Title: ~~Low-P, h~~Granulite-facies ~~igh-T metamorphic~~ overprint in ultramafic and mafic eclogite-facies rocks of the Central Alps: clues from srilankite ($ZrTi_2O_6$)~~-~~ and ~~spinel ±~~ sapphirine ± corundum-bearing symplectites

Running title: ~~LP-~~HT overprint in eclogites from Central Alps

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Abstract: max 300 words no abbreviations and citations

Eclogite-facies garnet peridotites and different types of eclogites with a broadly MOR~~B~~ signature ~~crop out~~ around Monte Duria (Italy~~;) in the~~ Adula nappe of the Central Alps~~)~~ display ~~. High~~ pressure peaks at ~~P~~ P ~~=>~~ 2.6–3.0~~9~~ GPa and ~~T~~ T = ~~860~~720–~~740~~900°C for peridotites, and at ~~P~~ P ~~<~~= 2.8–3.0 GPa~~2.5~~ and ~~T~~ T ~~=~~≈ 720–~~700~~740°C for eclogites~~, have been~~ retrieved by conventional thermobarometry~~,~~ and thermodynamic modelling ~~and on the basis of the presence in eclogites of pargasite and K-feldspar~~. High-pressure minerals are replaced both in peridotites and in eclogites by lower–P, high-T assemblages. In peridotites, the zirconium titanate srilankite ~~($Zr_{0.33}Ti_{0.66}$)O_2~~ occurs as µm-sized crystals in textural equilibrium with spinel, clinopyroxene and orthopyroxene in coronas and symplectites surrounding ~~garnet~~olivine. By using a new ZrO_2–TiO_2 ~~solid~~ solid-solution model, we ~~interpreted~~ evidence that srilankite ~~has formed after~~is stable in peridotites against zircon + rutile at ~~T~~ T ≈ ~~>~~ 900~~800~~°C at P ≈ 1.0 GPa. ~~,~~which is consistent with ~~$T \geq 850°C$ P~~ T ~~at P ≤ 1.58 GPa~~ estimate~~d~~s ~~by conventional thermobarometry of~~for symplectites replacing garnet bearing ~~ic phases~~sapphirine + spinel + orthopyroxene + amphibole (T ≈ 850 °C at 1.0 GPa).~~-~~

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In eclogites, ~~high-P phases~~ kyanite ~~and zoisite are~~is replaced by symplectites made of anorthite-rich plagioclase + spinel ± ~~Al-rich~~peraluminous sapphirine ± corundum. Thermobarometry suggests that these symplectites formed at ~~*T*~~, *T* ≈~~>~~ 850°C ~~at~~and ~~*P*~~, *P* = ~~1~~0.~~8~~0 – 1.0~~2~~ GPa, conditions which are ~~similar~~ coincident to the ~~low-P,~~ high-*T* overprint observed in peridotites. Thermodynamic modelling coupled with a material-transfer study suggests that at these ~~*P*, *T*~~ *P*, *T* conditions corundum and sapphirine are stable only in the ~~micro-domain surrounding~~pseudomorphs after kyanite ~~and zoisite~~, resulting from the local ~~enrichment~~ high content in aluminium of these micro-domains, which could not fully equilibrate with the surrounding rock due to the "inert" character of this component (i.e., mosaic equilibrium). This is the first report of eclogite-facies rocks showing a ~~LP-HT~~granulite-facies metamorphic overprint in the Central Alps, which is instead well documented in other pre-Alpine complexes. On these basis, alternative than available models are needed to explain the subduction-exhumation evolution of garnet peridotites and hosting eclogites of the Adula-Cima Lunga unit.

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INTRODUCTION

Outcrops of eclogite-facies rocks showing granulite-facies overprint are worldwide restricted to a few localities. These rocks often show spectacular examples of metamorphic reactions, where relicts of high-pressure (HP) minerals are partially replaced by ~~low-pressure (LP),~~ high-temperature (HT) symplectitic assemblages (e.g., ~~(~~Morishita *et al.*, 2001; Nakamura and Hirajima, 2000; Scott *et al.*, 2013)~~, commonly forming symplectitic intergrowths~~. The study of these symplectites is not always straightforward, because of the tiny dimension of the phases and the possible differences in bulk composition between the symplectite micro-domain and the surrounding rock due to variable element mobility and the opening of the system (e.g., ~~(~~Godard and Mabit, 1998; Godard and Martin, 2000). Nevertheless, their understanding can provide unrivalled records of the eclogite-granulite-facies transition.

~~LP-HT s~~Spinel + orthopyroxene + clinopyroxene symplectites (kelyphites) surrounding HP garnet in deep mantle peridotites are relatively common and similar, resulting from the ~~LP-HT~~retrograde reaction between garnet and olivine (see review of Godard & Martin, 2000). In the Alps, ~~nice~~ examples can be found in garnet peridotites from the Central Alps (Adula-Cima Lunga unit) and the Eastern Alps (Ulten zone, ~~) (~~see review of ~~(~~Morten and Trommsdorff~~,~~ -2003).

~~LP-~~HT overprint in eclogites can lead to complex assemblages, varying in function of the

bulk chemistry and the availability of fluids. In kyanite-bearing eclogites, spinel ± corundum ± sapphirine symplectites have been described in different granulite terranes from the Precambrian to the Caledonides and the Variscides (Baldwin *et al.*, 2007; Carswell *et al.*, 1989; Johansson and Möller, 1986; Liati and Seidel, 1996~~);~~; O'Brien, 1992; Godard & Mabit, 1998; Möller, 1999).

Here we present an integrated approach to study the ~~LP~~ HT overprint on garnet peridotites and different types of eclogites cropping out in the Duria area in the southern part of the Adula Nappe in the Central Alps. In particular, we focused on: i) ~~a rare~~ Zr-bearing symplectites containing the zirconium titanate srilankite (Zr_xTi_2)O_{64}; ii) sapphirine + spinel-bearing symplectites replacing garnet ~~occurring~~ in ~~garnet~~ peridotite; iii) spinel ± sapphirine ± corundum-bearing symplectites replacing kyanite ~~and zoisite occurring~~ in eclogites. Thermodynamic modelling of Zr-bearing symplectites in peridotites has been accomplished by developing a new binary solution model between ZrO_2 (baddeleyite) and TiO_2 (rutile) with the intermediate compound srilankite, calibrated against published experimental data at high-pressure conditions. A ~~material~~ material-transfer study has been performed by calculating *P*–*T*–*X* and aH_2O–*X* phase diagrams to ~~address~~ assess the stability of spinel, sapphirine and corundum in symplectites replacing garnet (in peridotite) and kyanite (in eclogite). ~~and zoisite in eclogites~~.-The integration of conventional thermobarometry, thermodynamic modelling and ~~material~~ material-transfer study allowed to retrieve the petrological processes that occurred in these rocks from the eclogite to the ~~granulite~~ granulite-facies transition, and to provide new *P*–*T* estimates of the eclogite-facies peak and the ~~LP HT~~granulite-facies ~~metamorphism~~metamorphic overprint, which are discussed in the framework of the pre-Alpine and Alpine metamorphism of this polycyclic basement.

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GEOLOGICAL SETTING

The Adula-Cima Lunga nappe complex is located on the eastern flank of the Lepontine Dome (Fig. 1) and it represents the highest of the ~~so-called~~ Lower Penninic units of the Central Alps (e.g. (Milnes, 1974; Schmid *et al.*, 1996). Its position in the Central Alps edifice is comprised between the ~~Lower Penninic~~ nappe stack formed by the Leventina-Lucomagno (L-L)~~,~~ ~~Maggia~~ and Simano (Sm) units at the bottom, and the Middle Penninic~~e units at the top (Tambo~~ units~~,~~ ~~Chiavenna metaophiolites and Suretta unit,~~ (Maggia – Mg, Tambo – Tb, Suretta – Su; Fig.1). The contact with the Middle Pennninic nappes occurs along the Misox Zone, a thin unit made of metasediments, MORB-derived amphibolites and slivers of continental basement ((Steinmann and Stille, 1999; Stucki *et al.*, 2003). The lower contact of

the Adula nappe is somewhat less defined due do lithological similarities with the Simano gneiss and the Tertiary ~~high~~ high-grade metamorphism of the Lepontine Dome that overprinted existing tectonic structures (Nagel, 2008). To the south, a lithologically heterogeneous E-W trending zone, namely the Southern Step Belt (SSB) or Bellinzona-Dascio Zone (Schmid *et al.*, 1996), is interposed between the Adula nappe and the western tail of the Bergell pluton~~, which is dextrally displaced along the Insubric Fault~~ (Fig. 1). To the e~~E~~ast, the Gruf Complex, considered part of the Adula nappe ~~(~~(Berger *et al.*, 2005~~), but see (Galli *et al.*, 2013) for alternative interpretation~~), is separated from the main units of the nappe complex by the Forcola normal fault (Ciancaleoni and Marquer, 2006). It is worth noting here that the interpretation of the Gruf Complex as pertaining to the Adula Nappe has been recently challenged by Galli *et al.* (2013), who suggest a pre-Alpine history for this complex.

The Adula nappe largely consists of orthogneiss and paragneiss of pre-Mesozoic origin (Frey and Ferreiro-Mählmann, 1999; Liati *et al.*, 2009; Rubatto *et al.*, 2009), variably retrogressed eclogites preserved as boudins within paragneiss, minor ultramafic bodies and metasedimentary rocks of presumed Mesozoic age (Galster *et al.*, 2012), with references), the latter chiefly preserved in the middle and northern domains of the nappe.

Paleogeographic reconstructions locate the Adula nappe in the former distal European margin (Schmid *et al.*, 1990), to the north of the North Penninic Ocean, opened since the Jurassic and later closed during the Late Cretaceous-Eocene phase of ~~-~~convergence between Europe and Africa-Adria (Dewey *et al.*, 1989).

During the Tertiary Alpine orogenic cycle the Adula nappe and the crustal slivers that now made the SSB, were subducted to mantle depths (Becker, 1993; Evans and Trommsdorff, 1978; Gebauer, 1996; Heinrich, 1986). Metamorphic conditions at peak pressure are found to increase southward, from ~~≈~~≈ 1.7 GPa and ~~≈~~≈ 650°C in the north, to 2.5~~–~~3.0 GPa and ~~≈~~≈ 750°C in the south (Brouwer *et al.*, 2005; Dale and Holland, 2003).

Even more severe ~~higher~~ conditions have been estimated for the peridotite and metaperidotite lenses that occur at the southern, western and eastern margins of the nappe (Fumasoli, 1974; Pfiffner and Trommsdorff, 1998). Garnet lherzolite bodies crop out at three localities, from west to east: Cima di Gagnone, Alpe Arami and Monte Duria (Fig. 1). Such mantle-derived rocks equilibrated at pressure ~~in excess~~ of ≈ 3.0 GPa and temperature of 800-850°C (e.g. (Hermann *et al.*, 2006; Nimis and Trommsdorff, 2001).

An older ~~high~~ high-pressure event of Variscan age (Herwartz *et al.*, 2011; Liati *et al.*, 2009) is seldom preserved within eclogitic boudins of the central and northern sector of the Adula nappe.

After the partial subduction of the European distal margin beneath the ~~Africa~~ Adria margin, the ~~high~~ high-pressure rocks of the Adula nappe and the SSB were overprinted by an upper ~~amphibolite~~ amphibolite-facies metamorphism (Todd and Engi, 1997; Wenk, 1970), which ~~that~~ postdates the main phase of nappe-stacking. In the southern sector of the Lepontine Dome, adjacent to the Insubric Fault (Fig. 1), metamorphic conditions promoted extensive migmatization of both metasedimentary and metagranitoid rocks ("Migmatite belt"~~;~~ (Burri *et al.*, 2005)). Partial melting occurred in the 32-22 time interval (Rubatto *et al.*, 2009) and was promoted essentially by fluid-present processes (Berger *et al.*, 2008), whereas fluid-absent melting of white mica was restricted to a narrow zone between Bellinzona and Lake Como (Fig. 1) in the Adula nappe and the SSB (Burri *et al.*, 2005).

Field aspects of peridotites and hosting crustal rocks

Two sites of the Duria area have been investigated in detail: (i) the outcrop of Borgo and (ii) outcrops within sight to Monte Duria (Figs. 1, 2).

At Borgo (Fig. 2), a hm-sized peridotite body is in contact with amphibole-bearing migmatites with preserved boudins of mafic eclogites. The peridotite body and its mafic rocks rim are hosted within migmatitic gneisses, like those hosting peridotites at Monte Duria (Fig. 2). In the peridotite body, garnet was not observed ~~(Fig. 3a,b)~~, but rounded chlorite-rich pseudomorphs that likely formed after garnet porphyroclasts are abundant; ~~-~~ m~~M~~m- to cm-sized garnet (up to 3 cm), often partially replaced by chlorite and/or kelyphite, has been found ~~downstream~~ in close-by loose blocks ~~on~~ downstream in the Rio Ledù stream bed (Fig. 3 a). In the Borgo body, a compositional layering marked by chlorite-rich and chlorite-poor layers represents the main fabric element at the mesoscale (Fig. 3 b). Such layering is locally transposed by a second foliation marked by chlorite. The contact between the peridotite and hosting crustal rocks is characterized by the occurrence of ~~a few decimeters~~ decimeter-thick metasomatic rim rich in amphibole (amph) and phlogopite (phl). Lenses rich in amph + phl have been also found as cm-sized boudins embedded in the surrounding mafic rock (Fig. 2). A phl-rich pegmatite intruded the peridotite-mafic rocks contact and is folded together with chlorite-defined foliation in the peridotite and the main foliation of hosting mafic gneiss. -The heterogeneous rocks association that makes~~de~~ the rim of the peridotite body consists chiefly of amphibole-bearing migmatitic gneiss (AG in Fig. 2) with boudins of mafic rocks (Fig. 2, 3c, 3d) that show differences in terms of mineralogical composition and deformation. Fine grained, partially retrogressed, dark green eclogites (ME in Fig. 2) occur as boudins (dm to m in size, Fig. 3c) included in plagioclase (pl)- and amphibole-rich gneisses. A second type of

eclogite occurs in larger light-green ~~colored~~ boudins (Fig. 2 and 3d). The contact between the second type eclogites (E in Fig. 2) and surrounding pl+amph gneisses is locally marked by mm-sized layers (Fig. 3e, HAE in Fig. 2), where cm-sized crystals of emerald-green zoisite surrounded by reddish coronae have been found (Fig. 3f).

On the southest ridge of Monte Duria, about 250 m from the summit (Fig. 1), several scattered peridotite bodies (Fig. 3g) occur within migmatitic gneisses (Fumasoli, 1974). Peridotites are often garnet-bearing, although garnet (gt) (mm- to cm-sized) is invariably surrounded by symplectitic intergrowths ("kelyphite", Fig. 3h; cf. Godard and Martin, 2000) and commonly retrogressed to pseudomorphic assemblages. Orthopyroxene (opx) and emerald-green clinopyroxene (cpx) ~~are often visible~~occur often as mm- to cm-sized ~~crystals embedded in an oriented~~ porphyroclasts in an oriented dark fine-grained olivine matrix. Cpx ± gt-rich veins cut at places these peridotite bodies.

The peridotite lenses commonly display a strongly foliated rim (Fig. ~~3h~~3g), with a chlorite foliation parallel to the main foliation of hosting gneisses, and a core where a compositional layering with gt- rich and gt-poor levels occur.

MATERIALS AND METHODS

~~More than 50 thin sections of rocks from the Duria area have been analysed at the petrographic and scanning electron microscopes. For this study, we selected 12 rocks, representative of peridotite and mafic rocks cropping out at Monte Duria and Borgo.~~

Major-elements whole-rock analysis was performed by inductively-coupled plasma mass spectrometry (ICP-MS) and LECO combustion analysis (total C, S) (Bureau Veritas ACME Mineral Laboratories, Canada). Bulk-rock chemistry has been evaluated by using bivariate plots (supplementary Fig. SM 1) and ~~using the~~ principal component analysis (supplementary Fig. SM 2)~~PCA)~~. ~~In particular, this method was used to classify mafic rocks in groups showing similar element correlation. PCA is a statistical procedure that transforms a number of possibly correlated variables into the same number of uncorrelated variables given by the eigenvectors of the covariance matrix, and called principal components. The first principal component (F1) account for as much of the variability in the data as possible, and thus corresponds to the highest eigenvalue of the covariance matrix; each of the succeeding components (F2, F3…) accounts for as much of the remaining variability as possible. For other details and examples of PCA applied to geosciences, refer for instance to (Tumiati *et al.*, 2005, 2008, 2010, 2013).~~

Quantitative analyses of minerals were performed using a JEOL 8200 wavelength-dispersive electron microprobe (EMP), at 15-kV accelerating potential, 5-nA sample current and 1-µm beam diameter. Standards used were omphacite (Na), grossular (Ca, Al and Si), fayalite (Fe), olivine (Mg), orthoclase (K), rhodonite (Mn), ilmenite (Ti), niccolite (Ni), pure Cr (Cr) and zircon (Zr, Hf). A counting time of 30 s was applied for all elements. ~~Ti traces in quartz and~~ Zr traces in rutile have been measured at 15-kV accelerating potential and 100-nA sample current, with a counting time of 300 s (150 s for background). Hf traces in µm-sized zircon, srilankite and baddeleyite in peridotite have been measured at 15-kV accelerating potential and 5-nA sample current (15 nA for larger zircon crystals in eclogite), with a counting time of 300 s (150 s for background). The Fe^{3+}/Fe_{TOT} ratio in minerals reported in Table 2 has been calculated by stoichiometry. Cathodoluminescence images of quartz has been collected at 15-kV accelerating potential and 100-nA sample current.

Thermodynamic modelling has been performed~~–~~ using the software package Perple_X (http://www.perplex.ethz.ch; ~~(~~Connolly, 2005), using the thermodynamic database of ~~(~~Holland and Powell~~,~~ (1998) revised to 2002 (hp02ver.dat), and the following solution models, described in ~~(~~Holland and Powell~~,~~ (1998) (HP), ~~(~~D~~iener~~IENER and ~~POWELL~~Powell~~,~~ (2012) (GHP2), ~~(~~Holland and Powell~~,~~ (2003) (I1,HP), and ~~(~~Dale *et al.*~~,~~ (2000) (DHP): Gt(HP) for garne~~t~~t, Opx(HP) for orthopyroxene, O(HP) for olivine, Cpx(HP) for clinopyroxene, Chl(HP) for chlorite, Sp(HP) for spinel, Pheng(HP) for white mica, Sapp(HP) for sapphirine, Omph(GHP2) for ~~clinopyroxene~~omphacite, Pl(~~H1~~I1,HP) for ternary feldspars, ~~Sp(HP) for spinel, Pheng(HP) for white mica,~~ Amph(DHP) for amphibole, ~~and Sapp(HP) for sapphirine~~and the water equation of state of Holland and Powell (1998). Thermodynamic modelling of Zr-bearing systems was accomplished first by creating the ordered srilankite end-member as a linear combination of 2/3 rutile (TiO_2) and 1/3 baddeleyite (ZrO_2). The srilankite Gibbs free energy of formation was corrected according to ~~(~~Cancarevic *et al.*~~,~~ (2006). A ~~The bb~~addeleyite-srilankite-rutile solution model was then~~we presented in this study is~~ calibrated against the experimental data of ~~(~~Troitzsch *et al.*~~,~~ (2004) and ~~(TOMKINS~~ Tomkins *et al.*~~,~~ (2007) at 2 GPa and 800–1200° C. Retrieved activity-composition relations are expressed according to the van Laar formulation (Holland & Powell, 2003), which allows describing asymmetrical miscibility gaps. Other details about the solid solution model are provided as Supplementary Information.

PETROGRAPHY, BULK-ROCK CHEMISTRY AND MINERAL CHEMISTRY OF DURIA ROCKS

Garnet peridotites

Garnet-bearing peridotites from the Duria area have been sampled from: i) one of the several migmatite-hosted boudins occurring close to Monte Duria (A2C2, MD20 and MD25 in Table 1 and 2); ii) loose blocks found downstream in the Rio Ledù stream bed cutting the Borgo outcrop (B1 and B3A in Table 1 and 2). Borgo peridotites are indistinguishable from the peridotite of Monte Duria in terms of microtexture, mineral assemblage and bulk-rock/mineral chemistry. Slight variations in SiO_2, CaO, Al_2O_3 (Table 1) are imputable to differences in modal proportion of cpx, gt and opx.

Garnet-bearing peridotites are composed by more than 90 vol% of polygonal olivine (100-200 μm), partially serpentinised especially along late fractures (Fig. 4a,b,c). The occurrence of serpentine accounts for the relatively high bulk loss-on-ignition (LOI) (Table 1). The *X*Mg (=Mg/Fe+Mg) of olivine is 0.89-0.91 (Table 2), comparable to the bulk rock *X*Mg = 0.90. Minor phases are clinopyroxene (cpx), orthopyroxene (opx), garnet, spinel (sp), amphibole and accessory ilmenite, pyrrhotite and pentlandite. In sample A2C2, we observed tiny crystals (~1 μm) of srilankite ($Zr_{0.33}Ti_{0.66}O_2$) ~~and a single crystal of baddeleyite ($Zr_{0.99}Ti_{0.01}O_2$)~~ in ~~a~~ double corona~~s~~ formed at the contact between olivine and garnet (Fig. 5a). ~~These Zr phases~~Srilankite occur both in the opx corona replacing the former olivine (Fig. 5b) and in the opx+ cpx + sp ~~opx+cpx+sp crystals in~~ kelyphite replacing garnet (Fig. 5 d). In this latter intergrowth, we found also few crystals of zircon and baddeleyite ($Zr_{0.99}Ti_{0.01}O_2$) (Fig. 5 c, e , f). The Hf content in zircon, srilankite and baddeleyite is highly scattered (Table 3). Maximum contents are 0.72 wt% HfO_2 in baddeleyite [Hf/(Zr+Hf) = 0.005], 0.40 wt% HfO_2 in srilankite [Hf/(Zr+Hf) = 0.007] and 0.05 wt% HfO_2 in zircon [Hf/(Zr+Hf) = 0.001].

Gt occurs as porphyroblasts and porphyroclasts of variable size up to 3 cm (Fig. 4 a, c; Fig. 6 a). It is only slightly zoned from core to rim (supplementary figure SM3), ~~with~~ displaying an average *X*Mg = 0.~~80~~79 ($Py_{68}Alm_{19}Gr_9Uv_{4}$) in the core and an average *X*Mg = 0.7~~6~~7 ($Py_{67}Alm_{21}Gr_9Uv_{4}$) in the rim ~~in the rim, with Cr content up to 2.49 wt% Cr_2O_3 (0.14 a.p.f.u.)~~. In samples MD20 and MD25, symplectites developed along fractures in garnet contain sapphirine, in textural equilibrium with spinel, orthopyroxene and amphibole (Fig. 7a). Sapphirine is characterised by *X*Mg = 0.93–0.95 and is Al-rich (17.36–17.61 a.p.u.f. on a basis of 28 cations), close to the sapphirine end-member (7 : 9 : 3).

Cpx, opx, sp and amph occurs as mm- to cm-sized porphyroclasts, found both in the matrix (Fig. 4 b; Fig. 6 a) and included in garnet, and ~~as fine-grained kelyphite~~in coronas surrounding garnet (Fig. 4 c; Fig. ~~5b~~6 a).

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Porphyroclastic cpx is diopside-rich with *X*Mg = 0.95, Cr up to 0.04 a.p.f.u. and jadeite content up to 7%. Cpx in kelyphite displays negligible jadeite contents and higher Al (0.018 a.p.f.u.). In sample B3, µm-sized inclusions of edenitic amphibole (*X*Mg = 0.94) and dolomite ($Ca_{1.01}Mg_{0.94}Fe_{0.05}$)($CO_3$)$_2$ have been observed in cpx porphyroclasts.

Porphyroclastic opx is enstatite rich (*X*Mg = 0.92) and Al poor (0.03 a.p.f.u.), while opx ~~and~~ in the kelyphitic assemblage becomes richer in Fe (*X*Mg = 0.89–0.92) and Al (up to 0.08 a.p.f.u. in sapphirine-free symplectites; up to 0.20 a.p.f.u. in sapphirine-bearing symplectites) (Table 2) ~~in the kelyphitic assemblage~~.

Primary s~~S~~pinel occurs both as porphyroclasts in the matrix (Fig. 6 a) and rarely included in garnet. Often, former spinel inclusions in garnet are now embedded in kelyphites, which contain a second generation of spinel forming vermicular intergrowths with opx and cpx. Spinel composition shows dramatic variations, being spinel porphyroclasts and inclusions rich in Fe (*X*Mg = 0.47) and Cr (Cr/Al+Cr = 0.56), especially at the core, while ~~kelyphitic~~ symplectitic spinel and rims of spinel porphyroclasts are ~~is~~ Fe poor (*X*Mg = 0.76–0.84) and Cr poor (Cr/Al+Cr = 0.04) (Fig. SM 3 b).

Amphibole porphyroclasts are pargasitic to edenitic in composition, while kelyphitic amphibole is tschermakite to magnesiohornblende~~ic~~. In sample B3A, we observed a late generation of kelyphitic intergrowth composed of chlorite, anthophyllite and phlogopite.

Mafic rocks

Mafic rocks were sampled systematically in the Borgo outcrop, where these rocks are in contact with peridotites (Figs. 2, ~~.~~ 3). ~~The different types of mafic rocks are not easy to distinguish in the field. Therefore, these r~~Rocks have been classified on the basis of their bulk-rock chemistry (Table 1) and petrographic features described below. ~~In particular, the principal component analysis (PCA) has been applied in order to identify groups of rocks showing similar element correlation (Fig. 6).~~ Overall, ~~As a general consideration, t~~the compositions of the Borgo mafic rocks are broadly ~~comparable~~ ascribable to ~~N~~-MOR~~B~~ ~~basalts~~ gabbros showing various degrees of differentiation~~(cf. Klein, 2003)~~, ~~showing~~ resulting in variable *X*Mg (from 0.61 to 0.84), and Al_2O_3 (from 14.61 to 20.83 wt%), CaO (from 9.57 to 13.24 wt%) and TiO_2 (from 0.16 to 1.65 wt%) contents (supplementary Fig. 1). A more detailed characterization of these rocks is beyond the purpose of this paper and will be given elsewhere. In this study, the principal component analysis (PCA) has been applied in order to identify groups of rocks showing similar element correlation (supplementary Fig. SM 2).

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PCA distinguishes among mafic rocks: i) kyanite eclogites (E),~~:~~ samples D3 and B5, showing an~~the lowest covariance~~ average content for all elements; ii) mafic eclogites (ME),~~:~~ samples D6 and D4, showing the highest contents in Fe, Ti,~~ P~~, P and Mn (dark green on the field); iii) high-Al eclogites (HAE),~~:~~ samples D1, D8 and D9, showing the highest contents in Al, Si, Na and K; iv) pl+amph gneisses (AG),~~:~~ samples D5 and D2, showing the highest contents in Ca and Cr. The mineralogy and petrography of these lithotypes is provided below.

Kyanite eclogites (E)

In these rocks, a symplectitic matrix composed of diopside-rich and jadeite-poor clinopyroxene ($Di_{81}Hed_{15}Jd_{6}$~~*XMg = 0.87-0.88*~~) and albite-rich plagioclase (up to ~~Ab_{73}~~Ab_{43}) is dominant (Table 2; Fig. ~~4e~~6b; Fig. ~~7~~5b,c~~e~~). In sample D3, these symplectites appear as pseudomorphs after former mm-sized stubby prismatic crystals embedded in quartz, associated to Ca-rich plagioclase pseudomorphs likely after zoisite (Fig. 7f; see also eclogites HAE below). The average bulk composition of a representative cpx + pl symplectite has been measured by averaging 400 EMP analyses (1 µm step) over a 20 µm × 20 µm area, and it would correspond~~s to a mixed composition between quartz and~~ to a mixed composition of 83.7 mol% omphacitic clinopyroxene $Di_{58}Jd_{32}Hd_{10}$ and ~~.~~16.3 mol% quartz, strongly suggesting that symplectites formed due to the reaction Ab (in pl) = Jd (in cpx) + qtz (Holland, 1980). A ~~It is noteworthy that f~~few inclusions of relict omphacite have been observed in ~~a~~ kyanite (Fig. 6c) and garnet porphyroclast~~s (Fig. 5d) in sample B5~~, displaying an almost identical composition $Di_{58}Jd_{33}Hd_{9}$ (Table 2). Other porphyroclasts consist of slightly zoned ~~homogeneous~~ garnet (core: Py_{38}~~$_{41}$~~Alm_{37}~~$_{36}$~~$Gr_{24}Sp_{1}$; rim: $Alm_{42}Py_{35}Gr_{20}Sp_{2}$; see also supplementary Fig. SM 4 a, b~~$_{3}$~~), quartz, ~~K-feldspar (Or_{97}~~-~~$_{98}$ in sample D3) and~~ pargasitic amphibole (*X*Mg = 0.82) (Fig. ~~5c~~6b) and~~.~~ K-feldspar (Or_{97}~~-~~$_{98}$) in sample D3. Cathodoluminescence images of monocrystalline quartz revealed a grain core showing a peculiar layered zonation, resembling twinning planes of a former phase surrounded by a polycrystalline rim (Fig. 6 d), now fully recovered. Rutile is an accessory mineral, commonly found included in garnet and kyanite porphyroclasts. Other accessory phases are ilmenite (replacing rutile in symplectites), zircon and apatite. ~~Traces of Zr in rutile included in garnet, and of Ti in porphyroclastic quartz have been measured for thermometric purposes and will be given in the next Section.~~ Garnet and kyanite are typically replaced by symplectitic intergrowths (Fig. 7 b, c~~5e~~). Symplectites surrounding garnet ~~(Fig. 4e,f)~~ usually consist of plagioclase and magnesiohornblende, although relict symplectites containing orthopyroxene ~~(*X*Mg = 0.74; Table 2)~~ and plagioclase have been observed (Fig. 7 b). Symplectites

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surronding kyanite (Figs. 4 d, e ,f; 6 b, c,;~~4 d, e , f~~7 c) consist of anorthite-rich plagioclase (An_{84}), spinel (*X*Mg = 0.5~~8~~) and minor ~~Al-rich~~peraluminous sapphirine (*X*Mg = 0.8~~4~~; Al ~~4.77~~19 a.p.f.u. on the basis of ~~7~~ 28 cations). An outer corona of orthopyroxene (*X*Mg = 0.70; Table 2) surrounds sometimes these symplectites (supplementary Fig. SM e, f). Sapphirine in these symplectites is very rich in Al (19.00 a.p.f.u. on the basis of 28 cations), being intermediate between the (7 : 9 : 3) and the (3 : 5 : 1) end-members.

Mafic eclogites (ME)

Compared to the kyanite ~~the~~ eclogites E, mafic eclogites (ME) contain a higher amount of garnet (Fig. 4 g). Garnet is zoned (supplementary figure SM4 c, d), displaying an average core composition $Alm_{40}Py_{35}Gr_{24}Sp_1$, which is only slightly enriched in Fe compared to garnet cores in type E eclogites. However, garnet rims in contact with surrounding plagioclase + magnesiohornblende symplectites are considerably Fe-and Mn-richer up to $Alm_{55}Gr_{20}Py_{19}Sp_6$. Often, garnet porphyroclasts are completely replaced by amph + pl symplectitic intergrowths. Magnesiohornblende, associated with albite-rich plagioclase, is a common phase also in symplectites after omphacite. In ME eclogites, cpx + pl symplectites are rarely preserved. One of these cpx + pl symplectites has been analysed using the same method described above for eclogites E, yielding the composition $Di_{58}Jd_{28}Hd_{15}$ for the former omphacite, showing higher Fe and lower Jd contents compared to eclogites E. Among relict eclogite-facies minerals, quartz occurs in mafic eclogites, but its modal abundance is lower compared to eclogites E. Zoisite, K-feldspar (Or_{99}) and pargasitic amphibole (*X*Mg = 0.68) occur as >100 µm porphyroclasts (Fig. 6 ~~5~~e, f). Accessory ~~phases~~ rutile, ilmenite, apatite and Fe–Cu sulphides are abundant. A single 30-µm crystal of dolomite $(Ca_{1.00}Mg_{0.88}Fe_{0.12})(CO_3)_2$ has been observed included in a garnet core (supplementary figure SM4 d). ~~Nor k~~Either kyanite ~~neither~~ nor symplectites after kyanite were observed in mafic eclogites.

High-Al eclogites (HAE)

These rocks contain no or very minor garnet. Porphyroclastic kyanite, quartz, emerald-green Fe- and Cr-bearing zoisite (up to 2 cm in size, Fig. 3f; 0.95 wt% FeO and 0.24 wt% Cr_2O_3) are accessory minerals. Zoisite contains minor inclusions of pargasite, and is commonly replaced by symplectites consisting of almost pure anorthite (An_{99}) (Fig. 4 h).~~.~~

The rock matrix is mainly constituted by simplectites made of ~~cpx+pl~~low-Jd clinopyroxene, high-Ab plagioclase and magnesiohondblende. ~~and pl+sp+sapp+cor symplectites in equal amounts (Fig. 5).~~ On the basis of the modal abundance of cpx and pl in

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symplectites after omphacite, the composition of the latter has been reconstructed as $Di_{59}Jd_{33}Hd_8$, which is nearly identical to that of omphacite observed in eclogites E. Similarly to eclogites E, s~~S~~ymplectites after kyanite contain anorthite-rich plagioclase (An_{87}~~$_8$~~), spinel (*X*Mg = 0.59~~61~~) and Al-rich sapphirine (*X*Mg = 0.85~~7~~; Al ~~4.89~~19.50 a.p.f.u. on the basis of ~~7~~28 cations)~~, similarly to eclogites E. Symplectites after kyanite contain anorthite-rich plagioclase (An_{88}), spinel (*X*Mg = 0.61) and Al-rich sapphirine (*X*Mg = 0.87; Al 4.89 a.p.f.u. on the basis of 7 cations), similarly to eclogites E.~~ However, in HAE eclogites these symplectites often contain also corundum (Fig. 7 d, e) ~~(Fig. 5h)~~. Late margarite and laumontite are~~is~~ also commonly observed as alteration products of~~in~~ these symplectites. ~~Corundum has been found also in symplectites surrounding zoisite (Fig. h), associated to anorthite-rich plagioclase (An_{93}), spinel and sapphirine (Fig. 5g).~~

Amphibole-plagioclase gneisses (AG) - retrogressed eclogites

These rocks display a broadly layered microtexture both at~~y~~ the meso- and microscale, with mm-sized layers rich in plagioclase and layers rich in amphibole. Plagioclase is typically Ca-rich (An_{90}), comparable to plagioclase found in coronas surrounding zoisite (cf. eclogites HAE) and in symplectites replacing kyanite (cf. eclogites E and HAE). However, neither spinel nor sapphirine nor corundum were observed in these plagioclase layers. Amphibole is magnesiohornblende (*X*Mg = 0.82), partially replaced by tremolite. Phlogopite also occurs, partially replaced by chlorite. Occasionally, relict cpx + pl symplectites after omphacite can be observed. The reconstructed composition of the former omphacite is $Di_{67}Jd_{24}Hd_9$, displaying lower jadeite content with respect to the more preserved eclogites described above.

PETROLOGY AND GEOTHERMOBAROMETRY OF DURIA ROCKS

In the previous sections, we characterized different types of rocks from the Duria area displaying relict eclogite-facies minerals, namely garnet in peridotites, and omphacite, garnet~~,~~ and kyanite ~~and zoisite~~ in eclogites, partially replaced by symplectitic intergrowths containing at times srilankite and sapphirine in peridotites, and sapphirine, spinel and corundum in eclogites. ~~In detail, we focused on i) garnet-bearing peridotites from Monte Duria and Borgo, and ii) eclogites, from the Borgo outcrop only.~~ In order to constrain the petrological processes occurred in these rocks and the *P*~~, T~~ -*T* conditions in force during eclogite-facies and post-eclogitic metamorphism, we performed classical thermobarometry and thermodynamic modelling of both peridotites and mafic rocks.

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Garnet peridotites

Thermobarometry

P, T Temperature conditions of the eclogite facies and post-eclogitic metamorphism have been estimated in peridotites using i) the cpx-opx pyroxene solvus thermometers of (Brey and Koehler, 1990) and (Taylor, (1998) (TaOpx/Cpx; red in Fig. 8); ii), and the Ca-in-opx thermometer of Brey & Köhler (1990) corrected by (Nimis and Grütter, (2010) (BKOpx_corrNG; purple in Fig. 8); iii) the thermometer of Nimis and Grütter (2010), based on the Fe–Mg exchange between opx and gt (NGOpx/Gt; black in Fig. 8) and iv) the single cpx thermometer of (Nimis &and Taylor, (2000), based on the enstatite content of cpx (NTCpx; pink in Fig. 8).

Minimum pPressure estimates of the eclogite facies were retrieved using i) the barometer of (O'Neill, (1981) (P$_{O'N81}$), based on the transition between spinel lherzolite and garnet+spinel lherzolite, which is dependent on the Cr/Al+Cr ratio of spinel (O'NSp/Gt; blue in Fig. 8); ii) the barometer of Taylor (1998), based on the Al exchange between opx and gt (TaOpx/Gt; grey in Fig. 8); iii) the Cr-in-Cpx barometer of (Nimis &and Taylor, (2000), based on the Cr exchange between cpx and gt (NTCrCpx; green in Fig. 8). Because O'NSp/GtP$_{O'N81}$ estimates were retrieved using the most Cr-rich composition of relict spinel included in garnet or in the matrix, they should be considered as minimum estimates.

Other estimates of the eclogitic peak were retrieved using also the thermometer of (Nimis and Grütter, 2010), based on the Fe-Mg exchange between opx and gt, and the barometer of Taylor (1998), based on the Al exchange between opx and gt.

The minerals inEstimates for the Duria peridotite sample A2C2 have been retrieved by considering the core compositions of porphyroblastic garnet, of orthopyroxene and spinel in the matrix, and of clinopyroxene included in garnet (Table 2). Minerals display a good degree of equilibration, as the seven independent geothermobarometers yield concordant values and intersect one to another at 2.8 ± 0.2 GPa and 730 ± 20 °C (Fig. 8). In the other peridotites from Mt. Duria (MD20, MD25) and Borgo (B1, B3), are not in equilibrium with respect to all elements, resulting in Fe–Mg and pyroxene-solvus temperatures are often discordant, suggesting disequilibrium among the considered phases (Fig. 7). In particular, although the TaOpx/Cpx and the NTCpx thermometers are broadly comparable to sample A2C2, intersecting the barometers at 700–760°C (with the remarkable exception of sample B3 at *T* = 830–840°C), the BKOpx_corrNG thermometer yields generally lower temperatures, down to 680°C in sample MD20. On the contrary, the NGOpx/Gt appears to be shifted at higher

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temperatures, intersecting the O'NSp/Gt barometer at 2.8 GPa and 880°C in sample B1 and at 3 GPa and 920°C in sample B3. Excluding sample A2C2, in all other samples the NGOpx/Gt thermometer displays a second intersection point with both the barometers TaOpx/Gt and NTCrCpx at anomalously high *P*–*T* conditions, up to around 4 GPa and 1100°C in sample B3 (Fig. 8)..~~The apparently highest temperatures for the eclogite-facies stage are those based on the pyroxene solvus thermometers in sample A2C2 from Monte Duria (T = 869° C at $P_{O'N81}$ = 2.69 GPa) and those based on the Fe-Mg exchange between opx and gt in sample B1 from Borgo (T = 903°C at $P_{O'N81}$ = 2.87 GPa). In sample B3 from Borgo, the thermometers of Brey & Köhler (1990) and (Nimis and Grütter, 2010) yields concordant T = 860 ± 2 °C at $P_{O'N81}$ = 2.86 GPa. Because $P_{O'N81}$ estimates were retrieved using the most Cr-rich composition of relict spinel included in garnet or in the matrix, they should be considered as minimum estimates.~~

Temperature for the post eclogitic peak were estimated by using the thermometers TaOpx/Cpx, BKOpx_corrNG, NTCpx and the experimentally calibrated thermometer of Sato *et al*. (2006), based on the Fe–Mg exchange between spinel and sapphirine (SSp/Sapp; brown in Fig. 9). Maximum pressure estimates were retrieved by using the barometer O'NSp/Gt, which represent the upper boundary of the garnet-free field in the presence of low Cr/Al+Cr keyphitic spinel. The composition of minerals forming kelyphites replacing garnet and opx coronas replacing olivine was considered for the calculations.

Mineral compositions in ~~symplectites~~ kelyphites post-dating eclogite-facies metamorphism result in discordant temperature estimates, suggesting also in this case a high degree of disequilibrium. The highest ~~apparent~~ temperatures of T = 880°C at P_{max} = 1.6–1.7 GPa, ~~based on~~retrieved using the the SSp/Sapp thermometer~~pyroxene solvus thermometers~~, ~~has~~ have been observed in Monte Duria peridotites MD20 and MD25 (Fig. 9) ~~(*T* = 858°C at $P_{O'N81}$ = 1.58 GPa)~~. Similar temperatures have been calculated for sample A2C2 using the pyroxene-solvus thermometers TaOpx/Cpx and NTCpx, which yield concordant temperatures of 840°C at P_{max} = 1.4 GPa. However, in the same sample the thermometer BKOpx_corrNG provides lower temperatures of 635°C at P_{max} = 1.4 GPa. Pyroxene–solvus temperatures are low and often discordant also in the other peridotites~~Given the partial low-P (LP), high-T (HT) re-equilibration~~, suggesting that these temperatures merely represent minimum estimates of the ~~LP~~ post-eclogitic peak temperature.~~e, while $P_{O'N81}$ estimates should be considered as maximum estimates of the LP-HT sp-bearing, gt-free metamorphic stage~~.

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Thermodynamic modelling of sapphirine-bearing symplectites

In all Duria peridotites we observed kelyphites developing at the contact between olivine and garnet consisting of orthopyroxene, spinel and clinopyroxene. By mass-balancing the mineral compositions of sample MD20 (sympl1 in Table 2), we obtained the following reaction accounting for the formation of these kelyphites:

$$1.25\ ol + 1.00\ gt = 1.73\ opx + 1.00\ sp + 0.42\ cpx + 0.25\ Fe_{+1}Mg_{-1} \quad (1)$$

However, in the same sample we observed also kelyphites containing sapphirine associated with low-Cr spinel, Al-rich orthopyroxene and magnesiohornblende, developed along garnet fractures. The chemical bulk composition of the symplectite (MD_20 X1 in supplementary Table SM2) has been retrieved using the kelyphite mineral compositions (sympl2 in Table 2) and the phase proportions obtained by image analysis of elemental X-ray maps (supplementary Fig. SM7). The reaction accounting for the formation of sapp-bearing kelyphites is:

$$0.88\ ol + 0.81\ gt + 0.17\ H_2O + 0.4\ Al_2O_3 + 0.04\ Na_2O = 1.00\ sympl2 + 0.33\ Fe_{+1}Mg_{-1} \quad (2)$$

where sympl2 is the reconstructed bulk composition of the sapph-bearing kelyphite normalized to 10 cations, and $Fe_{+1}Mg_{-1}$ represents a vector accounting for the Fe–Mg exchange between reactants and products. Reaction (2) suggests that the growth of sapp-bearing kelyphites requires higher gt/ol ratios compared to reaction (1), the presence of water and the addition of Na and extra Al in the system.

The *P–T* pseudosection calculated for sympl2 composition in the system NCFMASH at water-saturated conditions shows that sapphirine is stable only at relatively low pressure, below 1.0–1.1 GPa for temperatures ranging from 800 °C to 1000°C (Fig. 10 a). Sapphirine associated with orthopyroxene, spinel and amphibole is restricted to a narrow field extending from 0.8 to 1.0 GPa and $T > 720$°C. The intersection of this field and the thermometer SSp/Sapp occurs at $P = 0.8$–0.9 GPa and $T \approx 850$°C.

A *T–X* binary phase diagram has been calculated at fixed $P = 0.9$ GPa (Fig. 10 b), where $X = 0$ represents the composition of opx + cpx + sp kelyphites (sympl1 in Table 2), derived from reaction (1), and $X = 1$ represents the bulk composition sympl2 (Fig. 10 b). Sapphirine is never stable for bulk compositions towards $X = 0$, where the assemblage opx + cpx + sp is stable for $T > 790$°C. For $X > 0.7$ and $T > 780$°C, sapphirine becomes stable against chlorite +

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corundum, forming at X = 1 the assemblage opx + sapp + amph + sp + cpx for T > 820°C. With the exception of clinopyroxene, this last assemblage is consistent with that observed in sapp-bearing kelyphites.

Thermodynamic modelling of srilankite-bearing symplectites

The occurrence of srilankite ($Zr_{0.33}Ti_{0.66}O_2$) and zircon in a corona replacing garnet and olivine in sample A2C2 from ~~Monte~~ Mt. Duria (Fig. 5) gave us the opportunity to perform ~~a~~ thermodynamic modelling in order to retrieve additional ~~*P*,~~*P*–~~*T*~~ *T* constraints for the post-eclogitic metamorphic stage.

Although it is known that the Zr content in rutile is temperature dependent (e.g., ~~(~~Zack *et al.*, 2004), the solid solution between TiO_2 and ZrO_2 has been investigated experimentally in detail only in a few works (McHale & Roth, 1983; ~~(TOMKINS *et al.*, 2007;~~ Troitzsch *et al.*, 2004; Troitzsch and Ellis, 2004; Tomkins *et al.*, 2007). In particular, Troitzsch *et al*. (2004) dealt with the solid solutions among rutile (TiO_2), baddeleyite (ZrO_2) and the intermediate compound srilankite ~~$(Zr,Ti)_2O_4$~~ at 800–1220°C up to 2 GPa~~, demonstrating that the composition of ordered srilankite is depending on *P* and *T*, ranging from *X*Ti ($=TiO_2/ZrO_2+TiO_2$) 0.60 at 1200°C and 2 GPa, to 0.68 at 800°C and 2 GPa~~. These experimental data allowed us to develop a solid solution model and to calculate *T*-*X* and *P*-*T* phase diagrams in petrological systems of increasing complexity (Fig. ~~8~~10; supplementary Fig. SM6). Details on the solution model can be found as Supplementary information.

~~The *T*-*X* phase diagram calculated for the TiO_2–ZrO_2 system at 2.0 GPa (Fig. 8a) reproduces almost perfectly the experimental Ti contents of baddeleyite and the Zr content of rutile in function of *T*. However, the model overestimates the *X*Ti of the intermediate compound $(Zr,Ti)_2O_4$ (XTi^{sril}) at *T* > 800°C. On the basis of the experimental data of Troitzsch *et al.* (2004), the measured composition of srilankite in sample A2C2 (XTi = 0.66) is consistent with *T* ~ 900°C, which is close to the temperatures estimated for the post-eclogitic peak using the pyroxene solvus thermometers.~~

Because srilankite has been found included in an opx corona replacing olivine (Fig. 5 b), and associated to opx+cpx+sp in a kelyphite replacing garnet (Fig. 5 d), thermodynamic modelling has been performed ~~also in the more complex~~ in the systems ~~MS~~MgO–SiO_2–~~+~~TiO_2–ZrO_2 (grey chemographies and dashed line in Fig. 11) and CaO–FeO–MgO–Al_2O_3–SiO_2–~~FMAS+~~TiO_2–ZrO_2 (black solid lines in Fig. 11).

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In the system MgO–SiO_2–TiO_2–ZrO_2~~MS+TiO_2+ZrO_2~~, chemographies ~~in Figure 8b~~ show that the assemblage ~~a peridotitic assemblage~~ forsterite + enastatite ~~should always coexist with~~ + zircon + ~~and~~ rutile is stable independently from the bulk composition at relatively low temperatures (e.g., T < 830° C at ~~,~~ P = 0.9 GPa; Fig. 11).~~relatively low temperatures~~.~~-~~At higher temperatures, the stable assemblage is dependent on the bulk XTi ratio ~~([~~XTi^{bulk} = TiO_2/(ZrO_2+TiO_2)~~, -~~)], becoming eith~~h~~er forsterite+enastatite+zircon+srilankite for XTi^{bulk} < XTi^{sril} (green star above the sril–en tie line) or forsterite+enastatite+srilankite+rutile for XTi^{bulk} > XTi^{sril} (blue star below the sril–en tie line). The reaction leading to the formation of srilankite in the MgO–SiO_2–TiO_2–ZrO_2 system ~~therefore~~ is:

Mg_2SiO_4 (fo) + 2 TiO_2 (ru) + $ZrSiO_4$ (zrc) = ~~(~~Zr~~,~~Ti~~)~~$_2O_{64}$ (sril) + $Mg_2Si_2O_6$ (en)

(~~1~~3)

which is represented with a grey dashed line in the P–T field ~~shown on a P-T diagram in Figure 8 b~~(Fig. 11). Our model predicts that the above univariant reaction occurs at temperatures of ~~about~~79~~-10300~~°C at 0.5~~1~~ GPa and 900°C at 1.7 GPa ~~in the MS+TiO_2-ZrO_2 system~~.

A P~~-~~–T pseudosection (i.e., isochemical section) has been calculated for the system CaO–FeO–MgO–Al_2O_3–SiO_2–TiO_2–ZrO_2~~.CFMAS+TiO_2+ZrO_2~~ in order to check how the stability of srilankite is influenced by ~~other~~ components CaO, FeO and Al_2O_3. ~~In this system~~By adding FeO, the srilankite-forming ~~reaction~~univariant above becomes divariant, because olivine and orthopyroxene form solid solutions between their Mg- and Fe-endmembers~~-~~. By adding also CaO and Al_2O_3, ~~(unbalanced) becomes~~:clinopyroxene and spinel become stable, so that the actual phase assemblage of the srilankite-bearing kelyphite observed in sample A2C2 can be modelled.

~~(Mg,Fe)$_2$SiO$_4$ (ol) + (Mg,Fe,Ca)$_3$Al$_2$Si$_3$O$_8$ (gt) + ZrSiO$_4$ (zrc) + TiO$_2$ (ru) =~~

~~= (Mg,Fe)$_2$Si$_2$O$_6$ (opx) + Ca(Mg,Fe)Si$_2$O$_6$ (cpx) + (Mg,Fe)Al$_2$O$_4$ (sp) + (Zr,Ti)$_2$O$_4$ (sril)~~

~~(2)~~Therefore, in order to calculate the pseudosection ~~In order to model the low-P, high-T reaction between garnet and olivine in a Zr- and Ti-bearing system, w~~we considered ~~a~~ the bulk composition of the kelyphite, retrieved by mass-balancing the compositions of the reactant gt + ol, and the kelyphite products opx + cpx + sp occurring in sample A2C2 (Table 2), doped with 3 mol% rutile and 1 mol% zircon (Table SM 2), ~~consisting of garnet and~~

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~~olivine in equal amounts, using the mineral compositions measured in garnet peridotite A2C2, and~~ assuming a bulk *X*Ti = 0.75 ~~(Fig. 9c) and *X*Ti=0.25 (Fig. 9d)~~. In this more complex system, the stability of srilankite is ~~expanded~~shifted at lower temperatures ~~at lower temperatures~~by around 20°C (Fig. 11) ~~and is not dependent on the bulk *X*Ti~~. ~~In this system, the srilankite-forming reaction (unbalanced) becomes:~~

~~$(Mg,Fe)_2SiO_4$ (ol) + $(Mg,Fe,Ca)_3Al_2Si_3O_8$ (gt) + $ZrSiO_4$ (zrc) + TiO_2 (ru) =~~
~~= $(Mg,Fe)_2Si_2O_6$ (opx) + $Ca(Mg,Fe)Si_2O_6$ (cpx) + $(Mg,Fe)Al_2O_4$ (sp) + $(Zr,Ti)_2O_4$ (sril)~~
~~(2)~~

meaning that

~~In the pseudosections,~~ srilankite in equilibrium with opx~~,~~ ± sp ~~a±nd~~ cpx ~~is~~ should be ~~formed~~ stable against~~at the expenses of either~~ zircon + ~~(Fig. 8c) or~~ rutile ~~(Fig. 8d), depending on *X*Ti~~^{bulk}~~,~~ at ~~T~~ *T* ~~=>~~ 810~~970–1000~~°C at 0.9 GPa. This temperature is ~~higher~~ consistent with~~compared to that estimated~~ those retrieved for the post-eclogitic peak by using the TaOpx/Cpx and NTCpx thermometers (820–830°C at 0.9 GPa; sample A2C2) and the SSp/Sapp thermometer (850°C at 0.9 GPa; samples MD20 and MD25). ~~for the post-eclogitic peak using the pyroxene solvus thermometers.~~

~~However, at this stage the uncertainties associated to the temperatures retrieved from this new thermodynamic model are difficult to predict. Looking forward to experimental constraints in more complex systems, we can infer that in natural systems the stability field of srilankite could be shifted most likely at lower temperatures by 50–100°C.~~

Eclogites

Thermobarometry

~~*Temperatures*~~ *P–T* conditions of the eclogite-facies and of the post eclogitic peaks have been estimated for type "E" eclogites (sample B5), representative of the average mafic rocks of Duria.

Temperatures for the eclogitic peak have been retrieved by using the thermometer of ~~(~~Krogh~~-~~Ravna~~,~~ (2000), based on the Fe~~–~~–Mg exchange between cpx and gt (cpx-gt in Fig. 12 a). Peak pressures were estimated by using the barometer of Ravna and Terry (2004), based on the net transfer reaction diopside + kyanite = grossular + pyrope + quartz/coesite (gt-cpx-ky-qtz/coe in Fig. 12 a). The composition of preserved omphacite crystals included in kyanite and of porphyroclastic garnet cores have been used for the calculations (Table 2). Additional ~~T~~ *T* estimates have been retrieved using the trace-based thermometer~~s : i)~~ Zr-in-rutile

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calibration ~~after~~by Tomkins et al. (~~,~~2007) (Zr-in-ru in Fig. 12).~~calibration after Tomkins et al., 2007~~), considering the Zr content in rutile included in garnet (343–352 ppm Zr; see Table 4). ; ii) Ti-in-quartz (calibration after Wark & Watson, 2006), considering the Ti content of porphyroclastic quartz. Zr-in-rutile ranges from 343 to 621 ppm, which corresponds to a T range from 660°C to 712°C, while the average Ti content in quartz is 43 ppm, corresponding to T = 654°C (Fig. 9). This temperature range intersects the temperatures estimated using the cpx-gt thermometer at pressures between 1.5 and 2.5 GPa.**

The intersection of the thermometers cpx-gt and Zr-in-ru with the barometer gt-cpx-ky-qtz/coe provides a concordant estimate of peak conditions at *P* = 3.0 GP a and *T* = 740–750°C, slightly above the quartz/coesite transition (dashed line in Fig. 12 a)~~These pressures are higher than those estimated by using the Jd-in-cpx barometer of Holland (1980) (1.35 GPa at 700°C), based on the reaction albite = jadeite + quartz and the jadeite content in omphacite, which provides minimum estimates for omph-bearing assemblages. P~~ ~~≤ 2.5 GPa at T ~ 700°C are consistent with the presence of pargasitic amphibole in the eclogite-facies peak assemblage, which should disappear at ~2.4 GPa at 700°C for MORB compositions at H_2O-saturated conditions ((Schmidt and Poli, 1998);~~ Fig. 9). It is noteworthy ~~that the estimated P, T conditions for the eclogitic peak are close to the experimental wet solidus of MORB basalts, but dehydration melting temperatures in fluid-absent zoisite-bearing eclogites are as high as ~1000°C at 2.4 GPa (Skjerlie and Patino Douce, 2002).~~

The *P*~~,~~ ~~T~~ –*T* conditions of the post-eclogitic peak have been estimated using the compositions of the minerals forming symplectites replacing kyanite, garnet and omphacite, and those of garnet rims in contact with them. In particular, orthopyroxene found in a ~~relict opx+pl~~ symplectite replacing ~~garnet~~ kyanite in contact with relict garnet (Fig. 7 c; supplementary Fig. SM7) was~~as~~ considered for the Ca-in-opx thermometer of Brey & Köhler (1990) corrected by Nimis and Grütter (2010), and for the barometer of Lal (1993), based on the net transfer reaction~~reactions~~ enstatite -+ anorthite -= pyrope -+ grossular -+ quartz (gt-opx-pl-q in Fig. 12 b). Clinopyroxene forming cpx+pl symplectites replacing omphacite in contact with relict garnet was used for the barometer of (Eckert *et al.*, 1991), based on the ~~reaction~~ net transfer diopside -+ anorthite = pyrope -+ grossular -+ quartz (gt-cpx-pl-q in Fig. 12 b). Temperature for the post eclogitic peak were estimated also by using the thermometer of ~~(~~Sato *et al.*~~,~~ (2006), based on the Fe-~~–~~Mg exchange between spinel and sapphirine (sapp-sp in Fig. 12), assemblage found in symplectites replacing kyanite (e.g., Fig. 7 c), and by using the thermometer Zr-in-ru, considering the Zr content of rutile embedded in symplectites (567–845 ppm Zr; Table 4).~~

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The highest ~~*P*~~, *P*–*T* conditions ~~and *T*~~, *T* = ~~85~~840–~~850~~8°C at *P* = ~~1.2~~ 0.8–1.0 GPa, are provided by the intersection of the barometers gt-opx-pl-q and gt-cpx-pl-q, ~~barometer~~ and the thermometer sapp-sp ~~thermometer~~, while ~~*T*~~, *T* estimated using the Ca-in-opx (755–760°C at 0.85–0.95 GPa) and the Zr-in-ru (690–740°C at 0.85–0.95 GPa) ~~themrometer~~thermometers ~~is~~ are ~~slightly~~ considerably lower, suggesting partial ri-equilibration during retrogression ~~(822°C at 1.2 GPa)~~.

Peak ~~These *P*, *T*~~ *P*–*T* conditions retrieved for type "E" eclogites~~, which are very close to the experimental gt-in and well above the wet solidus reported by Schmidt & Poli (1998) (grey dashed lines in Fig. 9),~~ are comparable to *P*, ~~*T*~~ –*T* conditions ~~retrieved~~ estimated in Duria peridotites for both the eclogite-facies (*P* ≈ 3.0 GPa and *T* ≈ 750°C) and the post-eclogitic ~~LP-HT~~ metamorphism (*P* ≈ 0.9 GPa and *T* ≈ 850°C) ~~in peridotites~~.

Thermodynamic modelling

The bulk composition of type "E" eclogite B5 was considered for the calculation of *P*–H_2O and ~~*P*, *T*~~ *P*–*T* ~~(Fig. 10a) and P-X (Fig. 10b, Fig. 11a)~~ pseudosections in the system KNCFMASH (Fig. 13). The *P*–H_2O pseudosection (Fig. 13 a), calculated at fixed *T* = 750°C in the light of *T* estimated by means of conventional thermometry, serves to estimate the amount of the component H_2O accounting for the presence of K-feldspar in Duria mafic rocks, occurring as a relict eclogite-facies phase together with garnet, omphacite, kyanite and quartz. In figure 13 a, *X* represents the H_2O component added to the dry bulk composition B5 (Table 1; see also supplementary Table SM2). K-feldspar is stable with garnet, omphacite, kyanite quartz and phengite for *P* > 1.8 GPa and a maximum bulk H_2O content of 0.1 wt%, above which K-feldspar disappears. Therefore, a ~~*H_2O undersaturated conditions with bulk H_2O contents below 1 wt% are needed to stabilise K-feldspar at P > 1.7 GPa (Fig. 10b), observed as porphyroclasts in Borgo eclogites type "E" and "ME". However, at these pressures bulk H_2O contents > 1 wt% are necessary for the stability of pargasitic amphibole, often found in type "E" eclogites.*~~ *P*, ~~*T*~~ –*T* pseudosection ~~shown in Figure 10a is~~has been calculated ~~with~~ assuming an intermediate bulk H_2O content of~~=~~ 0.~~0~~05~~1~~ wt% (Fig. 13 a). Pseudosections indicate that the *X*Or of K-feldspar increases as pressure increases, being 0.97 at 2.5 GPa, 0.98 at 2.7 GPa and 0.99 at 3.0 GPa and 750°C. These values are comparable to the K-feldspar compositions measured in samples D3 (0.970–0.978; eclogite type E) and D6 (0.986; eclogite type ME), thus confirming high-pressure conditions up to 3 GPa for these rocks, suggested by conventional thermobarometry.

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For this relatively low H_2O~~For this low water~~ content, the amphibole-out is shifted at lower ~~P,~~ *P* compared with the wet amphibole-out found experimentally by Schmidt & Poli (1998) (black dashed line in Fig. ~~10a~~13 b)~~, and the predicted phase assemblage at 2.5 GPa and 700°C is omphacite (57 vol%), garnet (29 vol%), quartz (6 vol%), kyanite (5 vol%), K-feldspar (2 vol%) and phengite (<1 vol%)~~. At *T* = 750°C, amphibole (pargasite) is predicted to be stable only at *P* < 1.75 GPa in equilibrium with Na-rich plagioclase, so it is not thought to be a peak high-pressure phase.~~Amphibole + K-feldspar assemblage is stable at P < 1.7 GPa and T = 700°C independently form the bulk H_2O content. However, at these *P*, T conditions the predicted composition of K-feldspar is relatively Ab-rich and Or-poor (Or_{75} at 1.65 GPa and 700°C). K-feldspar compositions *X*Or = 0.970-0.978, measured in type "E" eclogites, are stable at P = 2.4-2.6 GPa at 700°C (fig. 10 a, b), which are comparable to P, T conditions estimated for the eclogitic peak through conventional thermobarometry.~~

~~In the *P*, T pseudosection, o~~Orthopyroxene~~ and spinel~~, found in symplectites replacing ~~garnet and~~ kyanite and garnet, ~~respectively, are~~is stable at ~~P~~ *P* < ~~0.9~~1.0 GPa at 850°C (Fig. 13 b). However, symplectites after kyanite contain also sapphirine + spinel, which are~~is~~ never stable for the composition B5. Bearing in mind that aluminium is a relatively inert component, we modelled ~~LP-HT~~coronitic reactions involving kyanite by calculating a *PT*–*X* pseudosection at fixed *P* = 0.9 GPa in the system KNCFMAS, where the sliding composition *X* represents a decreasing amount of kyanite component added to ~~the~~ a bulk ~~rock~~ symplectite composition ~~B5~~ from 25~~30~~ wt% (*X* = 0 in Fig. 14 ~~11~~a) to 0 wt% (*X* = 1 in Fig. 14 ~~1~~a) (see supplementary Table SM2). The symplectite compositions has been retrieved by considering the phase proportions in the micro-domain, obtained by means of image analysis of X-ray maps, and the phase compositions (sample B5 - Symp2 in Table 2). The retrieved phase proportions in this micro-domain, excluding the non-symplectitic phases garnet, quartz, amphibole and rutile, is: Ab-rich plagioclase 37 vol%; clinopyroxene 25 vol%; An-rich plagioclase 21 vol%; spinel 10 vol%; orthopyroxene 5 vol%; sapphirine 1.5 vol%. In this way, we modelled the phase stability fields for micro-domains close to kyanite porphyroclasts interacting with the surrounding rock assuming perfectly dry conditions. The ~~*TP*–~~*X* ~~pseudosection calculated at 850°C, assuming a low bulk H_2O content of 0.01 wt%,~~ shows that for kyanite-enriched compositions sapphirine

~~the orthopyroxene stability field is expanded at higher pressures, up to 1.25 GPa, which is nearly coincident with the P, T estimated using conventional thermobarometry. By balancing the phase compositions predicted by the thermodynamic model at 2.5 GPa and 700°C~~

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~~(reagents), and at 1.2 GPa, 850°C and X=0.33 (products), we obtained the following opx-producing reaction:~~

~~0.81 gt ($Py_{45}Alm_{0.32}Gr_{0.33}$) + 1.57 q =~~

~~1.00 opx (En_{72}) + 0.87 pl (An_{61}) + 0.56 $FeMg_{-1}$~~ ~~(3)~~

~~where $FeMg_{-1}$ represents a vector accounting for the Fe-Mg exchange between gt and opx~~.

The P-X pseudosection shows also that sapphirine-bearing assemblages become stable at ~~P~~ *P* < 0.88 GPa for bulk compositions enriched in ky (> 23 wt%; *X* < 0.25 in figure 11 a), but at these conditions sapphirine coexists with cordierite, which has never been observed in symplectites. The stability field of sapphirine is expanded up to ~~P~~ *P* = 0.91 GPa if ~~≈~~20 wt% kyanite is added to the bulk rock B5 (*X* = 0.33 in figure 11 a). At these P, T, X conditions, sapphirine is in equilibrium with opx, gt, amph and pl. By decreasing the ky content towards the composition B5, the adjacent fields contain also spinel. This suggests that a small fluctuation in the kyanite/bulk rock ratio in the micro-domain surrounding a kyanite porphyroclast that is getting destabilised during LP-HT metamorphism can lead to the assemblage plagioclase + sapphirine towards the inner part of the reaction front and plagioclase + spinel towards the outer part of the reaction front. By balancing the phase compositions predicted by the model at 2.5 GPa and 700°C (~~reagents~~reactants), and at 0.90 GPa, 850°C and X = 0.33 (products), we obtained the following sapp-producing reaction:

7.83 ky + 5.31 omph (Jd_{38}) + 0.25 gt ($Py_{45}Alm_{0.32}Gr_{0.33}$) =

= 5.63 pl (An_{63}) + 1.25 albite + 1.00 sapp ($Sapp_{85}$) (4)

(cf. Carswell ~~at~~ et al., 1989)

and, using the sp and pl compositions predicted at 0.88 GPa, 850°C and X=0.4, the following sp-bearing reaction:

1.54 ky + 0.58 omph (Jd_{38}) + 0.25 gt ($Py_{45}Alm_{0.32}Gr_{0.33}$) =

= 0.94 pl (An_{61}) + 1.00 sp (Sp_{68}) + 0.38 albite (5)

Corundum has been found in symplectites replacing kyanite in eclogites type "HAE", associated to sapphirine, spinel and An-rich plagioclase. In order to constrain the stability field of this assemblage, we performed also for these rocks a P-X pseudosection at fixed ~~T~~ *T*

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Commento [OU1]: wo plagioclases: this is typical of a "mosaic" equilibrium, with An at the place of kyanite (and zoisite?) and An59 after omphacite.

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= 850°C, where X = 1 accounts for the bulk composition of sample D9 + 0.01 wt% H_2O, and X = ~~O~~ 0 represents bulk D9 with 30 wt% added kyanite (Fig. 11b). At these conditions, corundum is stable with sapphirine at ~~P~~ *P* = 1.28 GPa for the composition D9 (X = 1). By increasing the kyanite/rock ratio, the assemblage corundum + sapphirine becomes stable at lower P, down to 1.03 GPa at X = 0. Considering the omphacite composition predicted at 2.5 GPa and 700°C, a possible corundum-forming reaction could be:

2.8 omph (Jd_{35}) + 1.00 kyanite = 1.82 cpx ($Di_{0.93}Hed_{0.07}$) + 1 corundum + 1 albite (6)

(Johansson and Möller, 1986).

The P-X pseudosection of Figure 11b shows that spinel never coexists with corundum + sapphirine. Spinel occurs with sapphirine at ~~P~~ *P* < 0.87 GPa and X > ~~≈~~0.3, corresponding to < ~~≈~~20 wt% of kyanite added to the bulk rock D9, or at ~~P~~ *P* up to 1.23 for composition D9 without addition of kyanite.

Togliere il discorso zoisite A double corona replacing cm-sized zoisite has been found in the HAE eclogite D1 (Fig. 5g). The inner corona consists of An-rich plagioclase, while the outer part is formed by a symplectitic intergrowth of pl+sapp+sp+cor. Because this symplectite is almost identical to symplectites surrounding kyanite, we developed a model in order to investigate whether this assemblage can develop also by LP-HT reactions involving zoisite. Analogously to P-X pseudosections calculated at 850 °C for samples B5 and D9, we considered a sliding composition from bulk rock D1 + 0.01 wt% of H_2O (X = 1 in figure 12a) to D1 enriched with 100 wt% of zoisite (X = 0). Furthermore, we calculated also a X-aH_2O pseudosection at fixed ~~P~~ *P* = 1.2 GPa and ~~T~~ *T* = 850°C (Fig. 12b) in order to investigate the role of H_2O. The P-X pseudosection shows that zoisite is stable down to ~~P~~ *P* = 1.0 GPa for X < 0.55, corresponding to 45 wt% of added zoisite. By decreasing the amount of added zoisite, the stability field of zoisite is shifted at higher pressures. At ~~P~~ *P* = 1.2 GPa, zoisite disappears at X > 0.55, where the stable assemblage is amph+pl+cpx+H_2O. At X > 0.9, sapphirine becomes a stable phase. For compositions close to D1, the assemblage corundum + sapphirine is stable slightly above 1.2 GPa while spinel + sapphirine are stable slightly below. However, X-aH_2O pseudosection calculated at 1.2 GPa and 850°C shows that LP-HT assemblages after zoisite are highly dependent on water activity (i.e., on the H_2O chemical potential). For aH_2O < -1.50, the breakdown of zoisite will produce An-rich plagioclase only up to X = 0.45 (added zoisite 54 wt%), which is accomplished by the following reaction:

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2 zoisite + 1 kyanite + 1 quartz = 4 anorthite + 1 H_2O (7)

By decreasing the zoisite content towards composition D1, corundum + plagioclase are stabilized first, suggesting the following reaction:

1 zoisite + 1 kyanite = 2 anorthite + 0.5 corundum + 0.5 H_2O (8)

(cf. O'Brien et al, 1992)

A further decrease in added zoisite results in the assemblages spinel + corundum + plagioclase, spinel + plagioclase, sapphirine + spinel + plagioclase and eventually sapphirine + plagioclase for the composition D1. The following reactions can be retrieved by considering as reactants the omphacite predicted at 2.5 GPa and 700°C, and as products spinel, sapphirine and plagioclase predicted at 1.2 GPa and 850°C.

2.83 kyanite + 1.00 zoisite + 0.27 omph (Jd_{31}) =
= 2.94 plagioclase (An_{77}) + 1.67 corundum + 0.21 spinel (Sp_{65}) + 0.5 H_2O (9)

and

1.47 kyanite + 1.00 zoisite + 0.69 omph (Jd31) =
= 2.18 anorthite + 0.51 pl (An_{59}) + 0.12 sapp ($Sapp_{86}$) + 0.5 H_2O (10)

Pseudosections suggest that in eclogites HAE the breakdown of both kyanite and zoisite can end up with anorthite-rich plagioclase associated to spinel, sapphirine and corundum at 1.2 GPa and 850°C, for low H_2O activities and a proper degree of interaction between kyanite/zoisite and the other surrounding high-pressure phases, in particular omphacite and garnet.

DISCUSSION

It is noteworthy that the estimated P, *T* conditions for the eclogitic peak are slightly above the experimental wet solidus of MOR compositions at H_2O-saturated conditions (Schmidt and Poli, 1998), but dehydration melting temperatures in fluid-absent zoisite-bearing eclogites are as high as ≈1000°C at 2.4 GPa (Skjerlie and Patino Douce, 2002).

In the Duria area, relict eclogite-facies assemblages are still preserved both in garnet-bearing peridotites and in different types of eclogites. In these rocks, high-pressure phases are partially or completely replaced by low-P/high-T symplectitic intergrowths (Fig. 4 and 5).

Thermodynamic models and thermobarometric data estimated for the Duria garnet peridotites are consistent with an equilibration at ~~90-100 km~~XX GPa depth and temperatures of 850-900°C. ~~In garnet peridotites, LP-HT r~~Reactions between garnet and olivine produced opx coronas on the olivine side, and opx+cpx+sp symplectites on the garnet side. Srilankite and zircon have been observed in textural equilibrium with these LP-HT minerals (Fig. 5a). Srilankite is a very uncommon phase in peridotites, and its presence suggests that a certain degree of metasomatism by a crust-derived Zr-bearing agent, has occurred during the post-eclogitic stage. Magmatic srilankite has been reported in gabbroic veins cutting oceanic peridotite in the Southwest Indian Ridge (Morishita *et al.*, 2004), and srilankite inclusions in upper-mantle pyrope-rich garnet equilibrated at 1.5-3.0 GPa and 600-800 °C have been found in xenoliths from the Navajo Volcanic Field on the Colorado Plateau (Wang *et al.*, 1999). Srilankite formed through reaction between ilmenite and baddeleyite has been reported also in mafic granulites from the Bergen Arcs in Western Norway equilibrated at ~~P~~ *P* < 1 GPa and 800-850°C (Bingen *et al.*, 2001). At Duria, srilankite composition $Zr_{0.33}Ti_{0.66}O_2$ suggests temperatures of equilibration of 850-900°C, which is consistent with temperatures estimated by Ca-in-opx and opx-gt thermometry. Coherently with the absence of garnet in LP-HT symplectites and the low Cr-content of symplectitic spinel, conventional barometry suggests that post-eclogitic ~~methamorphism~~metamorphism of garnet peridotites occurred below ~~50~~ 50-km depth. Chlorite, anthophyllite, phlogopite and magnesiohornblende represent late-stage, amphibolite-facies intergrowths overprinting high-temperature symplectites.

Eclogites from Duria are characterised by a broad major-element N-MORB signature. Kyanite eclogites (KE), mafic eclogites (ME) and high-Al eclogites (HAE) have been distinguished on the basis of the bulk chemistry using principal component analysis (Fig. 6). Magnesiohornblende+plagioclase gneisses (AG) are interpreted as rocks recrystallised in fluid-rich domains under amphibolite-facies conditions after the high-temperature event ~~and showing ductile flow deformation,~~ and t~~hey~~ have not been investigated in detail in this study. Thermodynamic models and conventional thermobarometric data suggest that kyanite eclogites from Duria underwent a high-pressure peak at ~80 km depth at temperature of about 700°C. The occurrence of K-feldspar as a high-pressure phase associated with pargasitic amphibole and zoisite indicates water undersaturated conditions during the eclogitic peak~~,~~

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~~therefore characterised by a very low amount of the component H_2O~~ (Fig. 10b). In eclogites, the following LP-HT symplectitic intergrowths have been observed: i) opx + pl replacing garnet; ii) Di-rich, Jd-poor cpx + Ab-rich pl replacing omphacite; iii) An-rich pl ± sp ± sapp ± cor replacing kyanite and zoisite. Conventional thermobarometry suggests that post-eclogitic assemblages should have equilibrated ~~below~~ above ~40 km depth at temperatures of about 850°C.

~~However, calculated P-T pseudosections (i.e. isochemical phase diagrams) fail to reproduce t~~The mineral assemblages ~~(iii)~~ observed in symplectites could only be stablilised in Al_2O_3-rich compositional microdomains derived from destabilisation of kyanite. ~~In particular, sapphirine-bearing assemblages are never stable if the bulk composition of kyanite eclogites (E) is considered. We approached this issue by performing a material transfer study, assuming that Al_2O_3 did not behave as a perfectly mobile component and, consequently, that the composition of the micro-domain surrounding a high-pressure Al_2O_3-rich phase replaced by LP-HT minerals (i.e., kyanite and zoisite) is not equivalent to the composition of the bulk rock.~~ Because of the "inert" character of the component Al_2O_3 (cf. (Korzhinskii, 1959), we preferred to express the variable content of Al_2O_3 as an extensive variable (weight amount of the component Al_2SiO_5 (kyanite) or $Ca_2Al_3Si_3O_{12}(OH)$ (zoisite) added to the bulk-rock composition), rather than an intensive variable (e.g., μAl_2O_3) (see also (Tumiati *et al.*, 2015)). In the phase diagrams performed in order to model the LP-HT symplectites replacing kyanite (Fig. 11a,b), X represents a sliding bulk composition where X=1 stands for the real bulk-rock compositions B5 (kyanite eclogite; Fig. 11a) and D9 (high-Al eclogite; Fig. 11b) reported in Table 1, and X=0 stands for 70 wt% of the same bulk compositions and 30 wt% of added kyanite component. ~~Phase diagrams demonstrate that sapphirine becomes stable in kyanite-eclogites only for a relatively high added kyanite component (X < 0.4) (Fig. 13) and, therefore, this mineral should form in those areas of the symplectite micro-domain where the component Al_2SiO_5 poorly riequilibrated with the surrounding rock.~~ The material transfer study performed through thermodynamic modelling is the best way to model the mineral distribution observed in symplectites,

Far from these domains, sapphirine-free, spinel+plagioclase symplectites ~~should~~ would occur. Thermodynamic modelling also ~~shows~~ predicts that ~~considering the kyanite-eclogite composition,~~ corundum ~~is~~ should never be stable in LP-HT symplectites replacing kyanite, consistent with the absence of ~~. In fact~~, corundum ~~has never been observed~~ in this eclogite type.

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~~Accordingly to petrographic observations, c~~Corundum is instead predicted to ~~may~~ form in high-Al eclogites. This is again consistent with petrographic evidence. since corundum occurs ~~The material transfer study performed through thermodynamic modelling is the best way to model the mineral distribution observed in symplectites, where corundum occurs~~ in the inner part of the symplectitic pseudomorph after kyanite (X < 0.2), and it disappears in the outer part of the symplectites, where sapphirine and eventually spinel form (Fig. 13).

Duria in the Alpine framework

The estimated *P~~-~~, ~~T~~ T* conditions of Duria rocks, 850°C and 1.0 GPa, point to a ~~granulitic~~ granulite-facies metamorphic stage, shared by both peridotites and mafic rocks, postdating a former eclogite-facies peak at 700-750°C and 2.5-3.0 GPa. Granulite-facies assemblages are in turn overprinted by late Barrovian amphibolite-facies metamorphism. Previous P-T estimates for the high-pressure metamorphism ~~displayed~~ evidenced in~~by~~ garnet peridotite from Duria (3.0 ± 0.2 GPa and 829 ± 33°C after (Nimis and Trommsdorff, 2001); 2.8 GPa and 830°C after (Hermann *et al.*, 2006)) are concordant with our new estimates. Hermann *et al.* (2006) provided also *P~~, T~~ T* estimates of 0.7~~–~~1.0 GPa and 720°C for opx+sp+amph symplectites surrounding garnet. These P~~, T~~ *T* conditions are lower compared to our estimates on opx+cpx+sp, amph-free symplectites replacing garnet~~,~~ Tthus, they may refer to the post-granulitic, amphibolite-facies stage that we observed in both peridotite and mafic rocks. On the basis of U-Pb SHRIMP data on zircons found in amph-bearing symplectites, this stage occurred at 33-34 Ma and corresponds to the equilibration in the spinel peridotite field (Hermann *et al.*, 2006)..

Ky-bearing eclogites from the Duria area were only briefly acknowledged by Heinrich (1986), but no evidence of high-temperature, post-eclogitic overprint was reported. However, the author stressed out that the eclogites from the southern Adula Nappe record an eclogite-facies peak characterized by higher pressure and temperatures (c. 800°C and 2.4 GPa) compared to northern Adula (500°C and 1.2 GPa).

Plagioclase + spinel coronas replacing kyanite have been reported by (Brouwer *et al.*, 2005) in eclogites from Borgoglio in Onsernone Valley, ~~~~ca. 50 km west from Monte Duria. However, the authors do not claim a post-eclogitic high-temperature event for these rocks, which are thought to have re~~i~~equilibrated at ~630°C and 0.6 GPa during regional Barrovian metamorphism. Plagioclase + spinel + corundum symplectites after kyanite were described in eclogite-amphibolites from Gorduno/Alpe Arami ~~(~~~~(ca.~~ 15 km W from Mt Duria) by

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(Brouwer, 2000), but the author did not provide P, ~~T~~ *T* constraints for symplectite formation, suggesting ~~T~~ *T* < 1050°C on the basis of the absence of sapphirine. In fact, except in eclogites from Duria described in our study, sapphirine was never observed in symplectites in eclogites from the Central Alps. However, sapphirine occurs as a rock-forming phase and as a symplectite constituent in granulites and charnokites from the Gruf Complex in Val Codera (Barker, 1964; Galli *et al*., 2011), ~ 20 km ENE from Monte Duria (Fig. 1). In these rocks, Permian in age, sapphirine occurs with opx, cordierite, gt, sillimanite and corundum, suggesting ~~T~~ *T* > 900°C and ~~P~~ *P* = 0.85-0.95 GPa (Galli *et al.*, 2011). The high temperatures attained in the Gruf Complex haves ~~been~~ considered so far an unique evidence for UHT metamorphism in the Central Alps.

Other significant occurrences of UHT metamorphism overprinting eclogite-facies rocks are reported from the Rhodope massif and various localities of the Variscan basement in Europe. Plagioclase ± sapphirine ± corundum ± spinel symplectites have been described in retrogressed eclogites from the central Rhodope in Greece (Liati and Seidel, 1996), and estimated *P*, ~~T~~ *T* conditions for the granulite facies were T > 800°C and ~~P~~ *P* > 1.5 GPa. Discussing Rhodope granulitized eclogites, the authors stressed out that kyanite eclogites overprinted under granulite-facies conditions are known from the Variscan basement in Europe but not from the eclogites of Alpine age (cf. also Galli *et al*., 2011), voicing the suspicion that these rocks could belong to a separate (pre-Alpine) tectonic unit. It should be noted, however, that this high-T granulite-facies metamorphism in central Rhodope was later questioned by (Moulas *et al.*, 2013). Nevertheless, similar sapphirine-bearing symplectites overprinting eclogit~~e~~ic phases have been described in Variscan units in Europe, for instance: i) Armorican Massif, France (Godard and Mabit, 1998); ii) Bohemian Massif, Moldanubian zone, Austria ((Carswell *et al.*, 1989; Faryad *et al.*, 2006; O'Brien, 1997); iii) Golfo Aranci, Sardinia, Italy (Franceschelli *et al.*, 2007; Giacomini *et al.*, 2005); iv) Lotru Metamorphic Suite, South Carpatians (Săbău *et al.*, 2002); v) Pohorje, Estern Alps, Slovenia (Vrabec *et al.*, 2012).

Although new pressure and temperature estimated for the eclogit~~e~~-facies~~e~~ peak in the Duria area are consistent with previous estimates concerning the Central Alps, in particular with garnet peridotites (e.g., Nimis & Trommsdorff, 2001) and eclogites (Brouwer et al., 2005) cropping out at Alpe Arami in the Southern Adula Nappe, a post-eclogit~~e~~ic, high-temperature overprint involving ultramafic and mafic rocks has been never reported so far in Central Alps. Peridotites and eclogites from the Southern Adula display Alpine ages (Becker, 1993; Brouwer *et al.*, 2005; Gebauer, 1996; Gebauer *et al.*, 1992). However, pre-Alpine high-

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pressure metamorphic events have been dated by Liati et al. (2009) at 330-340 Ma in the northern and c. 370 Ma in the middle Adula. Moreover, (Herwartz *et al.*, 2011) report the case of an eclogite of the Central Adula (Trescolmen) showing two distinct age populations, being the older Variscan (332.7 Ma) and the younger Alpine (38 Ma). Therefore, these authors suggested that Trescolmen eclogite was subducted during Varican orogeny and, later, it has been subducted again during the Alpine orogeny. Variscan eclogite-facies rocks, namely garnet peridotite and eclogite, dated back to ~330 Ma (Tumiati *et al.*, 2003, 2007) are known also in the Ulten zone (Eastern Alps; 150 km ENE from Duria). Pre-Alpine, low-P, high-T metamorphism has been evidenced in Central Alps in some rocks from the Gruf Complex, hosted in migmatites and characterized by UHT dated back to 282-260 Ma, followed by Alpine (34-29 Ma) amphibolite-facies metamorphism at 720-740°C and 0.65-0.75 GPa (Galli *et al.*, 2013, 2011). The latter P, ~~T~~ *T* conditions and ages are similar to those retrieved by Hermann *et al*. (2006) from amphibole-bearing symplectites in retrogressed garnet peridotites of Duria area.~~.~~ This LP-HT stage overprinting eclogite-facies rocks has never been reported before in the Adula-Cima Lunga nappe. Our new data add one more piece to the puzzle of the Central Alps, where Variscan and Alpine geodynamics interplayed, complicating the effort of deciphering the age and tectonometamorphic evolution of each unit (Biino *et al.*, 1997; Brueckner, 2011; Liati *et al.*, 2009).

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~~Our new low-P, high-T conditions estimated for the post-eclogitic peak suggest that a re-evaluation of the subduction-exhumation history and likely also of the age of pressure-peak in garnet peridotites and eclogites of Duria are needed.~~

CONCLUSIONS

Eclogite-facies rocks from Duria (Central Alps) share a common low-pressure, high-temperature metamorphic event at c. 1 GPa and 850-900°C. The metamorphic conditions and the petrological processes recorded by ~~occurred~~ in these rocks have been addressed by performing conventional thermobarometry and complex thermodynamic forward modelling of granulite-facies reactions involving Zr-bearing phases in peridotites and the high-pressure minerals kyanite and zoisite in eclogites, resulting in spinel ± sapphirine ± corundum symplectites. We have ~~readily~~ modelled the LP-HT mineral assemblages characterising these rocks by:

i) developing and integrating a new solid-solution model between ZrO_2 and TiO_2 with the intermediate compound srilankite $(Zr, Ti)_2O_4$, calibrated against previously published high-pressure experimental data.

ii) performing a material-transfer study using extensive properties, as the amount of poorly mobile chemical components, rather than intensive properties (i.e., chemical potentials), which are suitable only for perfectly mobile components.

~~This LP-HT stage overprinting eclogite facies rocks has never been reported before in the Adula-Cima Lunga nappe. Our new data add one more piece to the puzzle of the Central Alps, where Variscan and Alpine geodynamics interplayed, complicating the effort of deciphering the age and tectonometamorphic evolution of each unit (Biino *et al.*, 1997; Brueckner, 2011; Liati *et al.*, 2009).~~ Our new low-P, high-T conditions estimated for the post-eclogitic peak suggest that a re-evaluation of the subduction-exhumation history and likely also of the age of pressure-peak in garnet peridotites and eclogites of Duria are needed.

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REFERENCES:

Baldwin, J. a., Powell, R., Williams, M. L. & Goncalves, P. (2007). Formation of eclogite, and reaction during exhumation to mid-crustal levels, Snowbird tectonic zone, western Canadian Shield. *Journal of Metamorphic Geology* **25**, 953–973.

Becker, H. (1993). Garnet peridotite and eclogite Sm-Nd mineral ages from the Lepontine dome (Swiss Alps): New evidence for Eocene high-pressure metamorphism in the central Alps. *Geology* **21**, 599.

1012 Berger, A., Burri, T., Alt-Epping, P. & Engi, M. (2008). Tectonically controlled fluid flow
1013 and water-assisted melting in the middle crust: an example from the Central Alps. *Lithos*
1014 **102**, 598–615.
1015 Berger, A., Mercolli, I. & Engi, M. (2005). The central Lepontine Alps: notes accompanying
1016 the tectonicpetrographic map sheet Sopra Ceneri (1:100 000). *Schweizerische*
1017 *Mineralogische Und Petrographische Mitteilungen* **85**, 109–146.
1018 Biino, G. G., Marquer, D. & Nussbaum, C. (1997). Alpine and pre-Alpine subduction events
1019 in polycyclic basements of the Swiss Alps. *Geology* **25**, 751.
1020 Bingen, B., Austrheim, H. & Whitehouse, M. (2001). Ilmenite as a Source for Zirconium
1021 during High-grade Metamorphism? Textural Evidence from the Caledonides of Western
1022 Norway and Implications for Zircon Geochronology. *Journal of Petrology* **42**, 355–375.
1023 Brouwer, F. M. (2000). Thermal Evolution of High-Pressure Metamorphic Rocks in the Alps.
1024 Utrecht University.
1025 Brouwer, F. M., Burri, T., Engi, M. & Berger, a (2005). Eclogite relics in the Central Alps:
1026 PT-evolution, Lu-Hf ages and implications for formation of tectonic melange zones.
1027 *Schweizerische Mineralogische Und Petrographische Mitteilungen* **85**, 147–174.
1028 Brueckner, H. K. (2011). Geodynamics: Double-dunk tectonics. *Nature Geoscience*. Nature
1029 Publishing Group **4**, 136–138.
1030 Burri, T., Berger, a & Engi, M. (2005). Tertiary migmatites in the Central Alps: Regional
1031 distribution, field relations, conditions of formation, and tectonic implications.
1032 *Schweizerische Mineralogische Und Petrographische Mitteilungen* **85**, 215–232.
1033 Cancarevic, M., Zinkevich, M. & Aldinger, F. (2006). Thermodynamic Assessment of the
1034 PZT System. *Journal of the Ceramic Society of Japan* **114**, 937–949.
1035 Carswell, D. A., Moller, C. & O'Brien, P. J. (1989). Origin of sapphirine-plagioclase
1036 symplectites in metabasites from Mitterbachgraben, Dunkelsteinerwald granulite
1037 complex, Lower Austria . *Eur. Journal Mineral* **1**, 455–466.
1038 Ciancaleoni, L. & Marquer, D. (2006). Syn-extension leucogranite deformation during
1039 convergence in the Eastern Central Alps: example of the Novate intrusion. *Terra Nova*
1040 **18**, 170–180.
1041 Connolly, J. a D. (2005). Computation of phase equilibria by linear programming: A tool for
1042 geodynamic modeling and its application to subduction zone decarbonation. *Earth and*
1043 *Planetary Science Letters* **236**, 524–541.
1044 Dale, J. & Holland, T. J. B. (2003). Geothermobarometry, P-T paths and metamorphic field
1045 gradients of high-pressure rocks from the Adula Nappe, Central Alps. *Journal of*

Metamorphic Geology **21**, 813–829.

Dale, J., Holland, T. & Powell, R. (2000). Hornblende–garnet–plagioclase thermobarometry: a natural assemblage calibration of the thermodynamics of hornblende. *Contributions to Mineralogy and Petrology*. Springer Berlin Heidelberg **140**, 353–362.

Dewey, J. F., Helman, M. L., Knott, S. D., Turco, E. & Hutton, D. H. W. (1989). Kinematics of the western Mediterranean. *Geological Society Special Publications* **45**, 265–283.

DIENER, J. F. A. & POWELL, R. (2012). Revised activity-composition models for clinopyroxene and amphibole. *Journal of Metamorphic Geology*. Blackwell Publishing Ltd **30**, 131–142.

Eckert, J. O., Newton, R. C. & Kleppa, O. J. (1991). The DH of reaction and recalibration of garnet–pyroxene–plagioclase–quartz geo- barometers in the CMAS system by solution calorimetry. *American Mineralogist* **76**, 148–160.

Evans, B. W. & Trommsdorff, V. (1978). Petrogenesis of garnet lherzolite, Cima di Gagnone, Lepontine Alps. *Earth and Planetary Science Letters* **40**, 333–348.

Faryad, S. W., Perraki, M. & Vrána, S. (2006). P-T evolution and reaction textures in retrogressed eclogites from Svetlik, the Moldanubian Zone (Czech Republic). *Mineralogy and Petrology* **88**, 297–319.

Franceschelli, M., Puxeddu, M., Cruciani, G. & Utzeri, D. (2007). Metabasites with eclogite facies relics from Variscides in Sardinia, Italy: A review. *International Journal of Earth Sciences* **96**, 795–815.

Frey, M. & Ferreiro-Mählmann, R. (1999). Alpine metamorphism in the Central Alps. *Schweizerische Mineralogische und Petrographische Mitteilungen* **79**, 135–154.

Fumasoli, M. W. (1974). Geologie des Gebietes nördlich und südlich der Jorio-Tonale-Linie im Westen von Gravedone (Como, Italia). Universität Zürich.

Galli, A., Le Bayon, B., Schmidt, M. W., Burg, J. P. & Reusser, E. (2013). Tectonometamorphic history of the Gruf complex (Central Alps): Exhumation of a granulite-migmatite complex with the Bergell pluton. *Swiss Journal of Geosciences* **106**, 33–62.

Galli, a., Le Bayon, B., Schmidt, M. W., Burg, J. P., Caddick, M. J. & Reusser, E. (2011). Granulites and charnockites of the Gruf Complex: Evidence for Permian ultra-high temperature metamorphism in the Central Alps. *Lithos*. Elsevier B.V. **124**, 17–45.

Galster, F., Cavargna-Sani, M., Epard, J. & Masson, H. (2012). New stratigraphic data from the Lower Penninic between the Adula nappe and the Gotthard massif and consequences for the tectonics and the paleogeography of the Central Alps. *Tectonophysics* **579**, 37–

55.

Gebauer, D. (1996). A P-T-t Path for an (Ultra?-) High-pressure Ultramafic/Mafic Rock-Association and its Felsic Country-Rocks Based on SHRIMP-Dating of Magmatic and Metamorphic Zircon Domains. Example: Alpe Arami (Central Swiss Alps). *Geophysical Monograph Series* **95**, 307–329.

Gebauer, D., Grunenfelder, M., Tilton, G., Trommsdorff, V. & Sschimd, S. (1992). The geodynamic evolution of garnet-peridotites, garnet pyroxenites and eclogites of Alpe Arami and Cima Gagnone (Central Alps) from Early Proterozoic to Oligocene. *Schweiz. Min. Petr. Mitt.* **72**, 107–111.

Giacomini, F., Bomparola, R. M. & Ghezzo, C. (2005). Petrology and geochronology of metabasites with eclogite facies relics from NE Sardinia: Constraints for the Palaeozoic evolution of Southern Europe. *Lithos* **82**, 221–248.

Godard, G. & Mabit, J. L. (1998). Peraluminous sapphirine formed during retrogression of a kyanite-bearing ecologite from Pays de Leon, Armorican Massif, France. *Lithos* **43**, 15–29.

Godard, G. & Martin, S. (2000). Petrogenesis of kelyphites in garnet peridotites: A case study from the Ulten zone, Italian Alps. *Journal of Geodynamics* **30**, 117–145.

Heinrich, C. A. (1986). Eclogite facies regional metamorphism of hydrous mafic rocks in the Central Alpine Adula nappe. *Journal of Petrology* **27**, 123–154.

Hermann, J., Rubatto, D. & Trommsdorff, V. (2006). Sub-solidus Oligocene zircon formation in garnet peridotite during fast decompression and fluid infiltration (Duria, Central Alps). *Mineralogy and Petrology* **88**, 181–206.

Herwartz, D., Nagel, T. J., Münker, C., Scherer, E. E. & Froitzheim, N. (2011). Tracing two orogenic cycles in one eclogite sample by Lu–Hf garnet chronometry. *Nature Geoscience*. Nature Publishing Group **4**, 178–183.

Holland, T. (1980). The reaction albite = jadeite * quartz determined experimentally in the range 600-1200.c. *American Mineralogkt* **65**, 129–134.

Holland, T. J. B. & Powell, R. (1998). An internally consistent thermodynamic data set for phases pf petrological interest. *Journal of Metamorphic Geology* **16**, 309–343.

Holland, T. & Powell, R. (2003). Activity?composition relations for phases in petrological calculations: an asymmetric multicomponent formulation. *Contributions to Mineralogy and Petrology*. Springer-Verlag **145**, 492–501.

Johansson, L. & Möller, C. (1986). Formation of sapphirine during retrogression of a basaltic high-pressure granulite, Roan, Western Gneiss Region, Norway. *Contributions to*

Mineralogy and Petrology **94**, 29–41.

Korzhinskii, D. S. (1959). *Physicochemical Basis of the Analysis of the Paragenesis of Minerals*. New York: Consultants bureau, inc.

Krogh Ravna, E. (2000). The garnet – clinopyroxene Fe 2 + – Mg geothermometer□: an updated calibration. *Journal of Metamorphic Geology* **18**, 211–219.

Liati, A., Gebauer, D. & Fanning, C. M. (2009). Geochronological evolution of HP metamorphic rocks of the Adula nappe, Central Alps, in pre-Alpine and Alpine subduction cycles. *Journal of the Geological Society* **166**, 797–810.

Liati, A. & Seidel, E. (1996). Metamorphic evolution and geochemistry of kyanite eclogites in central Rhodope, northern Greece. *Contributions to Mineralogy and Petrology* **123**, 293–307.

Milnes, A. G. (1974). Structure of the Pennine Zone (Central Alps): a new working hypothesis. Bulletin of the Geological Society of America. *Bulletin of the Geological Society of America* **85**, 1727–1732.

Morishita, T., Arai, S. & Gervilla, F. (2001). High-pressure aluminous mafic rocks from the Ronda peridotite massif, southern Spain: Significance of sapphirine- and corundum-bearing mineral assemblages. *Lithos* **57**, 143–161.

Morishita, T., Maeda, J., Miyashita, S., Matsumoto, T. & Dick, H. J. B. (2004). Magmatic srilankite (Ti2ZrO6) in gabbroic vein cutting oceanic peridotites□: An unusual product of peridotite-melt interactions beneath slow-spreading ridges. *American Mineralogist* **89**, 759–766.

Morten, L. & Trommsdorff, V. (2003). Metamorphism and textures of dry and hydrous garnet peridotites. *EMU*, 443–466.

Moulas, E., Kostopoulos, D., Connolly, J. A. D. & Burg, J. P. (2013). P-T estimates and timing of the sapphirine-bearing metamorphic overprint in kyanite eclogites from Central Rhodope, northern Greece. *Petrology* **21**, 507–521.

Nagel, T. J. (2008). Tertiary subduction, collision and exhumation recorded in the Adula nappe, central Alps. *Geological Society, London, Special Publications* **298**, 365–392.

Nakamura, D. & Hirajima, T. (2000). Granulite-facies overprinting of ultrahigh-pressure metamorphic rocks, northeastern Su-Lu region, eastern China. *Journal of Petrology* **41**, 563–582.

Nimis, P. & Grütter, H. (2010). Internally consistent geothermometers for garnet peridotites and pyroxenites. *Contributions to Mineralogy and Petrology* **159**, 411–427.

Nimis, P. & Taylor, W. R. (2000). Single clinopyroxene thermobarometry for garnet peridotites. Part I. Calibration and testing of a Cr-in-Cpx barometer and an enstatite-in-Cpx thermometer. *Contributions to Mineralogy and Petrology*. Springer Berlin Heidelberg **139**, 541–554.

Nimis, P. & Trommsdorff, V. (2001). Revised Thermobarometry of Alpe Arami and other Garnet Peridotites from the Central Alps. *Journal of Petrology* **42**, 103–115.

O'Brien, P. J. (1997). Garnet zoning and reaction textures in overprinted eclogites, Bohemian Massif, European variscides: a record of their thermal history during exhumation. *Lithos* **41**, 119–133.

O'Neill, H. S. C. (1981). The transition between spinel lherzolites and garnet lherzolites, and its use as a geobarometer. *Contributions to Mineralogy and Petrology* **77**, 185–194.

Pfiffner, M. & Trommsdorff, V. (1998). The high-pressure ultramafic-mafic-carbonate suite of Cima Lunga-Adula, Central Alps: Excursions to Cima di Gagnone and Alpe Arami. *Schweizerische Mineralogische und Petrographische Mitteilungen* **78**, 337–354.

Ravna, E. J. K. & Terry, M. P. (2004). Geothermobarometry of UHP and HP eclogites and schists - An evaluation of equilibria among garnet-clinopyroxene-kyanite-phengite-coesite/quartz. *Journal of Metamorphic Geology* **22**, 579–592.

Rubatto, D., Hermann, J., Berger, A. & Engi, M. (2009). Protracted fluid-present melting during Barrovian metamorphism in the Central Alps. *Contributions to Mineralogy and Petrology* **158**, 703–722.

Săbău, G., Alberico, A. & Negulescu, E. (2002). Peraluminous Sapphirine in Retrogressed Kyanite-bearing Eclogites from the South Carpathians: Status and Implications. *International Geology Review* **44**, 859–876.

Sato, K., Miyamoto, T. & Kawasaki, T. (2006). Experimental Calibration of Sapphirine-Spinel Fe2+-Mg Exchange Thermometer: Implication for Constraints on P?T Condition of Howard Hills, Napier Complex, East Antarctica. *Gondwana Research* **9**, 398–408.

Schmid, S. M., O.A., P., Froitzheim, N., Schönborn, G. & Kissingl, E. (1996). Geophysical-geological transect and tectonic evolution of the Swiss-Italian Alps. *Tectonics* **15**, 1036–1064.

Schmidt, M. W. & Poli, S. (1998). Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth and Planetary Science Letters* **163**, 361–379.

Scott, J. M., Konrad-Schmolke, M., O'brien, P. J. & Günter, C. (2013). High-T, low-P formation of rare olivine-bearing symplectites invariscan eclogite. *Journal of Petrology*

54, 1375–1398.

Skjerlie, K. P. & Patino Douce, A. E. (2002). The Fluid-absent Partial Melting of a Zoisite-bearing Quartz Eclogite from 1{middle dot}0 to 3{middle dot}2 GPa; Implications for Melting in Thickened Continental Crust and for Subduction-zone Processes. *J. Petrology* **43**, 291–314.

Steinmann, M. & Stille, P. (1999). Geochemical evidence for the nature of the crust beneath the eastern North Penninic basin of the Mesozoic Tethys ocean. *Geologische Rundschau* **87**, 633–643.

Stucki, A., Rubatto, D. & Trommsdorff, V. (2003). Mesozoic ophiolite relics in the Southern Steep Belt of the Central Alps. *Schweizerische Mineralogische und Petrographische Mitteilungen* **83**, 285–299.

Taylor, W. R. (1998). An experimental test of some geothermometer and geobarometer formulations for upper mantle peridotites with application to the thermobarometry of fertile lherzolite and garnet websterite. *Neues Jahrbuch fur Mineralogie, Abhandlungen* **172**, 381–408.

Todd, C. S. & Engi, M. (1997). No Title. *Metamorphic field gradients in the Central Alps. Journal of Metamorphic Geology* **15**, 513–530.

TOMKINS, H. S., POWELL, R. & Ellis, D. J. (2007). The pressure dependence of the zirconium-in-rutile thermometer. *Journal of Metamorphic Geology*. Blackwell Publishing Ltd **25**, 703–713.

Troitzsch, U., Christy, A. G. & Ellis, D. J. (2004). Synthesis of ordered zirconium titanate (Zr,Ti)(2)O-4 from the oxides using fluxes. *Journal of the American Ceramic Society* **87**, 2058–2063.

Troitzsch, U. & Ellis, D. J. (2004). High-PT study of solid solutions in the system ZrO₂-TiO₂: The stability of srilankite. *European Journal of Mineralogy* **16**, 577–584.

Tumiati, S., Godard, G., Martin, S., Klötzli, U. & Monticelli, D. (2007). Fluid-controlled crustal metasomatism within a high-pressure subducted mélange (Mt. Hochwart, Eastern Italian Alps). *Lithos* **94**, 148–167.

Tumiati, S., Godard, G., Martin, S., Malaspina, N. & Poli, S. (2015). Lithos Ultra-oxidized rocks in subduction mélanges□? Decoupling between oxygen fugacity and oxygen availability in a Mn-rich metasomatic environment. *LITHOS*. Elsevier B.V.

Tumiati, S., Thöni, M., Nimis, P., Martin, S. & Mair, V. (2003). Mantle-crust interactions during Variscan subduction in the Eastern Alps (Nonsberg-Ulten zone): Geochronology

and new petrological constraints. *Earth and Planetary Science Letters* **210**, 509–526.

Vrabec, M., Janák, M., Froitzheim, N. & De Hoog, J. C. M. (2012). Phase relations during peak metamorphism and decompression of the UHP kyanite eclogites, Pohorje Mountains (Eastern Alps, Slovenia). *Lithos*. Elsevier B.V. **144**–**145**, 40–55.

Wang, L., Essene, E. J. & Zhang, Y. (1999). Mineral inclusions in pyrope crystals from Garnet Ridge, Arizona, USA: Implications for processes in the upper mantle. *Contributions to Mineralogy and Petrology* **135**, 164–178.

Wenk, E. (1970). Zur Regionalmetamorphose und Ultrametamorphose der Zentralalpen. *Fortschritte der Mineralogie* **47**, 555–565.

Zack, T., Moraes, R. & Kronz, a. (2004). Temperature dependence of Zr in rutile: Empirical calibration of a rutile thermometer. *Contributions to Mineralogy and Petrology* **148**, 471–488.

TABLES

Table 1: Bulk-rock composition of selected samples from Duria. All rocks were sampled at the outcrop of Borgo (Figs. 1, 2), with the exception of garnet peridotite A2C2 (Monte Duria).

Table 2: Representative microprobe analyses of olivine (Ol), clinopyroxene (Cpx), and orthopyroxene (Opx) in selected samples (see Table 1). Fine: fine-grained; C: core; R: rim; InGt: included in garnet; InCpx: included in clinopyroxene; Sym: in symplectite. Fe^{2+} and Fe^{3+} are calculated from stoichiometry.

Table 3: Representative microprobe analyses of garnet (Gt), amphibole (Amp), spinel (Sp), sapphirine (Sapp), plagioclase (Pl) and phlogopite (Bt) in selected peridotite and eclogite samples from Duria (see Table 1). Fine: fine-grained; C: core; R: rim; Sym: in symplectite. Fe^{2+} and Fe^{3+} are calculated from stoichiometry.

FIGURES

Figure 1. (a) Tectonic scheme of the Lepontine Dome in the Central Alps. Isotherms of the post nappe-stacking barrovian metamorphic event and the extent of the migmatite belt are from Todd and Engi (1997) and Burri *et al.* (2005), respectively. (b) Detailed geological

scheme of the Duria area with the locations of Monte Duria and Borgo outcrops. Main geological features are modified from Berger *et al.* (2005).

Figure 2. ~~Form surface mapping~~Map of the Borgo outcrop along the Ledù stream. AG: amphibolic migmatitic gneiss; E: kyanite eclogites; HAE: high-Al_2O_3 rim between kyanite eclogites and hosting amphibole-bearing migmatitic gneiss; ME: mafic eclogites; MG: migmatitic gneiss; OGN: orthogneiss; PDT: retrogressed garnet peridotite.~~(a)~~

Figure 3. Field aspect of peridotite lenses at Borgo (a, b, c, d, e, f) and Monte Duria (g, h). (a) Loose block of partially retrogressed garnet peridotite downstream of the Borgo outcrop; (b) compositional layering made by garnet-rich and ~~garnet~~ garnet-poor layers in the Borgo peridotite~~;~~, a pervasive chlorite-defined foliation overprinting the layering occurs within 4~~–~~5 m from the contact with hosting crustal rocks; (c) a boudin of mafic eclogite (ME) within amphibole-bearing migmatitic gneiss (AG); (d) a large (ca.~~.~~ 7 m x 5 m) boudin of kyanite eclogite (E); (e) detail of the contact between kyanite eclogite and hosting gneiss with the red- to pink-coloured Al_2O_3-rich rim (HAE); (f) emerald green zoisite crystal within the HAE rim; (g) peridotite lens on the SE ridge of Monte Duria (L. Pellegrino for scale): garnet porphyroclasts are preserved only at cores, whereas a chlorite foliation, associated to the retrogression in the spinel stability field occurs on the outer rim; (h) detail of anhedral to sub-euhedral garnet porphyroclasts with dark-coloured thin ~~symplectitic~~ kelyphitic rims.

Figure 4. ~~Representative transmitted light p~~Photomicrographs of Duria rocks: (a) peridotite sample B3A showing garnet porphyroclast (gt) surrounded by kelyphite, in a matrix of fractured olivine (ol); (b) detail of the olivine matrix showing a porphyroclast of orthopyroxene (opx); (c) detail of a double corona surrounding garnet, with secondary orthopyroxene developing towards olivine and kelyphite towards garnet.; (d) kyanite porphyroclast (ky) in eclogite sample B5, surrounded by symplectite and a plagioclase corona (pl) towards the host symplectitic matrix; (e, f) parallel- and crossed-polarised light micrographs showing the symplectitic matrix of sample B5, with garnet (gt), kyanite (ky) and amphibole (amp) porphyroclasts; (g) mafic eclogite D6, showing garnet porphyroclasts (gt) embedded in a symplectitic matrix; (h) zoisite porphyroclast (zo) replaced by symplectite in high-Al_2O_3 eclogite sample D1.

Figure 5. Back-scattered electron (BSE) images of Duria rocks: (a) olivine (ol) in former contact with garnet (out of sight) surrounded by a double corona consisting of orthopyroxene (opx) in the inner part, and orthopyroxene (opx) + clinopyroxene (cpx) and spinel (sp) in the outer part; apatite (ap), zircon (zrc), baddeleyite (bdy) and srilankite (sril) occur in textural equilibrium the coronitic assemblages (sample A2C2); (b) overview of garnet (gt) in former contact with olivine (ol), replaced by opx+cpx+sp kelyphite; olivine is replaced by secondary orthopyroxene (opx); Cr-rich spinel (Cr-sp) and clinopyroxene (cpx) porphyroclasts occur in the peridotite matrix (sample B1); (c) mineral assemblages in eclogite B5, showing kyanite (ky), garnet (gt), amphibole (amp) and quartz (q) porphyroclasts embedded in a symplectitic intergrowth of clinopyroxene (cpx) and plagioclase (pl). Coronitic assemblages are plagioclase + amphibole surrounding relict garnet and plagioclase + spinel (sp) + sapphirine (sapp) replacing kyanite; (d) relict omphacite (omph) in kyanite porphyroclast replaced by pl+sp sumplectite (sample B5); (e) relict coronitic assemblage pl+orthopyroxene (opx) replacing garnet in mafic eclogote D6; (f) K-feldspar porphyroclasts in mafic eclogite D6; (g) zoisite porphyroclast replaced by a corona of plagioclase in the inner part and a pl + corundum (cor) + sapp + sp symplectite in the outer part towards the eclogite matrix (sample D1); (h) kyanite porphyroclast completely replaced by a composite symplectite~~, cor-rich in the core, pl-rich in the rim and sp+sapp-bearing in the middle~~ (sample D9).

Figure 6. Principal component analysis of the bulk-rock compositions shown in Table 1. Kyanite-eclogites (E) B5 and D3 display the lowest absolute ~~eigenvalues~~ F1–F2 coordinates and their composition can be considered the reference point for eclogites outcropping at Borgo. Mafic eclogites (ME) D4 and D6 display the highest ~~value~~ coordinate for the principal component F1, which represent the relative enrichment of Fe, Mn, Ti and P. The high-Al_2O_3 ecl~~c~~ogites (HAE) D1, B8 and D9 are characterised by the lowest F1 ~~value~~coordinate, being ~~enriched~~ rich in Al_2O_3 and SiO_2, while the retrogressed amphibole-gneisses (AG) D2 and D5 show relatively high contents in CaO and MgO.

Figure 7. Conventional thermobarometry of Duria peridotites. HP, LP: calculations performed using the compositions of the phases belonging to the high-pressure and low-pressure assemblages, respectively. NG: Nimis and Grütter, 2010; Ta: Taylor, 1998; BK: Brey and Köhler, 1990; O'N81: O'Neill (1981). Further details provided in text.

Figure 8. Thermodynamic modelling of Zr-bearing symplectites. (a) Binary ZrO_2-TiO_2 T-X diagram calculated at fixed ~~P~~ *P* = 2.0 GPa using the Perple_X package (http://www.perplex.ethz.ch) and a new baddeleyite-rutile solid-solution model calibrated against the experimental data of Troitzsch et al. (2004) (red dots). Activity-composition relations among baddeleyite, rutile and srilankite are retrieved using the van Laar formulation (Holland and Powell, 2003), which allows describing asymmetrical miscibility gaps (α_{bdy} 0.35, 0.000546, 0.0; α_{sril} 1.1, 0.0, 0.0; α_{ru} 0.7, 0.0, 0.0); (b) Calculated P-T diagram showing the univariant srilankite-in reaction forterite + rutile + zircon = srilankite + enstatite in the system ~~MS~~MgO+SiO_2+TiO_2+ZrO_2. Ternary SiO_2-~~+~~TiO_2+ZrO_2chemographies (forsterite always in excess) are calculated at ~~T~~ *T* < srilankite-in and ~~T~~ *T* > srilankite-in. Rutile-enriched (blue star) and zircon-enriched (green star) bulk compositions are shown for reference; (c, d) P, ~~T~~ *T* pseudosections in the system CFMAS+TiO_2+ZrO_2 calculated for a fixed bulk composition corresponding to 1 mol garnet + 1 mol olivine, with components TiO_2 and ZrO_2 added in minor amounts with XTi (=TiO_2/ZrO_2+TiO_2) = 0.75 in (c) and 0.25 in (d); the srilankite-in reaction in the MS- TiO_2+ZrO_2 is shown for reference as dashed line.

Figure 9. Conventional thermobarometry of Duria eclogites. (a) blue lines: clinopyroxene-garnet thermometer after Krogh (2000) and jadeite-in-clinopyroxene barometer after Holland (1980); green shaded field: range of temperatures retrieved using the Zr-in-rutile thermometer of Tomkins et al. (2007); red dashed line: Ti-in-quartz thermometer of Wark and Watson (2006); grey dashed lines: experimental amp- and zo-out from Schmidt and Poli (1998), and coesite-quartz transition; (b) blue lines: Ca-in-orthopyroxene thermometer of Brey and Köhler (1990) and barometers of Lal (1993) (gt-opx-pl-q) and Eckert et al. (1991) (gt-cpx-pl-q); green line: sapphirine-spinel thermometer of Sato et al. (2006); grey dashed lines: experimental wet solidus and garnet-in from Schmidt and Poli (1998).

Figure 10. Thermodynamic modelling of E-type kyanite eclogites from Duria. (a) P-T isochemical section calculated for the composition B5, assuming H_2O = 0.01 wt%; isopleths of the calculated molar fraction of the component $KAlSi_3O_8$ in K-feldspar (XOr) are shown as dotted lines; the experimental wet solidus of Schmidt and Poli (1998) is shown for comparison as dashed line; (b) P-X isothermal section calculated at fixed ~~T~~ *T* = 700°C, where X = ~~O~~ 0 stands for the anhydrous bulk composition B5 and X = 1 represents the composition B5 with wt% added H_2O component.

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Figure 11. Thermodynamic modelling of symplectites replacing kyanite in E-type and HAE-type eclogites from Duria. ~~(c, d)~~ P-X isothermal sections calculated at fixed ~~T~~ *T* = 850°C, where X = 1 represents composition B5 (c, E-type clogites) or D9 (d, HAE-type eclogites) with 0.01 wt% added H_2O, and X = 0~~O~~ accounts for 30 wt% added kyanite component Al_2SiO_5.

Figure 12. Thermodynamic modelling of symplectites replacing zoisite in HAE-type eclogites from Duria (e) P-X isothermal section calculated at fixed ~~T~~ *T* = 850°C, ~~where X = 1 represents composition D1 with 0.01 wt% added H_2O, and X = O accounts for 50 wt% added zoisite component $CaAl_3Si_3O_{12}(OH)$~~; (f) log aH_2O vs. X section calculated at fixed ~~P~~ *P* = 1.2 GPa and ~~T~~ *T* = 850°C, where X = 1 represents composition D1 with 0.01 wt% added H_2O, and X = 0~~O~~ accounts for 50 wt% added zoisite component $CaAl_3Si_3O_{12}(OH)$.

Figure 13. Schematic cartoon showing symplectites replacing kyanite in type E eclogites (a, b) and HAE eclogites (c, d) on the basis of the thermodynamic modelling and related material-transfer study. (a) Former HP kyanite porphyroclast in kyanite eclogite B5 redrawn from the BSE inset (detail of Fig. 5c), embedded in a matrix of omphacite and garnet; (b) LP-HT reactions 4 (ky + omph + gt = pl + sapp) and 5 (ky + omph +gt = pl + sp) (see text) result in symplectites made of An-rich plagioclase together with sapphirine (sapp; blue fields in inset, cf. Fig. 11a) or spinel (sp; pink fields), depending on the amount of Al_2SiO_5 (kyanite) component added to the bulk rock. Compositional isopleths can be drawn in the symplectite in order to reproduce the microstructure of the symplectite. (c, d) In eclogite D9, symplectite replacing kyanite, shown in the inset (cf. Fig. 5h) contains corundum (cor) in its inner part (green fields in inset, cf. Fig. 11b), due to reaction 6 (ky + omph = cpx + pl + cor). Sapphirine + corundum (grey fields), sapphirine + spinel (yellow fields) and spinel only (pink fields) occur in symplectite towards the rock matrix. The observed microstructure can be modelled perfectly assuming also in this case a decreasing amount of the component Al_2SiO_5 from the core to the rim in the micro-domain surrounding the kyanite crystal that has been replaced by LP-HT mineral assemblages. Dashed red arrows in figures b and d indicates possible paths from the Al_2SiO_5-rich symplectite core towards the host ~~bulk~~ rock.

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