Re-equilibration of primary fluid inclusions in peritectic garnet from metapelitic enclaves, El Hoyazo, Spain

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Primary-appearing fluid (FI) and melt (MI) inclusions occur in peritectic garnet from restitic enclaves from El Hoyazo (Spain). The inclusions were trapped under conditions of immiscibility during partial melting of the enclaves. Trapped fluids in Bt–Grt–Sil and Spl–Crd enclaves have been characterized by microthermometric, Raman spectroscopic, electron microprobe (EMP) and transmission electron microprobe (TEM) analyses to better constrain melt and fluid products and pressure conditions of the partial melting event. In Bt–Grt–Sil enclaves, FI are one phase and contain a CO2–N2 mixture, sometimes with graphite as trapped phase. In Spl–Crd enclaves, FI are two phase and contain an H2O-rich (≤50 mol%) mixture, with minor amounts of CO2, N2, and traces of H2S and CH4. Graphite often occurs as a trapped phase in the H2O-rich FI, and rare carbonates and other accessory minerals are also observed. Although decrepitation features are not recognized during examination with a petrographic microscope, FI densities based on mass balance constraints are always lower than expected at the inferred PT conditions of entrainment, 5–7 kbar and 800–900 °C. Extremely low densities (≈0.1 g cm−1) of FI in Bt–Grt–Sil enclaves suggest a pressure ≤500 bar at 800–900 °C, while densities up to 0.53 g cm−1 in Spl–Crd enclaves indicate P ≤ 3 kbar at 800–900 °C. Re-equilibration is likely to have occurred via partial decrepitation, as suggested by TEM studies that show rare partially annealed sub-mm cracks, containing small cavities, which may have been the pathways for fluid movement out of the inclusions. MI coexisting with FI have a rhombohedral, peraluminous composition, with higher H2O contents of MI in Spl–Crd enclaves (≈9 wt.%) compared to MI in Bt–Grt–Sil enclaves (≈3 wt.%). Based on published data, peritectic garnet in Spl–Crd enclaves grew in the presence of a leucogranitic melt saturated in an H2O-rich fluid, in good agreement with the inferred garnet PT growth conditions. The composition of the fluid phase coexisting with melt in Bt–Grt–Sil enclaves cannot be evaluated owing to the almost complete decrepitation and fluid loss from FI, and may only be inferred to have been more CO2-rich, based on the lower H2O content of the coexisting melt.

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1. Introduction

Partially melted metapelitic enclaves are abundant in dacitic lavas from the Neogene Volcanic Province (NVP) in southern Spain, and contain anatecti melt, preserved as an amorphous phase (glass) in intergranular layers, in microfractures and in melt inclusions. Studied enclaves underwent partial melting at 9.3–9.9 Ma, after which they resided at high-temperature (HT) conditions for 3 Ma before host dacite extrusion (Cesare et al., 2003; 2009b). Because of their unusual history, they represent a unique case of “migmatites-in-progress” rapidly brought to the surface by a volcanic eruption. Rapid cooling froze the residual melanosomes and allowed the preservation of many of the features that were present at depth. Preserved glass in these samples permits a direct characterization of the anatectic melt as it forms during crustal melting. In fact, many of the typical problems related to slow cooling of leucosomes in classic migmatite terrains, such as fractional crystallization, cumulus phenomena, and mixing with other source melts (Sawyer and Brown, 2008; Marchildon and Brown, 2001), are absent or minimized in these samples. Melt inclusions (MI) occur in many minerals in these samples and their microstructural and compositional characterization (Acosta-Vigil et al., 2007; Cesare et al., 2007) along with trace element studies (Acosta-Vigil et al., 2010), support the hypothesis that glass within MI is the anatectic melt produced during peritectic reactions. Moreover, the possibility of finding anatectic melt trapped as MI in more classic high-temperature settings is supported by an increasing number of case studies on migmatites from low-pressure settings (i.e., Ronda migmatites; Cesare et al., 2009b), from medium- to high-pressure rocks (i.e., Kerala Khondalite Belt; Cesare et al., 2009a) and from ultrahigh-pressure migmatites (i.e., Ulten Zone; Braga and Massonne, 2001).
2008). In the studied rocks, the host mineral and the melt trapped in glassy inclusions is co-genetic, i.e. products of the same dehydration melting reaction, and in this respect they differ from MI from deep-seated rocks reported in literature in terms of their origin and significance (e.g. Thomas and Klemm, 1997; Webster, 2006). In fact, most MI in deep-seated rocks reported in the literature occur in plutonic rocks, and the trapped melt has a genetic relationship with the host crystal. Moreover, granite-hosted MI normally show a compositional trend in major elements and volatiles (Webster and Thomas, 2006) caused by fractional crystallization of the melt, while the compositional variation of MI in El Hoyazo enclaves reflects the prograde history of the rock during partial melting, i.e., contributions from different minerals during the progress of dehydration–melting reactions (Acosta-Vigil et al., 2007, 2010).

Another peculiar aspect of the El Hoyazo enclaves is the occurrence of fluid–melt immiscibility. Anatectic melt was trapped along with a COH fluid phase in different minerals, including cordierite and plagioclase (Cesare et al., 2007) and garnet (Alvarez-Valero et al., 2005; this study). Fluid–melt immiscibility is a well known phenomenon that has been extensively studied using fluid inclusions (FI) (Roedder, 1992 and references therein), and has been recognized in mafic melts (Andersen and Neumann, 2001), silicic melts (De Vivo and Frezzotti, 1994), as a secondary feature accompanying the crystallization and/or outgassing of magma during cooling (Roedder, 1992), in ore-forming magmatic systems (Student and Bodnar, 2004), and has been reproduced experimentally using synthetic silicate melt and fluid inclusions (Student and Bodnar, 1999). In high grade, partially melted rocks, COH fluids are commonly reported (Touret, 2009), and the coexistence of a CO2–rich phase and a melt is expected because experimental studies (Holloway, 1976; Tamic et al., 2001) demonstrate the low solubility of CO2 in silicate melts. However, fluid–melt immiscibility is only seldom reported for granulites and migmatites (Touret, 1971, 1981), probably because MI and FI in HT peak minerals are likely destroyed by deformation and re-crystallization during the retrograde PT evolution. The enclaves from El Hoyazo have not experienced a long retrograde history, and therefore they preserve original formation conditions. We are aware that the P–T path suggested for the enclaves (e.g., Alvarez-Valero et al., 2007) is less favorable for the preservation of primary MI densities, as it should normally lead to inclusion decrepitation (see Touret, 2009, Fig. 3). However our choice was supported by numerous examples of preservation of high densities in FI from both crustal and mantle xenoliths (e.g., Ladenberger et al., 2009; Ertan and Leeman, 1999; Szabó et al., 1996), and by the fact that some of these previous studies dealt with inclusions with preserved densities in garnet (Pretorius and Barton, 2003; Tokor et al., 2005).

By focussing on garnet, one of the first peritectic phases to crystallize along with plagioclase (Acosta-Vigil et al., 2010), the present study aims to characterize the fluid phase during the initial stage of partial melting of the thinned crust beneath the NVP. From a more general point of view, our results add new constraints to the composition of the fluid phase coexisting with anatectic melt during partial melting of a metapelitic protolith.

2. Geological setting

The NVP is located in the Betic Cordillera, which forms the western termination of the Alpine orogen in the Mediterranean region, along with the Moroccan Rif (Fig. 1). The area is characterized by a thinned lithosphere, a consequence of the opening of the Alboran Domain in the late Tertiary (Comas et al., 1999). The upwelling of asthenospheric mantle caused anomalous heat flow, still present in the area, with partial melting of the lower crust and subsequent eruption or emplacement of large volumes of magmas of variable composition, ranging from basaltic andesites to rhyolites, between 15 and 2 Ma (Comas et al., 1999; Zeck and Williams, 2002; Duggen et al., 2004). Investigated enclaves were emplaced in a shallow submarine environment during the Upper Miocene (Zeck, 1970; Cesare et al., 1997) by upwelling high-K calc-alkaline to shoshonitic magmas. The
host lavas are considered largely syngenic with respect to the enclaves themselves, based on petrographic and isotopic evidence (Zeck, 1970; Munskgaard, 1984; Munskgaard, 1985; Perini et al., 2009), although the extent of contamination by mantle-derived magmas is still under debate (Benito et al., 1999; Turner et al., 1999; Duggen et al., 2005; Acosta-Vigil et al., 2007). The studied enclaves come from El Hoyazo, a small dome of peraluminous dacite in the SW of the NVP. This site is characterized by abundant crustal material (10–15 vol.%; Zeck, 1992) that mainly consists of Bt–Grt–Sil and Sp–Crd crustal enclaves. Petrological features of both enclave types have been characterized by several past studies (Zeck, 1970; Cesare, 2000; Cesare et al., 1997, 2000; Cesare et al., 1997, 2000; Cesare and Gomez-Pugnaire, 2001; Alvarez-Valero and Kriegsman, 2009; Alvarez-Valero and Waters, 2010; Kriegsman and Alvarez-Valero, 2009; Acosta-Vigil et al., 2007, 2010). Despite differences in their microstructures and mineral assemblages, probably reflecting compositionally different protoliths, both enclave types show 1) residual bulk composition, with quartz only present as mineral inclusions, due to extensive melt-extraction (30–60 wt.%, Cesare et al., 1997); 2) abundant graphite (≥ 1 wt.%, Cesare and Maineri, 1999) both as mineral inclusions and as large flakes parallel to foliation, accounting for a graphite-rich protolith, and 3) abundant glass, interpreted as anatectic melt (Cesare et al., 1997).

The occurrence of primary MI in almost every mineral of the assemblage suggests coexistence among melt and growing crystal phases such as garnet, ilmenite, biotite, spinel and plagioclase. While garnet and ilmenite commonly occur as peritectic phases from biotite melting, and therefore are expected to trap inclusions of anatectic melt, other minerals such as plagioclase and biotite are commonly reactants in melting reactions, and should not be enclosed melt. Cesare and Maineri (1999) explained this apparent paradox by suggesting that rapid heating induced disequilibrium melt production in Bt–Grt–Sil enclaves, according to a reaction such as:

\[ \text{Chl} + \text{Ms} + \text{Qtz} + \text{Ilm} + \text{COH fluid} = \text{Grt} + \text{Pl} + \text{Sil} + \text{Bt} + \text{Melt} + \text{Gr} \]

that involved a low-grade, graphite-rich protolith, similar to phyllites and schists outcropping in the Alpurrjade Complex of the Betic Cordillera. In the proposed process, the rocks quickly evolved from a low-temperature mineral assemblage to a melt-bearing one, bypassing several intermediate mineral equilibria reactions of the upper amphibolite facies. The products of the proposed reaction (in particular garnet, plagioclase and biotite) are consistent with the observed MI-bearing minerals in the studied samples. The petrological model for the anatectic of Bt–Grt–Sil enclaves has been recently refined by Acosta-Vigil et al. (2010) who proposed that MI trapped in garnet and plagioclase represent the melt produced during prograde heating of the sample, at 690 °C, before the metamorphic peak was reached at 850 °C (Cesare et al., 1997). The age of anatexis beneath El Hoyazo (9.3–9.9 Ma) was determined by Cesare et al. (2003, 2009b) via U–Pb dating on MI-bearing zircons and monazites, while the host dacite extrusion occurred at 6.3 Ma (Zeck and Williams, 2002).

The presence of a free fluid phase during partial melting of El Hoyazo enclaves, suggested by Cesare and Maineri (1999), is evidenced by the coeval entrapment of FI and MI, indicating melt-fluid immiscibility. Primary FI and MI in plagioclase and cordierite from Bt–Grt–Sil enclaves were studied by Cesare et al. (2007) to characterize their composition and to better constrain the depth at which anatexis took place. These FI contain a CO₂–N₂–CH₄ mixture, with > 85 mol% CO₂ and their densities define pressures of ≤ 0.5 kbar at the inferred temperature of trapping (800–900 °C), much lower than the pressure of 5–7 kbar estimated for the partial melting event. Back-calculated compositions of the original fluid phase coexisting with anatectic melt suggest that FI lost about 25 mol% of the original H₂O during leakage. Therefore, despite their primary appearance, FI inclusions underwent extensive re-equilibration, and the pressures derived from calculated isochores are, therefore, not representative of entrainment conditions. Cordierite from the same enclaves is almost H₂O-free and not in chemical equilibrium with melt at the estimated P–T conditions of formation (Della Ventura et al., 2009). In this case, it was proposed that H₂O loss from cordierite channels was due to the rapid decompression accompanying lava transport to the surface.

3. Petrography of the samples

Samples from the two main types of enclaves occurring at El Hoyazo — Bt–Grt–Sil and Sp–Crd enclaves — were examined in this study. Bt–Grt–Sil enclaves are the most abundant and occur as fragments ≤60 cm in maximum dimension. Their phase assemblage consists of variable proportions of garnet, plagioclase, biotite, sillimanite and glass, along with graphite, apatite, zircon and monazite, with ilmenite, cordierite, hercynitic spinel, or quartz irregularly distributed (Zeck, 1970; Acosta-Vigil et al., 2007). Generally, a fine-grained matrix surrounds large garnet porphyroblasts (≤ 1 cm in diameter) wrapped by Bt-rich folia (Fig. 2a). The matrix mainly consists of plagioclase and a fine-grained, sponge-like aggregate of fibrolitic sillimanite and glass (named “mix” by Cesare et al., 1997), forming irregular to elongated domains. Garnet porphyroblasts often show an inclusion-rich dark core containing biotite, graphite, MI and FI, surrounded by an inclusion-free rim of variable thickness (up to 2 mm). Porphyroblastic biotite, ranging from tens of μm to 4 mm, occur in the matrix of the rock. Plagioclase forms anhedral poikilitic crystals with dusty appearance owing to the abundance of inclusions of graphite and glass, along with minor fibrolite and biotite. Cordierite, when present, displays a similar inclusion assemblage, with additional FI.

Fibrolitic sillimanite is abundant both as a component of the “mix” and as inclusions in garnet, while in plagioclase and cordierite it is locally oriented, along with graphite, parallel to the main foliation of the samples. Around garnet, fibrolitic sillimanite and biotite-rich layers may define folded patterns, indicating a syn-anatectic deformation (Cesare, 2008).

In the field, Sp–Crd enclaves are smaller than Bt–Grt–Sil enclaves, with fragments ≤10 cm. Sp–Crd enclaves are fine-grained and show a closely spaced foliation, defined by oriented biotite and fibrolite, overprinted by porphyroblasts of hercynitic spinel ≤2 mm (Fig. 2b). Foliation often anastomoses around granoblastic domains formed by euhedral garnet, cordierite and plagioclase. Fibrolitic sillimanite and glass are present but not as abundant as in the Bt–Grt–Sil enclaves. Ilmenite, ± garnet, ± plagioclase, ± quartz, ± K-feldspar may also be present. Spinel porphyroblasts range from subhedral to euhedral in shape and are often surrounded by small coronas of cordierite or K-feldspar. Cordierite and plagioclase are often associated, the first as porphyroblasts interstitial among garnet crystals, the latter forming elongated grains parallel to foliation at the borders of the unfoliated domains. As in Bt–Grt–Sil enclaves, both cordierite and plagioclase are dusty, and contain mainly FI, MI and graphite. In places, partially resorbed biotite and oriented fibrolite also occur. Garnet in Sp–Crd enclaves is less abundant, and smaller in size (≤2 mm), than in Bt–Grt–Sil enclaves. It crystallizes in euhedral or elongated crystals, depending on its microstructural environment. Garnet is euhedral and inclusion-free in statically re-crystallized domains, while it is subhedral and inclusion-rich in strongly foliated domains, where it displays a variable aspect ratio of up to 10:1 (Alvarez-Valero et al., 2005) and is characterized by a dark, dusty, sometimes circular core (Figs. 2b, 3a). Dark domains are surrounded by an asymmetrical inclusion-free external area up to 150 μm thick, which is better developed parallel to foliation. Inclusions at the garnet core are the same as in garnets in the previous enclave type, along with rare plagioclase. Where garnet cores host large (≤50 μm across) biotite flakes, inclusions define a circular pattern around the core, with
inclusion-free zones surrounding biotite (Alvarez-Valero et al., 2005). The process of elliptical garnet formation is due to a process of localized dissolution-re-precipitation, as defined by Alvarez-Valero et al. (2005).

Glass, representing former anatectic melt, is abundant in both Bt–Grt–Sil and Spl–Crd enclaves. Glass may occur as layers (≤ 100 μm), parallel to foliation, as thin films coating garnet and spinel porphyroblasts and as inclusions (≤ 50 μm) in almost all minerals, the most important being garnet, cordierite, biotite, spinel and plagioclase. Melt inclusions often occur in the interior of the host minerals, in a microstructural position that suggests primary trapping (Roedder, 1984) during host growth. MI are not present in sillimanite.

![Fig. 2](image-url)

**Fig. 2.** a) Common occurrence of garnet in Bt–Grt–Sil enclaves. Garnet porphyroblasts, with inclusion-rich core in a matrix formed by biotite, fibrolite and sillimanite in a fine sponge-like aggregate (Mix). Plagioclase porphyroblasts display a typical dusty aspect, as a result of the abundance of inclusions. Scale bar: 3 mm. b) Elliptical garnets, with inclusion-rich core, in Spl–Crd enclaves. A well-developed foliation, defined by biotite and mix is clearly visible. Biotite also grows in garnet pressure shadows, locally overgrowing garnet (black arrow). Cordierite forms poikiloblastic crystals in less deformed domains. White arrow: well-developed elliptical garnet. Scale bar: 500 μm.

![Fig. 3](image-url)

**Fig. 3.** Photomicrographs of FI and MI in garnet from Spl–Crd enclaves. a) Characteristic round garnets in sample AVHZ13. The garnet core is dark because of the high abundance of small FI and other mineral inclusions. The rim of the garnet is usually clear and inclusion-free. Scale bar: 100 μm. b) Inclusions in the dark core. Biotite, fibrolite (Fib), FI and MI, along with graphite (white arrows) can be recognized. Scale bar: 100 μm. c) Two-phase, vapor-rich inclusions. Black arrow: graphite trapped in a FI. White arrows: two small FI secondary FI arrays. Scale bar: 40 μm. d) Mixed inclusion with a two-phase fluid portion, formed by liquid H₂O, wetting the lower part of the bubble, and vapor CO₂. The clearest portion is glass. Scale bar: 40 μm.
however this phase is genetically associated with melt represented by the glass in the mix aggregate, and probably only the small crystal size prevented sillimanite from trapping MI. Acosta-Vigil et al. (2007, 2010) studied in detail the microstructural features and compositions of MI in different minerals and matrix from Bt–Grt–Sil enclaves. The glasses have a leucogranitic and peraluminous composition, with systematic differences among melts trapped in different minerals, possibly related to melt evolution during partial melting process of metapelites. In Spl–Crd enclaves, chemical compositions are available only for interstitial melt layers (Alvarez-Valero et al., 2005), where glass shows a peraluminous and rhyolitic composition, similar to that from Bt–Grt–Sil enclaves.

4. Samples and methods

Approximately 20 normal thin sections and doubly polished thick sections from two Spl–Crd enclaves (samples HO19 and AVHZ13) and from one Bt–Grt–Sil enclave (sample HO50) were examined to characterize fluid inclusions, melt inclusions and garnet host. Sample preparation and petrographic examination were conducted at the Department of Geosciences, University of Padua, Italy. The microthermometric (MT) study and Raman analyses were performed at the Department of Geosciences, Virginia Tech, USA. About 40 FI, recognized as primary and belonging to the same fluid inclusion assemblage (FIA, Goldstein and Reynolds, 1994), were analyzed using a USGS-type gas-flow heating and cooling stage (Werre et al., 1979), mounted on an Olympus BX51 microscope and a Linkam THMSG 600 °C programmable heating/cooling stage, mounted on an Olympus BX60 microscope. The accuracy of measurements is ±0.1 °C in the range −100/−31 °C and ±1 °C in the range 250/340 °C. Stage calibration was done using synthetic CO2–H2O synthetic FI standards (Sterner and Bodnar, 1984).

Raman analyses were accomplished using a Jobin-Yvon Horiba HR 800 LabRAM microprobe equipped with an Ancor electronically cooled charge-coupled device (CCD) detector and operated in confocal mode with the slit width set to 150 μm and confocal aperture set to 400 μm. The excitation source is a 514.57 nm Ar-ion laser, and the microprobe is coupled with an Olympus BX 41 petrographic microscope. The irradiation power measured on the samples was 3–4 mW. For quantitative measurements, spectra were acquired using an 80× objective and spectra were collected between 1000 cm−1 and 4200 cm−1, integrating 5 cycles of 10–20 s for each measure and using a grating of 600 g mm−1. Spectral resolution was about 1.5 cm−1. Qualitative Raman analyses were conducted on ~200 FI. The gas (vapor-bubble) portion of 68 FI was also quantitatively analyzed, and the gas density was estimated for 21 of the 68 analyzed FI, using the densimeter developed by Kawakami et al. (2003) and improved by Fall et al. (2011). The densimeter is based on the relative position of the CO2 Fermi diad of Raman peaks, whose separation distance is density-dependent (Wang and Wright, 1973). These analyses were conducted using an 80× objective, spectral window between 1150 and 1450 cm−1, integrating 5 cycles of 20–30 s for each determination, and using a grating of 2400 g mm−1. The spectral resolution using these analytical conditions is ~0.3 cm−1. Molar ratios of the gaseous phases, χa, were calculated using the relation

\[ \chi_a = \frac{A_\alpha}{(\alpha_\alpha A_\alpha) / \sum_i(A_i / (\alpha_i A_i))} \]

where \( A_\alpha \) is the area of the characteristic Raman peak (or band), \( \alpha_\alpha \) the Raman scattering cross section (Burke, 2001) and \( \alpha_i \) is the Raman instrument correction factor for the component a. The correction factors, previously determined for the Raman instrument in the Fluids Research Laboratory at Virginia Tech using a standard gas mixture are IFCO2 = 0.9, IFN2 = 1.1, IFH2S = 1.

Electron microprobe (EMP) analyses of MI in garnet from Spl–Crd samples were performed at the High Temperature/High Pressure Laboratory, I.N.G.V. (Istituto Nazionale Geofisica e Vulcanologia), Rome, using a Jeol JXA 8200 Superprobe. Analyses were conducted with a 1.5 μm beam, 10 kV accelerating voltage and 2.96 nA current, using as standard a rhodochrosite glass. Na, K, Al and Si were analyzed first to eliminate the influence of alkali loss on the counting statistics on the two most abundant elements (Si, Al), using 10 s counting times on the peak and 5 s on the background, and applying a ZAF data correction.

Transmission electron microscopy (TEM) was carried out in the Earth Science Department, University of Siena, Italy using a JEOL 2010 microscope, operating at 200 kV, with LaB6 source, ultrahigh resolution pole pieces and 0.19 nm point-to-point resolution. The microscope is equipped with an ultra-thin window energy dispersive spectrometer (EDS – ISIS Oxford). TEM grids were extracted from polished thin sections of two garnets and thinned by Ar+ ion-milling (Gatan Dual Ion Mill), at 20°–5 kV and at 12°–1.5 kV. In TEM samples, electron-transparent portions are typically thinner than ~100 nm, thus micrometer-sized inclusions would have lost their fluid content during ion-milling.

5. Results

5.1. Fluid and melt inclusion petrography

In Spl–Crd enclaves HO19 and AVHZ13, most FI are <5 μm (Fig. 3b), and only a very few are up to 25 μm (Fig. 3) and suitable for microthermometry. The analyzed FI are two phase (L+V), and vapor-rich (ca. 60–80 vol%) at room temperature. Their shape ranges from isometric to tubular (Fig. 3c). Toward the garnet rim the abundance of FI can decrease both abruptly or gradually and sometimes the boundary between the fluid inclusion-present zone and the fluid inclusion-absent zone defines a surface resembling the crystallographic face of the garnet. Most often the outer part of the host garnet is FI-free (Fig. 3a). The largest FI are often entrapped close to the cluster boundary. Locally the FI-rich core extends to the grain boundary, probably due to a strain-solution process (Alvarez-Valero et al., 2005). In a few cases, FI form pseudosecondary arrays that do not cross the cluster boundaries. Almost all the garnets display some cracks crossing the entire crystal. Studied FI have been selected from domains free of visible microfractures.

The presence of melt inclusions (Fig. 3b–d) in Spl–Crd enclaves was reported by Alvarez-Valero et al. (2005), and here we expand on their description and analyses. MI are ≤8 μm in size, ovoidal to tubular in shape, and contain a clear, homogeneous glass with a shrinkage bubble. A third type of inclusion contains both melt and fluid in proportions ranging from ~100% fluid (end-member FI) to almost 100% melt (end-member MI with shrinkage bubble). These inclusions are referred to as mixed inclusions (Lowenstern, 2003; Frezzotti et al., 1994; Cesare et al., 2007), and occur locally in the Spl–Crd enclaves, seldom with a two-phase fluid portion (Fig. 3d). Mixed inclusions are usually larger (≤40 μm) than both MI and FI, and may contain graphite as a trapped mineral phase. Both MI and mixed inclusions are less abundant in this type of enclaves compared to Bt–Grt–Sil xenoliths.

The occurrence of FI, MI and mixed inclusions in clusters in the garnet core suggests a primary origin for the inclusions and that they all belong to the same FIA. The three inclusion types would have been trapped during a single event, under conditions of immiscibility between anatectic melt and fluid (Roedder, 1992; Cesare et al., 2007). Many garnets show partially healed fractures that contain secondary FIAs comprised of small, highly irregular one phase FI (Fig. 3c).

Preliminary Raman data from these FI show a CO2-rich vapor at room T and minor amounts of CH4. No further studies have been carried out on these secondary FI.

In the garnet, graphite is the most abundant mineral inclusion, forming lamellae 10 to 200 μm in width. Anhedral biotite, ≤200 μm,
and needles of fibrolite, with diameter ≤ 1 μm, are often present in the garnet. The presence of biotite and sillimanite often appears to inhibit the formation of FI and MI in their immediate vicinity inside the cluster (see also Acosta-Vigil et al., 2007). Conversely, graphite appears to favor the entrapment of FI and MI during crystal growth. In places, FI may contain a few crystalline phases, and the most common is graphite. Because of its size, which is always too large to be reasonably considered a daughter mineral, and because of its random distribution with respect to the fluid or melt inclusion, graphite is considered a trapped mineral (Fig. 3c, see also Cesare and Maineri, 1999). Rare carbonates have been identified via Raman analyses and FESEM imaging in a few FI (<5% of total observed inclusions). Rare zircon and xenotime are also present and are likely to be phases trapped during FI formation. Except for graphite, present in 5 of the 40 studied inclusions, no accessory minerals were found in FI analyzed in the microthermometric study.

In the Bt–Grt–Sil enclave, garnet porphyroblasts display an inclusion-rich core (Fig. 4a), with the outer limits of the inclusion-rich zone often resembling crystal faces (Fig. 4a, b). As in the Spl–Crd enclaves, FI, MI, mixed inclusions and mineral inclusions (mainly graphite and biotite) occur in the same cluster. Several secondary assemblages of FI are visible, often crossing the cluster borders (Fig. 4b). Many cracks are visible in the garnet, both in the core and in the rim, often intersecting both mineral and fluid/melt inclusions. Nonetheless, several crack-free domains were identified, hosting FI suitable for microthermometric study. Generally, FI in Bt–Grt–Sil enclaves are smaller (≤ 15 μm) and less abundant than in the Spl–Crd enclaves. All of the fluid inclusions are one phase at room temperature, with isometric shape varying from spherical to negative-crystal (Fig. 4c). Raman analyses were performed at elevated T to search for evidence of H2O, according to the technique of Berkesi et al. (2009), but no H2O was detected. Graphite is the only solid phase found in the FI.

Most inclusion assemblages in garnet consist of MI and mixed inclusions. As in the Spl–Crd enclaves, this occurrence confirms the primary origin of the inclusions (Roedder, 1984) and the presence of melt-fluid immiscibility during garnet growth. Melt inclusions are ≤ 150 μm, with irregular (Fig. 4d) to negative-crystal shape (Fig. 4c). Acosta-Vigil et al. (2007) provide a detailed description of microstructures and compositions of melt inclusions from sample H050, the same sample studied here. Anhedral graphite, both fine-grained (∼5 μm) and coarser, and subhedral biotite (≤ 200 μm) are present (Fig. 4d), but are less abundant compared to the Spl–Crd enclaves.

5.2. Microthermometry

FI from the Spl–Crd enclaves showed phase transitions during microthermometry (MT), while no phase transitions were detected within FI from Bt–Grt–Sil enclaves.

![Photomicrographs of FI and MI in garnet from Bt–Grt–Sil enclaves. a) Subhedral garnet, surrounded by a foliation defined by biotite and sillimanite (enlargement of Fig. 2a). Inclusions of various types (MI, FI, mixed inclusions, and mineral inclusions) display a clear zonal arrangement, often with straight boundaries (black arrow), and characterize the garnet core. Scale bar: 2 mm b) Limits of the cluster in Fig. 4a. In this sample cluster borders often resemble the crystallographic face of the garnet. Black arrow: secondary FI array. Scale bar: 100 μm. c) Detail of a cluster, showing the occurrence of FI (white arrow), MI (black arrow) and mixed inclusions (gray arrow) with different volume percentages of fluid portions, trapped under conditions of immiscibility. Scale bar: 25 μm. d) Irregularly-shaped mixed inclusions with different proportions of trapped fluid. White arrows: Graphite is visible as a trapped phase inside both the melt and the fluid portion of the mixed inclusions and as mineral inclusions in the host garnet. Euhedral biotite is visible on the right side of the picture. Scale bar: 40 μm.](image-url)
In Spl–Crd samples, on heating from −180 °C, the melting of solid CO₂ \( (T_m^{CO_2}) \) and total homogenization \( (T_h) \) were observed, while homogenization of the CO₂-rich portion \( (T_h^{CO_2}) \) was never detected. The MT study shows slight differences among FI from sample HO19 and those from sample AVHZ13. FI in garnet from sample HO19 show a \( T_m^{CO_2} = -60 \) to \(-56.8 \) °C and the total \( T_h = 332-339 \) °C; they homogenize via critical behavior with fading of the meniscus between vapor and liquid. In a few FI, the formation of clathrates was also recognized, with \( T_m^{cla} = +9.2 \) to \(+9.8 \) °C. FI in garnet from sample AVHZ13 have \( T_m^{CO_2} \) in the range −64.7 to −58.3 °C, and total \( T_h = 335-339 \) °C to vapor. MT data are plotted in histograms on Fig. 5a and b.

Measured \( T_m^{CO_2} \) values in both samples are generally lower than −56.6 °C, suggesting the presence of volatiles other than CO₂ in the vapor portion of the inclusion for both samples, with slightly higher amounts in AVHZ13 (see Fig. 5a). The clathrate melting, observed in a few inclusions, indicates a low salinity for the aqueous phase. The high \( T_h \) values are consistent with a high \( X_{H_2O} \) in the inclusion, probably \( \geq 0.80 \) mol% (Takenouchi and Kennedy, 1964; Bodnar et al., 2009), with a density equal to (HO19) or lower than (AVHZ13) the critical density. The CO₂-rich fluid portion of the inclusions appears to contain a single phase, even at the melting point of the CO₂-solid. However, we cannot exclude the possibility that a thin film of liquid CO₂ may be

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**Fig. 5.** Microthermometric data for 36 FI from the Spl–Crd enclaves. a) Histogram of the CO₂ melting temperature; b) Histogram of the total homogenization temperature.

---

**Fig. 6.** Example of Raman spectra of FI in garnet from Spl–Crd enclave (see inset and Fig. 3c). The blue spectrum, indicating a CO₂-rich fluid, has been collected in the vapor portion (blue dot) of the FI; the H₂O-rich red spectrum was collected in the liquid portion (red dot).
present around the outer portion of the CO₂ bubble and be optically unresolvable. In any case, the microthermometric data are consistent with a low density CO₂-rich mixture in the vapor phase of the inclusions.

The total density and bulk composition of the inclusions could not be estimated from microthermometric data, owing to the lack of Th values. For this reason, composition and density were estimated using a mass balance calculation, based on available MT and Raman data (method described in Appendix A).

### 5.3. Raman spectroscopy

In Spıt–Crd enclaves, the gas portion of two-phase FI consists mainly of CO₂ and N₂, while the liquid portion contains H₂O (Fig. 6). All analyzed FI show CO₂ peaks (ν₁ and ν₂) at 1388 cm⁻¹ and 1285 cm⁻¹, respectively, an N₂ peak at 2336 cm⁻¹, and a broad band for H₂O between 3100 and 3600 cm⁻¹. Sample HO19 may also contain H₂S both in the gas phase (2611 cm⁻¹) and in the liquid H₂O phase (2579 cm⁻¹), and also CH₄ (2916 cm⁻¹) in a few cases. One-phase FI from Br–Grt–Sil enclaves contain CO₂ and N₂, whereas H₂O was not detected.

In sample HO19, the average composition of the vapor phase is 84 mol% CO₂, 15 mol% N₂ and 1 mol% H₂S (Table 1). CH₄ has been detected in only 5% of the analyzed inclusions, with an average content of 3 mol%. The vapor portion of FI from sample AVHZ13 has a similar average composition, 80 mol% CO₂ and 20 mol% N₂, with higher compositional variation towards higher amounts of N₂ (up to 60 mol% N₂ in one FI), compared to sample HO19. The fluid trapped in FI from Br–Grt–Sil enclaves is a mixture of CO₂ and N₂ in variable proportions (CO₂ = 41–81 mol%), with an average composition of 55 mol% CO₂ and 45 mol% N₂. Results for Br–Grt–Sil enclaves are summarized in Table 1 and reported in detail in Table 3.

### 5.4. Total composition, density and isochore determination

#### 5.4.1. Composition and density of FI from Spıt–Crd enclaves

As previously stated, failure to recognize a homogenization transition for the carbonic portion of FI in Spıt–Crd enclaves prevented us from estimating total composition and density based on microthermometric data alone (see Diamond, 2001, Fig. 7). Bulk compositions and total densities of FI in Spıt–Crd enclaves were thus determined using data from petrographic observation and Raman analysis, employing the CO₂ densimeter of Fall et al. (2011) and the mass balance calculation method described in Appendix A. Calculated densities (ρ_g), and bulk compositions (mol%) of trapped fluid obtained by this approach are reported in Table 2.

Fluid inclusions trapped in HO19 contain 78–91 mol% H₂O, 7–18 mol% CO₂ and 0–4 mol% N₂, while fluid composition in AVHZ13 shows a wider range in H₂O (44–84 mol%) and N₂ content (2–21 mol%). Knowing the molar fractions of the components, total densities of fluid inclusions were calculated using the same mass balance method as before (Table 2). Densities range from 0.27 to 0.53 g cm⁻³, where the highest value corresponds to a composition of 90 mol% H₂O, 8 mol% CO₂ and 2 mol% N₂.

#### 5.4.2. Densities of FI from Br–Grt–Sil enclaves

Total density was calculated using LonerW, from Software Package FLUIDS, v.2 (Bakker, 2009), assuming T = 22 °C (ambient temperature during Raman analysis) and FI internal pressure derived for each FI using the NIST database (Lemmon et al., 2009). Resultant FI densities (Table 3) range from 0.05 to 0.10 g cm⁻³ and are notably lower than densities of FI from Spıt–Crd enclaves.

#### 5.4.3. Isochore calculation

The fluid trapped in Spıt–Crd enclaves can be approximated by the CO₂–H₂O binary, and this is especially appropriate for the highest

### Table 1

<table>
<thead>
<tr>
<th>Enclave type</th>
<th>Sample</th>
<th>CO₂ mol%</th>
<th>N₂ mol%</th>
<th>H₂S mol%</th>
<th>CH₄ mol%</th>
<th>Accessories</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spıt–Crd</td>
<td>HO19A</td>
<td>75–100 (av. 84)</td>
<td>24-0 (av. 15)</td>
<td>≤ 3</td>
<td>≤ 7</td>
<td>± Gr ± Cal</td>
</tr>
<tr>
<td>Grt–Br–Sil</td>
<td>HOS0</td>
<td>35–90 (av. 80)</td>
<td>65–10 (av. 18)</td>
<td>0</td>
<td>0</td>
<td>± Gr ± Cal ± Zn ± Xtm</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Spıt–Crd enclaves</th>
<th>Raman data on vapor portion</th>
<th>Values from NIST database</th>
<th>Mass balance calculation results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>FI name</td>
<td>CO₂ mol%</td>
<td>N₂ mol%</td>
</tr>
<tr>
<td>HOS19</td>
<td>flincAgtr11</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>flincBgrt11</td>
<td>78</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>flincCgtrt1</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>flincDgtrt1</td>
<td>81</td>
<td>18</td>
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<tr>
<td></td>
<td>flincEgrt1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>flincEgtrt1</td>
<td>83</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>flinc1</td>
<td>80</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>flinc2</td>
<td>82</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>flinc3</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>flincBgrt1</td>
<td>82</td>
<td>17</td>
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<td></td>
<td>flincCgtrt1</td>
<td>81</td>
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<td></td>
<td>flincEgtrt1</td>
<td>90</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>flinc10</td>
<td>84</td>
<td>15</td>
</tr>
<tr>
<td>AVHZ13</td>
<td>A</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>74</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>M</td>
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<td>P</td>
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<td>F</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>97</td>
<td>3</td>
</tr>
</tbody>
</table>
density Fl from sample HO50. The calculated bulk compositions and densities were used as input data in the software NEWTWO (Connolly and Bodnar, 1983; Bodnar et al, 2009), to determine the isochores for every measured fluid inclusion. This software uses a modified Redlich–Kwong equation of state, developed to calculate the volumetric properties in the CO₂–H₂O system. The required input parameters are $X_{CO_2}$, $T_h$ and $P_h$ (pressure at homogenization). $P_h$ is grossly derived from available thermophysical data (Lemmon et al., 2009). Then the value is refined and more precisely estimated by performing several iterations and comparing the total density and CO₂ density predicted by the algorithm with the same parameters obtained via mass balance calculation and Raman analyses, until the output parameters match the mass balance calculation parameters. Isochores for Fl in Bt–Grt–Sil enclaves were determined using the software package FLUIDS, Program 2: ISOC, version 01/03 (Bakker, 2003), applying the EOS developed by Holloway (1977) and Flowers (1979) for CO₂–N₂ mixtures. The isochore determined for the lowest density Fl of sample HO50 are almost flat (Fig. 7) and provide hypothetical entrapment pressures of ~500 bar (in the 700–900 °C range), far from the inferred P–T trapping conditions of 800–900 °C and 5–7 kbar.

### 5.5. TEM study of host garnet from Bt–Grt–Sil enclaves

Calculated fluid densities show that, if Fl in Bt–Grt–Sil enclaves were trapped at the peak P–T conditions, they have experienced a larger density decrease compared to Fl in Spl–Crd enclaves (see below). For this reason, sample HO50 was characterized by TEM, to search for cracks, dislocations or other structural discontinuities at the nanometer scale that could have been pathways for fluid loss from the Fl during re-equilibration. Dark cores (containing abundant Fl) from two different garnet crystals were selected for this investigation. Low magnification TEM images show several subospherical Fl (Fig. 8a), larger than 1.5 μm and representing approximately the smallest size Fl detectable using the optical microscope. As a consequence of thinning procedures, these “large” inclusions are always empty in the TEM sample, and the surrounding garnet is poorly transparent to electrons. Fig. 8a shows a “large”, 2.5 μm, subospheral to negative-crystal-shaped inclusion. The surrounding garnet structure appears to be free of dislocations or other defect structures. Low magnification TEM images also revealed the occurrence of other “large” pockets and cracks containing a poorly-crystalline to amorphous material, very likely representing glass in microfractures such as those shown in Fig. 4b, c.

### Table 3

Summary of compositional data (based on Raman analysis and mass balance calculation) on Fl from Bt–Grt–Sil enclaves. $pCO_2$ = density estimated from Raman-based CO₂ densimeter (Fall et al., 2010). For explanation of the calculation method see Appendix A.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fl name</th>
<th>CO₂ mol%</th>
<th>N₂ mol%</th>
<th>$\rho_{CO_2}$ NIST (g cm$^{-3}$)</th>
<th>$\rho_{NIST}$ Database (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO50 1a</td>
<td>60</td>
<td>40</td>
<td>0.086</td>
<td>38</td>
<td>0.07</td>
</tr>
<tr>
<td>HO50 2a</td>
<td>47</td>
<td>53</td>
<td>0.086</td>
<td>38</td>
<td>0.07</td>
</tr>
<tr>
<td>HO50 3a</td>
<td>81</td>
<td>19</td>
<td>0.106</td>
<td>43</td>
<td>0.09</td>
</tr>
<tr>
<td>HO50 4a</td>
<td>58</td>
<td>42</td>
<td>0.059</td>
<td>28</td>
<td>0.05</td>
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<tr>
<td>HO50 5a</td>
<td>65</td>
<td>35</td>
<td>0.094</td>
<td>40</td>
<td>0.07</td>
</tr>
<tr>
<td>HO50 6b</td>
<td>42</td>
<td>59</td>
<td>0.225</td>
<td>60</td>
<td>0.10</td>
</tr>
<tr>
<td>HO50 7b</td>
<td>42</td>
<td>58</td>
<td>0.098</td>
<td>41</td>
<td>0.06</td>
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</table>

### Table 4

Electron microprobe (EMP) data for melt inclusions in Spl–Crd enclave sample HO19.

<table>
<thead>
<tr>
<th>No. analyses</th>
<th>15 (Std dev)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>68.95</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.10</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.85</td>
</tr>
<tr>
<td>FeO</td>
<td>1.32</td>
</tr>
<tr>
<td>MnO</td>
<td>0.16</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
</tr>
<tr>
<td>CaO</td>
<td>0.68</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.25</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.56</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.16</td>
</tr>
<tr>
<td>F</td>
<td>0.01</td>
</tr>
<tr>
<td>H₂O by diff.</td>
<td>8.97</td>
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<tr>
<td>#Mg</td>
<td>0.03</td>
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<tr>
<td>ASI</td>
<td>1.30</td>
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</table>

<table>
<thead>
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<th>Normative minerals</th>
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<tbody>
<tr>
<td>Cor</td>
</tr>
<tr>
<td>Qtz</td>
</tr>
<tr>
<td>Ab</td>
</tr>
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<td>Or</td>
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</tr>
<tr>
<td>Hyan</td>
</tr>
<tr>
<td>Ilm</td>
</tr>
<tr>
<td>Ap</td>
</tr>
</tbody>
</table>

Fig. 7. PT diagram with isochores of Fl in garnet from Spl–Crd and Bt–Grt–Sil enclaves. Each isochore represents a single fluid inclusion. Box A: inferred P–T conditions of the metamorphic peak/anatectic event for enclaves from El Hoyazo (after Cesare et al., 1997). Box B: proposed P–T conditions of formation of Fl-bearing garnet from Bt–Grt–Sil enclaves (after Acosta-Vigil et al., 2010). Box C: P–T conditions of enclaves after eruption of host dacite on the sea floor.
In addition to the “large” micrometer-sized inclusions, the dark garnet cores also host trails of nanometer-sized FI (Fig. 8b, c). These FI are often aligned along dark contrast features, indicative of crystal structural strain, and reasonably corresponding to structural discontinuities such as nanofractures or dislocations. These structural discontinuities connect all inclusions in the trail and are similar to features observed by Vityk et al. (2000) associated with FI in quartz that had been experimentally re-equilibrated to cause fluid leakage. The shape of nanometer-sized inclusions ranges from rounded, “drop-like” to negative-crystal shaped (Fig. 8d and e, respectively). Fig. 8e shows the details of the connection between an inclusion and structural defects (i.e. the linear feature on the right side of image).

Microstructures associated with partially decrepitated FI include linear crystal defects, or trails of secondary fluid inclusions if the cracks are partially annealed, often with a radial arrangement around decrepitated FI (Vityk et al., 2000; Viti and Frezzotti, 2001). Unfortunately, due to the small field of view on electron-transparent areas, the geometric relationships between isolated micrometer-sized inclusions and trails of nanometer-sized inclusions are not clear, and direct emanation of trails from large inclusions could not be observed. However, it seems realistic to consider these nanometer-sized trails as the path for fluid transport out of inclusions during re-equilibration.

5.6. Composition of MI in Spl–Crd enclaves

The glass in MI from Bt–Grt–Sil enclave HO50 was thoroughly characterized by Acosta-Vigil et al. (2007, 2010). In the present study, we analyzed the glasses hosted in MI and mixed inclusions from Spl–Crd enclaves by EMP. Sodium loss during EMP analysis is on average 57% relative, estimated using a rhyolitic standard analyzed at the same operating conditions: although such a Na loss is notably high, similar values have been already reported by Cesare et al. (2009a). Therefore, melt analyses have been corrected by increasing Na2O by 57% relative, and decreasing SiO2 and Al2O3, in a manner similar to that discussed in Cesare et al. (2009a). Results (Table 4) indicate a peraluminous, rhyolitic and felsic melt composition, with average SiO2 = 69 wt.%, K2O = Na2O (average values 4.5 and 2.2 wt.% respectively), low CaO (0.6 wt.%), and (FeO+MgO+TiO2) b 1.5 wt%. The magnesium number is low (X_Mg = 0.03). The H2O content has been assumed to be the difference between the EMP total and 100%. This approach allows the estimation of the water content of granitic glasses with a precision of 10% relative, as shown by Morgan and London (1996) and Acosta-Vigil et al. (2003). The H2O values obtained by this difference method are variable, but generally high and compatible with a melt saturated in an H2O-rich fluid at the inferred PT conditions of garnet growth, as also suggested by the average ASI value (1.30). Except for the markedly higher average H2O content (8.9 wt.% vs. 2.7 wt.%) of melts in the Bt–Grt–Sil enclaves, these melts from the Spl–Crd enclave are similar to those occurring in MI from sample HO50 (Acosta-Vigil et al., 2007).

6. Discussion

El Hoyazo enclaves were rapidly transported and emplaced on the surface by upwelling magmas. In this setting, crystals hosting FI are subject to a sudden change in confining pressure. This can lead to FI reequilibration in the form of partial (leakage) to total (decrepitation), with formation of microfractures on the FI walls or decrepitation haloes surrounding the original FI (Szabó and Bodnar, 1996). In garnet from Spl–Crd and Bt–Grt–Sil enclaves, FI lack optical evidence of decrepitation, and their microstructural features suggest that they
were trapped during garnet growth and in a condition of fluid–melt immiscibility. Although few partially healed cracks are visible in the garnet core in the studied samples, portions of the Fl + MI clusters seem completely unaffected by this brittle deformation event (Figs. 3b, 4d). Assuming that these inclusions are primary, their calculated low densities are incompatible with those expected for the inferred garnet growth conditions.

6.1. Density decrease: causes and conditions

The reported discrepancy in PT conditions inferred by Fl isochores and geothermobarometry suggests that the Fl density decreased after entrapment, and may have occurred either in a closed system (with no loss of material), or by more extensive leakage of components and their removal from the vicinity of the Fl.

The first hypothesis, i.e closed-system density decrease, may be ruled out. In fact, mass balance calculations and lack of noticeable amounts of carbonates indicate the impossibility that either Fl stretching (for details see Bodnar, 2003) or step-daughter precipitation processes (Kleinefeld and Bakker, 2002; Heinrich and Gottschalk, 1995) took place. Similarly, closed-system re-equilibration of a COH fluid along a decreasing temperature path (Cesare, 1995) would have produced easily detectable amounts of graphite within inclusions, and can be also ruled out.

The most likely process to cause the decrease of Fl density is a (partial) decrepitation (see e.g. Bodnar, 2003 and references therein). Although such re-equilibration process should be expected in the El Hoyazo enclaves, owing to their large departure from an isochoric P–T path, we could not identify any microstructural evidence of decrepitation by optical investigation. TEM imaging of garnet from Bt–Grt–Sil enclaves revealed the presence of trails of sub-micron (≤200 nm) Fl. Although no trails were observed that originated from larger Fl, we propose that they may represent escape pathways for the fluid that was originally trapped in inclusions. No TEM images were collected on Spl–Crd enclaves, but the presence of similar cracks may be inferred based on the recorded densities, suggesting that Fl opened and resealed during uplift of the enclaves to the surface.

Trapped fluids in the two different enclave types appear to have leaked to different extents. In Spl–Crd enclaves, the highest density Fl would have lost 50 wt.% of the original water, assuming only H2O removal and an original density of 0.73 g cm−3 (an isochore drawn for this density would intersect the PT field defined by box “A” in Fig. 7). The required loss would be even greater for the other measured inclusions in the Spl–Crd enclaves. In Bt–Grt–Sil enclaves the loss of components from Fl was almost complete, given the low density of the Fl (0.1 g cm−3). Petrological characterization of the same sample (Acosta-Vigil et al., 2010) indicates that Fl must have contained H2O at entrapment, but water is no longer detectable, suggesting total H2O removal. Relative amounts of CO2 and N2 in Fl in Bt–Grt–Sil enclaves are more variable than in Spl–Crd enclaves. This fact, combined with the extremely low densities, suggests that, in addition to water, some CO2 may have also been lost from the inclusions during re-equilibration.

Isochores for the Fl clearly define two groups, depending on the enclave type, and represent different degrees of re-equilibration. Isochores are steeper and more scattered for Spl–Crd enclaves, while isochores are almost flat and are more tightly grouped for the Bt–Grt–Sil enclaves (Fig. 7). Given the assumption that both samples followed the same PT path, such a difference in isochores must reflect different Fl behavior during decompression.

Hard minerals such as quartz and garnet are expected to re-equilibrate by brittle deformation of the Fl walls when overpressure in the Fl reaches a critical value (ΔP = Pinternal − Pexternal). In this present study, Fl in garnet in Spl–Crd enclaves partially decrepitated at ΔP ≥ 3 kbar, while in Bt–Grt–Sil enclaves the ΔP was around 5.5 kbar. The common result is the formation of micro-(nano-) cracks, as observed at TEM observation scale. These cracks may or may not connect the inclusions to the exterior of the garnet host. In the first case, fluid loss and the resultant Pfluid (and density) would be controlled by Pext at the moment of Fl resealing, whereas, in the second case, microcracking would decrease density by increasing Fl volume (through cracks opening) and by fluid leakage, but with no influence from the Pfluid, and then Fl resealing would have been instantaneous. In the latter case, however, garnet would have to increase its volume to accommodate the space needed for the fluid expansion in the host.

Isochores for Spl–Crd enclaves span a range of 3 kbar at 850 °C. If the cracks extended to the edge of the garnet host, Fl re-equilibration at El Hoyazo occurred as a diachronous process, in which the Fl re-equilibrated at different depths during uplift, each re-equilibration event independent from the others. Assuming that enclaves remained at T—800 °C until the eruption, then the highest density Fl would have been the first ones to open (and reseal) at ≈3 kbar. Conversely, the lowest density Fl would have been the last to reseal at ≈1 kbar. Such a spread in the re-equilibration P within the same host mineral (even within the same grain) may reflect the effect of Fl size. Generally, smaller Fl (average size = 15 μm) tend to re-equilibrate at higher ΔP values, compared to larger ones (Bodnar, 2003). In the case of El Hoyazo, ΔP increases as the enclaves is brought toward the surface, and the last re-equilibrated Fl should be the smaller ones. However, the lack of a size-density correlation for the El Hoyazo Fl precludes this possibility. It also seems unlikely that several primary Fl, belonging to the same FaA and in the same host, would have behaved so differently by re-equilibrating at different depths. If the microcracks were not connected to the exterior of the garnet host, then Fl re-equilibration at El Hoyazo was a synchronous process. As stated before, there is no density-size correlation among measured Fl, so it is likely that every inclusion underwent decrepitation at the same depth of ≈3 kbar (re-equilibration depth for the less re-equilibrated Fl). The resulting densities would depend only on the ability of garnet to develop a more or less extended system of micro-(nano-) cracks around each Fl, with variable volume increase and density decrease. Based on these considerations, synchronous partial decrepitation seems more likely for Spl–Crd enclaves. Conversely, in Bt–Grt–Sil enclaves, the abundance of cracks of different scales, ranging from mm to nm (Figs. 4b, c, 8b, c), may have allowed Pfluid to be controlled by Pext. Therefore, calculated isochores suggest that Fl resealed at a shallow depth (at a pressure of about 500 bar), very close to the time of eruption of the enclaves onto the seafloor.

Although both enclave types followed the same PT path, their Fl underwent different extents of fluid loss. One factor that may have influenced host garnet behavior during decompression is the amount of inclusions, especially MI, in the garnet core. MI (and Fl) are much more abundant in Bt–Grt–Sil enclaves than in Spl–Crd enclaves. Inclusions act as defects in the crystal lattice, likely weakening its structure and making the large garnets in the Bt–Grt–Sil enclaves most susceptible to fracturing. In this case, Fl may have opened at depth, during uplift, and resealed later, when enclaves reached shallower crustal levels, allowing a more extensive fluid loss.

The occurrence of re-equilibrated Fl in garnet is consistent with re-equilibration of inclusions found in cordierite and plagioclase in other samples (Cesare et al., 2007), and demonstrates that enclaves lost part of their fluid component during their uplift to the surface. Loss of channel H2O from cordierite during decomposition from 5 kbar and equilibration at shallow levels has also been reported by Della Ventura et al. (2009) for El Hoyazo enclaves.

6.2. Composition of fluids and implications for anatexis

Fl in garnet from Spl–Crd enclaves contain an H2O–CO2 mixture, although they experienced a significant density decrease. Because water and carbon dioxide tend to behave differently when leakage

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occurs (Hollister, 1990), we should consider how the variable leakage of components affected the bulk composition of the fluid.

Generally, because of its higher wetting angle (Watson and Brenan, 1987), H$_2$O is more likely than CO$_2$ to infiltrate any microcracks opened on the FI walls, if leakage occurs when H$_2$O and CO$_2$ are unmixed. In this study, enclaves were brought to the surface by a magma with a temperature of ~800 °C. Therefore, trapped fluid was in a supercritical, homogeneous state until final cooling (after the enclaves were emplaced on the seafloor), since the two-phase (liquid + vapor) field does not extend to such high temperatures for low salinity H$_2$O—CO$_2$ mixtures (Takenouchi and Kennedy, 1964; Schmidt and Bodnar, 2000). Preferential water removal from quartz-hosted FI with homogenous H$_2$O—CO$_2$ fluids is discussed by Hollister (1990), who proposes that water may be selectively removed from the inclusions if the host mineral undergoes ductile strain, even if the fluid is in the one-phase (supercritical) state. However, this type of strain environment is unlikely for the El Hoyazo enclaves, because the enclaves were rapidly transported to the surface in a fluid medium (magma), and observed nanocracks likely developed because of the sudden decompression during eruption.

If leakage of a homogeneous fluid occurred, only the density of the FI would have changed and the original composition would be preserved. Conversely, if H$_2$O is preferentially removed, both the density and the composition would have changed. Estimated compositions for Sp–Crd enclaves show a range of H$_2$O/CO$_2$ from 13 to 1 that is consistent with H$_2$O preferential leakage. However, the extremely low densities found in Bt–Grt–Sil enclaves HO50 suggest the leakage involved all fluid components.

The original fluid composition in Sp–Crd enclaves may be back-calculated, assuming that H$_2$O removal occurred during re-equilibration. Since the highest density FI would have lost around 50 wt.% of the original H$_2$O content (see Section 6.2), the original trapped fluid composition is estimated to have contained around 95 mol% H$_2$O.

Given the microstructural evidence, the aqueous fluid was trapped along with a peraluminous leucogranitic melt, now enclosed in garnet as MI, under conditions of fluid–melt immiscibility. The estimated fluid composition is consistent with compositions reported for a COH fluid in equilibrium with a saturated melt (Eggler and Kadik, 1979; Tamic et al., 2001) in the range 700–800 °C. The water content of the melt within MI of Sp–Crd samples, estimated by difference from EMP totals, is ~9 wt.% (Table 4). This value is close to saturation values of 10–12 wt.% H$_2$O (Johannes and Holtz, 1996; Holtz et al., 2001) proposed for a rhyolitic melt at 700 ± 20 °C and 6 kbar (Acosta-Vigil et al., 2010) in the presence of a pure H$_2$O fluid. The average ASI value of the Sp–Crd samples is 1.30, and is close to values of 1.31–1.37 predicted for H$_2$O-saturated melting at 700–800 °C (Acosta-Vigil et al., 2003).

Fluid was also trapped under conditions of fluid–melt immiscibility in garnet in Bt–Grt–Sil inclusions, and as in Sp–Crd enclaves, glass is peraluminous and leucogranitic, and has similar major element composition, but lower average H$_2$O and ASI (2.7 wt.%, and 1.17, respectively; Acosta-Vigil et al., 2007). Because the fluid coexisting with such melt is expected to contain H$_2$O (Johannes and Holtz, 1996), H$_2$O loss from the currently H$_2$O-free FI must have been complete.

To our knowledge, this is the first case study in which partially melted metapelites — the Sp–Crd enclaves— contain H$_2$O-rich FI that are in clear microstructural coexistence with anatectic melt. FI studies on HT rocks from the lower crust commonly report other types of compositions, such as CO$_2$–rich fluids or brines (Touret, 2009). Conversely, low salinity, H$_2$O-dominated fluids are common in upper-crustal, subvolcanic rocks.

The presence of H$_2$O-rich fluids in partially melted metapelites should be the rule rather than exception, as long as anatectic occurs at relatively low temperatures. This general premise is clearly supported by experimental evidence (e.g., Holtz et al., 2001) showing that the mole fraction of H$_2$O in the fluid in equilibrium with melt is >0.4 for T <750 °C. In the case of El Hoyazo, at least for Sp–Crd enclaves, the presence in the core of garnet crystals of an almost pure aqueous phase coexisting with a water-rich (~10 wt.%) leucogranitic melt is in agreement with the model of anatexis proposed by Acosta-Vigil et al. (2010) of garnet nucleation and growth during the first stages of the partial melting history of the residual enclaves.

After partial melting, the fast quenching during eruption preserved the Sp–Crd enclaves from the post entrapment processes (including preferential H$_2$O loss) commonly recognized in retrogressed granulites.

Although rare, FI in garnet from Sp–Crd enclaves provide important evidence for the existence of an H$_2$O-rich fluid during the production of anatectic leucogranitic melt in metapelites in nature, until now only predicted by melting experiments. Moreover, the occurrence of both melt and fluid inclusions in garnet supports the possibility for trapping in peritectic minerals the products of the partial melting of metapelitic rocks, in accordance with previous work on El Hoyazo enclaves (Cesare et al., 2007; Acosta-Vigil et al., 2007).

7. Summary

Primary-looking fluid inclusions in garnet in El Hoyazo enclaves re-equilibrated following entrapment, as has been observed in other host phases from the same rocks (Cesare et al., 2007). Re-equilibration occurred via partial decrepitation, without leaving detectable evidence at the optical scale. Higher resolution studies (TEM) document the occurrence of rare, partially annealed cracks at sub-μm scale, containing small cavities, which may have been the escape pathways for fluids that leaked from inclusions. Peritectic garnet in Sp–Crd enclaves trapped an H$_2$O–rich (≤95 mol%) fluid during growth, under conditions of fluid–melt immiscibility with a water-rich leucogranitic melt. Melt and fluid compositional parameters (H$_2$O content, ASI value) suggest garnet growth around 700 °C, in agreement with a model proposed by Acosta-Vigil et al. (2010). Owing to the almost complete decrepitation and fluid leakage, it is not possible to estimate the original composition of fluids hosted in garnet from Bt–Grt–Sil inclusions. Based on the H$_2$O content of coexisting melt inclusions (Acosta-Vigil et al., 2007) we infer that this fluid was more CO$_2$–rich than the fluid in the Sp–Crd enclaves.

The present study expands the dataset on fluid inclusions formed during anatectic in the lower crust of the Alboran Domain, by characterizing the garnet-hosted fluid phase that coexisted with anatectic melt, as has been done previously for melt and fluid inclusions in cordierite and plagioclase (Cesare et al., 2007). Although final results clearly show that enclaves lost part of the original fluids, this work adds further compositional constraints to the characterization of anatectic of metapelites in the lower crust.

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Appendix A

Mass balance calculation method

The bulk composition of H2O-bearing fluid inclusions was estimated using a mass balance calculation. The reader is also referred to Bodnar et al. (1985) and to Lin et al. (2007) for a detailed description of the assumptions and limitations of this method. The first step to determine the composition and density of the two-phase FI in Spl–Crd xenoliths is to determine the volume proportions of the aqueous and gas phases at room temperature. This was accomplished by first collecting a digital image of each inclusion and determining the areas of the aqueous and vapor phases using image-analyses software, and then converting these values into volume percentages of the liquid and vapor phases assuming a tubular cylindrical shape (see Bodnar et al., 1985; Fig. 5.3, 5.7, 5.12). This assumption may underestimate the volume of the carbonic vapor phase by about 10–20% relative. The mole percent CO2 in the inclusion will be similarly slightly underestimated based on this volume error. However, a more accurate estimate of the volume percentages cannot be accomplished without complete knowledge of the exact shape of the inclusions (see Anderson and Bodnar, 1993).

The density of the CO2 phase in the FI was estimated using the Fall et al. (2011) densimeter, previously described. Peak positions were measured at 35 °C, which is above the critical temperature of CO2 (31.1 °C), using a Linkam THMSG600 heating/cooling stage mounted on the Raman microprobe, to assure that the CO2-rich phase was homogeneous during the analyses. For each inclusion, the pressure corresponding to the calculated CO2 density was determined, and then the density of N2 was estimated at this same pressure and 35 °C using the available thermophysical data (Lemmon et al., 2009). The density of H2O is assumed to be 1 g cm−3 in all of the inclusions at the conditions of analyses (35 °C).

Using the compositions, volume proportions and densities of individual phases estimated as described above, the total inclusion composition and density were calculated based on mass balance considerations. Assuming that the total mass of “vapor” (CO2 + N2) in the FI = Mgas, total, the masses of the individual gas species are given by

\[ m_{\text{species}} = \text{wt. fraction}_{\text{species}} \times M_{\text{gas, total}} \]  

(1)

where \( \text{wt. fraction}_{\text{species}} \) represents the weight fractions of the individual gas species (CO2 or N2) determined by Raman analyses, and \( M_{\text{gas, total}} \) represents the sum of the masses of CO2 and N2 in the FI. For simplicity, we have assumed that the total mass of gas equals 1 g (the actual mass does not matter, as the final calculation involves only mass fractions and not total mass). The volume occupied by each gas species \( V_{\text{species}} \) in the FI is given by:

\[ V_{\text{species}} = m_{\text{species}} / \rho_{\text{species}} \]

(2)

where \( \rho_{\text{species}} \) represents the density of each component that has been determined previously from Raman analyses. The total volume of the gas phase, \( V_{\text{gas, total}} \), equals the sum of the volumes of the individual gas species according to:

\[ V_{\text{gas, total}} = V_{\text{CO2}} + V_{\text{N2}} \]

(3)

Then, the total volume of the FI \( (V_{\text{FI, total}}) \) is given by

\[ V_{\text{FI, total}} = V_{\text{gas, total}} / \text{vapor fraction} \]

(4)

where \( \text{vapor fraction} \) is the volume fraction of the inclusion that is occupied by the gas phase that was determined as described above. The volume of H2O in the FI is given by:

\[ V_{\text{H2O}} = V_{\text{FI, total}} - V_{\text{gas, total}} \]

(5)

and the mass of H2O in the inclusion is given by:

\[ m_{\text{H2O}} = V_{\text{H2O}} \times \rho_{\text{H2O}} \]

(6)

where \( \rho_{\text{H2O}} \) = 1 g cm−3. The total density of the FI is then given by:

\[ \rho_{\text{FI, total}} = \left( m_{\text{CO2}} + m_{\text{N2}} + m_{\text{H2O}} \right) / V_{\text{FI, total}} \]

(7)

References


