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Metamorphic peak estimates of the Marguareis Unit (Briançonnais Domain): New constrains for the tectonic evolution of the south-western Alps

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Abstract

In the Western Alps, while many P - T constraints are available for the high-grade units, the dataset for the low-grade units located along the westernmost edge of the belt remains scarcer and incomplete. To face these uncertainties, we quantify for the first time the metamorphic peak conditions of the Marguareis Unit, a fragment of European margin (Briançonnais Domain) regarded till now as very-low-grade unit, exposed along the boundary between Maritime and Ligurian Alps (South-Western Alps), whose deformation history is well constrained. The Marguareis Unit is regarded as a thinned portion of the European continental margin involved in the Alpine collision. Metamorphic peak conditions reconstructed using the chlorite–phengite multi-equilibrium approach on the Eocene siliciclastic deposits indicate that the Marguareis Unit recorded high-pressure and low-temperature conditions during its subduction, accretion and subsequent exhumation into the Alpine wedge.

1 | INTRODUCTION

It was widely recognized that quantitative pressure–temperature–time (P - T - t) paths extracted from metamorphic units portray the thermo-mechanical evolutions of orogens (e.g. England and England & Thompson, 1984; England & Richardson, 1977). The latter are usually reconstructed by means of the P - T conditions of high-grade units. However, the reconstruction of P - T paths, especially high-pressure metamorphism, in low- to very low-grade metamorphic rocks, is of paramount importance to better understand the geodynamic evolution of orogens. Indeed, under low-temperature condition reaction, kinetics is sluggish and consequently chemical equilibrium is rarely achieved at the whole-rock scale impeding to unambiguously constrain P - T conditions of metamorphism (Frey & Robinson, 1999; Lanari & Engi, 2017). It is all the more difficult

to determine P - T conditions in meta-sediments in which detrital minerals remain as relict phases, so making the so-called reactive rock composition (Lanari & Engi, 2017 and reference therein), to be taken into account in order to model the chemical equilibrium, still questionable.

This is the case of the very low-grade Marguareis Unit (Briançonnais Domain), a European fragment of continental crust (Decarlis et al., 2013), located at the boundary between Maritime and Ligurian Alps. This unit was involved in the Alpine collision since middle Eocene age (Seno et al., 2005). The deformation history of the Marguareis Unit has been deeply investigated (Brizio et al., 1983; Sanità et al., 2021), whereas the reconstruction of metamorphic conditions remains partly unconstrained and interpreted as the result of very shallow tectonic events (anchizone, Messiga et al., 1981). Contrarily, some authors (i.e. Lanari et al., 2014; Michard et al., 2004;

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Strzeczynski et al., 2011) reconstructed high pressure–low temperature (HP–LT) metamorphic paths for the Briançonnais Units cropping out in other sectors of the Alpine belt. The Marguareis Unit being located at the top of a SW-verging stack of low- to very low-grade units (Brizio et al., 1983; Sanità et al., 2020). Particularly, above the Late Cretaceous non-metamorphic Helminthoid Flysch Unit (Figures 1 and 2), the quantification of metamorphic peak conditions is crucial to reconstruct the vertical motions of tectonic units during the edification of the Alpine wedge of the South-Western Alps.

Our goal is to propose the first quantification of the peak conditions, and subsequent *P–T* evolution, for the Marguareis Unit obtained after detailed meso- to microstructural investigations. This involved a careful identification of sites where local chemical equilibrium was possibly achieved. In these, the composition of chlorite and phengite pairs was assumed to be in equilibrium; here, use for the *P–T* determination using the chlorite–phengite (Chl, Phg) multi-equilibrium approach (Lanari, 2012; Vidal et al., 2006) is a powerful tool for *P* and *T* calculations in meta-sediments (minerals abbreviations are from Warr, 2021).

1.1 | Geological context and deformation history

The Marguareis Unit (Monte Marguareis area—Figures 1 and 2) is tectonically stacked with units stemming from Ligure Piemontese Ocean and the neighbouring Europa continental margin (Vanossi, 1986; Vanossi et al., 1984). Its finite structural pattern results from a deformation history mainly dealing with superposed fold systems developed at different structural levels (Sanità et al., 2020, 2021). However, some authors regarded the structural architecture of the area as the result of a faulting event that is part of an E–W-direct shearing (Bertok et al., 2018; D’Atri et al., 2016; Piana et al., 2009). According to Sanità et al. (2021), this unit recorded two micro- to map-scale folding events (D1 and D2, Figure 3), and subsequently, mostly developed at large scale, D3 and D4 folding systems (Figures 2 and 3, syn-stacking and post-stacking structures—Sanità et al., 2020), regarded as the results of underthrusting and accretion into the Alpine collisional wedge (Brizio et al., 1983; Carminati, 2001; Carminati & Gosso, 2000; Sanità et al., 2020, 2021). The D1 phase produced similar and isoclinal SW-verging folds with scattered fold axes and NW–SE striking axial planes, whereas the D2 phase developed similar-to-parallel tight NE-verging folds with NW–SE trending fold axes and NW–SE striking axial planes. During the D1 and D2 phases, metamorphic re-crystallization took place along the S1 and S2 foliations associated with the F1 and F2 folding systems (Figure 3). S1 is a slaty cleavage marked by the preferred orientation of Chl+Phg+Qz+Ab+K-Fsp+Ep±Cal metamorphic assemblage and stylolitic surfaces (Figure 3). Within the S1, chlorite grains are stocky, sometimes with re-crystallization tails, and reach 30µm in size, while phengites are more elongated and range in length between 20 and 30µm. Both shows undulose extinction and sharp edges. The S2 is a crenulation cleavage (Figure 3) marked by syn-metamorphic Phg+Chl+Qz+Ab+K-Fsp±Cal association. Both Chl

Significance statement

We quantify the *P–T* conditions recorded by the European-derived Marguareis Unit (Briançonnais Domain) cropping out along the south-western sector of the Marguareis Massif (South-Western Alps). This unit was buried at depth corresponding to blueschists facies conditions during the Alpine collision. The reconstruction of the *P–T* path of the Marguareis Unit permitted to better constrain the tectonic evolution of this sector of the South-Western Alps.

and Phg along the S2 are thin, not exceeding 10 µm in length and show sharp edges. Big altered crystals of detrital chlorite (~80µm in length) and white mica (40µm in length) both characterized by frayed edges, chemical zoning and re-crystallization tails are also present (Figure 3, Material S1).

The subsequent D3 and D4 folding events produced a regional-scale NE–SW trending fold with north-eastward dipping axial plane (Sanità et al., 2020) and open-fold system with sub-horizontal axial planes (Figure 3) respectively. The associated tectonic foliations marked by stylolitic surfaces without evidence of metamorphic re-crystallization suggest their development at shallower structural levels (Sanità et al., 2021).

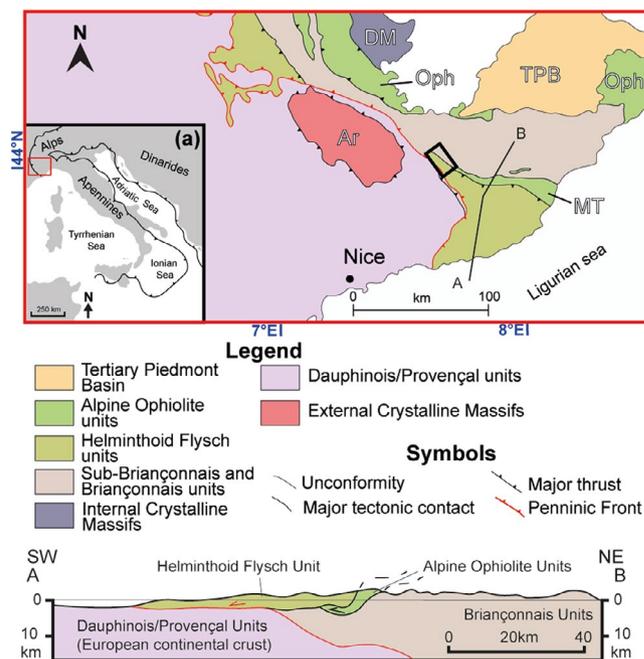


FIGURE 1 (a) Geographic location of the study area. (b) Simplified geological sketch of the South-Western Alps (modified and redraw by Molli et al., 2010) with regional-scale geological cross-section (redraw and modified from Bonini et al., 2010). Black box indicates the study area of Figure 2. In the cross-section, red line indicates the Penninic front. TPB, Tertiary Piedmont Basin; Oph, Alpine Ophiolitic Units; MT, Mglio-Testico Unit; DM, Dora Maira Massif; Ar, Argentera Massif

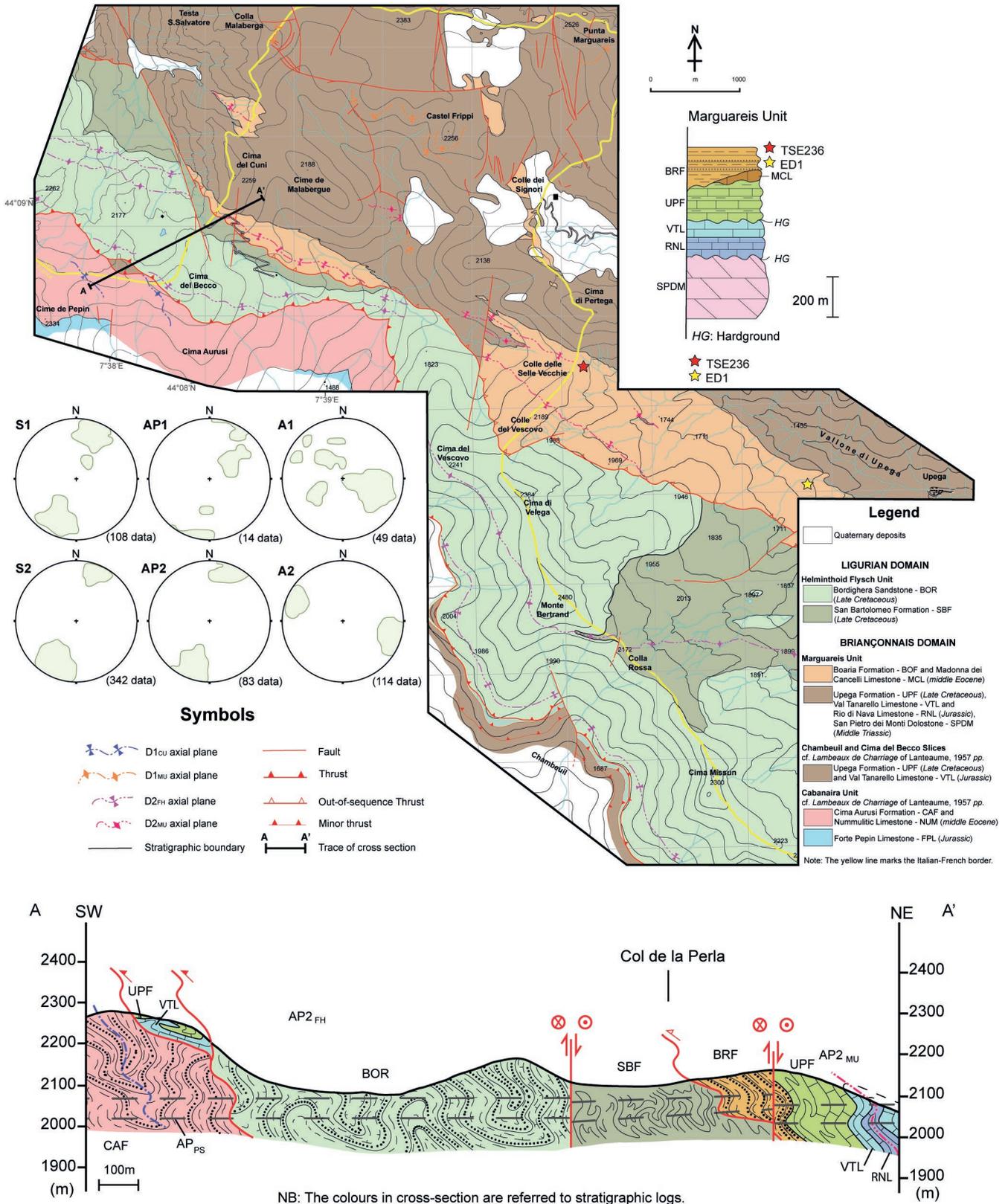


FIGURE 2 Structural sketch of the south-western sector of the Marguareis Massif with geological cross-section. Stereographic plots show the spatial relationships between planar and linear structural features recognized in the Marguareis Unit. The stratigraphic log (Middle Triassic–Middle Eocene age) of the Marguareis Unit is reported on the right corner (by Sanità et al., 2020). Red and yellow stars indicate the sample location

The last deformation event is represented by high angles normal to transensional faulting that did not produce profound modification in the previous architecture.

2 | METHODS

Meso-structural analysis combined with rigorous microstructural observations aimed to attest for costability of a given mineral pair, in our case chlorite and white mica, which allowed us to reasonably assume that conditions of local chemical equilibrium were attained and calculate P and T conditions of this equilibrium. Thus, calibrating X-ray maps on two samples collected from the middle Eocene meta-pelites of the Marguareis Unit (ED1 and TSE236), we closely linked the composition of chlorite and phengite to microstructural domains (S1 and S2). For each chlorite–phengite pairs grown along the S1 and S2 foliation planes, we calculate the temperature and pressure estimations by means of XMapTools software (Lanari et al., 2014) and ChlMicaEqui software (Lanari, 2012, the description of the method is in the Material S1). Our results are compared to classical chlorite thermometry (the chemical analyses of chlorite and phengite are provided in the Material S1). This has been progressively improved (Bourdelle & Cathelineau, 2015; Lanari et al., 2014) following the pioneering calibrations of Cathelineau and Nieva (1985) and Cathelineau (1988) and successfully applied in low-grade

metamorphic and/or hydrothermal systems (e.g. Beauchamps et al., 2021; Bourdelle, 2021; Favier et al., 2021; Vérati et al., 2018).

3 | RESULTS

Combining microstructural evidence with the compositional variability of chlorite (Figures S1–S3), three different compositions have been distinguished. The first composition is related to detrital chlorites which remain metastable during Alpine metamorphism. The second and the third compositions are related to chlorite re-crystallized along the S1 and S2 foliations respectively. D1 chlorites (Chl1) are characterized by low Si content (2.65–2.80 a.p.f.u.), and Al content which vary from 2.60 to 3 a.p.f.u. in both samples (Figure 4a and Material S1). D2 chlorites (Chl2) are aligned on the S2 and have Al content which is basically low (2.40–2.90 a.p.f.u.), whereas Si content is higher (2.75–3.00 a.p.f.u.) than those of Chl1 (Figure 4a and Material S1). The differences between the two samples are more evident by observing the composition of end-members: clinocllore+daphnite content is always higher than 50% in ED1, while in TSE236 it is lower than 40% in the Chl1 and range between 50% and 40% in the Chl2. In the sample ED1, small differences between Chl1 and Chl2 are given by the Amesite content which is higher and lower than 20% respectively. In both samples, XMg in chlorite tends to be higher in Chl1 than those of Chl2, even if the total range is between 0.37 and 0.45.

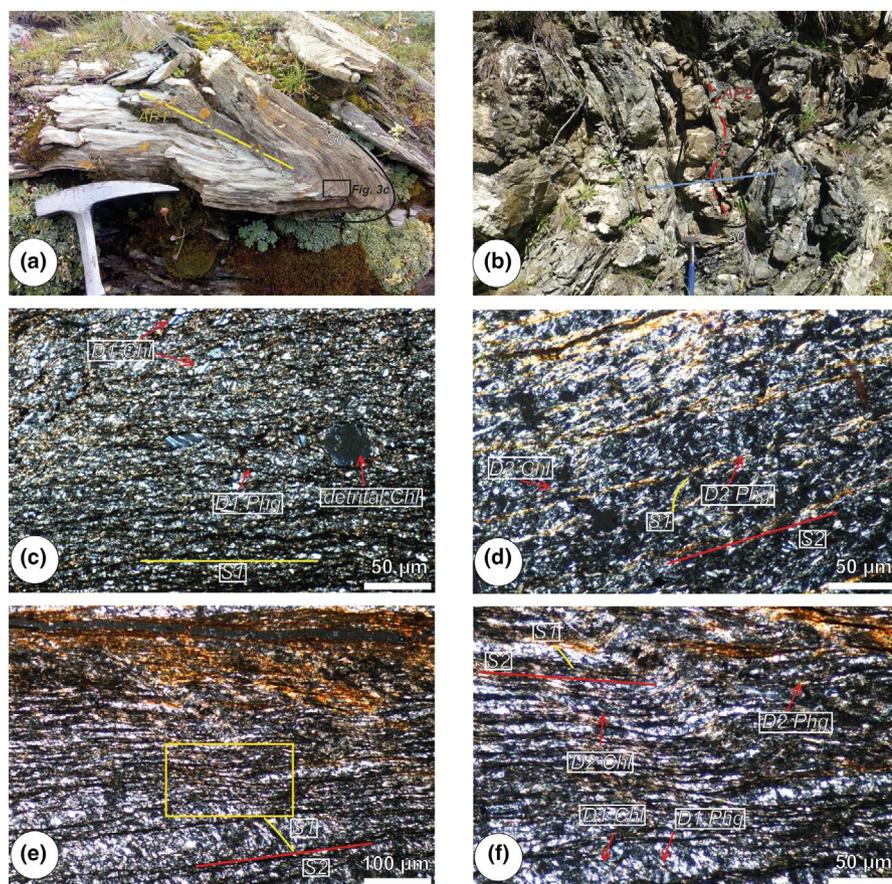


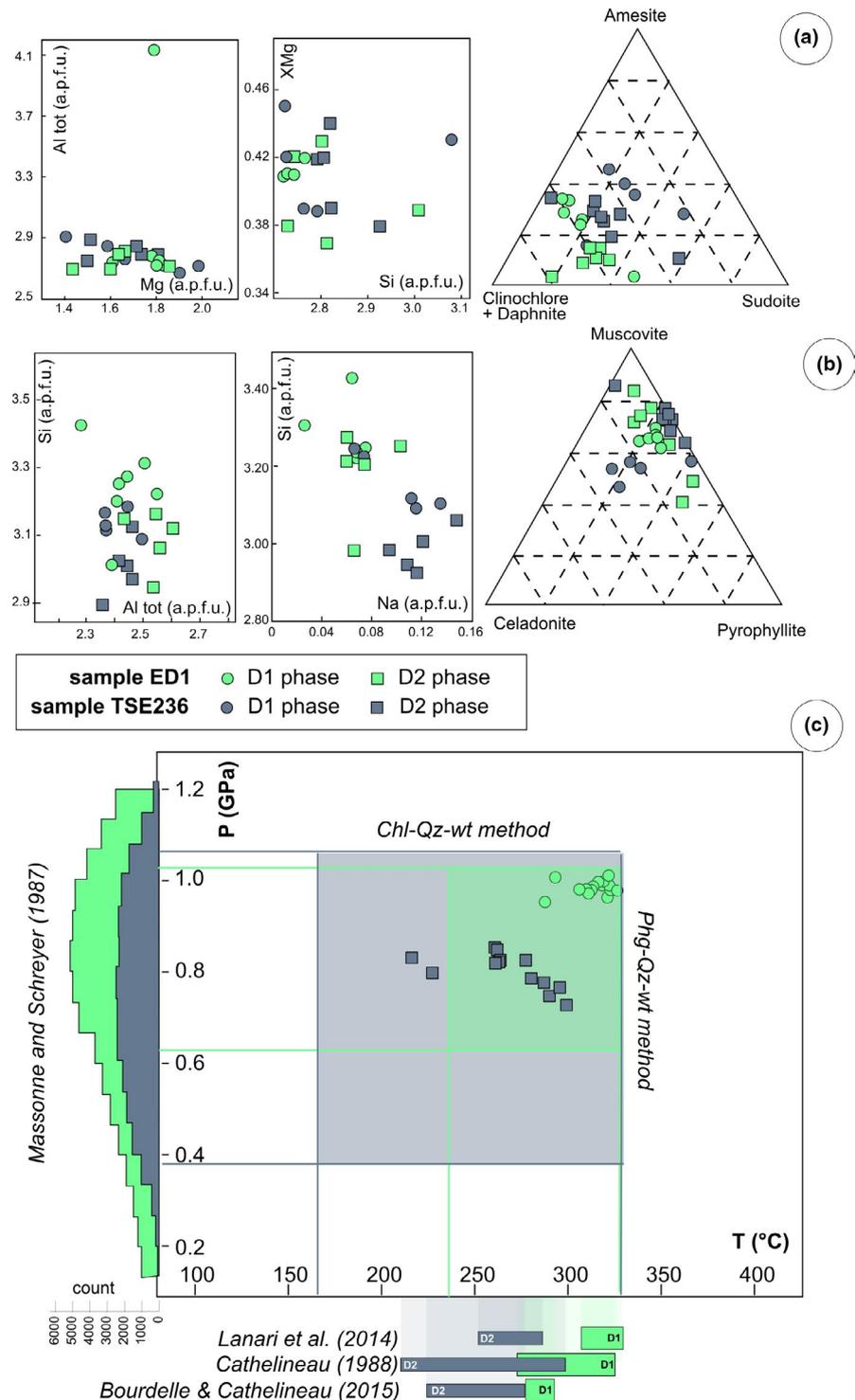
FIGURE 3 Meso- and micro-scale D1- and D2-related structural features of the Marguareis Unit. F1 and F2 folds (a, b) in the middle Eocene meta-pelites. (c–f) Microphotographs of the S1 and S2 foliations. The cross-cutting relationships are reported. AP1: F1-related axial plane; AP2: F2-related axial plane; AP4: F4-related axial plane

Similarly, phengite composition varies according to the different microstructural sites (S1 and S2 foliations and detrital phengites, Figure 3c, Figures S1–S3). Al and Si contents in mica related to the D1 (Phg1) and D2 (Phg2) phases are quite homogeneous into the two samples (Si: 2.90–3.40 a.p.f.u. in ED1, 2.90–3.20 a.p.f.u. in TSE236; Al: 2.35–2.60 a.p.f.u. in ED1, 2.30–2.70 a.p.f.u. in TSE236) (Figure 4b). In both the samples, a clear trend from Si-rich–Na-poor Phg1 to Si-poor–Na-rich Phg2 is identified. Phengites of ED1 sample are characterized by celadonite content always lower than 20% with

Phg1, which tend to be more muscovitic. In the sample TSE236, the celadonite content is more variable (higher in Phg1 than Phg2) but never exceeds 35%. However, both Phg1 and Phg2 are classifiable as impure muscovite.

P–T estimates based on the activity of chlorite and phengite end-members and the water activity were obtained through the Chl–Qz–wt, Phg–Qz–wt and Chl–Phg–Qz–wt methods. These methods were applied on chlorites and phengites related to the D1 phase in the sample ED1 and those of the D2 phase in the sample TSE236.

FIGURE 4 Geochemistry of (a) chlorite and (b) phengite sampled into ED1 and TSE236. Chlorite and phengite structural formula are calculated assuming 14 and 11 oxygen, respectively. (c) *P/T* diagram showing the results of the thermobaric methods applied to samples ED1 and TSE236. In the *P/T* space, the pale squares indicate the areas constrained by the Chl–Qz–wt method (Vidal et al., 2006) and the Phg–Qz–wt method (Dubacq et al., 2010); the position of data indicates the *P–T* equilibrium conditions of single Chl–Phg couples obtained with Chl–Phg–Qz–wt method (Vidal & Parra, 2000). Histograms along the Y-axis indicate the results of Massonne and Schreyer (1987) geobarometer. Along the X-axis, the used thermometers are reported with range values related to D1 and D2 phases



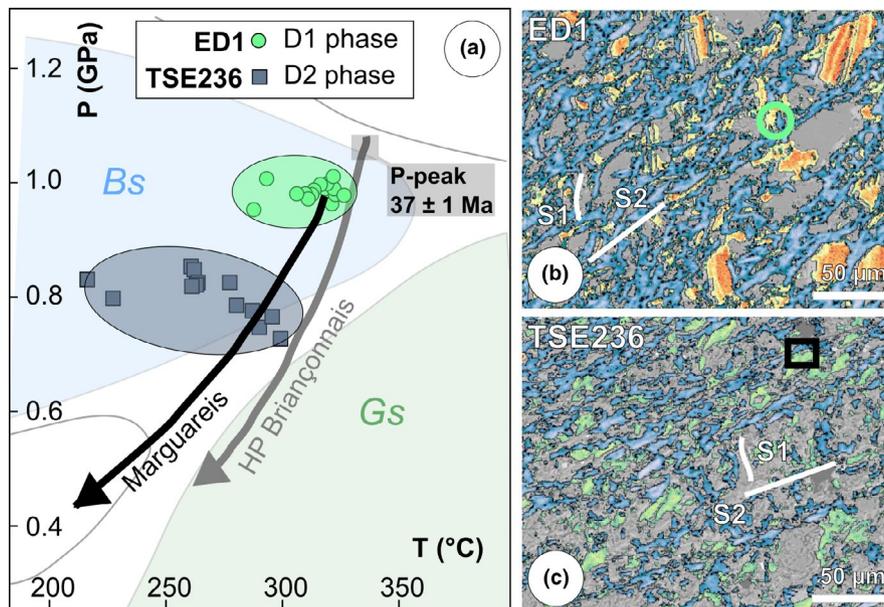


FIGURE 5 (a) P - T path of the Marguareis Unit (black arrow in the P - T space) obtained in this study. The paths related to the HP Briançonnais (grey arrow) are also plotted (data from Michard et al., 2004). The microdomains, in which the Chl-Phg couples used to constrain the P - T conditions of D1-D2 phases were sampled, are evidenced (b) in the sample ED1 with the green circle and (c) in the sample TSE236 with black rectangle. In (b) and (c), chlorite shadows are referred to the Fe-content (green-yellow-red colours) and phengite shadows represent the K-intensity (blue to white colours); other mineral phases (quartz, calcite, titanite and feldspar) are in grey

With the Chl-Qz-wt (Vidal et al., 2006), T ranges were calculated setting the equilibrium tolerance to 30°C and the percentage of Fe^{3+} for each Chl analysis fixing a starting pressure value (in this case, 0.6 GPa) following the procedure of Lanari and Duysterhoef (2019). The water activity was set to 1 in the sample ED1 and to 0.8 in the sample TSE236 based on the presence/lack of calcite (Frassi et al., 2022). Temperature ranges related to the D1 and D2 phases are 230–330°C and 160–330°C respectively. The Phg-Qz-wt (Dubacq et al., 2010) was applied in order to quantify the P conditions of the Marguareis Unit during the D1 and the D2 phases. The P range related to the D1 phase was estimated with Phg1 of the sample ED1 grown along the S1, setting an average temperature of 300°C and assuming 0.95% of water as optimized value (Material S1, Frassi et al., 2022). Pressure range for the D1 phase is between 1.05 and 0.65 GPa (Figure 4c). Pressure values related to the D2 phase were calculated using Phg2 of the sample TSE236, assuming an average T of 300°C and the water optimized values of 0.95% (Material S1, see Frassi et al., 2022). Pressure range of the D2 phase is 0.38–1.10 GPa (Figure 4c).

The Chl-Phg-Qz-wt (Vidal & Parra, 2000) method allowed to find the chlorite-phengite couples related to the D1 (sample ED1) and D2 (sample TSE236) phases (see Material S1). Only the couples equilibrated with a tolerance <1000J and included between the T - and P -ranges of the Chl-Qz-wt and Phg-Qz-wt method were considered. The P - T conditions for the D1 phase are 1.00–0.90 GPa and 280–330°C and those related to the D2 phase are 0.85–0.7 GPa and 230–300°C (Figure 4c).

The results obtained were compared with T and P values estimated with classical thermobarometry (Figure 4c). We first used

the semi-empirical calibration proposed by Cathelineau (1988) and this thermometer yields a temperature range 275–327°C for chlorites in S1 and 215–300°C for chlorites in S2. However, Lanari et al. (2014) proposed a calibration for low-temperature conditions (i.e. $T < 400^\circ\text{C}$) even when the amount of Fe^{3+} in chlorite is unknown. Using this calibration, we obtained a temperature range 310–330°C for chlorites in S1 and a T range 250–280°C for chlorites in S2. Moreover, we used also the calibration established by Bourdelle and Cathelineau (2015), which is also an efficient tool for chlorite thermometry between 100 and 400°C, even if the non-ideal contribution of site mixing is not considered. This thermometer yields temperatures of 275–285°C for chlorite in S1 and of 225–275°C for chlorites in S2. Altogether, chlorite solid-solution thermometry indicates T conditions of $300 \pm 30^\circ\text{C}$ for the D1 phase and T conditions of $250 \pm 40^\circ\text{C}$ for the D2 phase.

The geobarometer of Massonne and Schreyer (1987) was applied on the samples ED1 and TSE236 (XMapTools, Lanari et al., 2014) to obtain the pressure range related to the D1 and D2 phases respectively (Figure 4c). The pressure range calculated on phengite of the sample ED1 grown along the S1 is 0.63–1.03 GPa (>3000 pixel/map), while that of the sample TSE236 related to the S2 is 0.38–1.07 GPa (>1000 pixel/map).

4 | DISCUSSION

The polyphase deformation history recorded in the Marguareis Unit is regarded as the result of underthrusting, accretion and subsequently exhumation into the Alpine wedge (Brizio et al., 1983;

Carminati, 2001; Sanità et al., 2021). This structural pattern is marked by the superposition of folding systems (D1–D4) developed at different structural levels. Only during the D1 and D2 phases, metamorphic re-crystallization chlorite and phengite grains occurred. The thermobarometric estimations performed in this study show that the prograde path is not recorded and the chlorite–phengite pairs grown along S1 and S2 foliations depict the retrograde path of the Marguareis Unit (Figure 5). The exhumation already started during the D1 phase and it continues during the D2 phase up to shallower crustal levels into the Alpine wedge. P-peak conditions of 1.00–0.90 GPa and 280–330°C were registered by phengite–chlorite couples related to D1 phase (Figures 4c and 5a). The retrograde path of the Marguareis Unit is constrained by the re-crystallization of chlorite and phengite during the D2 phase at 0.85–0.7 GPa and 230–300°C (Figure 5a). No significative heating events during the D2 exhumation phases were identified from the thermobarometry for the Marguareis Unit. The different p values constrained on Phg1 and Phg2 are considered as the witnesses of the vertical movement of the Marguareis Unit inside the Alpine wedge. Thus, the reconstructed pathway strongly suggested that the metamorphic imprint of the Marguareis Unit was recorded in a continental subduction setting, the latter already documented in other similar sectors of the Alpine belt (Di Rosa et al., 2019; Lanari et al., 2012; Michard et al., 2004; Sterzynsky et al., 2011). Our results allow us to re-interpret the Marguareis Unit, till now regarded as a very low-grade unit (Messiga et al., 1981), as a HP–LT unit. In the South-Western Alps, HP–LT units were documented by others authors (Goffé et al., 2004; Lardeaux, 2014), and similar HP–LT paths were reconstructed for the Briançonnais Units in more internal sector of the belt (Lanari et al., 2014; Sterzynsky et al., 2011).

Michard et al. (2004) reconstructed the P – T path for the Briançonnais Units outcropping in the Embrunais–Ubaye area. The authors proposed that the Briançonnais Units recorded their metamorphic peak during the D1 phase (HP Briançonnais path in Figure 5a) immediately followed by the onset of the exhumation which begins at the end of D1 phase. The P – T path proposed for the HP Briançonnais Units by Michard et al. (2004) shows clear similarities with those we propose for the Marguareis Unit (Figure 5a). For the HP Briançonnais Units, the late Bartonian age is proposed (Monié, 1990) as age constraint for the metamorphic peak conditions (similar timing was proposed by Lanari et al., 2012). Therefore, based on the close relationships between Marguareis Unit and the Briançonnais Units in this work, we can suppose the Bartonian age as timing for the achievement of the metamorphic peak conditions also for the Marguareis Unit (as suggested by Sanità et al., 2020). The final exhumation of the Marguareis Unit through the D3 and D4 folding events as well as the faulting concludes the geological framework from Late Eocene onward.

5 | CONCLUSIONS

We quantified the metamorphic peak conditions and P – T evolution of the Marguareis Unit (Briançonnais Domain) exposed at the

boundary between Maritime and Ligurian Alps (South-Western Alps). Our results indicate that:

- The reconstructed P – T path suggests that the Marguareis Unit experienced HP–LT metamorphism during the building of the Alpine belt (P-peak: 1.00–0.90 GPa and T-peak: 280–330°C), and should therefore no longer be considered as the only Briançonnais Unit affected by anchizone metamorphism.
- The Marguareis Unit preserved only evidence of retrograde (de-compression) metamorphism into the Alpine wedge.
- The metamorphic peak conditions were achieved during the D1 deformation stage. The exhumation started during the late D1 and continued during the D2 phase as already proposed by previous authors for Briançonnais Units exposed in other sectors of the belt. The exhumation towards shallower structural levels concludes with the subsequent D3 and D4 folding and faults.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

Material S1. Thermobarometry.

Figure S1. Fe in chlorite in the micromap of sample ED1 (intensity map: Fe K α)

Figure S2. K in phengite in the micromap of sample TSE236 (intensity map: K K α)

Figure S3. Distribution of temperature based on Cathelineau (1988) geothermometer in sample TSE236.

Table S1. Representative chlorite EPMA analysis.

Table S2. Representative phengite EPMA analysis.

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