Coesite and diamond inclusions, exsolution microstructures and chemical patterns in ultrahigh pressure garnet from Ceuta (Northern Rif, Spain)

M.D. Ruiz-Cruz a,⁎, C. Sanz de Galdeano b

a Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain
b Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Facultad de Ciencias, 18071 Granada, Spain

A R T I C L E   I N F O

Article history:
Received 9 November 2012
Accepted 9 June 2013
Available online 17 June 2013

Keywords:
Ultrahigh pressure metamorphism
Betic–Rif cordilleras
Electron back-scattered diffraction
Exsolution

A B S T R A C T

Garnet from diamondiferous granulites of Ceuta (Betic–Rif cordillera, Spain and Morocco) contains a variety of inclusion types. To better understand the evolution of these rocks during the ultrahigh pressure event, two samples (1 and 2) were selected for the detailed study of garnet. Primary inclusions of apatite, quartz, coesite, rutile and retrograded pyroxene, and exsolution microstructures of rutile characterize garnet from sample 1, whereas exsolution microstructures of quartz, coesite, apatite and rutile, and inclusions formed from a melt characterize garnet from sample 2, indicating that peak metamorphic conditions were recorded by sample 2. In contrast, the chemical patterns of garnet suggest an inverse situation. Garnet from sample 1 has high Ca- and low Mn contents and high XMg, characteristic of growth at high pressure and temperature whereas garnet from sample 2 shows high Mn and low Ca contents and low XMg, characteristic of garnet formed at lower temperature and pressure. The contrasting compositions are interpreted as reflecting differences in the position of the metamorphic path followed by both samples relative to the solidus: Garnets from sample 1 are interpreted as formed below the solidus whereas garnets from sample 2 are interpreted as formed in the presence of a melt, which caused notable enrichment of garnet in Mn and depletion in Ca relative to garnet from sample 1. Due to extensive low-pressure Hercynian melting that caused generalized migmatization and melt mobilization, whole-rock composition of the samples notably changed, thus preventing the accurate estimation of the physical conditions characterizing the older ultrahigh pressure event. Estimations based on experimental determinations of the phosphorous solubility in garnet suggest that peak pressure conditions were on the order of 6–7 GPa, which put the origin of the studied crustal rocks at depths greater than 200 km.

© 2013 The Authors. Published by Elsevier B.V. All rights reserved.

1. Introduction

Discoveries of coesite and diamond in regional ultrahigh pressure (UHP) metamorphic rocks (e.g. Chopin, 1984; Chopin and Sobolev, 1995; Smith, 1984) demonstrated that continental material can be subducted to depths of at least 140 km, and subduction to depths of 150–300 km have been inferred for orogenic garnet peridotites (Bozhilov et al., 1999; Dobzhinetskaia et al., 1996; Hwang et al., 2000; Song et al., 2004; van Roermund and Drury, 1998; Yang et al., 1993; Zhang et al., 2003). Nevertheless, determining the subduction depth of UHP metamorphic crustal rocks is difficult because of extensive late-stage recrystallization and lack of suitable pressure (P) indicators. Inclusions and exsolution microstructures play, then, an important role in recognition and characterization of UHP metamorphism. Here we report the presence of high concentrations of exsolution microstructures of apatite, rutile and quartz in garnet from crustal rocks of the Betic–Rif UHP metamorphic belt. In other HP terrains, comparable inclusions have been interpreted as exsolution from majoritic garnet originated at pressures on the order of 6–7 GPa (Mposkos and Kostopoulus, 2001; Okamoto and Maruyama, 2004; Tompson, 1975; Ye et al., 2000; Zhang et al., 2003). In this paper we provide a detailed study of inclusion compositions and orientations and compare the chemical composition of host garnet in order to establish the growth sequence and the possible physical conditions of the UHP event.

2. Geological background

The Betic–Rif cordilleras in Southeast Spain and North Morocco make up part of the peri-Mediterranean Alpine orogenic system (Fig. 1A). These cordilleras were structured during the Alpine convergence between the African and Eurasian plates but their pre-Alpine
pressure studies have established that Permo-Triassic rocks record a high rocks, which have been dated to the Middle to Late Triassic. Previous which are thought to be Permo-Triassic in age; and 3) carbonate (Betic) or Sebtide (Rif); and the Maláguide (Betic) or Ghomaride (Rif).

The Alpujárride–Sebtide sequence includes: 1) pre-Permian granulites, gneisses and micaschists; 2) fine-grained schists or phyllites, which are thought to be Permo-Triassic in age; and 3) carbonate rocks, which have been dated to the Middle to Late Triassic. Previous studies have established that Permo-Triassic rocks record a high pressure–low temperature (HP–LT) Alpine metamorphic event, followed by low pressure–high temperature (LP–HT) one related to decompression (e.g. Bouybaouene et al., 1995; Goffé et al., 1989). Regardless of the polyphase metamorphic history K–Ar and Rb–Sr ages in micas cluster in a range between 23.4 and 15.5 Ma, only reflecting the exhumation of the complex. Based on these ages, the metamorphism affected the pre-Triassic formations has also been interpreted as Alpine (e.g. Balanyá et al., 1993). Nevertheless, most robust thermochromometers have provided Hercynian ages in different zones of the belt (e.g. Montel et al., 2000; Zeck and Whitehouse, 1999).

Although closely associated, peridotites and crustal rocks have been considered to be independent formations and studied separately. It was proposed that during an initial stage, dated between 1400 and 1300 Ma (Reisberg et al., 1989), the peridotites were removed from the asthenospheric mantle and incorporated into the sub-continental lithosphere. It was also assumed that diamond, now graphitized (Davies et al., 1993; Pearson et al., 1989; Slodkevich, 1980), formed during this stage. Nevertheless, the mechanism and age of emplacement of the peridotite massif within the nappe pile of the Betic–Rif orogen are yet matter of debate (e.g., Garrido et al., 2011; Pearson and Nowell, 2004; Platt et al., 2003; Saddiqi et al., 1988; Zeck, 1996).

In the Ceuta zone (Northern Rif, Spain), two different pre-Triassic crustal-rocks units have been identified (Ruiz Cruz and Sanz de Galdeano, 2012a): a) a meta-sedimentary unit consisting of variably migmatitic granulites overlying a small peridotite body; and b) a meta-magmatic unit (Hacho unit) consisting of meta-rhyolites and porphyritic meta-granites with textural characteristic of orthogneisses at the field scale. The first unit outcrops in the Hacho unit (Fig. 1B). Although the orthogneisses from the Hacho unit have been described and dated (Bernard-Griffith et al., 1977; Durand Delga and Kornprobst, 1963; Kornprobst, 1962, 1974), the meta-sedimentary unit, which outcrops in a rocky beach with a difficult access, had not been previously described in detail. Despite the mineralogical and textural differences between both units, the presence of diamond in restite garnet, apatite and zircon from the meta-magmatic rocks and the bulk-chemical data suggest a genetic relation between both types of units. Based on a model of restite fractionation, we interpreted that incipient melting would produce migmatites whereas more advanced melting and mobilization could lead to formation of felsic liquids enriched in silica and alkali cations which originated leucocratic rhyolites and granites during the Hercynian event (Ruiz Cruz and Sanz de Galdeano, 2012a).

In the meta-sedimentary unit we have found a variety of rocks in terms of whole-rock composition and texture. Presence of diamond and coesite inclusions in garnet from this unit has been recently described by Ruiz Cruz and Sanz de Galdeano (2012b). That study was especially focused to identification of diamond and coesite in specific type of garnet, which was characterized by the presence of a variably sized core with large and generally oriented silicate inclusions surrounded by a mantle containing aligned rutile inclusions and smaller idiomorphic inclusions, and by a thin inclusion-poor rim. Small inclusions in the mantle mainly consisted of K-feldspar, quartz, diamond and zircon (Ruiz Cruz and Sanz de Galdeano, 2012b, Fig. 2B).

3. Sample location and petrography

Two very close samples (samples 1 and 2) were selected for the present study. Location of the samples is shown in Fig. 1B and Table 1. Sample 1 is a migmatitic granulite (Coutinho et al., 2007), which was taken in the less modified remnant of the parent rock (Fig. 2A). The sample, which was cut perpendicular to the foliation, shows a porphyroblastic texture with slightly elongated mineral grains displaying some preferred
The mineral assemblage, deduced on the basis of the Rietveld analysis of the X-ray diffraction patterns (see below), is homogeneous in the several fractions of the sample and consists of quartz (48 wt.%) + K-feldspar (15 wt.%) + plagioclase (12 wt.%) + biotite (8 wt.%) + garnet (5 wt.%) + sillimanite (2 wt.%) and minor amounts of ilmenite, graphite, rutile, apatite, zircon, spinel, corundum, cordierite and margarite. Most of these phases, excluding garnet, apatite, rutile, mesoperthite and kyanite, represent a retrogressive assemblage, which is well-represented in a variety of coronas (spinel–plagioclase, corundum–plagioclase–cordierite, phengite–margarite and spinel–phengite symplectites), developed at the kyanite–quartz, kyanite–garnet and kyanite and phlogopite boundaries (Fig. 2B). Excluding coronas, the mineral assemblage in the matrix rock mainly consists of quartz, feldspars, biotite, sillimanite, graphite and ilmenite.

Sample 2 was taken in a garnet-rich migmatite (Wimmenauer and Bryhni, 2007), which seems to be representative of the melanosome at the field scale (Fig. 2C). The sample is, however, very heterogeneous even at the scale of the thin section, showing biotite + sillimanite + spinel-rich domains containing corroded garnet surrounded by thick spinel-rich coronas (Fig. 2D) and quartz-feldspatic domains with lower amounts of garnet. The average mineral composition consists of quartz (28.5 wt.%), K-feldspar (12.7 wt.%), plagioclase (6 wt.%), sillimanite (15.5 wt.%), garnet (15.3 wt.%), biotite (15.3 wt.) and chlorite (3 wt.%). Minor phases are cordierite, opaques and spinel (herzynite). The petrographical images indicate that, except for garnet and kyanite, which are the oldest preserved phases, the mineral assemblage mainly reflects different stages of retrogression in the biotite-rich domains, whereas the quartz-feldsparic domains are interpreted as crystallized from melt derived locally.

Whole-rock composition of both samples is characterized by high Al₂O₃ content (19.6–22.0 wt.%), which reflect the pelitic nature of the protolith (Table 1). Differences between the two samples studied affect to CaO, Na₂O and K₂O contents, which are higher in sample 1,
and to Fe₂O₃, MnO and MgO contents, which are higher in sample 2. These differences have been interpreted in terms of variable melting degree and melt mobilization, which were higher in sample 2 (Ruiz Cruz and Sanz de Galdeano, 2012a).

4. Analytical techniques

XRD patterns obtained in the Malaga University with Philips X’Pert PRO MPD, CuKα radiation and Ge monochromator, were used for semi-quantitative estimation of the mineral composition, using the X’Pert High Score software package (Philips), based on Rietveld analysis, and the PDF-2-2003 database (International Center for Diffraction data). Estimation of accessory minerals was carried out from the whole-rock P₂O₅ content (for apatite), the TiO₂ content (for rutile) and the Zr content (for zircon).

X-ray fluorescence analyses (XRF) of major elements and Zr were carried out using a Philips PW 1040/10 spectrometer (CIC, University of Granada, Spain). Glass beads with lithium tetraborate were employed to minimize the preferential orientation of phyllosilicates. The detection limit for major elements is 0.01 wt.%. Loss on ignition (LOI) was determined using 0.5 g of powdered sample, first dried at 110 °C and then heated to 1000 °C for 1 h. Typical precision was better than ±1.5% for an analyte concentration of 10 wt.%. Zirconium was determined by XRF on pressed pellets, with a precision better than ±4% for 100 ppm Zr.

Five thin sections from sample 1 and seven thin sections from sample 2 were used in this study. We have prepared two main types of thin sections: (a) normal diamond polished thin sections, which were used for the optical and the Raman study before coating and, after carbon coating, for electron microprobe (EMP A) and scanning electron microscopy (SEM) studies; and (b) thin-sections only polished with SiC and silica gel, which were used for the electron back-scattered diffraction (EBSD) study and for unambiguous identification of diamond by Raman spectroscopy and SEM.

The SEM-EDX study was carried out using an Environmental Scanning Electron Microscope FEI model Quanta 400, operating at 15–20 keV and the EMP A data were obtained with a Cameca SX100 equipment in the CIC (Granada University) and with a JEOL Superprobe JXA-8900M (University Complutense, Madrid).

EBSD data were obtained with an Inca Crystal equipment (Oxford Instruments) detector coupled to a Gemini-1530 (Carl Zeiss) FESEM (CIC, Granada University). We used an accelerating voltage of 20 kV, and beam current of 5 nA. Detailed description of the used methods is reported in Ruiz Cruz et al. (2011a).

Raman spectroscopic analysis was carried out at the Malaga University using a DILOR XY RMP operated in multichannel microanalysis mode with 1024 diodes and room temperature of 23 °C; the argon laser was operated at 514 and 488 nm and 100 mW power. Five to ten accumulations were made during 1–5 s time spans with slits of 300 mm and spectral range of 100 to 1800 cm⁻¹ and 100 to 4000 cm⁻¹.

5. Results

5.1. Garnet study

5.1.1. Sample 1

Several types of garnet have been distinguished in sample 1 on the basis of the inclusion types (Fig. 3). The most abundant are garnets containing large composite silicate inclusions (CI) described below (Type 1 garnet, Fig. 3A), which are similar to those described by Ruiz Cruz and Sanz de Galdeano (2012a, 2012b). Garnet contains variable amounts of oriented rutile needles and minor diamond cluster surrounding the CI-rich zone (see below) and an inclusion-free rim variably preserved.

Some other garnet types not described previously include: garnet with large fluorapatite inclusions in the core, a rutile-rich mantle and an inclusion-free rim (Type 2 garnet, Fig. 3B); garnet with a rutile-rich core and an inclusion-free rim (Type 3 garnet, Fig. 3C); and garnet with abundant euhedral quartz inclusions (Type 4 garnet, Fig. 3D). Scarce scattered diamonds have been identified in this later garnet type. In general, garnet appears as variably sized and corroded porphyroblasts, randomly distributed in the sample.

The chemical data (Table 2) obtained in the several garnet types show some similarities and some differences. All garnets have low content of spessartine (~1.5 mol%) and similar intervals of almandine (53–64 mol%) and pyrope content (21–31 mol%) (Fig. 4). In contrast, the grossular content and the almandine and pyrope profiles show important differences: in type 1 and 2 garnet the grossular content in the core is low (<10 mol%) (Fig. 4A and B), whereas in type 3 and 4 garnet the grossular content is higher in the cores (near 30 mol%) than in the rims (~10 mol%) (Fig. 4C and D). A notable and discontinuous increase of the grossular content is observed from the inclusion-poor cores to the inclusion-rich rims in garnet types 1 and 2, and in minor extent in type 3, whereas type 4 shows an inverse trend. Moreover, type 1 and 2 garnet show bell-shaped almandine and pyrope profiles, which are flatter in type 3 and 4 garnet.

These data reveal the presence of two garnet populations in this sample: a) type 1 and 2 garnet, which display profiles suggestive of growth under increasing P-T regimes and in which diamond has been identified; and b) type 3 and 4 garnet, type 3 being diamond-free, which have grown under more uniform conditions.

5.1.2. Sample 2

In sample 2 five garnet types can be distinguished on the basis of the dominant inclusion types and location (Fig. 5): Type 1 garnet (the most abundant) shows very variable size and appears located in the CI-rich zone and in quartz-feldspar-rich domains. It consists of a thick inclusion-free core and a rim containing scarce quartz inclusions (Fig. 5A); type 2 garnet, also showing variable size, consists of a core with abundant oriented euhedral quartz inclusions and a thick inclusion-free rim (Fig. 5B); diamond has been identified in the quartz-rich core; type 3 garnet is scarce and appears in quartz-rich domains, as large porphyroblasts containing quartz inclusions with a lobular shape in the core and scareaound quartz inclusions in the rim (Fig. 5C); type 4 garnet was only found in two of the studied thin-sections. It appears located in the biotite + sillimanite-rich domains and consists of a core with abundant inclusions of apatite and minor quartz and an inclusion-free rim (Fig. 5D); small diamonds are present as inclusions in phases associated with apatite; type 5 garnet only appears in the biotite + sillimanite-rich domains as small, strongly corroded porphyroblasts. It contains high concentration of rutile inclusions in the core, which increase in size toward the rim, and incomplete inclusion-free rims (Fig. 5E and F).

The chemical data (Table 3 and Fig. 6) show similarities for type 2, 3 and 4 garnet, with increasing content of pyrope from the core to the rim, and inverse trends for almandine and spessartine. The grossular content is very low except in the outer rim. The profiles suggest that these three garnet types grew during a common metamorphic event. Type 1 and 5 garnet show more homogenous compositions. Since type 5 garnet porphyroblasts appear strongly corroded, the several profiles do not clearly indicate the chemical changes from core to rim (Fig. 6E and F).

5.2. Inclusion study

5.2.1. Inclusions in garnets from sample 1

The main types of inclusions in garnets from sample 1 include large CI and smaller quartz, K-feldspar, rutile, zircon and diamond inclusions. We have identified several types of CI: 1) rounded or slightly elongated quartz/coesite + phengite inclusions (Fig. 7A), similar to those described by Ruiz Cruz and Sanz de Galdeano (2012b, Fig. 3E and F); polycrystalline quartz inclusions (Fig. 7B), interpreted as formed...
from precursor coesite; and euhedral inclusions in which plagioclase is the dominant phase (Fig. 7C and D). In this later CI type, plagioclase (Table 4, analyses 1 and 4) either is intergrown with quartz and minor phengite (Fig. 7D) or is surrounded by quartz/coesite + phengite (Table 4, analyses 3 and 5) palisades (Fig. 7C). Although most EMPA analyses are contaminated by adjacent phases, detailed chemical study of this inclusion type has permitted to find relics of clinopyroxene (Table 4, analysis 2), which had not been previously identified. This finding suggests that most of these CI are pseudomorphs after pyroxene.

Diamond inclusions from CI-rich type 1 garnet were described by Ruiz Cruz and Sanz de Galdeano (2012a, 2012b, Fig. 2B and following) and are also shown in Fig. 7D and E. The Raman spectra are not the typical of metamorphic microdiamond, being characterized by the presence of a complex band-set in the zone of the diamond band (Fig. 7F). In addition to the diamond peak (at 1331–1333 cm$^{-1}$), the spectra show extra features at lower and higher frequencies. Many bands can be attributed to Sp2- or Sp3-bonded carbon. Others may be due to luminescence. The bands at 1144, 1442–1468 and 1544 cm$^{-1}$ are common in the spectra of CVD nanodiamonds, being ascribed to either amorphous carbon or transpolyacetylene chains (CH) in diamond grain boundaries (Ferrari and Robertson, 2004). Both hypotheses are possible, based on Raman. Some of these bands could be due to complex carbonates, as in the case of halogen-bearing hydrated carbonates (Frost and Dickfos, 2007). This assumption is supported by the presence of a band at 1089–1095 cm$^{-1}$ in most diamond spectra, and by the presence of areas with light contrast in the back-scattered (BSE) and secondary electron (SE) images. The full width at half maximum (FWHM), determined in numerous spectra after fitting of the 1280–1420 cm$^{-1}$ zone with the Peakfit software (Jandel Scientific), is significantly wider (9.3–10.6 cm$^{-1}$) than in typical diamond, suggesting a disordered structure.

Type 2 and 3 garnet contain symmetrically oriented rutile rods and needles (Fig. 8A and B). In type 2 garnet, colorless rutile rods occupy the innermost part of the garnet, being surrounded by larger (up to 50 μm) rutile inclusions (Fig. 8A). The SEM study revealed that the small rutile rods are frequently composite inclusions made of rutile and a silicate phase with dark contrast in the BSE images (Fig. 8C). The Raman study has not permitted its unambiguous identification, since the rutile bands have a strong intensity. Nevertheless, bands at 996 and 1036 cm$^{-1}$ (Fig. 8D) suggest that the silicate phase

---

**Fig. 3.** Petrographical images of the main garnet types defined in sample 1. A: Type 1 garnet contains abundant composite silicate inclusions (CI). Aligned rutile inclusions are abundant. B: Type 2 garnet contains large apatite inclusions in the core, which is surrounded by a rutile-rich mantle and by an incomplete inclusion-free rim. C: Type 3 garnet shows a rutile-rich core and an incomplete inclusion-free rim. D: Type 4 garnet mainly contains euhedral quartz inclusions. Red arrows mark the position of the chemical profiles shown in Fig. 4.
can be pyroxene (Yang et al., 2009). The composite inclusions show elongation axis making angles of 45° and 90°, which are not coincident with the elongation direction of the single inclusions.

In type 3 garnet, large (up to 50 μm) rutile needles follow several preferred orientations, with angles of 30°, 60° and 90° (Fig. 8B). This variable orientation contrasts with the regular and uniform orientation described in other rutile exsolved microstructures in garnet (e.g. Song et al., 2004).

Clusters of small diamonds, in some cases containing carbonate inclusions, have been identified in the rim of type 2 garnet (Fig. 8E). The Raman spectra are simpler than in the case of diamond from type 1 garnet but also show broad diamond bands (Fig. 8F). In the non-treated spectra, it can be observed that the diamond band includes two very close bands at 1328 and 1333 cm⁻¹. The diamond band shows $FWHM$ values on the order of 10 cm⁻¹ (Fig. 8G). The double peak effect could be due to heating of diamond during analysis, with consequent down-shifting.

5.2.2. Inclusions in garnet from sample 2

Garnet from sample 2 contains, except for type 1, abundant inclusions of different nature (Fig. 5). Although locally coexisting, the several inclusion types appear concentrated in different porphyroblasts, following a common pattern: An inclusion-rich core is surrounded by an inclusion-free rim.

Quartz inclusions from type 2 garnet appear as large (up to > 100 μm), drop-shaped or prismatic inclusions and smaller (~5–20 μm) pseudo-cubic or prismatic inclusions (Fig. 9A and B). The small inclusions appear aligned following two perpendicular directions in the petrographic images (Fig. 9A), as also the large prismatic inclusions, these later in parallel to the elongation direction (Fig. 9B). The large inclusions contain, in turn, barrel-shaped or columnar graphite and diamond (Fig. 9A), which also appear directly included in garnet (Fig. 9B). Both phases have been differentiated on the basis of their Raman spectra (Nadala and Massonne, 2000; Pasteris and Wopenka, 1991) (Fig. 9C). The diamond vibration band again exhibits important broadening as expected for nanocrystalline domains or for coexistence of ordered and disordered phases (Yoshikawa et al., 1993). Coexistence of graphite and diamond in the same garnet suggests that one of the two phases grew metastably.

Large quartz inclusions show anomalous morphology and birefringence (Fig. 9C and D). The inclusions are surrounded by anomalous birefringent fields indicating a strong strain of garnet around them (Fig. 9D). In some cases, the strain results in mechanical disturbances in the host garnet to form small microfractures (Fig. 9E). The anomalous morphology can be better observed in the BSE images, in the case of the numerous hollows produced as a consequence of the inclusion loss during polishing (Fig. 9F). This behavior is suggestive of the presence of a silica polymorph with hardness higher than garnet. Very similar quartz inclusions in shape and morphology have been interpreted as formed from coesite (Tomilenko et al., 2009, Fig. 3). The Raman spectra are dominated by the bands of quartz although small bands (at 269 and 521 cm⁻¹) that can be interpreted as due to coesite (Boyer et al., 1985) are frequently present (Fig. 9C). The spectrum with the most intense coesite bands, obtained from the inclusion labeled as Qz + Coe in Fig. 9A, is shown in Fig. 9H. Despite coesite shows in most cases weak coesite bands, the 521 cm⁻¹ that can be interpreted as due to coesite (Boyer et al., 1985) are frequently present (Fig. 9C). The spectrum with the most intense coesite bands, obtained from the inclusion labeled as Qz + Coe in Fig. 9A, is shown in Fig. 9H. Despite coesite shows in most cases weak bands (e.g. Fig. 9I-a), the 521 cm⁻¹ one cannot be ascribed to garnet (Fig. 9I-b) or quartz (Fig. 9I-c).

Type 3 garnet contains large (~200 μm) quartz inclusions with a lobular shape in the core, and rounded inclusions toward the rim (Fig. 5C). The large quartz inclusions display morphologies (Fig. 10A) similar to the melt-derived quartz inclusions trapped by garnet during experimental melting of metapelites (Spandler et al., 2010, Fig. 1B). We have also identified similar quartz inclusions coexisting with “granitic” inclusions unambiguously derived from trapped melt in other zones of the Betic belt (unpublished data). Quartz includes, in turn, phengite, clusters of aluminosilicate (Fig. 10B) and minute inclusions of moissanite (Fig. 10C). Whereas moissanite is easily identified by Raman spectroscopy (Fig. 10D), the aluminosilicate phase shows bands suggesting the current coexistence of several phases (Fig. 10E).
In type 4 garnet the dominant inclusion type is apatite. The garnet cores show high density of apatite inclusions, which are seen either as short prisms (<10 μm in length) and rods (Fig. 11A), as needles (Fig. 11B), and as rarer hexagonal crystals (~30 μm) from which needles emerge (Fig. 11C). Apatite coexists with quartz, kyanite and with needles of a silica phase interpreted as coesite (Fig. 11D) on the basis of the lack of quartz bands and of the presence of bands at 178 and 521 cm$^{-1}$ in the Raman spectra (Fig. 11F). Zircon, xenotime, rutile and graphite are frequent phases associated with apatite (Fig. 11E). Small transparent inclusions in zircon and xenotime are diamonds, according to the Raman spectra (Fig. 11G), which are similar to those provided by diamond from type 1 garnet in sample 1. The geometrical pattern defined by prismatic apatite is difficult to deduced from the petrographical images (Fig. 11A) given the size variations, the high density of inclusions located at different depths and the presence of inclusions of other phases. Despite apatite and garnet show similar contrast in the BSE images, these indicate that apatite needles and prisms define equilateral triangles, whereas coesite needles show an orthogonal pattern. Both phases seem to share, however, one of the directions (Fig. 11D).

Type 5 garnet contains abundant rutile inclusions (<50 μm in length) showing several preferred orientations (Fig. 12A). Two populations of rutile are present: Brownish inclusions and lighter needles and rods. Rutile needles show frequent twinning and the elongation directions define a triangular pattern. The SEM study revealed that, as in the case of type 3 garnet from sample 1, most rutile needles and rods are associated with Si-rich phases (Fig. 12B, inset; Table 3, analyses 7 and 8), with variable contrast in the BSE images. The Raman spectra suggest that the associated phase is coesite in some inclusions and clinopyroxene in some others (Fig. 12C and D).

5.3. Orientation study

Although the geometrical patterns shown by apatite in sample 2 and by rutile in samples 1 and 2 strongly suggest exsolution microstructures, the distinction between these and the non-exsolution microstructures can be difficult (Liu et al., 2009) and confirmation must be based on accurate determination of the orientation relationships among inclusions and garnet. With this aim we have realized an EBSD study in selected zones of several garnet types from sample 2, which shows more variable types of possible exsolution microstructures.

The zone studied in type 2 garnet contained, according to the petrographical study, variably sized quartz inclusions. The diffraction-based map of phases (Fig. 13A) revealed, however, the presence of quartz-, quartz + coesite- and apatite + coesite + quartz inclusions, which could not be resolved at the scale of the petrographic microscope and only rarely at the scale of the SEM. Minor diamond was also detected in the larger inclusions. The orientation analysis indicated that most prismatic inclusions show elongation parallel to the equivalent [110] directions of garnet and that the quartz elongation is [0001].

---

Fig. 4. Chemical profiles obtained from garnets shown in Fig. 3. Green arrows and numbers indicate changes in slope of the grossular profiles, interpreted as reflecting changes in the P/T regime. See text for detailed explanation.
Fig. 5. Petrographical images (plane polarized light) of the main garnet types defined in sample 2. A: Type 1 garnet shows a large inclusion-free core and scattered quartz inclusions in the rim. B: Type 2 garnet shows a core with abundant euhedral inclusions of quartz and a thick inclusion-free rim. C: Type 3 garnet contains large lobular inclusions of quartz in the core and smaller quartz inclusions toward the rim. D: Type 4 garnet shows a core rich in small apatite and quartz inclusions, which increase in size in the outer zones, and an inclusion-free rim. E and F: Type 5 garnet shows a rutile-rich core and an inclusion-free rim (F). The zoning is not clear in the strongly corroded porphyroblasts (F). Red arrows mark the position of the chemical profiles shown in Fig. 6.
two of the larger quartz + coesite +apatite inclusions andapatite
inclusions (1 and 2 in Fig. 13A) show [0001]Qz//[100]Grt (Fig. 13B and F), small quartz, coesite andapatite display, with
minor angular variations, the orientation relationships [0001]Qz//
[001]Ap//[110]Grt (Fig. 13C). The orientation [001]Qz//[001]Coe
have been already described by Ruiz Cruz et al. (2011a) and
Ruiz Cruz and Sanz de Galdeano (2012b) in samples from Ceuta
and from other localities of the Rif. Larger inclusions (white circles in
Fig. 13A) show [0001]Qz // [100]Grt and [001]Rt// [110]Grt. In minute inclusions rutile
(Fig. 13G) and, in the composite inclusions, by the apatite orienta-
tions, that most apatite, coesite and rutile (in type 4 and 5 garnet),
associate with the small rutile inclusions. The elongation direction,
related with the small rutile inclusions. The elongation direction,
and from other localities of the Rif. Larger inclusions (white circles in
Fig. 13B, C and E) show [0001]Qz//[100]Grt and [001]Rt// [110]Grt. In minute inclusions rutile
(Fig. 13I and J). The large rutile
inclusion (4) does not show a unique orientation, suggesting
the presence of twinning (Fig. 13K). These results contrast with previ-
sionary determinations in rutile needles included in garnet, in which
the rutile c-axes are inclined at to the needle long axes, and the orientation
analyses indicate that [101] of rutile controls the orientation relations-
ships with garnet (e.g. Hwang et al., 2007). In our samples, the rutile
needles do not show oblique extinction and [101] of rutile do not control
the orientation relationships with garnet.

These results indicate, despite the complex orientation relationshi-
ship, that most apatite, coesite and rutile (in type 4 and 5 garnet),
and the small quartz ± coesite inclusions (in type 2 garnet) have all
characteristics of true exsolution microstructures (Liu et al., 2009),
including the idiomorphic shape (Figs. 9, 11 and 12), the dense and
homogeneous distribution in the garnet core (Fig. 5B, D and E) and
the crystallographic control by garnet (Ye et al., 2000). Never-
theless, in the smaller apatite + coesite inclusions and in the minute
inclusions, apatite shows [001] parallel to the three equivalent [100]
directions of garnet (Fig. 13B, C and E). The orientation of coesite
seems to be controlled, in contrast, by the [110] directions of garnet
(Fig. 13C) and, in the composite inclusions, by the apatite orienta-
tion with [001]Coe//[110]Grt. Rutile in the large inclusions shows [001]Rt//[100]Grt and [001]Rt//[111]Coe. In minute inclusions rutile
(Fig. 13F) and [110] directions of garnet

Study of type 5 garnet was realized in a small area from the
tutile-needle-rich zone in which only some inclusions were placed
at the depth appropriate for the EBSD study. The diffraction-based
map of phases (Fig. 13H) revealed that inclusions consist of rutile,
coesite and “non-solved” phases that appear as black pixels in the
map, confirming that other phase, different from quartz or coesite, is
associated with the small rutile inclusions. The elongation direction,
when it is discernable, is [011]. The orientation relationship between
rutile and garnet is [001]Rt//[110]Grt (Fig. 13I and J). The large rutile
inclusion (4) does not show a unique orientation, suggesting
the presence of twinning (Fig. 13K). These results contrast with previ-
sionary determinations in rutile needles included in garnet, in which
the rutile c-axes are inclined at to the needle long axes, and the orientation
analyses indicate that [101] of rutile controls the orientation relations-
ships with garnet (e.g. Hwang et al., 2007). In our samples, the rutile
needles do not show oblique extinction and [101] of rutile do not control
the orientation relationships with garnet.

6. Discussion

Although aligned rutile inclusions in garnet, such as those observed
in Fig. 7A, can be interpreted as primary or as formed by epitaxial
precipitation with the host, in agreement with some other authors
(e.g. Wang et al., 1999), most inclusions described here show several
symmetrically related orientations, and there is general agreement in
the interpretation of these patterns as formed from exsolution. Indeed,
exsolution microstructures similar to those described here have been
found in other UHP terrains and lithologies (e.g. Dobrzhinskaya et

al., 2002; Katayama et al., 2000; Mposkos and Kostopoulos, 2001; Ye et al., 2000; Zhang et al., 2002, 2005) and interpreted as generated from Si-, P-, Ti- and Na-rich garnet formed at very high P conditions. Nevertheless, whereas in the previously described cases the different phases appear associated (e.g. Mposkos and Kostopoulos, 2001; Ye et al., 2000), in our samples quartz, apatite and rutile appear concentrated in different garnet types, suggesting either that Ti-, Si-, and P-rich garnet formed under slightly different P–T conditions or that the initial garnet composition was dependent on the composition of the different microdomains.

6.1. Constraints on exsolution morphology and orientation

The exsolved phases occur with several morphologies: (1) euhedral equidimensional or prismatic quartz, and quartz + coesite (Fig. 9) and (2) coesite needles (Fig. 11D); (3) prismatic apatite (Fig. 11A) and (5)

---

**Fig. 6.** Chemical profiles obtained from the garnets shown in Fig. 5. Graphic symbols are as in Fig. 4. Brown arrows mark the increase in X$_{Mg}$, interpreted as reflecting temperature increase during the early decompression stage. See text for detailed explanation.
apatite needles (Fig. 11B); (6) rutile needles (Figs. 8C and 12A), and (7) composite silicate + rutile rods (Figs. 8B and 12B). Variations in morphology can be expected when a determined phase (for example rutile) precipitates from different hosts (for example, garnet and pyroxene) because the structure of the host controls in a great extent the shape and the orientation of the precipitates. In contrast, when exsolution...
occurs from the same phase (garnet, in our case) the variations in morphology can be related with external factors (e.g. T and P of exsolution or cooling rate).

Petrographic and BSE images also indicate that the exsolved phases described here show frequently a change in size, in some cases associated with a change in morphology. This is especially evident in the case of rutile, in which a notable increase in size is observed from the innermost zone to the outer rutile-rich zone (Figs. 3C and 8A). Similar exsolution systematics have been described in mantle rocks (e.g. Ali and Ashworth, 1983) but had not previously noted in UHP crustal rocks, probably due to lack of accurate orientation determinations. Sautter and Fabriès, 1990) and in experimental studies (e.g. Ried and Fuess, 1986; Weinbruch et al., 2003) and related with the exsolution kinetics.

Moreover, our results indicate that the exsolved phases do not show, with some exceptions, a unique orientation relationship with the host. For example, we have observed that exsolved phases can show {0001}_{Cr,Ap} and {001}_{Rt,Coe} parallel to {100}, {110} or {111} of the host. For example, we have observed that exsolved phases can show, with some exceptions, a unique orientation relationship with the exsolution kinetics.

Comparison of the chemical composition of garnets from samples 1 and 2 (Figs. 4 and 6) reveal evident differences: in addition to differences in the relative content of the components, the compositional breaks observed in the profiles of type 1 and 2 garnet from sample 1 are lacking in garnets from sample 2, which show gradual chemical zoning. Another difference regards the relative variations of almandine and pyrope. These components show parallel variations in garnets from sample 1, leading to scarce variations of \(X_{\text{Mg}}\) (except in the outermost rims), whereas they show inverse variations in garnets from sample 2, in which the main octahedral substitution is \(\text{Fe}^{2+} + \text{Mn} = \text{Mg}\). This means that \(X_{\text{Mg}}\) is, in garnets from sample 2, strongly dependent on the Mn content and notably lower than that expected in Mn-poor garnets.

Some other differences emerge from comparison of Tables 2 and 3: the Si content is < 3.0 apfu in garnets from sample 1, whereas it reaches values up to 3.07 apfu in type 5 garnet from sample 2; the \(\text{Na}_2\text{O}\) content is lower (0.08 wt.%) in garnets from sample 1, reaching values > 0.12 wt.% in type 2 and 3 garnet from sample 2; the Al content also reaches values > 2.0 apfu in some garnets from sample 2. In summary, garnets from sample 1 show normal formulae whereas garnets from sample 2 show frequently non-stoichiometric formulae (e.g. Table 3, analyses 7, 13 and 14), in some cases with high Si content, suggestive of a majorite substitution.

6.2. The contrasting chemical patterns of garnets from samples 1 and 2

Comparison of the chemical composition of garnets from samples 1 and 2 (Figs. 4 and 6) reveal evident differences: in addition to differences in the relative content of the components, the compositional breaks observed in the profiles of type 1 and 2 garnet from sample 1 are lacking in garnets from sample 2, which show gradual chemical zoning. Another difference regards the relative variations of almandine and pyrope. These components show parallel variations in garnets from sample 1, leading to scarce variations of \(X_{\text{Mg}}\) (except in the outermost rims), whereas they show inverse variations in garnets from sample 2, in which the main octahedral substitution is \(\text{Fe}^{2+} + \text{Mn} = \text{Mg}\). This means that \(X_{\text{Mg}}\) is, in garnets from sample 2, strongly dependent on the Mn content and notably lower than that expected in Mn-poor garnets.

Some other differences emerge from comparison of Tables 2 and 3: the Si content is < 3.0 apfu in garnets from sample 1, whereas it reaches values up to 3.07 apfu in type 5 garnet from sample 2; the \(\text{Na}_2\text{O}\) content is lower (< 0.08 wt.%) in garnets from sample 1, reaching values > 0.12 wt.% in type 2 and 3 garnet from sample 2; the Al content also reaches values > 2.0 apfu in some garnets from sample 2. In summary, garnets from sample 1 show normal formulae whereas garnets from sample 2 show frequently non-stoichiometric formulae (e.g. Table 3, analyses 7, 13 and 14), in some cases with high Si content, suggestive of a majorite substitution.
Fig. 9. Quartz inclusions in type 2 garnet from sample 2. A and B: Petrographical and BSE images showing sizes and orientation of the quartz inclusions. In A the blue lines mark two (110) directions of garnet (a and b: inclusions from which the Raman spectra are shown in G). C–E: Petrographical images showing the morphology, birefringence and cracks in garnet. F: BSE image of the trace of a lost inclusion. G: Raman spectra of diamond (a) and graphite (b) inclusions in quartz. Small bands at 269 and 521 cm$^{-1}$ can be ascribed to coesite. H: Raman spectrum of the inclusion labeled as Qz + Coe in A. I: Raman spectra of quartz + coesite (a), garnet (b) and quartz (c) from B.
grew. Differences in bulk-rock composition between both samples are evident and have been related with a more advanced melt mobilisation in sample 2 (Table 1). Although garnets from both samples coexist with other Fe–Mg–Ca–Mn phases (e.g. biotite, plagioclase and ilmenite), these phases are either retrogressive or formed during the Hercynian stage and the composition of the Fe–Mg–Ca–Mn phases present at the moment of garnet growth is unknown.

6.3. Main types of substitutions in garnets from sample 2

Testing the main types of substitutions in our garnets with several exsolution microstructures (sample 2) is difficult because exsolution has erased in a great extent the initial chemical composition of the garnet cores. The presence of abundant quartz (±coesite) inclusions in type 2 garnet suggests breakdown of Si-rich garnet. The proposed substitutions in majorite, Si4+ +M2+ = 2Al3+ (e.g. Akaogi and Akimoto, 1977; Ringwood, 1967, 1975) and Na+ +Si4+ =M2+ +Al3+ implies solid solution of garnet and pyroxene (Collerson et al., 2010; Irifune et al., 1986, 1994; Ringwood and Major, 1971) and are primarily P-dependent. The current chemical variations in our type 2 garnet are, however, controlled by the substitution 4Fe3+ → 3Si4+ + □+, whereas Al shows a positive- and Na a poor negative correlation with Si (Fig. 15A and B).

In type 4 garnet, apatite can be interpreted as result of exsolution from P + F-garnet (Barron and Barron, 2008; Haggerty et al., 1994; Mposkos and Kostopoulos, 2001; Ye et al., 2000). To account for apatite exsolution, PO4 may potentially substitute for SiO4 (Bishop et al., 1976; Tompsett, 1975). Phosphorus has been suggested (Tompsett, 1975) to enter the garnet structure through the coupled substitution of PO4 + Na+ → Si4+ + Ca2+. In the current composition of our apatite-bearing garnet, the slight excess of Si and Al are compensated by the presence of vacancies in the octahedral positions (Table 3, analyses 9–11). Although Na and Si show a negative correlation (Fig. 15D), the Na content is very low in these garnets, suggesting that Na was not involved in the substitution.

In type 5 garnet, presence of rutile indicates breakdown of Ti-rich garnet (Song et al., 2005; van Roermund et al., 2000; Yang and Liu, 2004). The main scheme of cation substitutions in Ti-rich garnet is M2+ + Ti4+ = 2Al3+ or Na+ + Ti4+ = Ca2+ + Al3+ (Zhang and Liou, 2003), combined with Na+ + Si4+ = Ca2+ + Al3+ (Sobolev et al., 1971; Zhang and Liou, 2003). In the current composition of our rutile-bearing garnet, the only evident substitution is Si4+ = Ti4+ (Fig. 15F), whereas Al defines two trends with opposite variations (Fig. 15E). Lack of correlation between Na and Si (not shown) suggests, moreover, that Na was not involved in the substitution.

All these data suggest that the typical substitutions invoked for the Si-, P- and Ti enrichment in garnet are not evident in our garnets, in which, with minor exceptions, Si and Al show positive correlations and Si and Na negative or very poor correlations. Nevertheless, it must be taken into account that the currently observed compositions of garnet do not represent the true substitutions acting in the initial garnet because of the presence of abundant exsolved phases. BSE image analyses using VISILOG have been used to estimate the amounts (vol. %) of the exsolution and the possible chemical composition of the initial garnet cores, after transformation in wt. %.

An accurate estimation was not possible in the case of type 2 garnet because of the coexistence of exsolution and non-exsolution quartz microstructures. Nevertheless, addition of variable amounts SiO2 (between 1 and 3 wt.%) to the composition of the garnet core leads to a notable increase of the Si content (from 3.023 to 3.106 apfu), which is coupled with both the loss of the Fe3+ content and vacancies in VI and VIII.

Fig. 10. Inclusions in type 3 garnet from sample 2. A: BSE image of a large lobular quartz inclusion, showing the relative size and location of moissanite, aluminosilicate and phengite. B: BSE image of the aluminosilicate inclusions (white rectangle in A). C: SE image of the moissanite inclusions (black rectangle in A). D: Raman spectrum of moissanite. E: Raman spectrum of aluminosilicate.
In type 4 garnet, addition of 2.8 wt.% apatite and 0.6 wt.% quartz, estimated from the BSE images, to the analysis of the garnet core (Table 3, analysis 9) leads to a stoichiometric formula (without excess of Al) and with P$_2$O$_5$ content of 1.20 wt.%. The Ca content increases in parallel, from 0.09 to 0.22 apfu (Table 3, analysis 12). This reveals that the main substitution was not P$^{5+}$ + Na$^+$ = Si$^{4+}$ + Ca$^{2+}$, as predicted by Tompsom (1975) and experimentally obtained by Brunet et al. (2006) and Hermann and Spandler (2008). Snoeyenbos and Koziol (2008) also noted that garnet from the Taconian Shelburne Falls arc with exsolved apatite needles show Na$_2$O content insufficient for a coupled P + Na substitution.

Fig. 11. Inclusions in type 4 garnet from sample 2. A: Petrographical image of a garnet core with high density of prismatic apatite inclusions. B: Petrographical image of a garnet core with high density of apatite needles. The elongation directions of the apatite needles define triangular patterns (inset). C: Petrographical image showing morphologic changes in apatite. D: BSE image showing sizes and orientation the apatite, quartz and coesite. Inset: Elongation directions of coesite needles (black lines) and apatite prisms (red lines). E: Petrographical image showing the inclusion types associated with apatite. Xenotime inclusions contain small transparent inclusions of diamond. F: Raman spectrum of a coesite needle. Asterisks mark the garnet bands. The band at 278 cm$^{-1}$ has not been identified. G: Raman spectrum of a xenotime inclusion containing diamond. Asterisks mark the xenotime bands. Not identified bands between 1409 and 1525 cm$^{-1}$ can be due to fluorescence.
substitution, suggesting that other compensatory mechanism such as Mg in VI or vacancy in VIII must act. In our case, the presence of a solid-solution between garnet ($M^{2+}_2Al_2Si_3O_{12}$) and apatite ($Ca_3Ca_2P_3O_{12}F$) seems more plausible, which would require the $P^{5+} + 0.66Ca^{2+} + 0.33F^{-} = Si^{4+} + 0.66Al^{3+} + 0.33□$ substitution.

Although experimental data testing the phosphorus solubility in garnet are very scarce and limited to mafic or ultramafic compositions, the experiments of Hermann and Spandler (2008) have shown that the phosphorus content in garnet increases with increasing P (between 2.5 and 4.5 GPa), reaching 0.56 wt.% at 4.5 GPa, and that the garnet is not majoritic. Recent experiments performed in the range 2.5–19 GPa and 800–1500 °C, using synthetic peridotite (Frost, 2012) also indicate that the $P_2O_5$ content in garnet is $\rho$-dependent, increasing from 0.07 wt.% at 2.5 GPa to 1.5 wt.% at 12.8 GPa. In this specific case, due to the low Na$_2$O content in the peridotite (0.6–0.7 wt.%), the substitution $P^{5+} + Na^{+} \rightarrow Si^{4+} + Ca^{2+}$ only plays a minor role in controlling the phosphorus content of garnet. This seems to be the case of our sample 2 with Na$_2$O content of 0.47 wt%. The $P^{5+} + Na^{+} \rightarrow Si^{4+} + Ca^{2+}$ substitution was, however, important in MORB type lithologies with Na$_2$O content on the order of 2.7 wt% (Konzett and Frost, 2009). Thus, the results of Konzett et al. (2012) clearly indicate that: a) the type of substitution controlling the phosphorus content in garnet is strongly dependent on the Na$_2$O content of the rock, the $P^{5+} + M^{2+} = Si^{4+} + Al^{3+}$ being prevalent in Na$_2$O-poor rocks; b) the phosphorus content in garnet increases with $P$ (and eventually with $T$) but decreases with $T$ once the solidus is crossed, due to preferential phosphorus partitioning into coexisting melt; and c) extreme preference of phosphorus to substitute for $PVSi$ irrespective of the chemical system.

Addition of 1.6 wt.% of rutile to the type 5 garnet core composition (Table 3, analysis 13) leads to a formula in which the main substitution is $Si^{4+} = Ti^{4+}$ (Table 3, analysis 17). Since Ti generally occupies the octahedral positions, coupled substitutions such as $Na^{+} + Ti^{4+} = Ca^{2+} + Al^{3+}$ or $M^{2+} + Ti^{4+} = 2Al^{3+}$ (Ringwood and Lovering, 1970; Song et al., 2004; Zhang et al., 2003) would be necessary for charge balance. Nevertheless, the mechanism for Ti-bearing garnet solid solution remains enigmatic. Experimental data indicate that Ti solubility in garnet increases with both $P$ and $T$ (Hermann and Spandler, 2008; Kawasaki and Motoyoshi, 2007; Zhang et al., 2003). Auzanneau et al. (2010), in experiments on a natural SiO$_2$–TiO$_2$-saturated greywacke and a natural SiO$_2$–TiO$_2$–Al$_2$SiO$_5$-saturated pelite, at 1.5–8.0 GPa and 800–1050 °C noted that the garnet composition changed drastically with $P$, $T$ and coexisting assemblage. Although Na is involved in the substitution, garnet is devoid of majoritic component, even at the highest $P$. Maximum Ti content was determined at 4 GPa, whereas the Ti content tends to decrease at higher $P$. In our Ti-rich garnet the compensatory mechanism would be the presence of vacancies in VIII, since alternative substitution mechanisms (Pertermann et al., 2004) are not possible with the obtained formula. Nevertheless, it must be taken into account that the addition of Si, Na$^{+}$ and K$^{+}$ from the silicate phases associated (e.g. Table 4, analysis 8) and presumably exsolved with rutile, would lead to Si-richer formulae with coupled
increase of Na and K, but quantification of these phases was not possible with the available data.

6.4. Sequence of garnet growth and thermobarometric interpretation

The rocks studied are poly-metamorphic and, based on textural, chemical and structural data, only garnet and the included phases (mainly coesite, K-feldspar, rutile, apatite and diamond) and kyanite can be unambiguously ascribed to the UHP paragenesis. Since most garnet was strongly corroded during the Hercynian melting stage (they are restitic), it seems clear that their growth occurred before this stage. The Hercynian paragenesis is mainly represented by the melt-derived phases (mainly quartz, K-feldspar, plagioclase and biotite). It is uncertain, however, if some garnet population or some garnet overgrowth was formed during this stage or during the subsequent Alpine event. It is also evident that the current whole-rock compositions must significantly differ from the initial ones, especially in sample 2, in which it seems very probable that important resorption and even overgrowth of the initial garnet occurred during or after the Hercynian melting stage.

Taking into account these incertitudes, we assume that the most reliable interpretation can be derived from garnets in sample 1. Both the natural observations and the experimental results indicate that the variations of the grossular content and X_{Mg} are function, respectively, of P and T in subduction-zone HP to UHP metamorphic rocks (Carswell et al., 2000; Hermann, 2002; Hermann and Green,
In the studied rocks, variations in Ca are only evident in type 1 and 2 garnet from sample 1 (Fig. 4) suggesting an increase of P from core to rim, associated with scarce T variations, except in the outermost zone of the rim, in which chemical modifications can be related to resorption and diffusion. We assume that, because both garnet types contain diamond near or within the rims, these profiles must characterize, in our samples, the prograde growth under high dP/dT. Although in most cases the profiles are incomplete, changes in slope of the grossular content suggest that a first stage (1, in Fig. 4A and B) of growth under P increase (garnet cores) was followed by a stage (2, in Fig. 4A and B) of growth under moderate P increase (garnet mantles). Although we have not found a continuous zoning, textures locally suggest that type 4 garnet postdated type 1 (Fig. 3D). Since diamond is scattered in type 4 garnet, we think that it is reasonable to assume that its profile is representative of the P climax and of the first retrogressive stage.

In sample 2, the profiles of type 2, 3 and 4 garnet show trends (Fig. 6B, C and D) typical of prograde garnet growth under low-to-medium P-T metamorphic conditions. Nevertheless, we have identified diamond in type 2 and 4 garnet, and the presence of apatite exsolution microstructures in the garnet cores suggests that these garnets record the P-peak and that most garnet growth occurred during decompression, under increasing T. Profiles of type 1 and 5 garnet (Fig. 7A, E and F), which are diamond-free, suggest in contrast, growth under uniform high-T and low-P conditions or, alternately, extensive diffusion or resorption. An exception is type 3 garnet, which is diamond-free and contains, instead, quartz inclusions probably formed from trapped melt. This evidence strongly suggests that the commonly used parameters (especially the Ca and Mn content) are not accurate markers of P and T in garnet from sample 2. Presence of inclusions assumed to be derived from melt suggests that, as in rocks from Erzgebirge (Massonne, 2003; Massonne and Fockenberg, 2012), partial melting occurred at UHP conditions.

If this assumption is true, the experimental results of Massonne and Fockenberg (2012) can provide additional information. These authors note that a drastic decrease in Ca content can be expected, according to the experimental results and the thermodynamic calculations in garnet formed above the solidus under UHP conditions, when the melt content increases considerably. In addition to the decrease of the Ca content, an increase of the Mn content can be
expected in garnet formed in the presence of a melt, since most Mn would be incorporated in garnet, whereas the melt itself would be depleted in Mn (e.g. Wu et al., 2009; Zeng et al., 2009). Thus, a reasonable assumption is that garnets from sample 1 grew below the solidus whereas most garnets from sample 2 grew above the solidus. This interpretation implies that a melting stage different from the generalized Hercynian melting, locally occurred during deep subduction.

In order to get information on the P-T evolution of these rocks, pseudosections were constructed with PERPLE_X (Connolly, 2009) and contoured by molar fractions of garnet components (XCa and XMg) (Fig. 16). The thermodynamical data are from Holland and Powell (1998) (hp02ver.dat) and the solution model that implemented in Perple_X solution model files (solution_model.dat). A system saturated in SiO₂, Al₂O₃ and TiO₂ was used in both cases.

The obtained pseudosections resulted to be different for samples 1 and 2, especially regarding the XCa content. In the pseudosection obtained for sample 1 (Fig. 16A), XCa shows range (between 0.02 and 0.22), which does not overlap, except for one case (rim of type 3 garnet), with the XMg range observed in garnet from this rock (Table 2), revealing that garnet is not in equilibrium with the current whole-rock composition. In the case of sample 2 (Fig. 16B), the several garnet populations have lower Ca content, and XCa intersects with some XMg isolines. Nevertheless, except for the core of type 1 garnet, which could be indicative of a Hercynian origin, only the rim compositions could be in equilibrium with the current chemical composition. The garnet rims plot in two specific zones of the pseudosection: between 500 and 570 °C and between 1.6 and 1.7 GPa for type 1, 2 and 4 garnet; and at ~820 °C and ~1.2 GPa for type 3 garnet. The first population could be compatible with Alpine overgrowths, whereas the position of the second population could point to Hercynian overgrowths.

Because the lack of accurate results for most garnets studied, the P–T–t evolution of the two samples can only be tentatively based on: 1) the observed variations in garnet composition; 2) the presence and location of diamond; and 3) the types of exsolved phases. In our interpretation, diamond-bearing type 1 and 2 garnet from sample 1 would have formed during the prograde UHP stage, as suggested by Ruiz Cruz and Sanz de Galdeano (2012a). Since diamond is

---

**Fig. 15.** Selected chemical plots for garnet with exsolution microstructures from sample 2, showing the main current chemical substitutions. In type 2 and 4 garnet Al shows a positive correlation with Si (A and C) and Na a poor or negative correlation with Si (B and D). In type 5 garnet Al defines two inverse trends (E). Trend 1 is mainly marked by analyses from the core and trend 2 by analyses from the rim. Several trends are evident in the Ti vs. Si plot (F). Trends 1 and 3 are defined by analyses from the core in which contamination with Ti (1) and Ti depletion (3) seems possible. Trend 2, which indicates a Si for Ti replacement, includes analyses from the core and from the rim. In the plots of type 5 garnet we have used the data of several profiles.
concentrated in the inner rims, it can be assumed that the cores grew below the stability field of diamond and the rims within the diamond stability field. Type 3 garnet from sample 1, which is diamond-free and shows rutile exsolution microstructures similar to those observed in the mantle of type 2 garnet, is interpreted as recording the prograde + retrogressive stages below the diamond stability field. It seems that Ti enrichment in garnet occurred as a consequence of breakdown of Ti-rich biotite, as suggested by Das et al. (2013). Type 4 garnet from sample 1 is interpreted as recording the P-peak and the retrogressive stage of the UHP event in this sample. Growth of type 1 and 2 garnet probably occurred under variable dP/dT regimes, as suggested the breaks in Ca content (Fig. 4A and B, green arrows). The beginning of the decompression stage must have occurred along a nearly isothermal path within the stability field of diamond, according to the profiles of type 4 garnet (Fig. 4D). Further cooling would lead to rutile exsolution.

In our interpretation, the cores of type 2 and 4 garnet from sample 2, which contain diamond, grew near the P-peak, under T above the solidus, and their chemical evolution would reflect decompression. Their profiles (Fig. 6B and D) indicate, however, that decompression occurred under increasing T (brown arrows in Fig. 6B and D). Similar temperature increase was deduced for rocks from Erzgebirge and the Kokchetav Massif by Massonne and Fockenberg (2012), on the basis of theoretical considerations. According to these authors, a considerable increase in T after passing the solidus would be required to consume the melt at UHP. This interpretation could be also valid in our rocks. Nevertheless, another explanation seems possible. Since peridotites are present in the same outcrop, the T increase could be explained as caused by emplacement of hot mantle drips near the deeply buried rocks. Indeed, partially graphitized diamond has been described in sim-ilar peridotites from other zones of the Rif belt (El Atrassi et al., 2011), strongly suggesting that diamond formed during a common event in both rock types.

Although on the basis of previous reports of apatite exsolution microstructures as well as on the basis of the experimental results of Konzett and Frost (2009) and Konzett et al. (2012) it can be assumed that P attained >6 GPa in sample 2, maximum T is uncertain. Indeed, the position of the solidus is strongly influenced by the amount of H2O in the rocks although the most discrepant solidus (e.g. Auzanneau et al., 2006; Massonne and Fockenberg, 2012) seems to converge near 1200 °C at high P. Previous estimations by Ruiz Cruz and Sanz de Galdeano (2012a, Fig. 9) based on the garnet-phengite thermometer provided T near 1100 °C for P near 4 GPa. Extrapolation of that path to higher P would indicate T ≥ 1150 °C for the P-peak.

7. Conclusions

The presented results confirm that exsolution microstructures play an important role in recognition and characterization of UHP metamorphism and that, except for the majorite substitution, the chemistry of the UHP garnet departs significantly from the familiar solid solutions observed at lower-P conditions.

Our results also indicate the exsolved phases show important variations in morphology, size, distribution and orientation, which seem to be dependent on the exsolution kinetics. The geometric patterns observed in the petrographical images do not accurately reflect the orientation relationships between host garnet and precipitates, as generally assumed. These relationships, which can vary even within a single garnet porphyroblast, can only be determined by orientation EBSD studies or by transmission electron microscopy.

The presented data suggest that, in addition to the Hercynian stage of melting, partial melting also occurred at UHP conditions. As a consequence, the parameters commonly used in T and P estimates, such as the Mn contents, XGr and XMg, were notably affected. Melting under UHP conditions caused, in appearance, depletion in Ca and enrichment in Mn in garnet, which strongly affects XMg.

Estimation of the garnet composition before exsolution indicates that rutile exsolution microstructures in garnet have probably formed from Si-rich majoritic garnet. In contrast, apatite exsolution microstructures are indicative of high P2O5 content in the initial garnet but not of a majorite composition.
With respect to the tectono-metamorphic evolution of the Betic–Rif belt, these new results suggest that P probably near 7 GPa, similar to those estimated for the Erzgebirge and for the Kokchetav Massif, were attained during the undated UHP metamorphic event. This puts the origin of the studied crustal rocks at depths greater than 200 km. Although the T increase during the first stage of decompression could have different causes, the more affordable and plausible, in the case of the Ceuta rocks, would be the emplacement of hot mantle portions in the deeply buried crustal rocks.

Acknowledgments

The authors are grateful to Marco Scambelluri, to Maria Luce Frezzotti and to an unknown Reviewer, whose comments, suggestions and corrections have notably improved the manuscript. This study has received financial support from the Projects CGL 2009-08186 (Ministerio de Ciencia e Innovación, Spain) and C2012-31872 (Ministerio de Economía y Competitividad, Spain).

References

Akaogi, M., Akimoto, S., 1977. Pyroxene-garnet solid solution equilibria in the systems Mg,SiO₄–Mg,Al₂O₃, and Fe,SiO₄–Fe,Al₂O₃ at high pressures and temperatures. Physica of the Earth and Planetary Interiors 15, 90–106.
Alfrezoa, T.A., Pokhilenkoa, L.N., Ovchinnikova, Y.I., Donnellyb, C.L., Richesb, A.J.V., 2009. Evidence of peridotite melting during exhumation of subducted continental crust. Contributions to Mineralogy and Petrology 156, 490–502.

Auzanneau, E., Vielzeuf, D., Schmidt, M.W., 2006. Complete solid-solution between Na₃–Fe₃Al₂Si₃O₁₂ at high pressures and temperatures. American Mineralogist 91, 1137–1145.
Bozhilov, K.N., Green, H.W., Dobrzhinetskaya, L., 1999. Clinoenstatite in Alpe Arami melanges. Comptes Rendus de l’Académie des Sciences – Series 2 (316), 1595–1601.
Brunet, F., Bonneau, V., Irifune, T., 2006. Complete solid-solution between Na₄Al₃(PO₄)₃ and Mg₃Al₂(SiO₄)₃ garnets at high pressure. American Mineralogist 91, 211–215.

Carwell, D.A., Wilson, R.N., Zhai, M.G., 2000. Metamorphic evolution, mineral chemistry and thermobarometry of schists and orthogneisses hosting ultra-high pressure eclogites in the Dabie Shan of central China. Lithos 52, 121–155.

Davies, G.R., Nixon, P.H., Pearson, D.G., Ohta, M., 1993. Tectonic implications of graphitized diamonds from the Ronda peridotite massif, southern Spain. Geology 21, 471–474.
Frezzotti, M., Marchesi, C., 2009. Garnet Iherzolite and garnet-sinelite mylonite in the Ronda peridotite: vestiges of Oligocene backarc mantle lithospheric extension in the western Mediterranean. Geology 39, 927–930.
Goff, B., Richaud, A., García-Dueñas, V., González-Lodeiro, F., Monié, P., Campos, J., Galindo-Zaldívar, J., Jableby, A., Martínez-Martínez, J.M., Simancas, F., 1989. Evidence of high-pressure, low-temperature metamorphism in the Alparguareñi nappes, Betic Cordillera (SE Spain). European Journal of Mineralogy 1, 139–142.
Haggerty, S.T., Fang, A.T., Bart, W.J., 2003. Apatite, phosphorus and Ti humility in eclogitic garnet from the upper mantle. Geophysical Research Letters 21, 1699–1702.
Hermann, J., 2002. Experimental constraints on phase relations in subducted continental crust. Contributions to Mineralogy and Petrology 143, 37–50.
Hermann, J., Green, D.H., 2001. Experimental constraints on high pressure melting in subducted crust. Earth and Planetary Science Letters 188, 149–186.
Hermann, J., Spandler, C.J., 2008. Subduction melts at sub-arc depths: an experimental study. Journal of Petrology 49, 717–740.
Holland, T.J.B., Powell, R., 1998. An internally consistent thermodynamic data set for phases of petrological interest. Journal of Metamorphic Geology 16, 309–343.
Wang, S.L., Shen, P., Chu, H.T., Yui, T.F., 2000. Nanostructure Si-K₂O in garnet: an experimental study at high pressure and temperature. American Mineralogist 85, 724–737.
Wang, S.L., Yui, T.F., Chu, H.T., Shen, P., Schertl, H.P., Zhang, R.Y., Liou, J.G., 2007. On the origin of oriented rutile needles in garnet from UHP eclogites. Journal of Metamorphic Geology 25, 343–362.
Irifune, T., Sekine, T., Ringwood, A.E., Hlibberson, W.O., 1986. The eclogite-garnet transformation at high pressure and some geographical implications. Earth and Planetary Science Letters 77, 245–256.
Irifune, T., Ringwood, A.E., Hlibberson, W.O., 1994. Subduction of continental crust and terrigenous and pelagic sediments: an experimental study. Earth and Planetary Science Letters 126, 351–368.
Katayama, I., Parkinson, D.C., Okamoto, K., Nakajima, Y., Maruyama, S., 2000. Supersilicic clinopyroxene and silico clinopyroxene in UHP eclogite and pelitic gneiss from the Kokchetav massif, Kazakhstan. American Mineralogist 85, 1368–1374.
Kawasaki, T., Motosyoji, Y., 2007. Solubility of TiO₂ in garnet and orthopyroxene: Ti thermometer for ultrahigh-temperature garnets, U.S. Geological Survey and The Geological Society of America, 84 pages.
Liu, L., Yang, J., Zhang, J., Chen, D., Wang, C., Yang, W., 2009. Exsolution microstructures from peridotite and eclogite xenoliths. Nature 260, 696.
Lü, Z., Zhang, L.F., Du, J.X., Kurt, B., 2009. Petrology of coesite-bearing eclogite from the upper mantle. Geophysical Research Letters 21, 1699–1702.

Marchesi, C., Jabaloy, A., Martínez-Martínez, J.M., Simancas, F., 1989. First evidence of natural and synthetic coesite. Physic and Chemistry of Minerals 12, 45–48.
Massonne, H.-J., 2003. A comparison of the evolution of diamondiferous quartz-rich rocks from the Saxson Erzgebirge and the Kokchetav Massif: are they diamondiferous greenschist and eclogite facies or diamondiferous granulite facies? Planetary and Space Science 51, 347–364.

Massonne, H.-J., Fockenberg, T., 2012. Melting of metasedimentary rocks at ultrahigh pressure–insights from experiments and thermodynamic calculations. Lithosphere 4, 269–285.
Mecerreyes, J.-C., Nicholas, A., 1975. Textures and fabrics of upper-mantle peridotites as illustrated by xenoliths from basalts. Journal of Petrology 16, 454–487.
