

# What can high-*P* sheared orthogneisses tell us? An example from the Curinga–Girifalco Line (Calabria, southern Italy)

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## Abstract

High-*P* (HP) mineral parageneses are usually poorly developed within metagranitoids, as these rocks are commonly affected by fluid-deficient conditions when experiencing a metamorphic cycle. However, since ductile shear zones can act as preferential pathways for fluids in the Earth's crust, if metagranitoids are involved in ductile shear under HP conditions, the presence of fluids during deformation can induce recrystallization and equilibration in these rocks. With this in mind, we investigate the formation and evolution of mineral assemblages in the orthogneisses of the Castagna Unit from the northern Serre Massif (Calabria, southern Italy). During Alpine tectonics, the thrusting along the Curinga–Girifalco Line juxtaposed these rocks, representative of the Hercynian intermediate crust, below the lithologies of the Hercynian lower crust. A detailed microstructural study of the orthogneisses, sampled along a progressively increasing ductile deformation gradient, revealed a variation in the mineral assemblage between the weakly deformed orthogneisses and those in the shear zone. Phase diagram calculations in the MnNCKFMASHTO system indicate that the progressive replacement of relict minerals by new, Alpine minerals in the shear zone, was related to the presence of fluids during deformation. This allowed equilibration of the sheared orthogneisses up to metamorphic peak conditions of ~0.9–1.0 GPa and ~560–590°C. Our integrated study highlights that both weakly deformed and mylonitic orthogneiss share the same peak metamorphic conditions, and that the new equilibrium mineral assemblage was stabilized in the mylonitic orthogneisses along a fluid-conservative prograde path, where no fluid was added or lost. After metamorphic peak, the fluid was channelled towards the inner part of the shear zone, with fluid-present conditions that were restricted to the mylonitic orthogneisses close to the tectonic contact. These mylonitic orthogneisses record cooling and exhumation to 0.6–0.7 GPa and 360–400°C, showing an overall anticlockwise *P–T* path. By comparing our findings with existing structural studies, we highlight that the Castagna Unit was under-thrusted to lower-crustal depths during the Alpine orogeny, before the re-activation of the Curinga–Girifalco Line during the Oligocene to Miocene extensional tectonic phase, that enabled the exhumation of this unit.

## KEYWORDS

Alpine Calabria, anticlockwise *P–T* path, ductile shear zones, fluid–rock interactions, HP metagranitoids

## 1 | INTRODUCTION

Modelling the pressure ( $P$ )–temperature ( $T$ ) path of metagranitoids that experienced high- $P$  (HP) metamorphism is one of the most intriguing challenges in metamorphic petrology. This is because, under closed-system conditions, the (very) low fluid content in these rocks, which is inherited from the magmatic protolith, commonly hinders the development of HP parageneses (e.g. Biino & Compagnoni, 1992; Compagnoni & Rolfo, 2003; Massonne, 2015; Proyer, 2003). The most recurrent HP index mineral in metagranitoids is garnet, which is characterized by a  $X_{Ca} > 0.2$  (Carswell et al., 2000; Le Goff & Ballèvre, 1990; Massonne, 2015; Proyer, 2003) and is commonly associated with quartz+K-feldspar+albite+phengite+epidote+spinel/rutile±biotite (Carswell et al., 2000; Giuntoli et al., 2018; Le Goff & Ballèvre, 1990; Maldonado et al., 2018; Massonne, 2015; Menold et al., 2009; Proyer, 2003; Xia et al., 2012; Young & Kylander-Clark, 2015; Zucali, 2011).

Le Goff and Ballèvre (1990) demonstrated the problematic uses of conventional thermobarometers to estimate  $P$ – $T$  conditions for the metamorphic peak in HP metagranitoids. According to these authors, (a) the garnet–biotite Fe–Mg thermometer suffers from problems related to the high-grossular activity of garnet when it is applied to these rocks, and (b) the phengite barometer of Massonne and Schreyer (1987) needs independent temperature estimate along with corrections for the Fe–Mg partitioning between phengite and biotite.

Another crucial aspect of HP metagranitoids concerns the usual presence of corona textures and non-concentric zoning patterns of garnet and white mica (e.g. Bruno et al., 2001; Zucali, 2011), which reflect local equilibration. In addition to the local equilibration affecting these rocks, the Fe-rich composition of garnet, at a  $P \geq 1.0$  GPa, suggests  $H_2O$ -undersaturated conditions (Proyer, 2003).

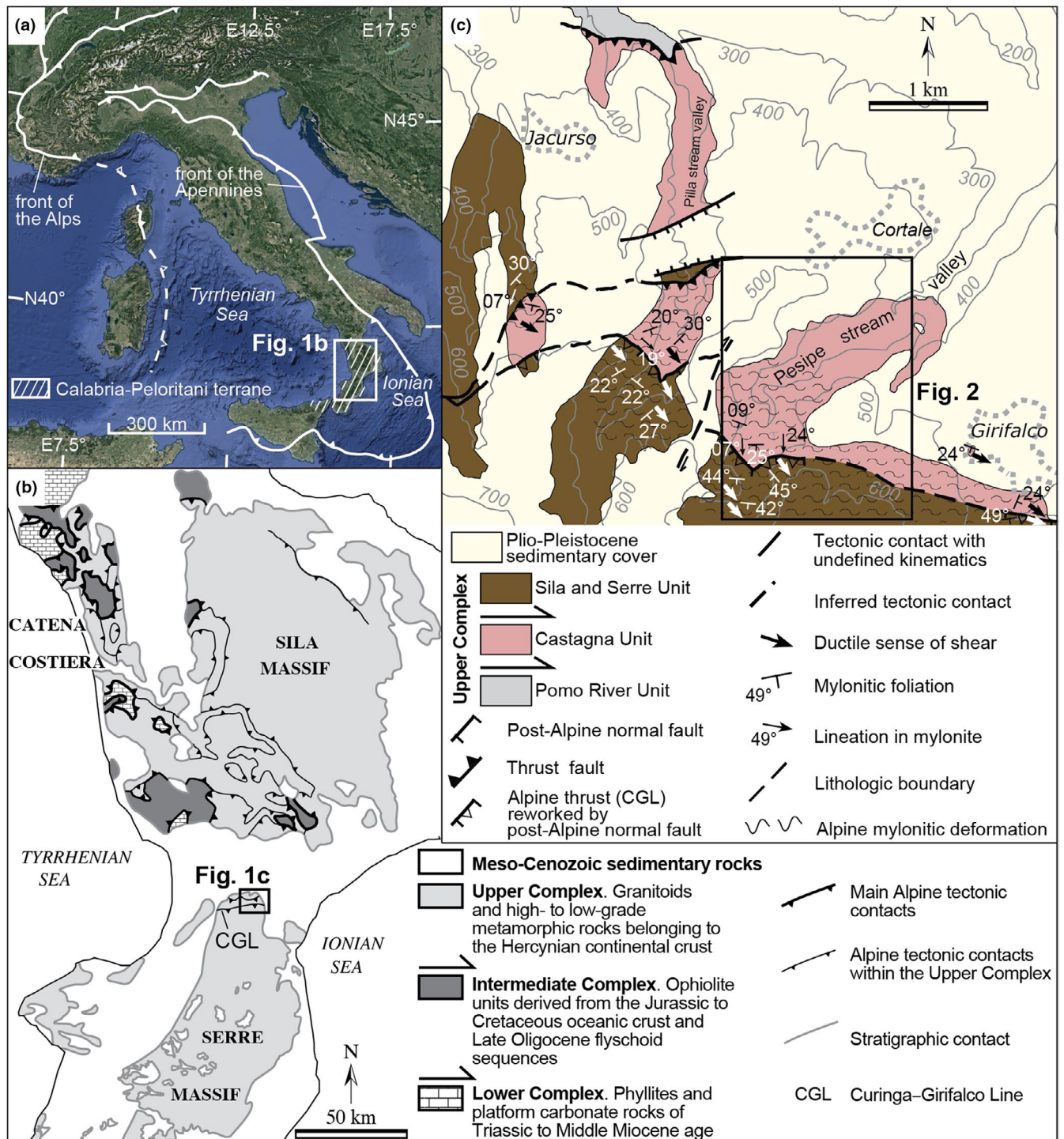
According to Pattison et al. (2011) and Pattison and Tinkham (2009), the catalytic role exerted by fluids on metamorphic reactions could be critical for the (a) stabilization of HP mineral assemblages in metagranitoids, and (b) their preservation or restoration during exhumation (Guiraud et al., 2001; Proyer, 2003; Young & Kylander-Clark, 2015). Proyer (2003) investigated the preservation of HP mineral assemblages in metagranitoids in relation to the rock's fluid budget. The author concluded that: "... Metagranitoids do not easily record or preserve high pressure conditions, either because of metastable persistence throughout the high-pressure section of the  $P$ – $T$  path or because of significant dehydration during exhumation ...". More recently, Young and Kylander-Clark (2015) conducted a comparative thermodynamic study among different lithologies that were metamorphosed at HP conditions, considering also metagranitoids. The authors investigated whether the mineral assemblage of these rocks was prograde or retrograde with respect to the peak metamorphic

conditions attained, considering the available fluid budget in the rock with respect to the modes of the OH-bearing minerals. In contrast to Proyer (2003), Young and Kylander-Clark (2015) concluded that HP metagranitoids should retain part of their prograde mineral assemblages but should not convert further without additional water influx. Moreover, the breakdown of OH-bearing minerals, such as white mica, during exhumation may not trigger a complete retrogression in HP metagranitoids, as a result of the low modal abundance of these mineral phases in these rocks. Furthermore, it is well known that deformation can also play a major role in promoting mineral stabilization (Bell & Hayward, 1991; Holyoke & Tullis, 2006; Waters & Lovegrove, 2002). In this sense, ductile shear zones that developed in felsic rocks are an ideal setting to study deformation-enhanced recrystallization, particularly if deformation was coupled to fluid–rock interactions during shearing (e.g. Tursi et al., 2018, and references therein).

Therefore, to investigate the role of fluid in the stabilization of mineral HP parageneses in deformed metagranitoids, a case where these rocks were affected by ductile shearing is considered in the present study. In particular, we focussed on the orthogneisses of the Castagna Unit that outcrop along the Curinga–Girifalco Line (CGL) in the northern Serre Massif (Calabria, southern Italy). The reconstruction of the  $P$ – $T$ –fluid path that was experienced by these rocks is attempted for the first time, relating the mineral compositions and zoning patterns of phengite and garnet to the fluid-present/deficient conditions during shearing.

## 2 | GEOLOGICAL SETTING

The Calabria–Peloritani terrane (Figure 1a; Amodio-Morelli et al., 1976; Bonardi et al., 2001) is an orogenic pile consisting of three main groups of stacked tectonic units (Figure 1b). From the bottom to the top, these can be summarized as follows: (a) the Lower Complex, which is characterized by Apennine units with Meso-Cenozoic phyllites and partly metamorphosed carbonate rocks showing a HP (~1.4 GPa) and low- $T$  (LT) (~390°C) metamorphic imprint (Iannace et al., 2007); (b) the Intermediate Complex, which is composed of ophiolite units of the Ligurian Tethys' oceanic lithosphere (Liberi et al., 2006), that records HP/LT Eocene metamorphism with peak conditions at ~2.0–2.1 GPa and 470–490°C (Tursi, Bianco, et al., 2020); (c) the Upper Complex, which consists of an Hercynian continental crust, showing a local Alpine metamorphic overprint at 0.3–0.7 GPa and 200–450°C in the Sila Massif and Catena Costiera (Acquafredda et al., 1994; Graessner & Schenk, 2001; Liberi et al., 2011; Ortolano et al., 2020; Piccarreta, 1981) and up to 1.1–1.2 GPa and 540–570°C in the Aspromonte Massif (Cirrincione et al., 2008).



**FIGURE 1** (a) Sketch of the current position of the Apennines and Alpine fronts. (b) Geological sketch map of central and northern Calabria-Peloritani terrane. (c) Structural sketch map of the Curinga-Girifalco Line (CGL) in the vicinity of the village of Girifalco; the light grey stippled lines delimit the villages of Jacurso, Cortale and Girifalco. Modified after Festa et al. (2020), according to Festa et al. (2004), Langone et al. (2006), Carminati and Doglioni (2012), and Altenberger et al. (2013)

In Calabria, the Upper Complex is composed from the bottom to the top, of: (a) the Fiume Pomo Unit (Colonna, 1998), (b) the Castagna Unit (Paglionico & Piccarreta, 1976), and (c) the Sila and Serre Unit (Figure 1b; Festa et al., 2004, and references therein). In this study we focus on the tectonic contact between the Castagna and the Sila and Serre units.

The Castagna Unit primarily consists of late-Hercynian, low-amphibolite facies orthogneisses, minor paragneisses, and amphibole-bearing lenses (e.g. Colonna & Piccarreta, 1975). The orthogneisses have magmatic protoliths dated at *c.* 545 Ma (Fornelli et al., 2020; Micheletti et al., 2007, 2011) and show bulk chemical compositions ranging from granite

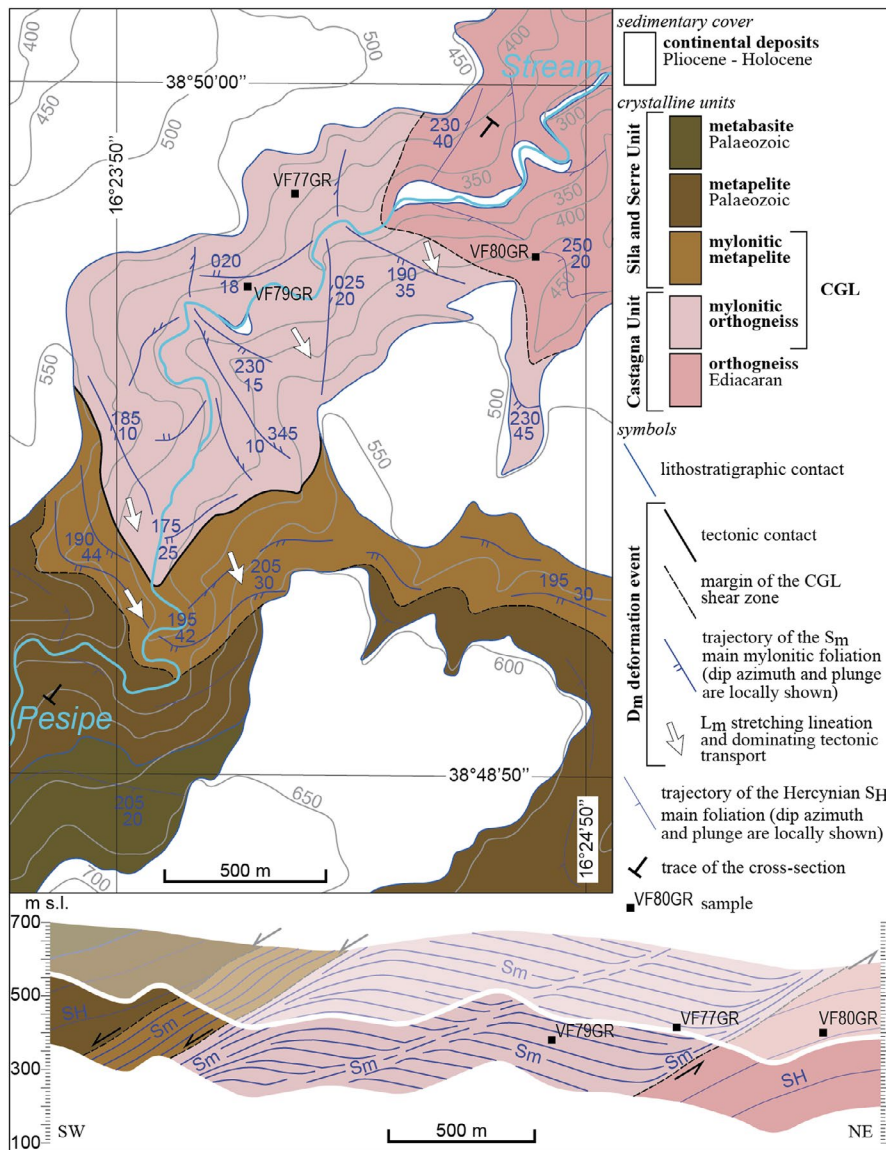


to granodiorite (Fornelli et al., 2007). The primary magmatic and sedimentary rocks of the Castagna Unit were involved in the Hercynian orogeny under lower amphibolite facies conditions (Brandt & Schenk, 2020; Ortolano et al., 2020), and subsequently in the Alpine tectonics.

The Sila and Serre Unit consists of a nearly complete Hercynian continental crust section with a thickness of ~22–23 km (e.g. Caggianelli et al., 2013). From the bottom to the top, the Sila and Serre Unit comprises: (a) lower crustal mafic and felsic granulites that are overlain by migmatitic paragneisses (Schenk, 1980); (b) tonalitic to granitic igneous bodies emplaced at mid-crust levels at around 280–300 Ma (Caggianelli et al., 2000, 2013; Langone et al., 2014); (c) upper crust amphibolite to greenschist facies paragneisses and phyllites (Angi et al., 2010; Festa et al., 2013, 2018; Tursi et al., 2020).

In the northern Serre Massif, the Castagna Unit and the lower crust rocks of the Sila and Serre Unit are juxtaposed

along a prominent Alpine tectonic contact: the CGL (Langone et al., 2006; Schenk, 1980, 1981; Spiegel, 2003), which is characteristically exposed in the Girifalco locality (Figure 1c). According to Schenk (1981) and Langone et al. (2006), the Castagna Unit is overlain by the Sila and Serre Unit along this shear zone (Figure 2). Here, ductile deformation dated at *c.* 43 Ma by Schenk (1980) through the Rb–Sr isotopic system on biotite, has developed a considerable thickness of mylonitic rocks (~200–400 m) in both units (Langone et al., 2006; Paglionico & Piccarreta, 1976, 1978; Spiegel, 2003). According to Langone et al. (2006), the Alpine metamorphic overprint is recorded in the orthogneisses of the Castagna Unit by garnet showing grossular-poor core with grossular-rich overgrowths, and by the occurrence of new, fine-grained phengitic white mica. These authors applied conventional geothermobarometers to orthogneisses and amphibolite lenses, and estimated the *P–T* conditions of ductile shearing



**FIGURE 2** Detailed structural geological map of the Pesipe Stream valley and cross-section throughout the CGL; the location of the samples studied in the present paper is indicated on the map and projected on the cross-section. In the cross-section, the white line represents the topography, and the light upper part is the extrapolation. The mylonitic foliation  $S_m$ , interpreted as map scale S-planes and C-type shear bands, can be appreciated (modified after Festa et al., 2020)

to be  $\sim 0.75\text{--}0.9$  GPa and  $525\text{--}570^\circ\text{C}$ . Similar  $P\text{--}T$  estimates were obtained for the sheared pseudotachylyte veins and the ultramylonitic layers that affect the mylonitic lower crustal rocks of the Sila and Serre Unit near the tectonic contact with the Castagna Unit orthogneisses (Altenberger et al., 2011, 2013). Later, (late Eocene?) early Oligocene–early Miocene (30–15 Ma) extensional shearing and reactivation occurred along the CGL (Festa et al., 2020), with cataclasites and un-sheared pseudotachylyte veins that developed at  $T < 300^\circ\text{C}$  (Thomson, 1998) in a brittle environment, in confinement to the tectonic contact (Langone et al., 2006; Spiegel, 2003).

## 2.1 | Orthogneiss field geology and sampling

The shearing effects produced by Alpine ductile deformation on the orthogneiss of the Castagna Unit are evident alongside transects from the host rock towards the contact with the Sila and Serre Unit, especially in the Pesipe Stream valley (Figure 2). Here, Festa et al. (2020) interpreted the mylonitic foliation  $S_m$ , in terms of map scale S-planes and C-type shear bands, and calculated a remarkable thickness of  $\sim 700$  m for the mylonitic orthogneiss of the CGL (Figure 2).

The weakly deformed orthogneiss (Figure 3a) contains centimetre in size K-feldspar and quartz porphyroclasts (or ‘augen’) (e.g. Figure 3b) in a grey–white quartzofeldspathic fine-grained matrix, that alternates with mica-rich layers, dominated by biotite. Moving towards the contact with the Sila and Serre Unit, a progressive grain size reduction of the K-feldspar and quartz porphyroclasts (up to millimetre in size), characterizes the mylonitic orthogneisses (Figure 3c–f). The variations in the mineral assemblage, that are associated with the grain size reduction along the transect in Figure 2, are highlighted in the following by referring to samples collected approaching the contact with the Sila and Serre Unit, namely from weakly deformed orthogneiss (sample VF80GR) to mylonitic orthogneiss (sample VF77GR) and mylonitic leucocratic orthogneiss (sample VF79GR).

## 3 | MICROSTRUCTURES AND MINERAL CHEMISTRY

### 3.1 | Methods

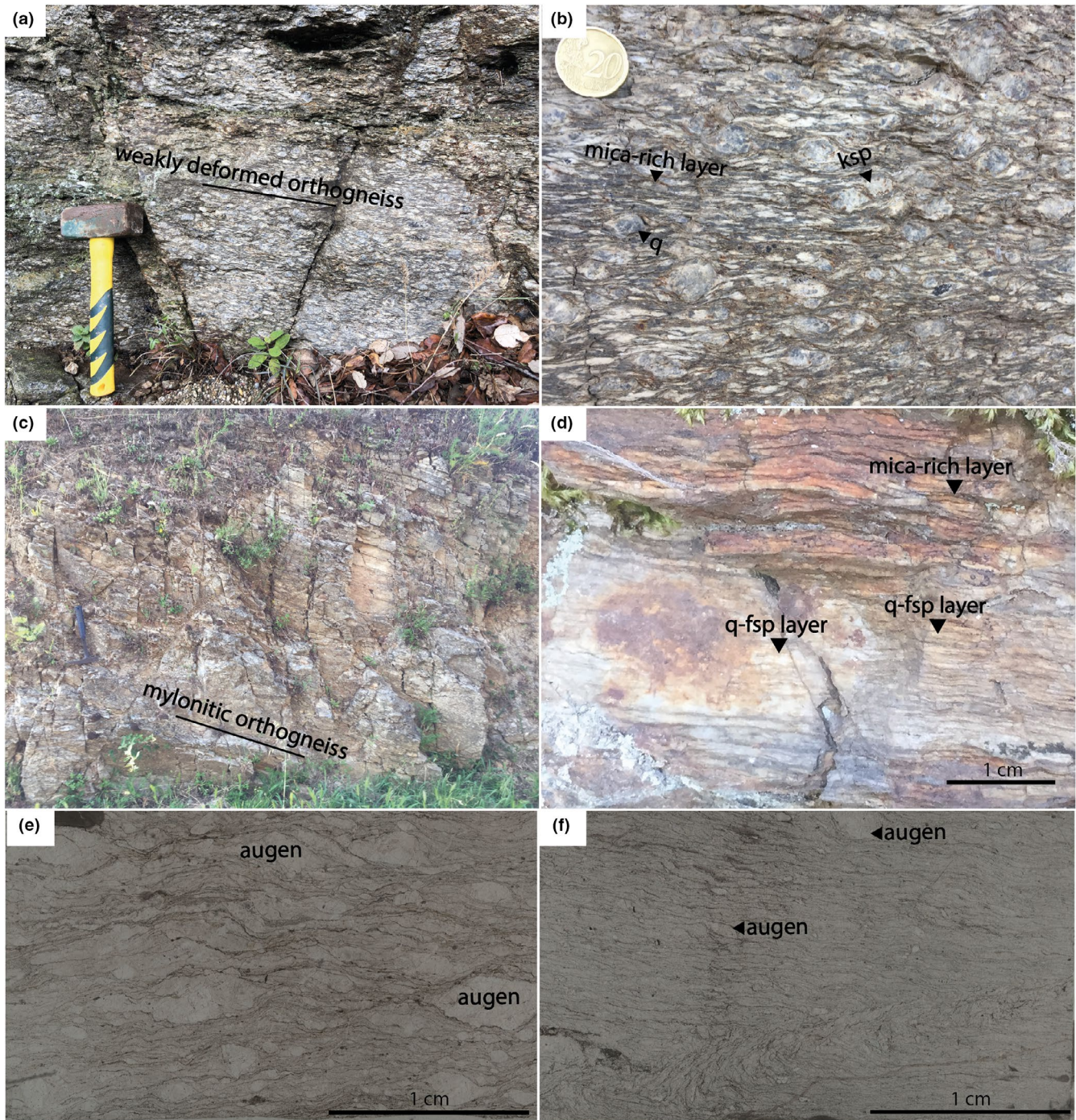
Samples have been characterized using a scanning electron microscope (SEM) of LEO, model EVO-50XVP, housed at the Department of Earth and Geo-environmental Sciences, University of Bari Aldo Moro, coupled with an X-max ( $80\text{ mm}^2$ ) energy dispersive (ED) Silicon drift Oxford detector (Oxford Instruments) equipped with a Super Atmosphere Thin Window ©. Microanalysis was performed with the Silicon

drift ED detector on polished thin sections. Quantitative results were obtained using operating conditions of 15 kV accelerating potential, 500 pA probe current,  $\sim 25,000$  output counts per second (cps) as average count rate on the whole spectrum, counting time of 50 s and 8.5 mm working distance. X-ray intensities were converted to wt% (w/w) oxides by XPP correction scheme developed by Pouchou and Pichoir (1988, 1991), granted as quantitative software support by Oxford-Link Analytical (UK). Given the composition of the analysed mineral phases, the  $1\sigma$  precision corresponded to the following values:  $\text{SiO}_2 = 0.10\text{--}0.20$  wt%,  $\text{TiO}_2 = 0.08\text{--}0.10$  wt%,  $\text{Al}_2\text{O}_3 = 0.08\text{--}0.13$  wt%,  $\text{FeO} = 0.05\text{--}0.15$  wt%,  $\text{MnO} = 0.04\text{--}0.6$  wt%,  $\text{MgO} = 0.08\text{--}0.13$  wt%,  $\text{CaO} = 0.04\text{--}0.14$  wt%,  $\text{Na}_2\text{O} = 0.04\text{--}0.06$  wt% and  $\text{K}_2\text{O} = 0.04\text{--}0.12$  wt%. The accuracy of the analytical data was also checked using several standard minerals manufactured by Micro-Analysis Consultants Ltd. (UK); four of the standards used for element calibrations (augite, almandine, pyrope, and orthoclase) are reported as supplementary data in Table S1. All the analyses of the relevant minerals (i.e. garnet, mica, and feldspars) used to constrain the thermobarometric evolution of the Castagna Unit's orthogneisses in this study are provided in the Table S2. The bulk rock compositions (Table 1) were obtained by X-ray fluorescence analysis using a Panalytical AXIOS-Advanced spectrometer equipped with a 4 kW Rh Super Sharp end window X-ray Tube at the Department of Earth and Geo-environmental Sciences, University of Bari Aldo Moro. XRF analysis was conducted on pressed powders of thin section back cut after a careful microstructural survey, in order to exclude any possible polymetamorphic chemical zoning of key mineral phases like garnet (e.g. Argles et al., 1999; Palin et al., 2016). The operating conditions of the XRF spectrometer were: 60 kV and 66 mA the X-ray tube power supply; a scintillator detector was used to collect the X-ray lines dispersed by a LiF 220 crystal. X-ray intensities were converted in oxide wt% using the mathematical matrix correction procedure as suggested by (Leoni & Saitta, 1976a, 1976b) and (Leoni et al., 2004). Two reference standards (AGV-1 from USGS-USA and NIM-G from NIM-South Africa) were used to check the accuracy of the analytical data: the precision is better than 3% for all elements. The water content of the rock was measured as loss on ignition, heating the powdered samples at  $900^\circ\text{C}$  for 12 hr. This value takes into account the loss of OH from hydrous silicates, the  $\text{CO}_2$  from carbonate dissociation and of S, Cl and other anions due to the dissociation of sulphides, sulphates, chlorides.

### 3.2 | Weakly deformed orthogneiss

Sample VF80GR is a weakly deformed orthogneiss (Figure 3a,b) with large K-feldspar, plagioclase, and quartz porphyroclasts (up to 2 cm in size) that are dispersed into





**FIGURE 3** (a, b) Typical field occurrence of the weakly deformed augen orthogneisses. (c) Typical field occurrence of mylonitic orthogneisses showing a marked mylonitic foliation. (d) Alternation of the thin mica-rich layers with the stretched quartzofeldspathic ones in the mylonitic leucocratic orthogneiss. (e) Scanned thin section (plane-polarized light) of the mylonitic orthogneiss showing a smaller grain size with respect to the weakly deformed augen orthogneisses. (f) Scanned thin section (plane-polarized light) of fine-grained mylonitic leucocratic orthogneiss. The mineral abbreviations are from Holland and Powell (1998)

a matrix with anastomosing quartzofeldspathic and mica-rich layers (Figure 4a,b). The mineral assemblage comprises quartz+K-feldspar+plagioclase+biotite+muscovite+epidot e+sphene-ilmenite+apatite. The plagioclase in the matrix is fine-grained recrystallized and shows an albite composition with an  $X_{An}$  of  $\sim 0.06$ , whereas the plagioclase porphyroclasts

are oligoclase in composition with an  $X_{An}$  of  $\sim 0.12$  (Table 2). Biotite occurs in flakes up to  $\sim 300$   $\mu\text{m}$  in size aligned to the main foliation (Figure 4b), and is characterized by  $\sim 1.55$  apfu (atoms per formula unit) of Al,  $\sim 0.11$  apfu of Ti, and an  $X_{Fe}$  ratio (as  $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$ ) of  $\sim 0.6$  (Table 2). In most of cases, biotite is observed to be wrapped by tiny (up to  $\sim 50$   $\mu\text{m}$  in



**TABLE 1** XRF bulk rock compositions (wt%) of samples VF80GR, VF77GR, and VF79GR

| XRF whole rock analysis (wt%) |                          |                  |                                |      |      |                                |                  |                   |                  |      |                               |        |
|-------------------------------|--------------------------|------------------|--------------------------------|------|------|--------------------------------|------------------|-------------------|------------------|------|-------------------------------|--------|
| Sample                        | H <sub>2</sub> O/<br>LOI | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | Na <sub>2</sub> O | TiO <sub>2</sub> | MnO  | P <sub>2</sub> O <sub>5</sub> | Total  |
| VF80GR                        | 1.98                     | 68.02            | 14.43                          | 1.30 | 1.97 | 4.33                           | 3.93             | 2.94              | 0.62             | 0.05 | 0.13                          | 99.70  |
| VF77GR                        | 0.93                     | 73.36            | 13.17                          | 0.83 | 0.79 | 2.55                           | 4.88             | 3.01              | 0.35             | 0.05 | 0.07                          | 99.99  |
| VF79GR                        | 1.10                     | 71.01            | 16.05                          | 0.74 | 0.44 | 1.63                           | 5.53             | 3.03              | 0.17             | 0.03 | 0.29                          | 100.02 |

size) white mica-rich layers (Figure 4b) that displayed Si = 3.28–3.36 apfu and  $X_{\text{Fe}} = 0.38\text{--}0.44$  (Table 2). The Si content of this tiny white mica is higher than 3.11–3.15 apfu measured on the larger muscovite flakes (up to ~250  $\mu\text{m}$  in size), the latter also characterized by  $X_{\text{Fe}} = 0.48\text{--}0.51$  (Table S2). The epidote grains have a subhedral shape (Figure 4a,c) and are found either replacing large plagioclase porphyroclasts (Figure 4a) or within the matrix aligned to the main foliation (Figure 4c). Epidote grains are characterized by ~2.42 apfu of Al and ~0.51 apfu of  $\text{Fe}^{3+}$  (Table 3). Ilmenite is the prevalent opaque mineral in the rock, characterized by ~0.10 apfu of Mn (Table 3). Ilmenite also commonly has overgrowths of small titanite coronae (Figure 4c), with Al and  $\text{Fe}^{3+}$  of ~0.08 apfu and ~0.01 apfu respectively (Table 3).

### 3.3 | Mylonitic orthogneisses

#### 3.3.1 | Sample VF77GR

Sample VF77GR is a garnet-bearing mylonitic orthogneiss (Figure 3c,d), which is characterized by K-feldspar, quartz, and minor plagioclase porphyroclasts, set in a fine-grained matrix with anastomosing quartzofeldspathic layers alternating with very thin white mica layers (Figure 4d,e). Quartz+K-feldspar+plagioclase+white mica+garnet+epidote+sphene±biotite±ilmenite constitute the mineral assemblage of this sample (Figure 4d–f). K-feldspar and plagioclase within the matrix are fine-grained and recrystallized (Figure 4d), with the plagioclase being close to the pure albite in composition ( $X_{\text{An}} = 0.01$ ) (Table 2). Garnet grains, up to ~200  $\mu\text{m}$  in size, are present in the rock (Figure 4e,f); they have an ellipsoidal shape and are wrapped by the main mylonitic foliation (Figure 4e,f). Garnet commonly host tiny inclusions of quartz, albite, white mica, and sphene (Figures 4f and 5a,b); epidote and chlorite are sometimes observed around the crystals (Figure 5a,b). Garnet have grossular-rich compositions (Table 4) and show appreciable core to rim zoning patterns (Figure 5a,b). Specifically, the patterns in Figure 5 display: (a) an increase in  $X_{\text{Gr}}$  from the inner core (0.48–0.50) towards its outer part (0.52–0.54) (Figure 5a,b), and constant values of ~0.54 in the rim (Figure 5a,b); (b) an increase in  $X_{\text{Alm}}$  from the core (0.20–0.23) towards rim (0.32–0.36) (Figure 5a,b), where in some cases

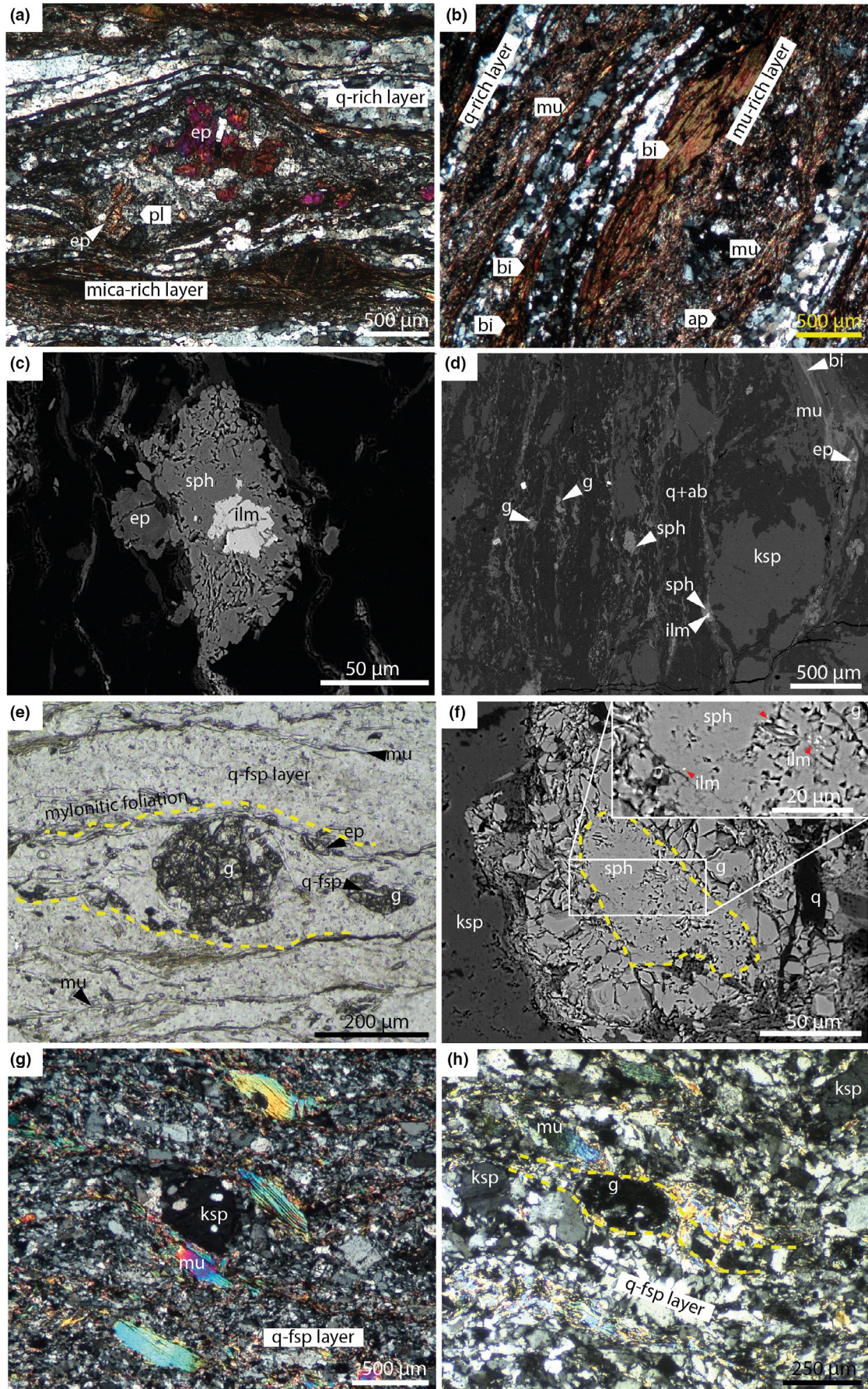
remains constant (Figure 5b); (c) a roughly bell-shaped zoning pattern in  $X_{\text{SpS}}$  (Figure 5a,b), with values of 0.20–0.24 in the core and 0.09–0.10 in the outermost part of the rim. Both the  $X_{\text{Andr}}$  (calculated as  $[2-(\text{Al}_{\text{apfu}}+\text{Ti}_{\text{apfu}}+\text{Cr}_{\text{apfu}})]$ ) in the Y site) and  $X_{\text{Py}}$  core–rim trends are below 0.10 mole fractions (Figure 5b), and are respectively characterized by: (a) almost constant values from the inner core towards the rim (~0.05), and (b) increasing values from the core (~0.00) towards the outermost part of the rim (~0.01).

White mica is mostly fine-grained (up to ~50  $\mu\text{m}$  in size) and aligned along the main mylonitic foliation  $S_{\text{m}}$  (Figure 4d,e), where it overgrows the relict biotite flakes (Figure 4e). It is enriched in the ferro-celadonite end-member with Si = 3.32–3.39 apfu and  $X_{\text{Fe}} = 0.59\text{--}0.69$  (Table 2) with respect to the larger muscovite flakes (up to ~300  $\mu\text{m}$  in size), which have Si  $\approx$  3.05 apfu and  $X_{\text{Fe}} \approx 0.59$  (Table S2). Subhedral to euhedral grains of epidote have been observed in the mica-rich layers either aligned along the main mylonitic foliation  $S_{\text{m}}$  (Figure 4d,e) or around small garnet grains (Figure 5b). The epidote has ~2.45 apfu of Al and ~0.51 apfu of  $\text{Fe}^{3+}$  (Table 3). Sphene is characterized by ~0.16 apfu of Al and ~0.02 apfu of  $\text{Fe}^{3+}$  (Table 3), and occurs in large coronae (up to ~100  $\mu\text{m}$ ) around ilmenite as well as in small euhedral grains within the mica-rich layers (Figure 4d). Moreover, sphene showing micro-inclusions of ilmenite is also found to be occasionally hosted within garnet (Figure 4f, top right inset).

#### 3.3.2 | Sample VF79GR

Sample VF79GR is a garnet-bearing, biotite-free mylonitic leucocratic orthogneiss (Figure 3e,f) with K-feldspar and quartz porphyroclasts within a fine-grained quartzofeldspathic matrix, which sporadically alternates with very thin white mica layers (Figure 4g). The mineral assemblage of sample VF79GR is composed of quartz+K-feldspar+plagioclase+white mica+garnet+epidote+sphene. K-feldspar, quartz, and albite ( $X_{\text{An}} \sim 0.01$ ) (Table 2) comprise the fine-grained recrystallized matrix (Figure 4g,h). Garnet (up to ~250  $\mu\text{m}$  in size) are wrapped by the main mylonitic foliation (Figure 4h), and have grossular-rich compositions (Table 4) that exhibit very similar end-members' zoning patterns from core to rim as those of the







**FIGURE 4** (a) Epidote grains replacing a plagioclase porphyroblast, which is wrapped by alternating quartz-rich and mica-rich layers (sample VF80GR, crossed polar microphotograph). (b) Microphotograph highlighting the replacement of relic biotite by fine-grained white mica within the mica-rich layers (sample VF80GR, crossed polar microphotograph). (c) SEM-BSE image of a titanite (sph) corona growing around a relic ilmenite core in the weakly deformed orthogneiss (sample VF80GR). (d) SEM-BSE image showing the entire fabric and mineral assemblage of mylonitic orthogneiss. Note the brighter biotite relics overgrown by the white mica along the mica-rich layers, the titanite (sph) coronae around the brighter ilmenite core, and the small garnets set within the matrix (sample VF77GR). (e) Pre-kinematic garnet, in the centre of the micrograph, wrapped by the main mylonitic foliation, highlighted by the yellow dashed lines (sample VF77GR, mylonitic orthogneiss, plane-polarized light). (f) SEM-BSE image of a highly fractured pre-kinematic garnet grain hosting titanite (sph) with micro-inclusions of ilmenite (red arrows in the top right inset) (sample VF77GR). (g) K-feldspar porphyroblast set in a fine-grained quartzofeldspathic matrix alternating to very thin white mica-rich layers (sample VF79GR, crossed polar microphotograph). (h) Pre-kinematic garnet wrapped by the main mylonitic foliation, highlighted by the yellow dashed lines (sample VF79GR, mylonitic leucocratic orthogneiss, crossed polar microphotograph). The mineral abbreviations are from Holland and Powell (1998)

**TABLE 2** Representative analyses of recrystallized plagioclase, white mica, and biotite from samples VF80GR, VF77GR, and VF79GR

|                                | Plagioclase |               |        |        | White mica                |                           |                           |                           |                           |                           | Biotite |
|--------------------------------|-------------|---------------|--------|--------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------|
|                                | VF80GR      |               | VF77GR | VF79GR | VF80GR                    |                           | VF77GR                    |                           | VF79GR                    |                           | VF80GR  |
|                                | Matrix      | Porphyroblast |        |        | min<br>Si <sub>apfu</sub> | max<br>Si <sub>apfu</sub> | min<br>Si <sub>apfu</sub> | max<br>Si <sub>apfu</sub> | min<br>Si <sub>apfu</sub> | max<br>Si <sub>apfu</sub> |         |
| SiO <sub>2</sub>               | 67.54       | 65.11         | 68.64  | 69.65  | 48.53                     | 50.01                     | 49.61                     | 49.31                     | 49.45                     | 49.06                     | 37.07   |
| TiO <sub>2</sub>               | 0.00        | 0.00          | 0.00   | 0.00   | 1.13                      | 0.41                      | 0.00                      | 0.00                      | 0.00                      | 0.21                      | 1.94    |
| Al <sub>2</sub> O <sub>3</sub> | 20.32       | 21.59         | 19.64  | 19.55  | 27.57                     | 26.85                     | 28.87                     | 26.00                     | 28.28                     | 26.85                     | 17.03   |
| Cr <sub>2</sub> O <sub>3</sub> | 0.00        | 0.00          | 0.00   | 0.00   | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| FeO <sub>t</sub>               | 0.00        | 0.00          | 0.00   | 0.00   | 4.20                      | 4.43                      | 5.32                      | 5.68                      | 5.52                      | 5.08                      | 20.42   |
| MnO                            | 0.00        | 0.00          | 0.00   | 0.00   | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| MgO                            | 0.00        | 0.00          | 0.00   | 0.00   | 2.74                      | 3.00                      | 1.34                      | 2.23                      | 1.46                      | 1.46                      | 8.49    |
| CaO                            | 1.20        | 2.41          | 0.21   | 0.21   | 0.24                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| Na <sub>2</sub> O              | 10.99       | 10.01         | 10.75  | 11.54  | 0.00                      | 0.00                      | 0.20                      | 0.15                      | 0.00                      | 0.16                      | 0.00    |
| K <sub>2</sub> O               | 0.12        | 0.09          | 0.14   | 0.13   | 10.67                     | 11.78                     | 11.41                     | 11.35                     | 11.39                     | 11.44                     | 9.12    |
| Total                          | 100.17      | 99.21         | 99.38  | 101.08 | 95.08                     | 96.48                     | 96.75                     | 94.72                     | 96.10                     | 94.26                     | 94.07   |
| O                              | 8.00        | 8.00          | 8.00   | 8.00   | 11.00                     | 11.00                     | 11.00                     | 11.00                     | 11.00                     | 11.00                     | 11.00   |
| Si                             | 2.95        | 2.88          | 3.01   | 3.01   | 3.28                      | 3.36                      | 3.32                      | 3.39                      | 3.34                      | 3.38                      | 2.86    |
| Al <sup>IV</sup>               | —           | —             | —      | —      | 0.72                      | 0.64                      | 0.68                      | 0.61                      | 0.66                      | 0.62                      | 1.14    |
| Al <sup>VI</sup>               | —           | —             | —      | —      | 1.48                      | 1.48                      | 1.60                      | 1.50                      | 1.59                      | 1.56                      | 0.40    |
| Al <sub>tot</sub>              | 1.05        | 1.13          | 1.01   | 0.99   | 2.20                      | 2.12                      | 2.28                      | 2.11                      | 2.25                      | 2.18                      | 1.55    |
| Ti                             | 0.00        | 0.00          | 0.00   | 0.00   | 0.06                      | 0.02                      | 0.00                      | 0.00                      | 0.00                      | 0.01                      | 0.11    |
| Cr                             | 0.00        | 0.00          | 0.00   | 0.00   | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| Fe <sup>3+</sup>               | 0.00        | 0.00          | 0.00   | 0.00   | 0.07                      | 0.01                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| Fe <sup>2+</sup>               | 0.00        | 0.00          | 0.00   | 0.00   | 0.17                      | 0.24                      | 0.30                      | 0.33                      | 0.31                      | 0.29                      | 1.32    |
| Mg                             | 0.00        | 0.00          | 0.00   | 0.00   | 0.28                      | 0.30                      | 0.13                      | 0.23                      | 0.15                      | 0.15                      | 0.98    |
| Mn                             | 0.00        | 0.00          | 0.00   | 0.00   | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| Ca                             | 0.06        | 0.11          | 0.01   | 0.01   | 0.02                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00                      | 0.00    |
| Na                             | 0.93        | 0.86          | 0.91   | 0.97   | 0.00                      | 0.00                      | 0.03                      | 0.02                      | 0.00                      | 0.02                      | 0.00    |
| K                              | 0.01        | 0.01          | 0.01   | 0.01   | 0.92                      | 1.01                      | 0.98                      | 1.00                      | 0.98                      | 1.01                      | 0.90    |
| Σ <sub>cations</sub>           | 4.99        | 4.99          | 4.95   | 4.98   | 6.99                      | 14.13                     | 14.07                     | 14.13                     | 14.05                     | 14.07                     | 15.41   |
| X <sub>Fe</sub>                |             |               |        |        | 0.38                      | 0.44                      | 0.69                      | 0.59                      | 0.68                      | 0.66                      | 0.57    |
| X <sub>An</sub>                | 0.06        | 0.12          | 0.01   | 0.01   |                           |                           |                           |                           |                           |                           |         |

**TABLE 3** Representative analyses of epidote, titanite, and ilmenite from samples VF80GR, VF77GR, and VF79GR. Titanite analyses of samples VF80GR and VF77GR are those typical of the coronae. Ilmenite represents the coronae core

|                                | Epidote |        |        | Titanite |        |        | Ilmenite |        |
|--------------------------------|---------|--------|--------|----------|--------|--------|----------|--------|
|                                | VF80GR  | VF77GR | VF79GR | VF80GR   | VF77GR | VF79GR | VF80GR   | VF77GR |
| SiO <sub>2</sub>               | 38.49   | 39.09  | 38.11  | 31.32    | 31.75  | 32.15  | 0.00     | 0.00   |
| TiO <sub>2</sub>               | 0.00    | 0.00   | 0.00   | 39.34    | 34.65  | 30.05  | 55.41    | 56.30  |
| Al <sub>2</sub> O <sub>3</sub> | 26.29   | 26.94  | 25.38  | 2.09     | 4.42   | 7.91   | 0.00     | 0.00   |
| Cr <sub>2</sub> O <sub>3</sub> | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| FeOt                           | 7.84    | 9.00   | 8.87   | 0.54     | 0.90   | 0.34   | 39.84    | 39.40  |
| MnO                            | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 4.58     | 6.03   |
| MgO                            | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| CaO                            | 24.54   | 23.48  | 24.05  | 29.93    | 28.71  | 29.64  | 0.00     | 0.00   |
| Na <sub>2</sub> O              | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| K <sub>2</sub> O               | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| H <sub>2</sub> O <sup>a</sup>  | 0.00    | 0.00   | 0.00   | 0.44     | 0.89   | 1.44   | 0.00     | 0.00   |
| Cl                             | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| F                              | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| Total                          | 97.16   | 98.51  | 96.41  | 103.72   | 101.42 | 101.57 | 99.83    | 101.73 |
| O                              | 12.50   | 12.50  | 12.50  |          |        |        | 3.00     | 3.00   |
| Si                             | 3.01    | 3.02   | 3.01   | 1.00     | 1.00   | 1.00   | 0.00     | 0.00   |
| Al <sub>tot</sub>              | 2.42    | 2.45   | 2.36   | 0.08     | 0.16   | 0.29   | 0.00     | 0.00   |
| Ti                             | 0.00    | 0.00   | 0.00   | 0.95     | 0.82   | 0.70   | 1.04     | 1.04   |
| Cr                             | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| Fe <sup>3+</sup>               | 0.51    | 0.51   | 0.59   | 0.01     | 0.02   | 0.01   | 0.00     | 0.00   |
| Fe <sup>2+</sup>               | 0.00    | 0.08   | 0.00   | 0.00     | 0.00   | 0.00   | 0.83     | 0.81   |
| Mg                             | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| Mn                             | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.10     | 0.12   |
| Ca                             | 2.06    | 1.94   | 2.04   | 1.02     | 0.97   | 0.99   | 0.00     | 0.00   |
| Na                             | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| K                              | 0.00    | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00     | 0.00   |
| OH                             | 0.00    | 0.00   | 0.00   | 0.09     | 0.19   | 0.30   | 0.00     | 0.00   |
| Σ <sub>cations</sub>           | 8.00    | 8.00   | 8.00   | 3.07     | 2.98   | 2.99   | 1.96     | 1.96   |

Note: Titanite formulae were recalculated on the basis of 1.00 apfu of Si.

<sup>a</sup>H<sub>2</sub>O recalculated as OH = Al + Fe<sup>3+</sup> - F; all Fe was assumed to be Fe<sup>3+</sup>.

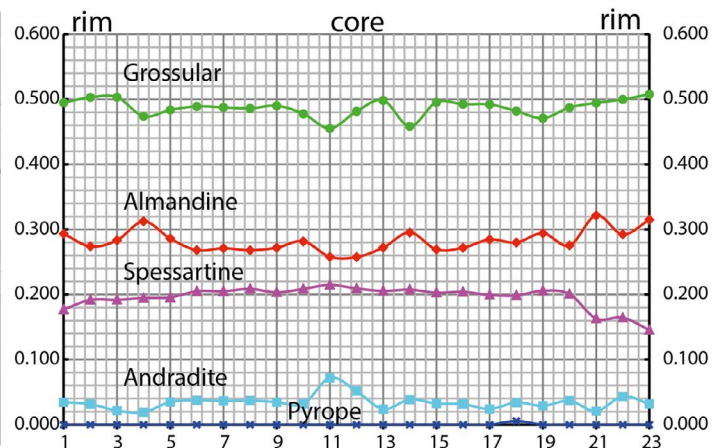
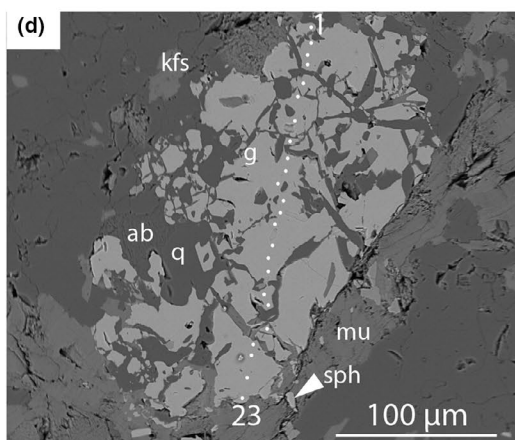
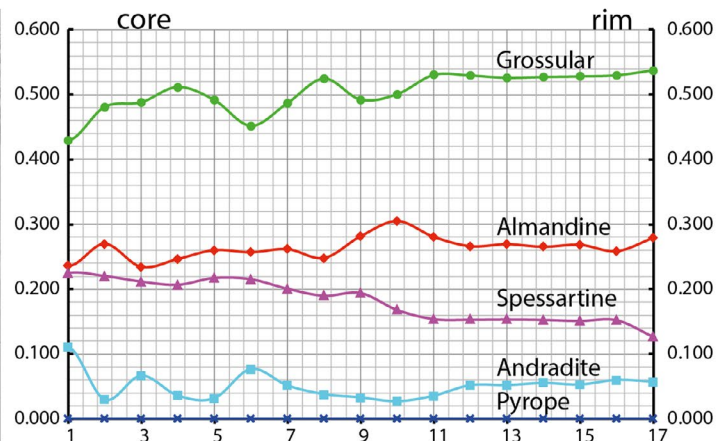
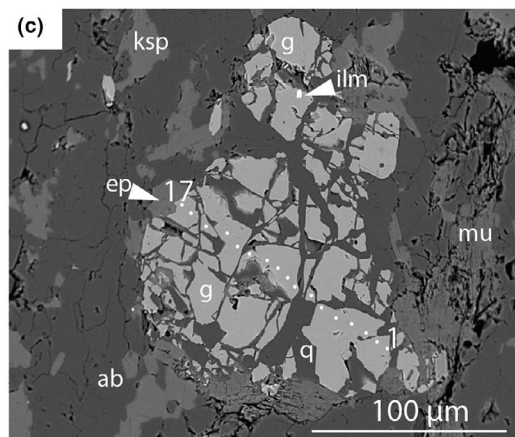
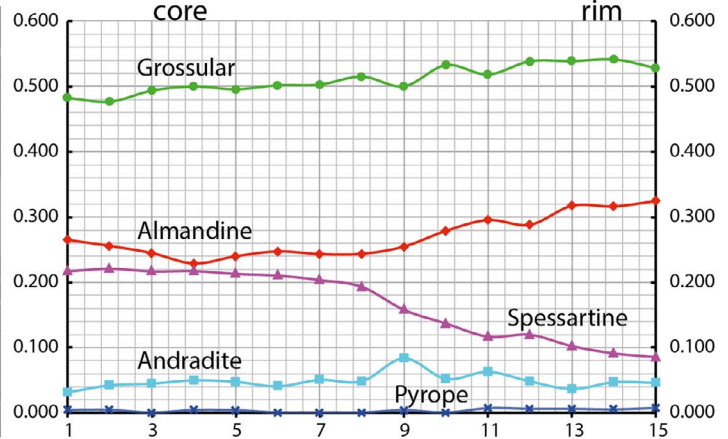
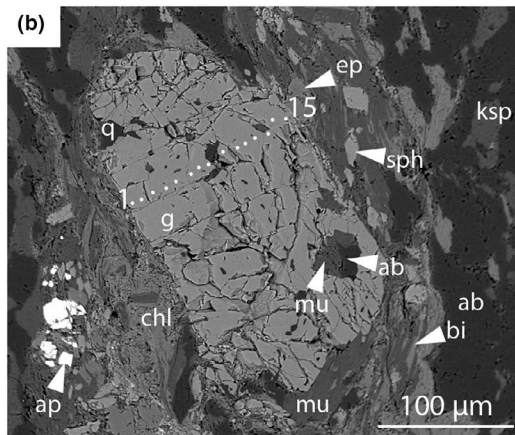
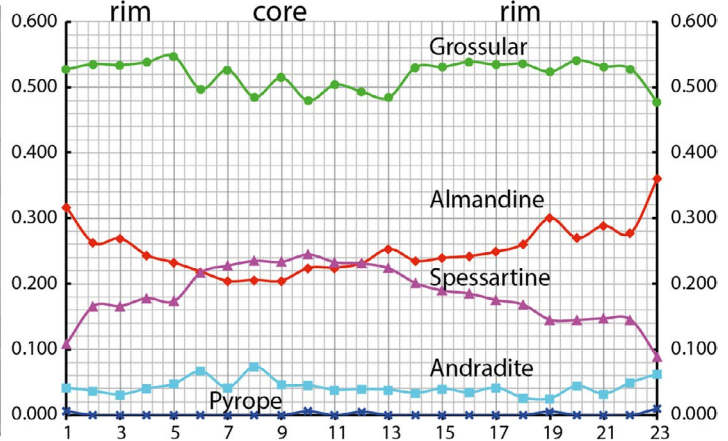
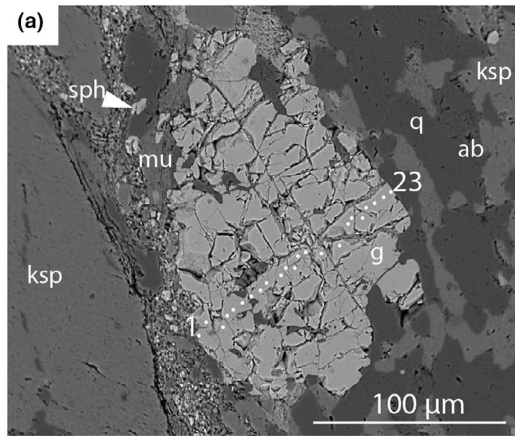
garnet from sample VF77GR (Figure 5c,d). In particular, the patterns in Figure 5 are characterized by: (a) a general increase in  $X_{Gr}$  from ~0.45 to 0.50–0.54 from the inner core to its outer part (Figure 5c,d, especially 5c), and almost constant values of ~0.53 and/or ~0.50 in the rim (Figure 5c,d); (b) an increase in  $X_{Alm}$  from the inner core (0.23–0.28) towards the outer part (0.30–0.32) (Figure 5c,d), and lower (~0.27) but roughly constant values in the rim; (c) a gentle decrease in  $X_{Sps}$  (Figure 5c) from 0.20 to 0.22 in the inner core to 0.15–0.16 in the outer

core, which is followed by nearly constant values in the rim and an eventual drop to 0.12–0.14. The core–rim trend in  $X_{Andr}$  is best highlighted in Figure 5c, which reveals: (a) variations in the core from ~0.03 to ~0.11 mole fractions followed by a decreasing trend up to plateau at ~0.06 mole fractions in the rim. On the other hand, the  $X_{Py}$  maintains at around zero mole fractions throughout the traverses (Figure 5c,d).

The white mica is fine-grained (up to ~30 μm in size), aligned along the main mylonitic foliation (Figure 4g) and

**FIGURE 5** SEM-BSE images of pre-kinematic garnets from sample VF77GR (a, b) and sample VF79GR (c, d) with the related compositional zoning profiles shown on the right-hand side. The point analysis traverses of the garnet are highlighted in the SEM-BSE images (a–d) with white dots along with the starting and ending points. The mineral phases in the matrix and hosted in garnets as inclusions (a–d) are also shown





**TABLE 4** Representative core, middle, and rim analyses of garnets from samples VF77GR and VF79GR. The reported analyses are from the garnet chemical profiles shown in Figure 5

|                                | VF77GR              |        |        |                     |        |        | VF79GR              |        |        |                     |        |       |
|--------------------------------|---------------------|--------|--------|---------------------|--------|--------|---------------------|--------|--------|---------------------|--------|-------|
|                                | Profile-1—Figure 5a |        |        | Profile-2—Figure 5b |        |        | Profile-1—Figure 5c |        |        | Profile-2—Figure 5d |        |       |
|                                | Core                | Middle | Rim    | Core                | Middle | Rim    | Core                | Middle | Rim    | Core                | Middle | Rim   |
| SiO <sub>2</sub>               | 37.50               | 38.08  | 37.58  | 37.50               | 37.91  | 39.33  | 37.71               | 37.87  | 37.96  | 37.44               | 37.49  | 37.40 |
| TiO <sub>2</sub>               | 0.00                | 0.00   | 0.22   | 0.00                | 0.00   | 0.00   | 0.23                | 0.32   | 0.00   | 0.00                | 0.00   | 0.00  |
| Al <sub>2</sub> O <sub>3</sub> | 20.43               | 20.35  | 20.29  | 20.43               | 20.74  | 21.14  | 20.71               | 20.71  | 20.22  | 20.67               | 20.94  | 20.64 |
| Cr <sub>2</sub> O <sub>3</sub> | 0.00                | 0.00   | 0.00   | 0.00                | 0.30   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| FeOt                           | 13.09               | 14.38  | 16.15  | 11.82               | 12.82  | 15.99  | 13.41               | 14.81  | 14.58  | 13.47               | 13.79  | 15.52 |
| MnO                            | 10.11               | 6.21   | 4.18   | 11.28               | 7.64   | 4.96   | 10.07               | 7.60   | 5.75   | 9.30                | 8.79   | 6.63  |
| MgO                            | 0.12                | 0.00   | 0.14   | 0.16                | 0.00   | 0.17   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| CaO                            | 18.75               | 20.98  | 21.43  | 19.15               | 20.53  | 20.63  | 18.47               | 18.89  | 21.38  | 19.12               | 18.99  | 19.47 |
| Na <sub>2</sub> O              | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| K <sub>2</sub> O               | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| Total                          | 100.14              | 100.19 | 100.15 | 100.49              | 100.02 | 102.36 | 100.71              | 100.29 | 100.09 | 100.11              | 100.07 | 99.77 |
| O                              | 12.00               | 12.00  | 12.00  | 12.00               | 12.00  | 12.00  | 12.00               | 12.00  | 12.00  | 12.00               | 12.00  | 12.00 |
| Si                             | 2.98                | 3.01   | 2.97   | 2.97                | 2.99   | 3.03   | 2.98                | 2.99   | 3.00   | 2.97                | 2.97   | 2.98  |
| Al <sub>tot</sub>              | 1.91                | 1.89   | 1.89   | 1.91                | 1.93   | 1.92   | 1.93                | 1.93   | 1.89   | 1.94                | 1.96   | 1.94  |
| Ti                             | 0.00                | 0.00   | 0.01   | 0.00                | 0.00   | 0.00   | 0.01                | 0.02   | 0.00   | 0.00                | 0.00   | 0.00  |
| Cr                             | 0.00                | 0.00   | 0.00   | 0.00                | 0.02   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| Fe <sup>3+</sup>               | 0.09                | 0.11   | 0.09   | 0.09                | 0.05   | 0.08   | 0.06                | 0.05   | 0.11   | 0.06                | 0.04   | 0.06  |
| Fe <sup>2+</sup>               | 0.79                | 0.84   | 0.98   | 0.69                | 0.79   | 0.95   | 0.83                | 0.93   | 0.85   | 0.83                | 0.87   | 0.97  |
| Mg                             | 0.01                | 0.00   | 0.02   | 0.02                | 0.00   | 0.02   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| Mn                             | 0.68                | 0.42   | 0.28   | 0.76                | 0.51   | 0.32   | 0.67                | 0.51   | 0.39   | 0.63                | 0.59   | 0.45  |
| Ca                             | 1.60                | 1.78   | 1.82   | 1.63                | 1.74   | 1.70   | 1.56                | 1.60   | 1.81   | 1.63                | 1.61   | 1.66  |
| Na                             | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| K                              | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| Σ <sub>cations</sub>           | 8.06                | 8.04   | 8.07   | 8.07                | 8.03   | 8.02   | 8.04                | 8.03   | 8.05   | 8.06                | 8.05   | 8.05  |
| X <sub>Alm</sub>               | 0.26                | 0.28   | 0.32   | 0.22                | 0.26   | 0.32   | 0.27                | 0.31   | 0.28   | 0.27                | 0.28   | 0.32  |
| X <sub>Sps</sub>               | 0.22                | 0.14   | 0.09   | 0.24                | 0.17   | 0.11   | 0.22                | 0.17   | 0.13   | 0.20                | 0.19   | 0.15  |
| X <sub>Gr</sub>                | 0.48                | 0.53   | 0.54   | 0.48                | 0.54   | 0.53   | 0.48                | 0.50   | 0.54   | 0.50                | 0.50   | 0.51  |
| X <sub>Py</sub>                | 0.00                | 0.00   | 0.01   | 0.01                | 0.00   | 0.01   | 0.00                | 0.00   | 0.00   | 0.00                | 0.00   | 0.00  |
| X <sub>Andr</sub>              | 0.04                | 0.05   | 0.05   | 0.05                | 0.03   | 0.04   | 0.03                | 0.03   | 0.06   | 0.03                | 0.02   | 0.03  |
| X <sub>Fe</sub>                | 0.98                | 1.00   | 0.98   | 0.97                | 1.00   | 0.98   | 1.00                | 1.00   | 1.00   | 1.00                | 1.00   | 1.00  |

enriched in the ferro-celadonite end-member ( $Si_{apfu} = 3.34$ – $3.38$  and  $X_{Fe} = 0.66$ – $0.68$ ; similar to sample VF77GR) (Table 2) with respect to the few, larger muscovite flakes (Figure 4g) that show  $Si = 3.09$ – $3.14$  apfu and  $X_{Fe} = 0.57$ – $0.59$  (Table S2). Epidote is widespread in the rock matrix and has a sub-euhedral to euhedral shape. It is characterized by  $\sim 2.36$  apfu of Al and  $\sim 0.59$  apfu of  $Fe^{3+}$  (Table 3). Sphene is present as small euhedral grains within the rock matrix, with  $\sim 0.29$  apfu of Al and  $\sim 0.01$  apfu of  $Fe^{3+}$  respectively (Table 3).

## 4 | PHASE EQUILIBRIUM MODELLING

### 4.1 | Models and modelling strategy

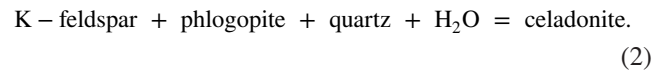
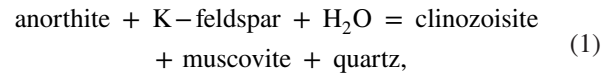
Phase equilibrium diagrams have been calculated using the THERMOCALC v3.45 software (Powell & Holland, 1988) with the updated version of the Holland and Powell (2011) data set (file tc-ds63.txt, created on 05/01/2015). The used activity–composition models are: clinopyroxene (Green



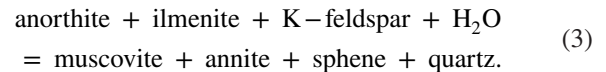
et al., 2016); garnet, biotite, muscovite, paragonite, margarite, cordierite, orthopyroxene, chlorite, and ilmenite (White et al., 2014); epidote (Holland & Powell, 2011) and feldspars (Holland & Powell, 2003). The quartz, albite, sphene, rutile, kyanite, sillimanite, andalusite, and aqueous fluid end-members have been assumed to be pure phases. The bulk rock compositions have been converted from weight percentages (wt%) to mole percentages (mol.%) in the MnNCKFMASHTO 11-component model system (Table 5). The modelled mole percentages of CaO have been reduced on the basis of the P<sub>2</sub>O<sub>5</sub> content, due to the presence of apatite. To determine the appropriate Fe<sup>3+</sup>/Fe<sub>tot</sub> ratio in samples VF80GR, VF77GR, and VF79GR, *P*–*X*(Fe)<sup>3+</sup> isothermal phase diagrams have been calculated at 500°C for each sample (Figure S1). Such temperature was chosen to investigate the mineral assemblages forming at the greenschist–amphibolite facies transition with respect to the Alpine *P*–*T* conditions obtained by Langone et al. (2006) (*P* = 0.75–0.90 GPa and *T* = 525 ± 50°C) for the mylonitic orthogneiss of the Castagna Unit. Hence, the *X*(Fe)<sup>3+</sup> used in the phase diagrams of Figures 6–9 was selected within the opportune stability fields, that is, at *X*(Fe)<sup>3+</sup> lower than that favouring hematite stabilization for the weakly deformed orthogneiss (Figure S1), and at *X*(Fe)<sup>3+</sup> in the centre of the *g*+*mu*+*bi*+*ep*+*ab*+*q*+*ksp*+*sph* stability field for the mylonitic orthogneisses (Figure S1).

## 4.2 | Principal reactions producing HP mineral assemblages

The mineral assemblages that developed in the weakly deformed orthogneiss (sample VF80GR) and mylonitic orthogneisses (samples VF77GR and VF79GR) during the main tectono-metamorphic events are summarized in Table 6. In sample VF80GR, the presence of subhedral epidote crystals together with tiny white mica overgrowths on large biotite flakes (Figure 4a,b), suggest the consumption of aqueous fluid within the simplified CKASH and KMASH systems respectively:

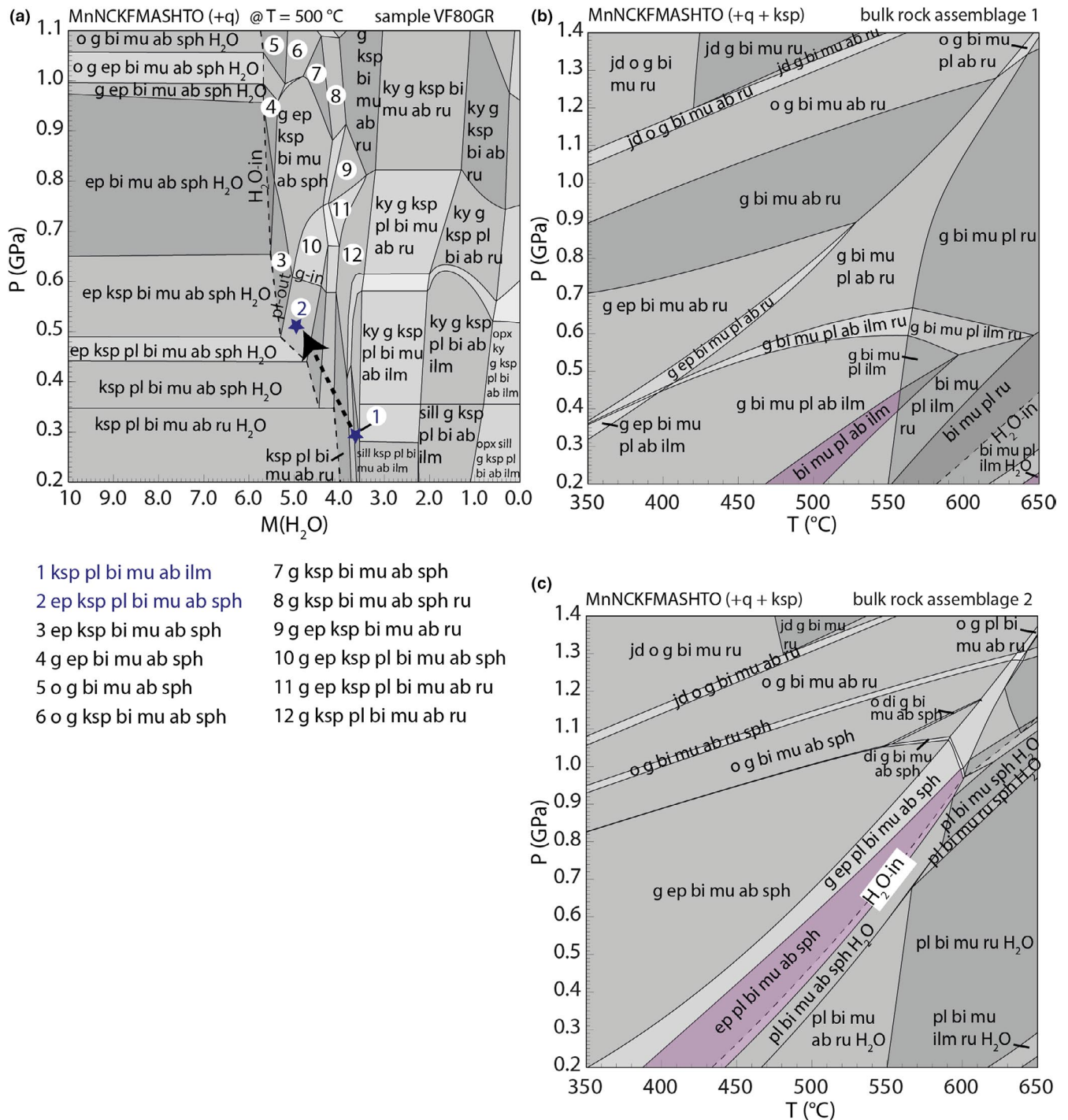


Equilibria 1 and 2 highlight the fluid (H<sub>2</sub>O) demand required to stabilize the clinozoisite and celadonite end-members of the epidote and white mica, respectively. Moreover, the sphene coronae around ilmenite in sample VF80GR (Figure 4c) may have formed in response to hydration reactions as that in the following CKFASHT system:



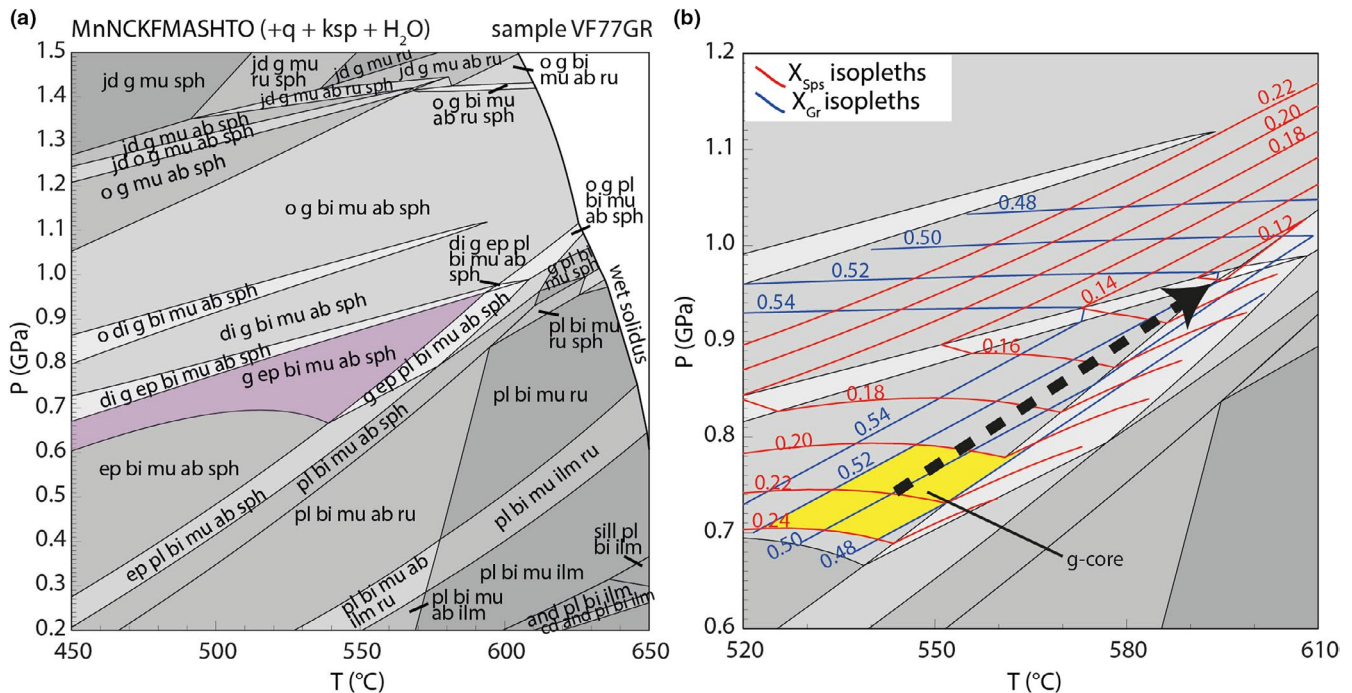
**TABLE 5** Modelled bulk rock compositions in Figures 6–9

| Figure   | Diagram                   | Modelled bulk rock compositions (mol%) |                  |                                |      |      |      |                  |                   |                  |      |      |        |                               |
|----------|---------------------------|----------------------------------------|------------------|--------------------------------|------|------|------|------------------|-------------------|------------------|------|------|--------|-------------------------------|
|          |                           | H <sub>2</sub> O/<br>fluid             | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | FeO  | K <sub>2</sub> O | Na <sub>2</sub> O | TiO <sub>2</sub> | MnO  | O    | Total  | X <sub>Fe</sub> <sup>3+</sup> |
| Figure 6 |                           |                                        |                  |                                |      |      |      |                  |                   |                  |      |      |        |                               |
| (a)      | <i>P</i> – <i>M</i> left  | 10.00                                  | 68.13            | 8.52                           | 1.21 | 2.94 | 3.26 | 2.51             | 2.85              | 0.47             | 0.04 | 0.06 | 100.00 | 3.68                          |
|          | <i>P</i> – <i>M</i> right | 0.00                                   | 75.70            | 9.46                           | 1.35 | 3.27 | 3.63 | 2.79             | 3.17              | 0.52             | 0.05 | 0.07 | 100.00 | 3.86                          |
| (b)      | <i>P</i> – <i>T</i>       | 3.60                                   | 72.97            | 9.12                           | 1.30 | 3.15 | 3.50 | 2.69             | 3.06              | 0.50             | 0.05 | 0.07 | 100.00 | 3.77                          |
| (c)      | <i>P</i> – <i>T</i>       | 4.90                                   | 71.99            | 9.00                           | 1.28 | 3.11 | 3.45 | 2.65             | 3.01              | 0.50             | 0.05 | 0.07 | 100.00 | 3.77                          |
| Figure 7 |                           |                                        |                  |                                |      |      |      |                  |                   |                  |      |      |        |                               |
| (a)      | <i>P</i> – <i>T</i>       | Excess                                 | 80.28            | 8.49                           | 0.86 | 1.29 | 2.10 | 3.40             | 3.19              | 0.29             | 0.04 | 0.05 | 100.00 | 4.76                          |
| Figure 8 |                           |                                        |                  |                                |      |      |      |                  |                   |                  |      |      |        |                               |
| (a)      | <i>P</i> – <i>T</i>       | 3.31                                   | 77.62            | 8.21                           | 0.84 | 1.25 | 2.03 | 3.29             | 3.09              | 0.28             | 0.04 | 0.05 | 100.00 | 4.44                          |
| (c)      | <i>P</i> – <i>M</i> left  | 3.31                                   | 77.62            | 8.21                           | 0.84 | 1.25 | 2.03 | 3.29             | 3.09              | 0.28             | 0.04 | 0.05 | 100.00 | 4.44                          |
|          | <i>P</i> – <i>M</i> right | 0.00                                   | 80.28            | 8.49                           | 0.86 | 1.29 | 2.10 | 3.40             | 3.19              | 0.29             | 0.04 | 0.05 | 100.00 | 4.76                          |
| (d)      | <i>P</i> – <i>T</i>       | 2.81                                   | 78.02            | 8.25                           | 0.84 | 1.25 | 2.04 | 3.31             | 3.10              | 0.28             | 0.04 | 0.05 | 100.00 | 4.41                          |
| Figure 9 |                           |                                        |                  |                                |      |      |      |                  |                   |                  |      |      |        |                               |
| (a)      | <i>T</i> – <i>X</i> left  | 4.90                                   | 71.99            | 9.00                           | 1.28 | 3.11 | 3.45 | 2.65             | 3.01              | 0.50             | 0.05 | 0.07 | 100.00 | 3.77                          |
|          | <i>T</i> – <i>X</i> right | 4.90                                   | 75.56            | 10.07                          | 0.41 | 0.70 | 1.31 | 3.75             | 3.12              | 0.14             | 0.03 | 0.03 | 100.00 | 4.58                          |
| (b)      | <i>P</i> – <i>T</i>       | 6.50                                   | 74.28            | 9.89                           | 0.40 | 0.69 | 1.28 | 3.69             | 3.07              | 0.13             | 0.03 | 0.03 | 100.00 | 4.98                          |



**FIGURE 6** (a)  $T$ - $M_{\text{H}_2\text{O}}$  pseudosection of sample VF80GR with quartz present in all fields. The thin dashed curve delimits the fields with  $\text{H}_2\text{O}$ -saturated mineral assemblages from the fields with  $\text{H}_2\text{O}$ -undersaturated mineral assemblages, and the black arrow joining the blue stars (referred to as assemblages 1 and 2) highlights the stabilization of epidote and sphene due to hydration. (b)  $P$ - $T$  pseudosection, with quartz and K-feldspar present in each field, for the bulk rock composition of assemblage 1 (with 3.6 mol% of  $\text{H}_2\text{O}$  bound in OH-bearing mineral phases), where the  $P$ - $T$  field of the bi-mu-pl-ab-ilm and bi-mu-pl-ilm- $\text{H}_2\text{O}$  mineral assemblages are shown in light magenta. (c)  $P$ - $T$  pseudosection for the bulk rock composition (with quartz and K-feldspar present in each field) of mineral assemblage 2 (with 4.9 mol% of  $\text{H}_2\text{O}$  bound in OH-bearing mineral phases), where the  $P$ - $T$  field of the new mineral assemblage is shown in light magenta. Note that the new mineral assemblage occurs in the  $P$ - $T$  space both under  $\text{H}_2\text{O}$ -saturated conditions, at higher temperature (in the quadra-variant ep+pl+bi+mu+ab+sph+ $\text{H}_2\text{O}$  stability field), and  $\text{H}_2\text{O}$ -undersaturated conditions, at lower temperature (in the penta-variant ep+pl+bi+mu+ab+sph stability field)

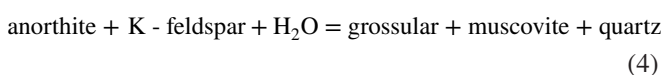




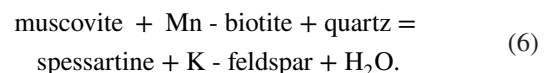
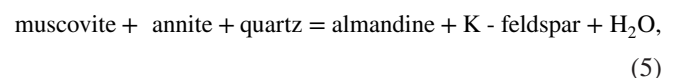
**FIGURE 7** (a)  $P$ - $T$  pseudosection for sample VF77GR (mylonitic orthogneiss) with quartz and K-feldspar present in each field, which shows the topology of the mineral assemblages under H<sub>2</sub>O-saturated conditions and the stability field of the stable mineral assemblage (in magenta). (b) Contouring of the  $X_{Gr}$  and  $X_{Sps}$  compositional isopleths for garnet with the  $P$ - $T$  path (black arrow) retrieved from the intersections of the core-rim compositions of the garnet in Figure 5a and core compositions in Figure 5b. The intersection area between the highest  $X_{Sps}$  values and the related  $X_{Gr}$  values in the very core of these garnets is highlighted in yellow

Accordingly, Harlov et al. (2006) demonstrated that ilmenite replacement by sphene is not solely a function of the  $P$ - $T$  conditions as previously believed (e.g. Enami et al., 1993), but may be strongly influenced by changes in fH<sub>2</sub>O and/or fO<sub>2</sub>.

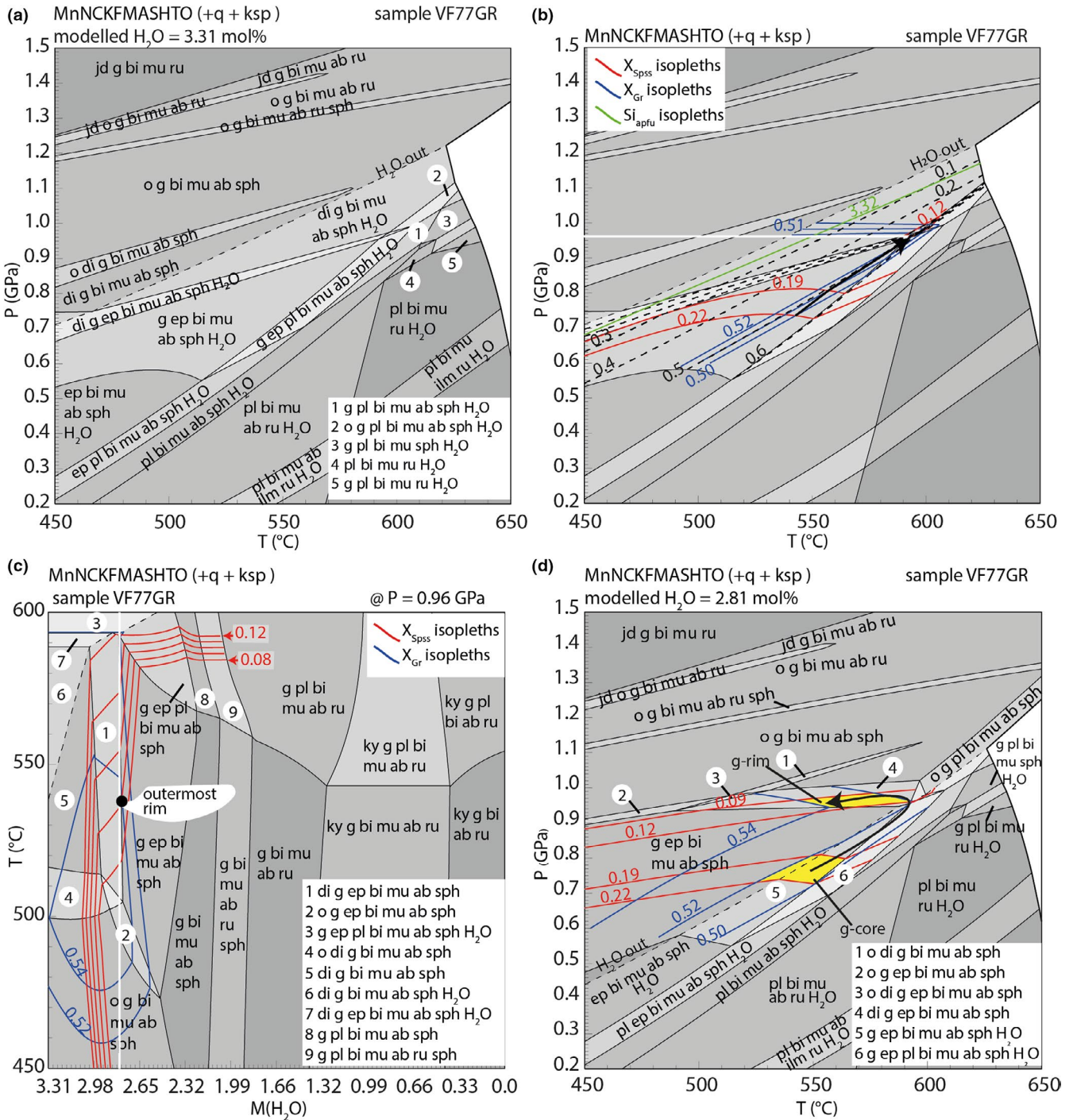
Within the mylonitic orthogneisses (sample VF77GR and VF79GR), the microstructural relationships evidence the overgrowth of tiny ferro-celadonite-rich white mica on large biotite flakes and the overgrowth of sphene on relict ilmenite (Figure 4e), as also recorded in the weakly deformed orthogneiss. This mineral paragenesis is consistent with the fluid consumption, as evidenced from Equilibria 2 and 3. In addition, grossular-rich garnet (Table 4) occur in the mylonitic orthogneisses (Figure 4e,h), as the main mineral phase indicative of the prograde metamorphism. These garnets host tiny quartz, albite, and white mica inclusions (Figure 5) as well as sphene coronae around ilmenite remnants (Figure 4f), thus suggesting that garnet started to grow when these minerals were already present. According to the petrographic evidences, the stabilization of grossular-rich garnet cores in the investigated mylonitic orthogneisses may have primarily occurred, via the following hydration reaction in the simplified CKASH system:



Equilibrium 4 evidences the linkage between the stabilization of the Ca-rich garnet (Table 4) and the availability of fluid in the system. However, biotite was also involved in the stabilization of garnet in mylonitic samples, providing Fe and Mn through Equilibria 5 and 6:



Equilibria 4–6 imply the consumption and release of fluid respectively, potentially suggesting H<sub>2</sub>O conservation during the garnet stabilization. Accordingly, it can be inferred that biotite may have been part of the mineral assemblage at least up to the peak metamorphic conditions, when it was either nearly (sample VF77GR) or completely (sample VF79GR) consumed as metamorphism progressed (Table 6). Around garnet and biotite, a further ferro-celadonite-rich white mica grew along the mylonitic foliation (Figure 4d,h), as indicative of the last metamorphic stage (Table 6). Therefore, the succession of the mineral assemblages in the weakly- to mylonitic orthogneisses was related to both hydration (i.e. Equilibria

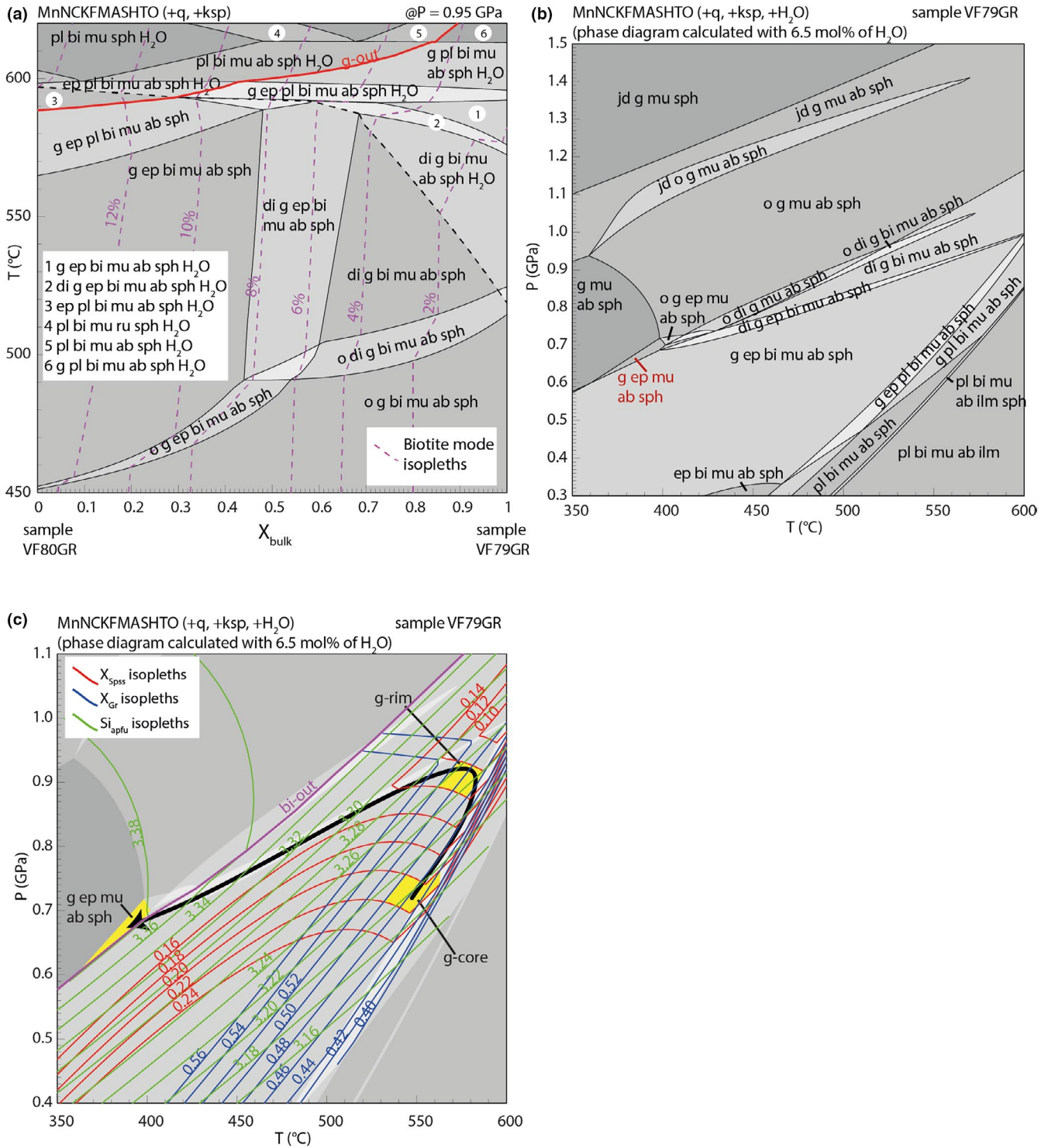


**FIGURE 8** (a)  $P$ - $T$  pseudosection of sample VF77GR, where the thick black curve is the wet solidus. The dashed line delimits  $H_2O$ -saturated fields. (b) Retrieved  $P$ - $T$  path (black arrow) corresponding to the intersections of the  $X_{\text{Gr}}$  and  $X_{\text{Spss}}$  compositional isopleths of the garnet from the very core to the peripheral core compositions in Figure 7b; the thick dashed lines are the contours of  $H_2O$  fluid modes, whereas the green thick line is the  $Si = 3.32$  apfu isopleth. (c)  $T$ - $M_{H_2O}$  pseudosection calculated at 0.96 GPa for sample VF77GR with excess quartz and K-feldspar. The black point refers to the outermost rim compositions of the garnet shown in Figure 5b, and the white line indicates the  $H_2O$  content required to reproduce the rim in Figure 5b. (d)  $P$ - $T$  pseudosection calculated with the  $H_2O$  content selected in (c), with the  $P$ - $T$  path (thick black arrow) experienced by the mylonitic orthogneiss of the Castagna Unit (sample VF77GR); the intersection areas between  $X_{\text{Gr}}$  and  $X_{\text{Spss}}$  compositional isopleths of the garnet from the very core to the outermost rim are highlighted in yellow

1-4) and dehydration reactions (i.e. Equilibria 5 and 6); hence, the phase equilibrium modelling is focussed on the investigation of the fluid-present and fluid-deficient

conditions when the former celadonite-rich white mica (produced by Equilibrium 1), epidote, sphene, garnet and the ferro-celadonite-rich white mica were stabilized.





**FIGURE 9** (a)  $T$ - $X_{\text{bulk}}$  pseudosection by varying the bulk rock composition from the weakly deformed orthogneiss ( $X=0$ ) to the mylonitic leucocratic orthogneiss ( $X=1$ ), but considering the same H<sub>2</sub>O mol.% in both samples. Note the progressive stabilization of garnet and the increased fluid content towards the core of the shear zone, highlighted by the garnet-out curve (red curve). The contouring of biotite mode isopleths (magenta dashed curves) is also shown. (b)  $P$ - $T$  pseudosection of the VF79GR sample assuming a fluid content of 6.5 mol% able to saturate all the fields at  $P < 1.5$  GPa, in the temperature range considered. The mineral assemblage of the mylonitic leucocratic orthogneiss is highlighted in red. (c)  $P$ - $T$  path (black thick arrow) obtained for the mylonitic leucocratic orthogneiss (sample VF79GR) through the contouring of the  $X_{\text{Gr}}$ ,  $X_{\text{Sps}}$ , and  $\text{Si}_{\text{apfu}}$  isopleths of garnet and white mica; the intersection areas between  $X_{\text{Gr}}$  and  $X_{\text{Sps}}$  in the very core and outermost rim of the garnets in Figure 5c,d are highlighted in yellow as well as the mylonitic mineral assemblage stability field. The biotite-out curve is highlighted in magenta

**TABLE 6** Mineral paragenesis developed during the different metamorphic stages in samples VF80GR, VF77GR and VF79GR

| Sample | Mineral phases and metamorphic stages |    |    |    |    |    |                  |   |     |     |   |    |            |    |    |     |   |     |    |    |     |   |     |   |
|--------|---------------------------------------|----|----|----|----|----|------------------|---|-----|-----|---|----|------------|----|----|-----|---|-----|----|----|-----|---|-----|---|
|        | Prograde                              |    |    |    |    |    | Metamorphic peak |   |     |     |   |    | Exhumation |    |    |     |   |     |    |    |     |   |     |   |
|        | g                                     | mu | bi | ep | pl | ab | ksp              | q | ilm | sph | g | mu | bi         | ep | ab | ksp | q | sph | mu | ab | ksp | q | sph |   |
| VF80GR | x                                     | x  | x  | x  | x  | x  | x                | x | a   | x   |   |    |            |    |    |     |   |     |    |    |     |   |     |   |
| VF77GR | x                                     | x  | x  | x  | x  | x  | x                | x | a   | x   | x | x  | x          | x  | x  | x   | x | x   | x  | x  | x   | x | x   | x |
| VF79GR | x                                     | x  | x  | x  | x  | x  | x                | x |     | x   | x | x  | ?          | x  | x  | x   | x | x   | x  | x  | x   | x | x   | x |

Note: a = inclusion in titanite; ? = no clear microstructural evidences.

### 4.3 | Post-Hercynian hydration in the weakly deformed orthogneiss

The occurrence of new epidote grains (Figure 4a) and sphene coronae (Figure 4c) in the weakly deformed orthogneiss (sample VF80GR) is explored in Figure 6a. A  $P$ - $M_{\text{H}_2\text{O}}$  pseudosection has been calculated near the greenschist–amphibolite facies transition in the pressure range of 0.2–1.4 GPa and at a constant temperature of 500°C. At this temperature, the mineral assemblage pl+bi+mu+ab (+q+ksp), where oligoclase and albite occur together at the peristerite solvus, is either  $\text{H}_2\text{O}$  saturated for  $M(\text{H}_2\text{O}) > 4.0$  mol% if rutile is stable, or  $\text{H}_2\text{O}$  undersaturated if ilmenite is stable (assemblage 1 in Figure 6a) for ~3.6 mol% of  $\text{H}_2\text{O}$  bound in OH-bearing minerals, that is, biotite and muscovite in this case. Although the stability of rutile and/or ilmenite is dependent on the oxidation state, ilmenite was observed in the studied rocks (Figure 4) while rutile was not detected (cf. Table 6). Therefore, moving at a constant 3.6 mol% of  $\text{H}_2\text{O}$  towards a higher pressure in the phase diagram (e.g. assemblage 12 in Figure 6a), epidote and sphene never stabilize in the mineral assemblages encountered. Indeed, to stabilize these phases, a higher fluid content in the bulk rock of ~4.9  $\text{H}_2\text{O}$  mol% (assemblage 2 in Figure 6a) is required.

To investigate the changes that can occur in the equilibrium mineral assemblages within the  $P$ - $T$  space when fluid is added to the rock, two  $P$ - $T$  pseudosections have been calculated for the bulk rock compositions of the mineral assemblages 1 (ksp-pl-bi-mu-ab-ilm-q) and 2 (ep-ksp-pl-bi-mu-ab-sph-q) (Figure 6b,c), whose difference is the previously inferred  $\text{H}_2\text{O}$  content (i.e. 3.6 and 4.9 mol%). The mineral assemblage (1) exhibits an upper pressure limit of ~0.45 GPa for a temperature ranging from 470 to 550°C, under  $\text{H}_2\text{O}$ -undersaturated conditions (Figure 6b). This mineral assemblage appears to have formed on a primary pl (oligoclase)+bi+mu+ilm+ $\text{H}_2\text{O}$  (+q+ksp) paragenesis, which is stable at low- $P$  amphibolite facies conditions from ~640°C (Figure 6b), and seems to correspond to the late-Hercynian metamorphic conditions (e.g. Ortolano et al., 2020). The  $P$ - $T$  stability field of the mineral assemblage (2) is composed of ep+pl (oligoclase)+bi+mu+ab+sph (+q+ksp), and is shown in the  $P$ - $T$  pseudosection in Figure 6c, which is calculated by considering 4.9 mol% of  $\text{H}_2\text{O}$ . Noticeably, Figure 6c reveals that the new mineral assemblage is stable in a pressure range of 0.2–1.0 GPa and temperature range of 390–590°C, which covers  $\text{H}_2\text{O}$ -undersaturated and  $\text{H}_2\text{O}$ -saturated conditions (Figure 6c).

### 4.4 | Alpine peak metamorphic conditions in mylonitic orthogneisses

Alpine peak metamorphic conditions have been firstly investigated in sample VF77GR (mylonitic orthogneiss) and



then in sample VF79GR (mylonitic leucocratic orthogneiss), moving towards the contact with the Sila and Serre Unit along the transect in Figure 2. To reproduce the garnet zoning patterns, equilibria in these rocks have been modelled by considering (a) fully H<sub>2</sub>O-saturated conditions (i.e. H<sub>2</sub>O set in excess) and (b) partly H<sub>2</sub>O-saturated conditions (Table 5).

#### 4.4.1 | Sample VF77GR: equilibria under fully H<sub>2</sub>O-saturated conditions

The case of complete rehydration of the relict metamorphic mineral assemblage during Alpine tectonics has been investigated by calculating a  $P$ – $T$  phase diagram with fluid (H<sub>2</sub>O) set in excess (Figure 7a). Under H<sub>2</sub>O-saturated conditions, garnet is present in the observed q+ksp+ab+g+ep+mu+bi+sph mineral assemblage from a minimum pressure of ~0.6 GPa, with the upper stability field of this assemblage limited at higher pressure by the diopside-in curve. To reproduce the core–rim compositional variation for the garnet (Figure 5a,b), the  $X_{Gr}$  and  $X_{Sps}$  isopleths have been plotted in Figure 7b. The  $X_{Gr}$  isopleths can be reproduced between the lowest (0.48) and highest (0.54) molar fractions (Figure 5a,b), whereas the lowest reproducible  $X_{Sps}$  molar fraction is 0.12 (Figure 7b). The composition isopleths in Figure 7b suitably represent the growth of the garnets' core (i.e.  $X_{Sps}$  of 0.24–0.20 and  $X_{Gr}$  of 0.48–0.52 in Figure 5a,b) as well as the rim compositions of some garnet (i.e.  $X_{Sps}$  of 0.14–0.16 and  $X_{Gr}$  of 0.52–0.54 in Figure 5a). The phase diagram in Figure 7b clearly shows that garnet grew at conditions of ~0.75 GPa and 540°C up to ~0.96 GPa and 590°C, in the g+ep+bi+mu+ab+sph (+q+ksp) stability field, if H<sub>2</sub>O saturation is assumed. The maximum  $P$ – $T$  conditions are recorded either in the latter part of the rim of some garnet (Figure 5a) or in the outer core of some other crystals ( $X_{Sps}$  of ~0.12 and  $X_{Gr}$  of ~0.54), as illustrated in Figure 5b.

The main outcome of modelling the mylonitic orthogneiss (sample VF77GR) with excess fluid is the irreproducibility of  $X_{Sps}$  values lower than 0.12 molar fraction, which are recorded in the rim of some garnets (Figure 5b). Therefore, fully H<sub>2</sub>O-saturated conditions do not completely satisfy the composition of growing garnet.

#### 4.4.2 | Sample VF77GR: equilibria under partly H<sub>2</sub>O-saturated conditions

Excluding the fully H<sub>2</sub>O-saturated conditions, phase equilibria in sample VF77GR were also investigated under variable degrees of hydration to reproduce the zoning patterns of the garnet in the same mylonitic orthogneiss. The first modelled

amount of H<sub>2</sub>O, was that required to saturate the wet solidus at 1.2 GPa and 620°C (i.e. 3.31 mol% of H<sub>2</sub>O), with quartz and K-feldspar present in all fields. This H<sub>2</sub>O content reproduces H<sub>2</sub>O-saturated conditions for the stability field of the observed g+ep+bi+mu+ab+sph (+q+ksp) mineral assemblage (Figure 8a), with an amount of fluid that is different (lower) from that modelled in Figure 7. Accordingly, both the phase diagrams of Figures 7a and 8a were calculated for the same sample, but the different amounts of H<sub>2</sub>O make them not completely identical. For instance, the LP tip of the g–ep–bi–mu–ab–sph stability field is at ~0.65 GPa and ~540°C in Figure 7a, whereas it is at ~0.55 GPa and ~515°C in Figure 8a, making this  $P$ – $T$  stability field in Figure 8a wider than in Figure 7a. However, the reproducible  $X_{Sps}$  isopleths of the garnet are the same as those in Figure 7b, and the garnet rim composition in Figure 5b is thus irreproducible, with the intersection in the outer part of the core ( $X_{Gr}$  = 0.52 and  $X_{Sps}$  = 0.12) occurring again at ~0.96 GPa and ~590°C. The  $Si_{apfu}$  isopleth is strongly affected by the fluid availability in the system; it runs parallel to the H<sub>2</sub>O-saturation curve and does not exhibit any reliable intersection with the  $X_{Gr}$  and  $X_{Sps}$  of the garnet (Figure 8b). To investigate the growth of garnet rims in relation to dehydration during the prograde path, the H<sub>2</sub>O-mode isopleths were contoured (Figure 8b). This contouring highlights how the H<sub>2</sub>O content of the rock does not vary during the growth of the garnet's core within the g+ep+bi+mu+ab+sph+H<sub>2</sub>O stability field (Figure 8b). This testifies that garnet formed while the rock was following a steep prograde path where the fluid, provided by devolatilization reactions (e.g. equilibria 5–6), was almost stored within simultaneously forming OH-bearing minerals like white mica (e.g. Equilibrium 2).

To investigate if the evolutionary path of the mylonitic orthogneiss of the Castagna Unit was characterized by fluid-deficient conditions, a  $T$ – $M_{H_2O}$  pseudosection was calculated at a constant  $P$  of 0.96 GPa, varying the H<sub>2</sub>O mol% from 3.31 to 0.00 (Figure 8c). This isobaric phase diagram shows that the outermost rim compositions of garnet (i.e.  $X_{Gr}$  = 0.54 and  $X_{Sps}$  = 0.09) are reproduced in the di+g+ep+bi+mu+ab+sph stability field under H<sub>2</sub>O-deficient conditions of 2.81 mol% of H<sub>2</sub>O bound within OH-bearing minerals, at a  $T$  of <590°C.

Consequently, a  $P$ – $T$  pseudosection was calculated considering the fluid content equal to 2.81 mol% (Figure 8d). The intersections between the  $X_{Sps}$  and  $X_{Gr}$  isopleths of the garnet, together with the slope of the H<sub>2</sub>O-saturated curve, setting the H<sub>2</sub>O-conservative character, indicate that the prograde path occurred from 0.70–0.75 GPa and 540–545°C ( $X_{Gr}$  = 0.48 and  $X_{Sps}$  = 0.22) up to the metamorphic peak at ~0.96 GPa and ~590°C ( $X_{Gr}$  = 0.52 and  $X_{Sps}$  = 0.12). The composition of the outermost rim of the garnet ( $X_{Gr}$  = 0.54 and  $X_{Sps}$  = 0.09), suggests that probably, retrogression with nearly isobaric cooling, down to ~540°C, resulted under H<sub>2</sub>O-undersaturated conditions.

#### 4.5 | Sample VF79GR: metamorphic peak and post-peak exhumation under fluid-present conditions

As reported so far, garnet is progressively stabilized and the modal abundance of biotite progressively decreases (Figures 2 and 3) when moving from the weakly deformed orthogneiss (sample VF80GR) towards the garnet-bearing, biotite-free mylonitic leucocratic orthogneiss (sample VF79GR). These variations are evident in the  $T$ - $X_{\text{bulk}}$  pseudosection in Figure 9a, calculated at 0.95 GPa from sample VF80GR to sample VF79GR, assuming for both samples 4.9 mol% of  $\text{H}_2\text{O}$  bound within OH-bearing minerals (see Table 5). In this phase diagram the expansion of the garnet stability field (cf. assemblages 1 and 3 at  $T < 600^\circ\text{C}$ , and assemblages 4 and 6 at  $T > 600^\circ\text{C}$ ) as well as the decrease in the biotite mode are illustrated. Accordingly, this isobaric phase diagram highlights the control of the bulk rock composition on mineral assemblages as well as how fluid-present conditions are favoured in mylonitic metagranitoids with lower  $\text{FeO}_t$ ,  $\text{MgO}$ , and  $\text{TiO}_2$  and higher  $\text{K}_2\text{O}$  contents (cf. Table 1, samples VF80GR and VF79GR). The calculated equilibria at 0.95 GPa for  $X_{\text{bulk}} = 1$  in Figure 9a, support the interpretation that the mylonitic leucocratic orthogneiss (sample VF79GR) is  $\text{H}_2\text{O}$ -undersaturated at a  $T < 510^\circ\text{C}$  for the fluid content considered. This results in small amounts of biotite expected to be stable in this rock under peak-pressure conditions, even at temperature of  $< 510^\circ\text{C}$ , which seems not corresponding to the absence of biotite within this rock (cf. Table 6). Therefore, since the equilibria consuming biotite require the presence of fluid, the phase equilibria considering a higher fluid content (i.e. 6.5 mol%; Table 5) are explored in the phase diagram in Figure 9b. Here, for this fluid content the biotite-free mylonitic mineral assemblage of sample VF79GR (cf. Table 6) is reproduced at pressure of 0.6–0.7 GPa and temperature of 360–400°C during retrogression: this is suggested by the contouring of composition isopleths of  $X_{\text{Sps}}$  and  $X_{\text{Gr}}$  of garnet in Figure 9c showing that garnet growth started in the bi-stability field at pressure of 0.70–0.76 GPa and temperature of 530–560°C ( $X_{\text{Sps}} = 0.20$ – $0.22$  and  $X_{\text{Gr}} = 0.46$ – $0.50$  of garnet cores, cf. Figure 5c,d) up to peak metamorphic conditions of 0.88–0.94 GPa and 560–590°C ( $X_{\text{Sps}} = 0.12$ – $0.14$  and  $X_{\text{Gr}} = 0.50$ – $0.54$  of garnet outermost rims, cf. Figure 5c,d). The contouring of Si in muscovite, together with the disappearance of biotite, highlight how the tiny recrystallized ferro-celadonite-rich white mica, having Si up to 3.38 apfu in sample VF79GR (Table 2), record the  $P$ - $T$  conditions of equilibration during retrogression around 0.6–0.7 GPa and 350–400°C, before entering the  $\text{g}+\text{ep}+\text{mu}+\text{ab}+\text{sph}$  ( $+\text{q}+\text{ksp}+\text{H}_2\text{O}$ ) stability field (Figure 9c). Noticeably, while the Si content of white mica is pressure sensitive in biotite-bearing mineral assemblages, it becomes temperature sensitive in biotite-free mineral assemblages (Figure 9c).

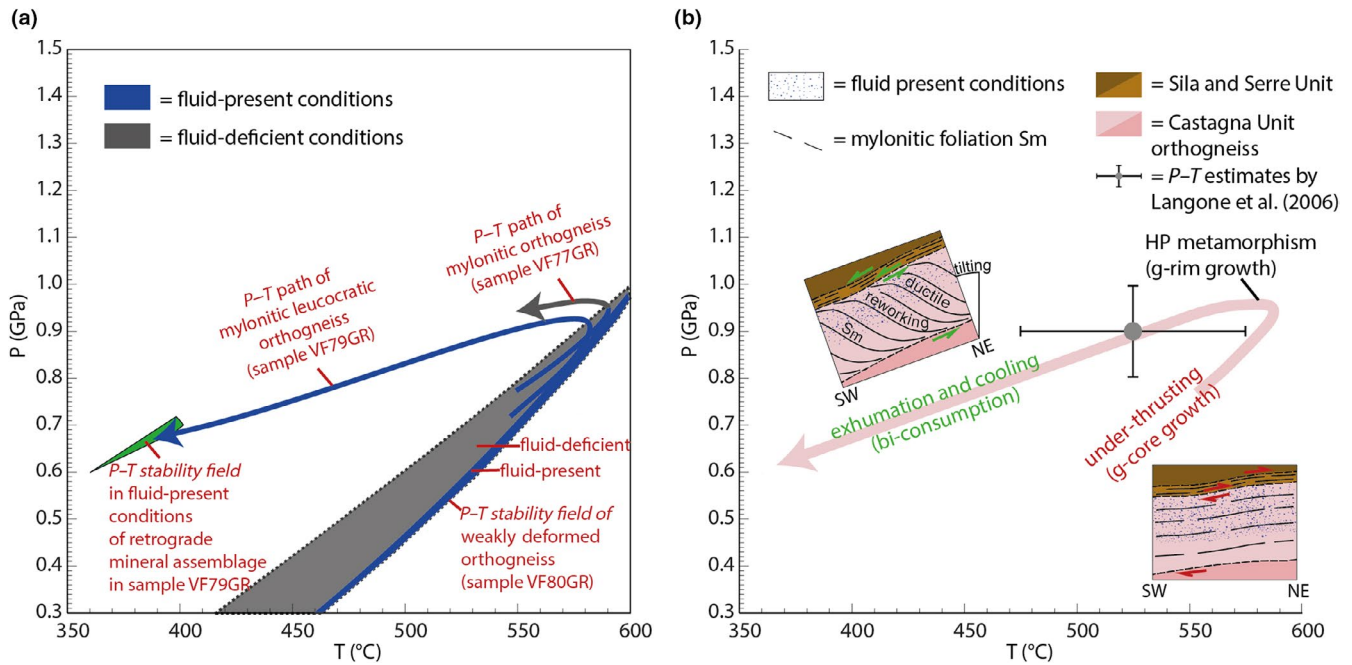
## 5 | DISCUSSION

The following discussion is focussed on: (a) the Alpine  $P$ - $T$ -fluid evolution experienced by the orthogneisses of the Castagna Unit, and (b) some general considerations regarding the evolution of the CGL during Alpine orogeny.

### 5.1 | Alpine $P$ - $T$ -fluid evolution of the orthogneisses

The modelling results are summarized in Figure 10a, where the  $P$ - $T$  stability field of the weakly deformed orthogneiss (VF80GR) and the  $P$ - $T$ -fluid paths of the mylonitic orthogneisses (VF77GR, VF79GR) are shown together. In particular, the stability field of the  $\text{ep-pl-bi-mu-ab-q-ksp-sph}$  mineral assemblage of the weakly deformed orthogneiss (from Figure 6c) is reported in Figure 10a. This mineral assemblage formed under conditions characterised by insufficient degrees of hydration to saturate the assemblage. Under these conditions, epidote and sphene were stabilised at the expense of an inherited, late-Hercynian metamorphic mineral paragenesis (i.e.  $\text{pl-bi-mu-q-ksp-ilm}$  in Figure 6b). On the whole, the  $P$ - $T$  space of the  $\text{ep-pl-bi-mu-ab-q-ksp-sph}$  mineral assemblage has an upper pressure limit of  $\sim 1.0$  GPa and a temperature range of  $\sim 420$ – $600^\circ\text{C}$  (Figure 10a). As regards the mylonitic orthogneisses (sample VF77GR and VF79GR), the modelling results show that garnet started to grow under  $\text{H}_2\text{O}$ -saturated conditions (Figures 7–9). These garnet, which host quartz, albite, muscovite, and sphene inclusions record the prograde path, up to peak metamorphic conditions of  $\sim 0.9$ – $1.0$  GPa and  $\sim 590^\circ\text{C}$  (Figures 7–9), within their core to rim zoning patterns (Figure 5a). Moreover, some of the garnets in sample VF77GR (Figure 5b) show rim equilibration in the temperature range of  $540$ – $590^\circ\text{C}$  at peak pressure conditions of  $\sim 0.96$  GPa, under fluid-deficient conditions (Figures 8 and 10a). Although the thermobarometric results obtained from intersections of garnet compositional isopleths have to be cautiously considered given the uncertainties related to the small core–rim differences in  $X_{\text{Gr}}$  values, along with the poorly constrained behaviour of Mn in many minerals, some general considerations on the obtained prograde  $P$ - $T$  evolution and the  $P$ - $T$  stability field of mineral assemblages can be, however, made. In fact, the prograde path obtained by modelling the garnet zoning patterns in mylonitic orthogneiss, roughly overlaps the stability field of the mineral assemblage in the weakly deformed orthogneiss, as illustrated in Figure 10a. Accordingly, it is possible to deduce that the whole orthogneiss body of the Castagna Unit shared the same peak metamorphic conditions under a geothermal gradient of  $\sim 16$ – $17^\circ\text{C}/\text{km}$  (assuming a granitic crust density of  $2,750 \text{ kg}/\text{m}^3$ ; Figure 10a). Moreover, within the mylonitic orthogneisses, biotite is less abundant





**FIGURE 10** (a)  $P$ – $T$  diagram highlighting the overlap of the  $P$ – $T$ –fluid paths in Figures 8d and 9c onto the stability field of the mineral assemblage of the weakly deformed orthogneiss in Figure 6c. Note how fluid-present conditions are promoted in mylonitic samples (VF77GR and VF79GR). (b)  $P$ – $T$  path obtained in this study for the orthogneisses of the Castagna Unit during Alpine reworking; the  $P$ – $T$  estimates (with uncertainties) by Langone et al. (2006) for the orthogneisses of the Castagna Unit are also plotted. The Alpine evolution of the orthogneisses is also schematically represented, by two frames (modified after Festa et al., 2020), for the Eocene under-thrusting and the late Oligocene extensional re-activation accompanied by ductile reworking of the CGL during (late Eocene?) Oligocene–early Miocene exhumation, tilting and cooling; sites of fluid-present conditions are highlighted

than in the weakly deformed orthogneiss or it is completely absent, as in the case of sample VF79GR, because replaced by tiny, ferro-celadonite-rich white mica (Table 2). This tiny white mica, which defines the main mylonitic foliation (Figure 4), records, in sample VF79GR, equilibration under  $H_2O$ -saturated conditions near the biotite-out curve, in proximity to the  $g$ – $ep$ – $mu$ – $ab$ – $q$ – $ksp$ – $sph$  mylonitic mineral assemblage (Figure 9c). The  $P$ – $T$  space of equilibration of this mineral assemblage is 0.6–0.7 GPa and 360–400°C, and allows the definition of the exhumation and cooling trajectory followed by the Castagna Unit mylonitic orthogneisses, along with the resulting anticlockwise shape of the  $P$ – $T$  path (Figure 10a). Comparing our results with the thermobarometric estimates by Langone et al. (2006) on orthogneisses of the Castagna Unit, the  $P$ – $T$  estimates by these authors suitably overlap along the exhumation and cooling path obtained in this study (Figure 10b).

Analysing the obtained  $P$ – $T$  paths with respect to the fluid-present/deficient conditions from the weakly deformed to the mylonitic orthogneisses (Figure 10a), it can be argued that the hydration event that favoured the stabilization of the new Alpine mineral assemblages in these rocks, probably occurred during the rifting phase preceding the Alpine compressive tectonics in Calabria (e.g. Liberi et al., 2011). In fact, as demonstrated in other case studies of prograde ductile shear zones set in metagranitoid rocks (e.g. Leydier et al., 2019),

an aqueous fluid could have infiltrated along planar discontinuities (e.g. old schistosity planes) and/or brittle structures (e.g. fractures) before the onset of the Alpine tectonics, with resulting fluid-present conditions in the orthogneisses when under-thrusting of the Castagna Unit below the Sila and Serre Unit commenced (Figure 10b). Successively, during the Eocene compressive tectonics, the Castagna Unit experienced burial and thrusting below the Sila and Serre Unit (Festa et al., 2020) (Figure 10b). The interpreted  $P$ – $T$  evolution for the Castagna Unit mylonitic orthogneisses shown in Figure 10a, evidences that  $H_2O$ -saturated conditions characterized the prograde path of these rocks up to the Alpine metamorphic peak ( $P$  of ~0.9–1.0 GPa and  $T$  of ~590°C) at  $c.$  43 Ma (Schenk, 1990). These peak conditions were reached following an almost  $H_2O$ -conservative trajectory (Figure 8), which resulted from the simultaneously operating reactions of devolatilization, due to biotite breakdown to form garnet (e.g. Equilibrium 5), and of fluid-consumption, to form the celadonite rich white mica (e.g. Equilibrium 2). Hence, it can be deduced that the stabilization of garnet in the mylonitic orthogneisses, rather than in the weakly deformed orthogneiss, was aided by the fluid-present conditions (Figures 8 and 9) which likely exerted a catalytic role to mineral stabilization (e.g. Rubie, 1986). After the cessation of under-thrusting, the Castagna Unit mylonitic orthogneisses experienced cooling at high- $P$  conditions (Figure 10a). This is recorded in the

rim compositions of some garnets from sample VF77GR, which evidence equilibration in H<sub>2</sub>O-undersaturated conditions during isobaric cooling at a pressure of ~0.9–1.0 GPa (Figure 10a). On the other hand, closer to the tectonic contact with the Sila and Serre Unit, the prograde to retrograde path of the mylonitic leucocratic orthogneiss (sample VF79GR) is H<sub>2</sub>O-saturated, as recorded in the core to rim compositions of the garnet and by the Si contents of the tiny white mica, respectively (Figures 9 and 10a). Therefore, it can be inferred that the remaining fluid in the mylonitic orthogneisses, was channelled towards the tectonic contact with the Sila and Serre Unit after the peak metamorphic conditions were reached, promoting fluid-present conditions in these rocks (Figure 10b) during the exhumation.

## 5.2 | Evolution of the CGL during Alpine orogeny

About the *P–T* path obtained, some final considerations on (a) the location of the CGL during the Eocene compressive tectonics with respect to the Alpine subduction, and (b) the re-activation of the CGL during the Oligocene–Miocene extensional tectonics in Calabria, can be outlined. The prograde part of the modelled path indicates stacking of the Calabria continental crust during Eocene Alpine compressive tectonics (Festa et al., 2020), with the Castagna Unit orthogneisses, under-thrusting the Sila and Serre Unit, that reached a depth of ~35 km under a geothermal gradient of ~16–17°C/km. After the cessation of under-thrusting, the peculiar isobaric cooling trajectory, under HP conditions (Figure 10b), indicates that the orthogneisses of the Castagna Unit started to experience cooling at HP conditions. Rocks that experienced this type of *P–T* evolution were interpreted by Wakabayashi (2004) and Willner et al. (2004) as recording involvement in the subduction process. Accordingly, it can be argued that the location of the CGL was in proximity to the cold subducting Ligurian Tethys' oceanic crust (Tursi, Bianco, et al., 2020), which promoted deflection of the isotherms in the obducting continental crust, and cooling, under HP conditions, in the Castagna Unit orthogneisses. This is also corroborated by the general cold character of the Alpine subduction zone in Calabria, where a geothermal gradient of ~6.6°C/km at peak metamorphic conditions, was obtained by Tursi, Bianco, et al. (2020) for the lawsonite–clinopyroxene blueschists of the oceanic crust subducting beneath the continental margin.

The subsequent exhumation and cooling of the orthogneisses of the Castagna Unit to 0.6–0.7 GPa and 360–400°C can be suitably reconciled with the evolutionary structural model for the CGL by Festa et al. (2020). According to this model, exhumation of the Castagna Unit's orthogneisses happened during ductile re-activation of the CGL under an extensional regime that likely occurred during

(late Eocene?) Oligocene to early Miocene. This tectonic re-activation is thereby supported by the microstructural evidence presented in this study, where the tiny, syn-kinematic ferro-celadonic white mica defines the main mylonitic foliation and shows equilibration in the retrograde path (e.g. Figures 9c and 10b). In addition, sphene in mylonitic orthogneisses, together with the modelled Ca-rich garnet (e.g. Figure 4), show equilibration during the prograde stage of metamorphism related to under-thrusting (Figure 10b), providing constraints for the extensional re-activation of the former compressive Curinga–Girifalco Line. The preservation of the prograde history of the Castagna Unit orthogneisses, along with the anticlockwise shape of the *P–T* trajectory, were therefore possible since no high-*T* overprint occurred during exhumation of these rocks (i.e. no Alpine magmatism is recorded in Calabria), which is the main factor for erasing these information (e.g. Wakabayashi, 2004).

## 6 | CONCLUSIONS

The present study provides the first reconstruction of the Alpine *P–T*–fluid evolution experienced by the orthogneisses of the Castagna Unit in Calabria, along with the useful information that can be retrieved from forward thermodynamic modelling of metagranitoids relating their mineral parageneses with respect to fluid-present/deficient conditions during metamorphism. The results showed that the Castagna Unit was first subjected to hydration during the rifting phase preceding the Alpine compressive tectonics in Calabria. During the Alpine orogeny, the Castagna Unit's orthogneisses experienced under-thrusting to lower crust depths along the CGL, with the mineral assemblage of these rocks varying in relation to the distance from the Sila and Serre Unit. Accordingly, the *P–T* evolutionary path of the mylonitic orthogneisses was either characterized by transient H<sub>2</sub>O-saturated and H<sub>2</sub>O-undersaturated conditions, far from the tectonic contact, or persistent H<sub>2</sub>O-saturated conditions close to the contact. These *P–T*–fluid conditions were primarily recorded in the core–rim composition of garnet and also in recrystallized phengitic white mica. The obtained paths, evidence under-thrusting in a 'closed system' along a fluid-conservative trajectory, up to the peak metamorphic conditions of ~0.9–1.0 GPa and ~560–590°C. Different degrees of fluid saturation affected the post-peak evolution of the mylonitic orthogneisses. Accordingly, isobaric cooling in H<sub>2</sub>O-undersaturated conditions is recorded in mylonitic orthogneisses far from the tectonic contact, whereas H<sub>2</sub>O-saturated conditions affected the mylonitic orthogneisses close to this contact. This resulted from the channelling, within the shear zone, of the fluid towards the tectonic contact with the Sila and Serre Unit during re-activation, under an extensional regime, of

the previously compressive shear zone. The overall anticlockwise  $P$ – $T$  evolution recorded by the Castagna Unit mylonitic orthogneisses thus evidence the involvement of this tectono-metamorphic unit into the Eocene subduction process in Calabria.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

**Figure S1.**  $P$ - $X\text{Fe}^{3+}$  phase diagrams for sample VF80GR of weakly deformed orthogneiss (left side) and for sample VF77GR of mylonitic orthogneiss (right side).

**Table S1.** Mean of 10 SEM-EDS microanalyses on four reference standards (Augite, Almandine, Pirope and Orthoclase) with the relative standard deviation (s) and the certified value from Micro-Analysis Consultants Ltd. (UK).

**Table S2.** Analyses of white mica and biotite in samples VF77GR, VF79GR, and VF80GR.

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