2	17.1	4.72	0.51	3.48	2.07
SEY07	Н	74.2	23.7	1.57	0.57	0.87	1.17
SEY11	Н	77.1	19.9	2.20	0.80	1.09	1.84
SEY14	Н	70.3	27.2	2.06	0.49	1.32	1.23
SEY15	D	96.2	0.1	2.2	1.5	1.2	1.5
SEY16	Н	72.8	25.1	1.68	0.45	1.02	1.10
SEY21	Н	74.1	22.0	2.58	1.27	1.56	1.70
SEY22	Н	80.5	16.8	1.82	0.80	1.21	1.01
SEY23	Н	84.1	13.4	1.74	0.77	1.18	0.94
SEY25	Н	77.3	19.9	1.99	0.75	0.86	1.88

Sample composition is represented by a single, standard-sized, thin section (~6,000 points)

Li Lithology, H harzburgite, L lherzolite, D dunite. Mineral abbreviations: Ol olivine; Opx orthopyroxene; Tot. Cpx total clinopyroxene; Tot. Sp total spinel; Cpx\* interstitial clinopyroxene grains not intergrown with spinel, and selvages on orthopyroxenes; S1 Type 1 clinopyroxene-spinel symplectites

The average composition of the 11 harzburgites/lherzolite is 76.5% Ol, 20.6% Opx, 2.1% Cpx and 0.7% Sp, in the average of the visually estimated composition of Hole 1274A harzburgites (Kelemen et al. 2004). No correlation was found between Cpx and Opx or Ol contents, and the lherzolite is especially poor in Opx. Base metal sulfides have been detected in 75% of the studied thin sections (Fig. 2b). Owing to the average degree of serpentinization, all the BMS assemblages except a few inclusions in the Opx described subsequently, systematically display partial replacement of primary sulfides (pentlandite  $Fe_4Ni_5S_8$  to Fe<sub>5</sub>Ni<sub>4</sub>S<sub>8</sub> (unpublished EMP data), chalcopyrite Cu-FeS<sub>2</sub>, bornite Cu<sub>5</sub>FeS<sub>4</sub>) by native copper, Ni<sub>3</sub>Fe alloys and/or magnetite, and occasionally by heazlewoodite Ni<sub>3</sub>S<sub>2</sub> and secondary Cu-rich sulfides (digenite Cu<sub>9</sub>S<sub>5</sub> and valleriite CuFe<sub>2</sub>S<sub>3</sub>,Mg(OH)<sub>2</sub>). This alteration sequence is common to abyssal peridotites (Luguet et al. 2003). Serpentinization-related opaque minerals preserved the original shape of magmatic sulfide grains, i.e. polyhedral (not euhedral) blebs with generally concave inward grain boundaries. Only such grains were used for modal abundance estimates.

Site 1274 peridotites may be as BMS-rich as fertile mantle lherzolites (up to 0.1 vol%), despite their average harzburgitic modal compositions. However, BMS are heterogeneously distributed, being concentrated in the uppermost 25 m of Hole 1274A and in the deeper Ol-rich harzburgite SEY23; two zones that yielded only harzburgites (Fig. 2a, b). The highest BMS concentrations correspond to high (>0.1) Cpx/ Opx modal ratios (SEY03; SEY04; SEY23) and the lowest to Opx-rich samples (>20% Opx). However, BMS are strongly heterogeneously distributed at the hand-sample scale which generated strong random sectioning effects. For example, one thin section in SEY09 contains almost no BMS whereas the other is the second richest one (0.08 vol% BMS). The nearzero BMS content of samples from 40 to 145 mbsf is worthy of note, because it seems to correspond with the occurrence of numerous dunites (although there are sampling gaps in our studied sample set).

# Microstructures and grain morphology

Centimeter-sized, rounded olivine domains are mosaics of 3-4 mm-sized grains. Gently curved to polygonal grain boundaries, with an occasional subgrain boundary, suggests recrystallization of very coarse primary crystals. Opx porphyroclasts are highly variable in grain shape and size. Coarse to very coarse (>1-2 cm), equant Opx are occasionally broken with formation of wedge-shaped fractures (Fig. 3a) which affect only the Opx grains and not adjacent Ol and display no specific orientation. Opx grain boundaries commonly display cuspate embayments filled with secondary Ol, varying in size from a few micrometer to a few millimeter. In many instances, Ol sides in contact with reacted Opx have developed faceted crystal boundaries, which suggests growth from, or re-equilibration with, a melt film that was present at the Ol-Opx interface; in some cases, this melt film is interpreted to have left behind a stringer of Cpx. With increasing degree of dissolution, some Opx grains become ovoid and define a flow structure. More typically, strong dissolution results in the formation of anhedral, thin, elongate grains, interstial to Ol. Replacive Ol commonly penetrates Opx along cleavage planes (Fig. 3b). Extensive replacement of Opx by Ol results in the parceling of the original, very coarse grains into what appears in thin section as clusters of variously shaped (angular to rounded) Opx clasts within a matrix of newly crystallized Ol. Ends of Opx porphyroclasts are preferentially corroded or intergrown with Sp several millimeters long and a few 100 µm wide (Fig. 3c). These aggregates are interpreted as recrystallized Opx parcels cemented by Sp and minor Cpx. This secondary material is arranged along the crystallographic directions of the host mineral and likely results from the infiltration of melt which reacted with the Opx, then precipitated  $Sp \pm Cpx$ . This material steps out the Opx in between adjacent Ol grains (Fig. 3c); at these sites, Ol is resorbed into tiny grains poikilitically enclosed in Sp. A few samples show high strain deformation, with mosaics of very fine grained (20-50 µm) Ol replacing Opx along kink bands and grain boundaries. However, Opx dynamic recrystallization was not observed in any samples.

Clinopyroxene occurs in two major textural types. The first type characterizes the lherzolite sample, where coarse (up to 5 mm) Cpx grains, with large exsolution lamellae of Opx and occasional twinning, form diffuse, one crystal thick, discontinuous veins (Fig. 4a); some partially replace Opx (Fig. 4b). Crystal boundaries show large embayments filled with Ol (Fig. 4a), similar to those in Opx porphyroclasts. However, in contrast with Opx, these Cpx have poikiloblastic rims, associated with tiny grains of Sp, that enclose adjacent Ol or Opx (Fig. 4a) and can be followed over several millimeters (Fig. 4c). Both cores and rims display intergrowths with magmatic sulfides (Fig. 4c, d). The second Cpx texture type, ubiquitous in the lherzolite and all harzburgites, consists of smaller grains, up to 2 mm in size, with thin exsolution lamellae of Opx and rare twinning. They typically form selvages on Opx, with Opx-Cpx contacts characterized by strong Opx resorption: Opx display convex-out grain boundaries and tends to be poikilitically enclosed by Cpx (Fig. 4e). Cpx selvages show thin extensions between adjacent Ol grains, locally widen into small to medium-sized, intergranular Cpx. Late-stage Cpx also fills low-angle triple junctions, V-shaped fractures in Opx, and small cracks in the Ol matrix.

Spinel is found with recrystallized Opx (described in Opx section) or associated with late-stage Cpx. Sp shapes range from anhedral to blocky, subhedral porphyroblasts up to 2 mm sized, that are often overgrown by a corona of Cpx in spatial continuity with the Cpx



Fig. 3 Photomicrographs of Site 1274 harzburgite textures, indicative of reactions with a porous melt. **a** Wedge-shaped fracture in a coarse orthopyroxene porphyroclast. The *broken part* had slightly rotated and fracture is filled by secondary clinopyroxene. In *bottom*, large embayment filled with a single olivine grain. Crossed polarizers. **b** Detail of oval, resorbed orthopyroxene. *Left end of the crystal* was corroded by melt that penetrated following a cleavage plane. Secondary olivine (ol) and clinopyroxene (cpx; *colored in white* for clarity) now fill the space. Transmitted light. **c** *Right end* of same orthopyroxene porphyroclast (opx1) as in **b** formerly percolated by melt that followed the cleavages before precipitating spinel (sp; *dark*)

selvages. Pyroxenes and Sp commonly form two types of fine-grained symplectites representing 0.5–2% of harzburgite modes. One symplectite type (S1) consists of Cpx grains intergrown with skeletal Sp in ~40:60 volume proportions, respectively, with no Opx (Fig. 3d). It occupies the same textural sites as the discrete Cpx, with both occurrences grading into each other. In particular, it fills Ol or Ol–Opx triple

brown) and clinopyroxene (cpx; colored in white) intergrowth. This new material seals texturally re-equilibrated subgrains of the orthopyroxene (opx2), and continues as intergranular extensions between adjacent olivine (arrows). Transmitted light. **d** Backscattered electron image of clinopyroxene (*light gray*) and spinel (white) S1 symplectite, filling serpentinized olivine (ol; dark) triple junction. **e** Backscattered electron image of clinopyroxene (*light gray*), orthopyroxene (*light gray*) and spinel (white) S2 symplectite developed at the interface of orthopyroxene porphyroclast (opx1) and olivine (ol). Scale bar for all micrographs represents 500  $\mu$ m

junctions, and surrounds the ovoid Opx. Thin stringers of S1 may also be observed at the edges of coarse Cpx in the lherzolite. A second symplectite type (S2) contains Opx in addition to Cpx and Sp rods. It forms bulbous, myrmekite-like assemblage, ~200  $\mu$ m across, at Opx–Ol interfaces, with convex side of Opx toward Ol (Fig. 3e) and Sp branching perpendicular to the adjacent Ol. Although separated by Sp, Opx in S2



Fig. 4 a-d Photomicrographs of Site 1274 lherzolite sample SEY04. a Part of vein-like, coarse-grained clinopyroxene in serpentinized olivine matrix. Arrow 1 shows embayment filled with secondary olivine. Arrow 2 shows intergranular extension of the grain boundary in adjacent (now serpentinized) olivine matrix. Arrows 3 show a stringer of Al-Cr-poor clinopyroxene rimming the coarse clinopyroxene. Transmitted light. b Coarse clinopyroxene (cpx) developed at the border of altered orthopyroxene porphyroclast (opx), and replacing it deeply inside. Note that the two pyroxenes share common (001) planes. Arrows at the top show a rim of secondary Al-Cr-poor clinopyroxene (left) grading to clinopyroxene-spinel intergrowth (right). The latter surrounds almost completely the orthopyroxene. Transmitted light. c Rims of coarse clinopyroxene with large BMS

symplectite is in optical continuity with the primary Opx grain.

The average size of BMS grains range between  $100 \times 50$  and  $200 \times 100 \mu m$ , but larger grains (up to  $500 \times 300 \mu m$  in maximum dimensions) occur in the lherzolite. BMS are not randomly distributed at the thin section scale. Most BMS grains occur at Opx–Ol or Cpx–Opx grain boundaries. Except in SEY23, very

blebs attached (*arrow 1*). These rims extent in thin intergranular veins associated with spinel (sp) and sulfide (*arrows 2*), suggesting that the melt reached interconnection through the silicate matrix. Reflected light. **d** BMS grains enclosed in cleavage planes of a coarse clinopyroxene (*white and arrows 1*). Note the large BMS grain attached on the clinopyroxene (*arrow 2*). Reflected light. **e** Continuous poikiloblastic clinopyroxene rim sealing BMS micrograins (*white and arrow*) at the outer margin of a highly resorbed orthopyroxene. Reflected light. **f** A large BMS grain penetrating into a corroded orthopyroxene (*arrow 1*). Note the secondary sulfide inclusion networks inside the orthopyroxene (*arrow 2*). Scale bar for all micrographs represents 500  $\mu$ m

few BMSs are surrounded by Ol alone. BMS occur in sites of Opx consumption, either protruding into Opx margins in contact with secondary Ol (15%) or as disseminated blebs adjacent Cpx selvages (50%). Respectively 40% and 30% of about 300 counted grains of BMS share a grain boundary with an Opx or a Cpx crystal, whereas the latter two silicates account for only 20 and 2%, respectively, of harzburgite modes. In

some cases. BMS are sealed at the Opx outer margins by a continuous poikiloblastic Cpx rims. Sulfide melts penetrated corrosion paths, thus creating secondary sulfide inclusion networks within the Opx (Fig. 4f). Their BMS assemblages (pentlandite + chalcopyrite + bornite in unfractured, closed inclusions; abundant native Cu in fractured, open inclusions) provide evidence for Cu-rich sulfide parent melts. Another sulfide population (25%) is intimately associated with the interstitial Cpx separate from the Opx, either as swarms of droplets  $(1-10 \ \mu m)$  or as convoluted patches showing low dihedral angles and grading into vein-like extensions. The diffuse discontinuous veins of coarse Cpx in the lherzolite are BMS-rich, BMS occupying the same microstructural sites as the Cpx (Fig. 4c, d). Large BMS blebs are attached to Cpx crystals that also contain concentrated sprays of hundreds of BMS inclusions oriented parallel to cleavage planes (Fig. 4d). In this peculiar sample, sulfide melt reached interconnection through the silicate matrix, as suggested by the thin sulfide veins that surround relict Opx crystals (Fig. 4c). A minor proportion of BMS (2-4%) is attached to Sp, especially S1 Sp. By contrast, no sulfide has been found in S2 symplectites.

#### Major element mineral compositions

Ol Mg# [= molar Mg/(Mg + Fe)] and NiO contents (eTable 1) from 0.903 to 0.917 and from 0.30 to 0.43 wt%, respectively, vary little, with identical withinand inter-sample standard deviations. Sample set average is Mg# 0.9107  $\pm$  0.0015 and NiO 0.38  $\pm$  0.03 wt%. CaO contents are very low (<0.1 wt%) except in the dunite (0.22 wt%) and one harzburgite (0.24 wt% in SEY18).

Orthopyroxene (eTable 2) shows limited withinand inter-sample compositional ranges for Mg# and CaO  $(0.911 \pm 0.024$  and  $1.91 \pm 0.34$  wt%, respectively). Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> are positively correlated (Fig. 5a), with the highest concentrations in the cores of the largest porphyroclasts ( $\geq 5$  mm). However, many coarse porphyroclasts have cores depleted in Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. There is no difference in concentration of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> between the smaller porphyroclasts and the grains forming intergrowths with Sp. In addition, Cr<sub>2</sub>O<sub>3</sub> is low (~0.9 wt%) relative to Al<sub>2</sub>O<sub>3</sub> concentrations (~3 wt%), and only a few Opx compositions plot on the extension of the abyssal Opx compositional trend, defined by the cores of similarly sized porphyroclasts (Fig. 5a; Seyler et al. 2003). This suggests that Hole 1274A Opx have been more extensively re-equilibrated to lower T than commonly observed in typical abyssal peridotites. Because Al<sub>2</sub>O<sub>3</sub>



**Fig. 5**  $Cr_2O_3$  versus  $Al_2O_3$  (wt%) in pyroxenes of Hole 1274A peridotites. *Point symbols* represent sample averages. **a** Pc = porphyroclast cores; Sym = in S2 symplectites and other intergrowths with spinel. Field of abyssal peridotite orthopyroxene porphyroclast cores  $\geq 5$  mm (Seyler et al. 2003). **b** Pc = coarse grain cores; Gc = medium grain cores; Pr/Gr = coarse and medium grain rims; IG = small interstitial grains and selvages on orthopyroxene; Sym = in S1 and S2 symplectites and in intergrowths with orthopyroxene and spinel. Field of abyssal peridotite residual clinopyroxene cores (Seyler et al. 2003)

and  $Cr_2O_3$  decrease together, Cr# decreases only slightly and can thus still be used to compare the different samples.

Clinopyroxene compositions are given in eTable 3. Overall, Cpx are characterized by low Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> contents compared with common abyssal Cpx and both oxides decrease simultaneously (Fig. 5b). The lherzolite coarse Cpx grains are slightly zoned, with the highest Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and the lowest CaO (in integrating exsolution lamallae) contents in cores. Coarse grain rims and small Cpx grains that crystallized at the edges of coarse crystals are poorer in Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> and richer in CaO. Similar compositional ranges also characterize all Cpx textural types in harzburgites, although some larger Cpx cores tend to have higher Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. It is noteworthy that within a thin section, tiny Cpx in symplectites has similar compositional ranges to the cores and rims of medium-sized grains not in intimate contact with Sp. In contrast with Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, Mg-numbers are systematically higher in the rims and tiny grains, indicating subsolidus Fe-Mg exchange reactions with the other silicate minerals and Sp upon cooling. Thus Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> variations cannot be attributed to simple subsolidus re-equilibration and will be discussed further. TiO<sub>2</sub> contents are very low ≤0.05 wt% in most samples, increasing to 0.15 wt% in a few samples. Na<sub>2</sub>O contents display a wide range of concentrations from near 0 up to 0.72 wt% (Fig. 2c). Most samples (75% of the sample set), including the lherzolite and the dunite, contain Cpx with very low  $Na_2O \le 0.13$  wt%; such concentrations are among the lowest Na<sub>2</sub>O concentrations reported in abyssal peridotites. Na<sub>2</sub>O and TiO<sub>2</sub> are positively correlated in these very low-Na<sub>2</sub>O Cpx. The other samples have Cpx moderately or strongly enriched in Na<sub>2</sub>O (0.15-0.3 wt% in six samples and >0.4 wt% in three samples, respectively) with no enrichments in TiO<sub>2</sub>. Such high concentrations of Na<sub>2</sub>O are at odds with the overall ultra-depleted compositions of the peridotites. Cpx grains are unzoned for Na<sub>2</sub>O and TiO<sub>2</sub>, and, at a thin section scale, their concentration ranges are similar within grains and from grain to grain. High Na<sub>2</sub>O samples cannot be distinguished from low Na<sub>2</sub>O samples by any textural features or other major element compositions. Eight of nine samples enriched in Na<sub>2</sub>O come from the base of the hole, in the section with gabbroic intercalations and fault gouges (Fig. 2a,c). In particular, the three samples with the highest Na<sub>2</sub>O contents (SEY23, SEY25 and HJBD13) were sampled in the bottom, close to fault gouge horizons. However, sample SEY24, extremely poor in Na<sub>2</sub>O and TiO<sub>2</sub>, is intercalated in the Na<sub>2</sub>O-rich section.

Spinel Cr# [= molar Cr/(Cr + Al)] vary in a very narrow range from 0.43 to 0.51 (average  $0.47 \pm 0.011$ ) in all the harzburgites and the lherzolite. Sample SEY02 is characterized by significantly lower Cr# (0.36); the dunite is only slightly higher with 0.52 (eTable 4). Within-sample variations do not exceed 5%, except in one sample (SEY05) where Cr# variation is up to 10%. TiO<sub>2</sub> contents vary from 0.01 to 0.15 wt% (average 0.07 wt%). Such values (<0.2 wt%) are commonly considered as a characteristic of plagioclase-free, spinel peridotites that did not react with MORB liquid at low-P (Dick 1989; Seyler and Bonatti 1997). In the entire sample set, except SEY02, Sp compositions thus define a unique, restricted, compositional field, with no correlation between Cr# and TiO<sub>2</sub>. Average Cr# and Mg# in Sp, Ol and Opx are well correlated from sample to sample. In Ol Mg# vs Sp Cr# diagram, Hole 1274A peridotites plot at the higher Cr# end-member (except SEY02) of the abyssal peridotite array (Fig. 6). These compositions are similar to those of dredged samples from the entire 14°–16°N region (Bonatti et al. 1992; Cannat et al. 1992, 1997) and also characterize abyssal peridotites from the 43°N area at the MAR (Shibata and Thompson 1986).

# Trace elements in clinopyroxenes

Six samples have been selected for trace element study, including five harzburgites and the lherzolite SEY04. Cpx in harzburgite samples SEY03, SEY21, SEY22 and the lherzolite have low to very low Na<sub>2</sub>O contents  $(\leq 0.3 \text{ wt\%})$ , whereas harzburgite samples SEY23 and SEY25 have Cpx enriched in Na<sub>2</sub>O (0.45–0.55 wt%). Within-sample variability for REEs, Sr, Zr and Ti was investigated by analyzing Cpx of several textural occurrences (selvages on Opx, intergranular grains, core and rim, symplectites, and crack-filling); in addition, three samples were analyzed in two thin sections cut from the same slab, to study centimeter scale variability. Results are presented in eTable 5. Trace element concentrations show no significant intra- or inter-grain variations at a sample scale (except in sample SEY25), and as a consequence, show no texturerelated variation. Thus, only average concentrations are hereafter considered for these samples. Near-homogeneous trace element contents in Cpx, suggestive of equilibrium at the thin section scale, is a typical feature of abyssal Cpx, for which with few exceptions, no significant texture-dependance is observed (Hellebrand et al. 2002). In contrast, the two grains analyzed in SEY25 show different compositions. The low-Na Cpx



**Fig. 6** Olivine forsterite contents versus spinel Cr# [= molar Cr/ (Cr + Al)] in Hole 1274A peridotites. *Point symbols* represent sample averages. *Bars* represent 1 $\sigma$  sample variations. Field of Mid-Atlantic Ridge (*MAR*) peridotites from Seyler et al. (2003). Field of peridotites from 43°N at the MAR after Shibata and Thompson (1986)

group has ultra-depleted trace element compositions, in accordance with the extreme depletion in major elements. HREE concentrations are twofold lower than in Cpx from the hotspot-influenced Bouvet FZ (Johnson et al. 1990). REE absolute and relative concentrations in Site 1274 low-Na Cpx are nearly identical to Cpx from Marie Celeste FZ harzburgites in the Central Indian Ridge. The latter are also the most depleted Cpx reported for abyssal peridotites (sample ANTP84-11 in Hellebrand et al. 2002; Fig. 7). Both sets of Cpx are characterized by very steep positive Nd to Lu slope, LREE upward inflection and downward inflection in Eu. This apparent negative Eu anomaly is not coupled with a negative Sr anomaly, which would have been the signature of coexisting plagioclase (this mineral has not been observed in Hole 1274A harzburgites). In contrast, Sr is strongly enriched relative to the adjacent REEs, a feature also commonly observed in the Cpx from very depleted harzburgites, which has been explained by increased difference between Sr and REE bulk partition coefficients, as continuous melting approaches the point of Cpx exhaustion (Parkinson et al. 1992). Because all these Cpx are selectively enriched in LREEs relative to MREEs, we interpret the  $(Sm/Eu)_N$  ratios >1 as an effect of Sm enrichment with respect to Eu. SEY23 REE patterns are characterized by higher concentrations in MREEs relative to HREEs and by less fractionated  $(Nd/Yb)_N$  ratios. La, Ce and Sr enrichments are similar to those observed in SEY21 and SEY22 Cpx, although Na<sub>2</sub>O is twice more concentrated. SEY25 Cpx are globally enriched in the trace elements. Starting from similar Lu and Yb concentrations, the magnitude of the enrichments increases toward the more incompatible REEs up to Ce, and then slightly decreases for La. Their REE concentrations thus define patterns characterized by a concave downward shape with  $(La/Ce)_N < 1$ , which are unusual in abyssal peridotites but have been reported from two ultra-slow spreading ridge segments, the Gakkel peridotites in the Arctic ocean (Hellebrand and Snow 2003) and the Southwest Indian Ridge near the Rodrigues Triple Junction (Toplis et al. 2003). SEY25 Cpx patterns display other unusual features for mantle peridotites equilibrated in the spinel stability field, such as strong negative Eu, Sr and Zr anomalies.

# Discussion

Constraints from textures and in situ major elements

Structures, textures and compositions of the high-T mineral assemblages confirm the highly refractory compositions of Site 1274 harzburgites. No evidence for truly residual Cpx has been found. Detailed microstructures clearly demonstrate that the variability of Opx mode results from two major melt-mineral reaction events leading to different extents of replacement of the Opx either by Ol (reaction 1) or by Cpx  $\pm$  Sp (reaction 2), and resulting in the dm to m scale alternation of harzburgites with variable Ol/Opx and Cpx/Opx ratios observed in the drill core. In addition to modal and textural changes, melt-mineral diffusive exchange reactions occurred concurrently, which allow us to better constrain some aspects of the late magmatic history.

#### Interpretation of orthopyroxene resorption

A first interpretation of reaction 1 textures is to consider them as "asthenospheric" textures formed in the



SEY23 -SEY25A -SEY25B B La Ce Sr Nd Zr Sm Eu Gd Ti Tb Dy Er Yb Lu

Fig. 7 Chondrite-normalized clinopyroxene rare earth element, Sr, Zr and Ti patterns of Hole 1274A peridotites. **a** Low-Na clinopyroxenes. **b** High-Na clinopyroxenes. *Upper hatched field* represents the range for abyssal peridotites after Johnson et al. (1990), Ross and Elthon (1997), Hellebrand et al. (2002) and

Brunelli et al. (2006). *Lower hatched field* is the range for Marie Celeste Fracture Zone peridotites in the Central Indian Ocean after Hellebrand et al. (2002). CI chondrite normalization values from Anders and Grevesse (1989)

upwelling melting mantle (Nicolas 1986; Ceuleneer et al. 1988). In this interpretation, secondary Ol is a reaction product of Opx + Cpx + Sp incongruent melting (Kinzler and Grove 1992). On the other hand, similar textures may develop where incremental or aggregated melts, generated at deeper levels, migrate upward through residual peridotites (Daines and Kohlstedt 1993). In this second interpretation, Ol precipitation and Opx dissolution result from reaction between adiabatically ascending melts that become saturated in Ol and undersaturated in Opx and surrounding mantle (Kelemen 1990). This reaction may occur in the convecting mantle, in regions of incipient melt focusing, where interaction between ascending partial melts and wall rock results in randomly distributed porous flow (Kelemen et al. 1995a,b; Aharonov et al. 1995), or at a higher level in the thermal boundary layer (TBL), where convection changes to, then is dominated by, conductive cooling. In Site 1274, the large (>1 mm) size of the replacive Ol grains suggests that the reaction mostly occurred at, or close to, the peridotite solidus; it continued at relatively low T and high stress as indicated by the few samples where Opx, affected by crystal plastic deformation, is also deeply corroded and replaced by tiny grains of Ol.

Reaction 2, characterized by  $Cpx \pm Sp$  replacing Opx, indicates that the melt was not only undersaturated in Opx (or silica) but also saturated in Cpx. Such reaction combined with reaction 1 may lead to wherlitic compositions through melt-peridotite interaction. Cpx replacing Opx textures are commonly observed in some mantle xenoliths (Zinnegrebe and Foley 1995; Klügel 2001) and lherzolite massifs (Fabriès et al. 1989) where mantle peridotites have been percolated by alkaline melts, but are not a characteristic feature of abyssal peridotites (Seyler et al. 2001). Similar textures are produced experimentally during Opx assimilation in basanitic liquid (Shaw 1999). In Shaw's (1999) experiments, crystallization of Ol and Cpx after dissolution of Opx occurs in two stages. Stage 1 produces Ol and a modified melt enriched in silica and saturated in Cpx, stage 2 crystallizes Cpx selvages on residual Opx by diffusion of Ca from the modified melt. In contrast, primitive, tholeiitic liquids, in equilibrium with mantle minerals at high pressure, become undersaturated in both Opx and Cpx and oversaturated in Ol as they begin to cool at a lower P, and Ol is the only silicate phase to crystallize within residual peridotites at the base of the TBL (Kelemen 1990; Kelemen et al. 1995a, b; Wagner and Grove 1998). Cpx precipitation will follow as Ol fractionation drives the liquids to saturation in Cpx at moderate P (0.7-1.2 GPa; Stolper 1980). At this stage, the liquid composition has significantly evolved and the peridotite has cooled well below its solidus, leading to the formation of thin metasomatic dykelets. Lack of Fe–Ti enrichments and diffuse Cpx textures in Site 1274 peridotites do not support such a conclusion. In contrast, the petrographic study indicates that both reactions, and thus the Cpx crystallization, occurred at similar conditions of low strain and high temperature of the solid matrix, prior to the formation of the lithosphere.

Additional evidence for high-T conditions comes from the observation that in spite of the fact that Opx was, in general, extensively dissolved, this mineral did not reprecipitate along with Cpx. Fractionating liquids are driven to Opx saturation if they derive from high-P partial melts that extensively reacted with wall peridotites, beyond the point of the exhaustion of Cpx (Kelemen et al. 1995a, b), or if they are silica-rich, low-P melts produced by partial melting of a depleted peridotite, in equilibrium with a Cpx-free residue. Indeed, in many ophiolites, mantle harzburgites as refractory as Site 1274 harzburgites, which show similar textures of Opx dissolution-Ol crystallization, do contain secondary Opx (Barth et al. 2003; Dijkstra et al. 2003). In addition, these Opx have very low CaO contents (<0.8%; Barth et al. 2003), in contrast with Site 1274 Opx (ave. CaO ~1.96%, Wo ~3.8%). Application of Ca-in-Opx geothermometer of Brey and Kohler (1990) leads to an equilibrium temperature of ~1,250°C at 1 GPa, suggesting that Hole 1274 peridotites cooled rapidly at depth in the TBL before uplift. This result also reflects probable dry melting Site 1274 peridotites as opposed to assumed hydrous condition in many ophiolites.

# Al–Cr exchange reactions and origin of late-stage Sp and Cpx

Although Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> behave in the opposite way during partial melting (Jacques and Green 1980), in Site 1274, both oxides decrease from core to rim in Opx, to the point where a large proportion of coarse Opx cores acquire low Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> contents. Enhanced Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> depletions indicate that re-equilibration of the Opx to lower P-T condition occurred in high-T peridotites in presence of melt, which increased Al and Cr diffusion out of Opx into the interstitial melt. This process, which occurred concurrently with the Opx resorption, leads to the complex  $Opx + Sp \pm Ol$  intergrowths through a suite of reactions : (1) dissolution of high-T (Al-, Cr-rich) Opx along grain boundaries and cleavages and reprecipitation of Sp, in situ, or at sites of low stress where the melt was driven by shearing of the matrix, according to the reaction  $Mg(Al,Cr)AlSiO_6 = Mg(Al,Cr)_2O_4 + (SiO_2)_{melt}$ , (2) dissolution of adjacent Ol by modified melt locally oversaturated in silica, leading to enclosure of Ol into Sp neoblasts. During these reactions, residual Opx and Ol texturally re-equilibrated with the newly formed minerals.

Clinopyroxene selvages on Opx may result from anmelt-to-mineral diffusive reaction: 0.5 other  $Mg_2Si_2O_6 + (CaSiO_3)_{melt} = CaMgSi_2O_6$ . Minor amounts of Cpx in the Opx + Sp  $\pm$  Ol intergrowths, as well as the formation of the S2 symplectictes at the Opx-Ol interfaces, may also involve Cpx exsolution from Opx and/or a calcic melt component according to the reactions:  $Mg_2SiO_4 + Mg(Al,Cr)AlSiO_6 + (CaSiO_3)_{melt} =$  $Mg(Al,Cr)O_4 + CaMgSi_2O_6 + 0.5$  $Mg_2Si_2O_6$ or  $Mg_2SiO_4 + (CaAl_2SiO_6)_{melt} = CaMgSi_2O_6 + MgAl_2O_4.$ In contrast, the Cpx grains that fill low-angle Ol and Ol-Opx triple junctions and the S1 symplectictes, for which no evidence for Opx- or Ol-melt reaction has been observed, probably precipitated from melt as Cpx or Cpx-Sp cotectic crystals, respectively. The ranges of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> concentrations in the Cpx likely reflect variable Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> saturations of the interstitial melt under condition of rapidly decreasing temperature as the peridotite entered into the TBL, conditions that also permit the preservation of the delicate symplectites.

#### Lherzolitic domains

Hole 1274A peridotites display lherzolitic domains, as exemplified by sample SEY04 which is enriched in both Ol and Cpx. The coarse Cpx crystals are constituents of the protogranular texture, and their orientation defines a high-T lineation; they show resorption features similar to Opx; they contain coarse (up to 4 µm) Opx exsolution lamellae; they also display Curich sulfide intergrowths. All these features are in contrast with textures and compositions of late-stage Cpx (+  $Sp \pm sulfides$ ) that overgrew the coarse Cpx as poikiloblastic rims or discrete crystals. Similar  $Cpx + Sp \pm$  sulfides are also abundant around reacted Opx. This second Cpx generation is characteristically small-sized, enriched in wollastonite (thin Opx exsolutions; high whole-grain CaO contents) and impoverished in  $Al_2O_3$  and  $Cr_2O_3$  relative to the coarse Cpx. The coarse Cpx crystals are thus interpreted to have crystallized from a sulfide-rich melt at higher P-Tconditions than the late-stage Cpx grains. However, elemental compositions which are mainly controlled by melt composition (Na, Ti and incompatible trace elements) are similar between coarse and late-stage Cpx. Therefore, texture and composition relationships between the two generations of Cpx might be interpreted as the result of a dissolution-reprecipitation process at decreasing P-T conditions, that partially preserved relicts of earlier Cpx. Because late-stage Cpx in the lherzolite shows mineral association, texture and compositions identical to the Cpx in the harzburgites, we suggest that Cpx saturation in the percolating melt might have been promoted by melting or selective dissolution of previous Cpx veins within residual mantle. During this process, the primary Cpx and the percolating melt evolved toward chemical equilibrium. Such melt will be especially reactive with Opx.

#### Constraints from trace element and mode modeling

A number of numerical models have been developed, which describe the behavior of trace elements during melt-rock interaction involving elemental exchanges both by diffusive and by mineral (e.g. with modal ± porosity changes) reactions (e.g. Godard et al. 1995; Vernières et al. 1997; Suhr et al. 1998). They show that extensive interaction between migrating melt, derived from adiabatic decompression, and depleted uppermost mantle approaches equilibrium between melt and peridotite and rapidly depletes the melt in incompatible elements. Because the least incompatible trace elements are controlled by mineral reactions and are buffered by the peridotite, the HREE patterns in melt and solid, after melt-rock interaction, reflect the composition of the residual solid (except at high melt/solid ratios in high-porosity channels). In contrast, concentrations of the most incompatible trace elements (LREEs) are mostly controlled by the porosity, being partially buffered by percolating melt. If melt-rock equilibration is not totally achieved, then REE patterns will show selective enrichments in LREEs quite similar to those observed in Site 1274 depleted Cpx.

As a first step in modeling the reactions, we assumed that melt–rock equilibration in Site 1274 peridotites was achieved through partial melting alone. Theoretical extents of melting of the solid residue was calculated using the concentrations of the Cpx moderately incompatible elements (Eu to Lu), that are the least sensitive to melt percolation. In this model, Cpx fractionated at the top of the melting zone from intergranular melt in equilibrium with a near-Cpx free residual harzburgite. Composition of this melt can be modeled as the composition of the last melt fraction generated at the shallowest pressure during continuous decompressional partial melting. The results of these calculations are then used as end-members to discuss the effects of additional reactions between percolating melt and residue. Our calculations, using nonmodal melting equations (Shaw 2000) and a conventional Splherzolite source, cannot reproduce the M/HREE fractionations of the low-Na Cpx, whatever the melting process (batch, Raleigh, critical). To reproduce simultaneously the low Lu and Yb contents and the very low Eu/Lu ratios, melting must begin in the garnet stability field, in agreement with previous modeling of strongly depleted abyssal Cpx compositions (Johnson et al. 1990; Hellebrand et al. 2002; Brunelli et al. 2006). Polybaric, near-fractional melting models (Brunelli et al. 2006) reproduce the M-HREEs contents in our four most depleted samples after 9-10% melting in the garnet stability field, followed by 12-14% melting in the spinel stability field (Fig. 8a-c). Na-rich Cpx SEY23 cannot be reproduced in a satisfying way. Best fits are obtained after 7-9% fractional melting in the garnet stability field followed by 14-16% melting in the spinel stability field with higher residual porosity (~2– 7%; Fig. 8d). This suggests that other processes, such as melt entrapment or melt mixing, contributed to the SEY23 REE pattern. SEY25 cannot be modeled by partial melting alone, except for Lu and Yb whose concentrations are nearly identical to those measured in the other samples.

Because melting reactions in the garnet stability field produced Opx (Kinzler 1997), calculated residual modes contain ~30 wt% Opx, a proportion which is very close to the Opx contents of the least reacted Site 1274 harzburgites (Opx ~28 vol%). Departure from this theoretical mode toward lower, variable, and heterogeneously distributed Opx/Ol proportions is one of the most convincing pieces of evidence for additional mineral reactions accompanying advecting melt percolation. Pervasive or poorly focused partial melt migrating upward in the upwelling molten mantle, or in the shallow mantle at a temperature close to the peridotite solidus, enhances pyroxene dissolution and Ol crystallization, the magnitude of which increases with the quantity of melt passing through the peridotite (Aharonov et al. 1995; Kelemen et al. 1995a, b; Asimow and Stolper 1999). Thus, an alternative model would be to assume that the peridotite underwent a lower degree of adiabatic melting than the one calculated above, leaving a substantial amount of residual Cpx (for instance ~10% upon 12% melting in the spinel field) that would disappear by additional dissolution. In this case, residual intergranular melt would equilibrate with Cpx-free harzburgites characterized by low and highly fractionated REE contents. During this process, both Opx and Cpx are subject to dissolution with Opx more rapidly dissolving as pressure decreases (Kelemen et al. 1995b). However, Site 1274 Opx-rich harzburgites are also devoid of residual Cpx; it is thus likely that low-P melt-rock interaction involved a harzburgite mantle already depleted in Cpx and, thus, that partial melting did start in the garnet stability field.

Selective LREE enrichments in the depleted Cpx, and the occurrence of Na-rich, REE-enriched Cpx (samples SEY23 and 25), may reflect incomplete or local equilibrium between percolating melt and residue, the former being more enriched in REE than the latter, or may be explained by a later event that occurred during or just after the Cpx crystallization (Navon and Stolper 1987; Bodinier et al. 1990; Takazawa

Fig. 8 Results of polybaric continuous (critical) melting models in the garnet, then the spinel peridotite fields (thick dashed lines). Equations for continuous melting from Shaw (2000). Polybaric model and melting parameters (initial and melt modes, source composition, melt/ peridotite partition coefficients) same as in Brunelli et al. (2006). Departure of Site 1274 samples from calculated patterns for Sm to La is attributed to late-stage chromatographic fractionation (not modeled here)



et al. 1992), in relation to the presence of former melt channels.

#### Additional constraints from BMS distribution

Base metal sulfides provide further evidence supporting variable degrees of reactions of a highly refractory mantle with a percolative melt. It is now well demonstrated that S behaves as a moderately incompatible element during mantle melting, because basaltic melts dissolve five to ten times more S than the estimated S content of the upper mantle (Lorand 1991; and references therein). At 1.5 GPa, conventional fractional melting predicts total consumption of BMS for  $F \le 12$ -16% if the depleted MORB mantle contains about 150 ppm S (Saal et al. 2002; Luguet et al. 2003). Because the solubility of S decreases with increasing pressure (Mavrogènes and O'Neill 1999), a partial melting event starting in the garnet lherzolite stability field would allow BMS to persist in residual solids at higher  $F (\leq 20\%)$ . The near-zero S contents of certain Site 1274 Opx-rich harzburgites are therefore consistent with a high degree of partial melting that has progressed beyond complete resorption of the sulfides.

The remainder of Site 1274 harzburgites is much too rich in BMS to be interpreted as simple melting residues. Assuming that all of the S is residing in BMS, the highest BMS content (0.1 vol%) corresponds to ca  $300 \pm 30$  ppm S (based on pentlandite and chalcopyrite S concentrations of 33 and 35 wt%, respectively; unpublished data). This bulk-rock S content is twice the "best estimate" for the convecting depleted mantle. In theory, the conventional fractional melting model predicts a regular decrease of S contents negatively correlated with melt depletion indexes such as Ol Mg# and Sp Cr#. There is no such correlation in Site 1274 harzburgites which, on the contrary, display huge variations of BMS modal abundances, sometimes at the hand-sample scale, in spite of nearly constant Ol Mg# and Sp Cr#. Such heterogeneous distribution can be understood if BMS are "cumulate minerals" of a heterogeneously distributed percolating melt in disequilibrium with harzburgites. The common occurrence of BMS in microstructural sites of melt-rock reactions (Opx-Ol and Cpx-Opx) provide strong support to this interpretation, as does the overabundance of Cu-rich sulfides in Opx-hosted inclusions and of native copper in intergranular BMS that have experienced strong reduction by serpentinization fluids. The assemblage Pn + Cp + Bo (which was protected from serpentinization) is characteristic of oceanic peridotites that have been refertilized in Cpx + Sp by basaltic melts (Lorand 1988; Luguet et al. 2003). Experimental phase diagrams in the Cu–Fe–Ni–S system (Craig and Kullerud 1969) show this assemblage to be a crystallization product of a Cu-enriched Ni–Fe sulfide melt with metal/sulfur atomic ratio >1.

The fact that the highest BMS concentrations correspond to rocks with high (>0.1) Cpx/Opx modal ratios (SEY03, SEY04, SEY23) outlines the main effect of Cpx fractionation. As suggested earlier, Cpx crystallization in Site 1274 harzburgites was promoted by rapid temperature decrease at relatively high pressure (~0.8–1 GPa). Such P-T conditions enhance BMS precipitation by reducing the solubility of S in the percolating melt (Naldrett 1989). In the lherzolite SEY04, the volume of sulfide liquid was high enough for sulfide melt films to be locally interconnected through the interstitial pores of the silicate matrix (Fig. 4c). Experimental data (Gaetani and Grove 1999) suggests that interconnection can occur for 0.1 vol% intergranular sulfides, which is very close to the BMS modal abundance measured in this sample. It is likely that, after such a massive coprecipitation of BMS and Cpx, S was exhausted from the residual silicate melt and no BMS precipitated inside S2 symplectites.

The BMS embedded in Opx porphyroclasts is a common occurrence in ophiolitic and abyssal harzburgites and interpreted as incompletely extracted residual sulfides that have survived partial melting (Lorand 1988; Luguet et al. 2003). This interpretation does not pertain to Site 1274 harzburgites that experienced high degrees of melting beyond complete resorption of BMS. In these rocks, the BMS embedded in Opx contain a high proportion of Cu-rich minerals and are often rimmed by Sp or discrete Cpx crystals. These chemical and microstructural criteria suggest that BMS actually precipitated from trapped, Cu-rich, melts and then infiltrated the corroded Opx at temperatures below the peridotite solidus via the numerous corrosion embayments and fractures. Cu-Ni sulfide melts have depressed solidus temperatures compared to major silicates of anhydrous peridotites (<1,000°C vs. 1,300°C at 1 GPa) and high wetting capacity (Ballhaus et al. 2001), which can explain the secondary sulfide inclusion networks within the Opx.

# A two-stage partial melting/melt-rock reaction model for Site 1274 peridotites?

The wealth of textural, mineralogical and geochemical data obtained from this study yields some contradictions and inconsistencies. A high degree of melting of peridotite, starting in the garnet stability field, is inconsistent with normal mantle temperature inferred from the chemistry of the basalts and gabbros sampled north of the 15°20'N FZ, which have normal MORB compositions (Dosso et al. 1991, 1993; Kelemen 2003) and from the structure of the lithosphere, which is typical of a slow-spreading ridge (thin crust but thick lithospheric mantle, in which a large quantity of gabbroic rocks have frozen; Cannat 1996). The Cu–Ni-rich composition of the metasomatic BMS also argues against a refractory percolating melt.

We propose to solve these inconsistencies by assuming that the convective mantle at the Mid-Atlantic Ridge, 15°–16°N contained harzburgitic blobs that have already been affected by early high-P history of melt depletion and refertilization before upwelling and remelting beneath the present-day ridge. Such a two-stage petrogenetic model has been suggested for other abyssal peridotites from ultra-slow spreading ridges (Seyler et al. 2004) and is supported by Os model ages indicating a long-term Re depletion (Brandon et al. 2000; Alard et al. 2005). For this to apply for Hole 1274A peridotites requires the garnet signature and the high Opx contents of the least reacted harzburgites.

Pyroxene layering in the peridotites may be partially inherited from former pyroxenite veins. This pyroxenitic component preferentially melted to produce a melt undersaturated in Opx and saturated in Cpx. Experimental melting of Cpx-rich lithologies with MORB affinity demonstrate that melts have major element compositions in the range of normal MORB compositions (Pickering-Witter and Johnston 2000; Schwab and Johnston 2001). In addition, experimental melting of Cpx + Sp layer enclosed within a peridotite matrix, with bulk composition similar to MORB composition, releases a melt strongly undersaturated in Opx, which upon reaction with surrounding residual harzburgite, yields normal MORB liquid and residual Ol + Sp assemblage (Bulatov et al. 2002). Mantle pyroxenites are four to five times more enriched in S and Cu than fertile lherzolite (Lorand 1991). Therefore a high degree of melting of Cpx-rich veins may produce a melt saturated in Cu-rich sulfide phases. This melt is just as capable to precipitate Cu-rich BMS as is a lowdegree melt of peridotite of similar major element composition in the percolated mantle column. In this interpretation, the coarse Cpx + Ol + sulfides assemblages in the lherzolite sample represent relics of early cumulate veins that partially melted and/or reacted with peridotitic melt. Lack of a geochemical anomaly in the regional basalts does not preclude our model, as very small amounts of Cpx-rich melt will be highly diluted after mixing with partial melts from the melting of surrounding depleted peridotites that had some remaining Cpx.

#### **Concluding remarks**

Leg 209 Hole 1274A harzburgites differ from common abyssal peridotites by extreme refractory compositions and by well-developed textures of Opx dissolution and Ol + Cpx + Sp + sulfides crystallization. They also show more extensive melt-mineral elemental exchange reactions, resulting in lower Al and Cr contents in residual Opx and in anomalously depleted, U-shaped REE patterns in Cpx. Although Site 1274 peridotites may resemble some ophiolitic and forearc mantle harzburgites, lack of secondary Opx and higher temperature of equilibration show that the extra-depletion was not caused by late-stage hydrous melting. Characteristics of Site 1274 samples indicate reaction with a melt in strong disequilibrium with the peridotite matrix at a temperature close to its solidus.

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