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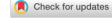
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RESEARCH ARTICLE





Subduction signature in the Internal Ligurian units (Northern Apennine, Italy): Evidence from *P-T* metamorphic peak estimate

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Abstract

The Internal Ligurian units (Northern Apennine) represent deformed and metamorphosed fragments of the oceanic lithosphere of the Ligure–Piemontese oceanic basin. Different tectonic models have been proposed for the geodynamic setting in which the deformation and metamorphism have been acquired. However, the lack of updated, clear, thermo-barometric data has made it hard to unambiguously discriminate between these different proposed models. In this article, we provide evidence for the deformation of the Palombini Shale, i.e., pelagic deposits belonging to the Internal Ligurian units, under *P* and *T* peak conditions of 230–300°C. and 0.6–0.9 GPa, respectively. These data indicate that the Internal Ligurian units were affected by a blueschist facies metamorphism achieved during the underplating within the accretionary wedge developed during the Late Cretaceous–Early Tertiary Alpine subduction. These data support the hypothesis of a unique, pre-Oligocene orogenic system for the Alpine belt and the westernmost sector of the Northern Apennines belt.

KEYWORDS

blueschist facies metamorphism, deformation, Internal Ligurian Apennine, Palombini Shale, subduction

1 | INTRODUCTION

The Internal Ligurian (IL) units (Figure 1a) represent fragments of the Ligure-Piemontese oceanic basin that opened in the Middle to Late Jurassic between the European and Adria continental margins and closed by subduction and subsequent continental collision from Late Cretaceous to Middle-Late Eocene (Marroni et al., 2017 and references therein). In the IL units, the record of the subduction part of this geodynamic evolution is represented by a pre-Oligocene polyphase deformation history (Meneghini et al., 2007 and references

therein). Due to their relevance in understanding the geodynamic history of the Ligure-Piemontese basin, the IL units have been studied in detail, both from a stratigraphic and structural point of view.

Despite all these contributions (see Meneghini et al., 2007 for a review), specific published data on the metamorphic conditions of the IL units are scarce, dated, and mainly concern thermal peak quantification (Ellero et al., 2001; Leoni et al., 1996; Malavieille et al., 2016; Reutter et al., 1980; Venturelli & Frey, 1977), while pressure conditions have remained largely undetermined. In the literature, the deformation of the IL units has been related to an

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involvement of these units in the Alpine subduction, with the model of accretion spanning from coherent underplating (Marroni et al., 2004; Meneghini et al., 2007), to frontal accretion (Principi & Treves, 1984; Treves, 1984). Other authors have proposed an evolution in an intraoceanic transpressional setting during the closure of the Ligure–Piemontese basin (Nirta et al., 2005) or achieved during an incipient continental collision of an oceanic trapped crust (Hoogerduijn Strating, 1994; Hoogerduijn Strating & Van Wamel, 1989; Principi & Treves, 1984). The lack of updated, clear, thermo-barometric data have made it hard to unambiguously discriminate between these different tectonic models.

As the Ligurian sector of the Northern Apennine represents the junction with the Ligurian sector of the Alpine chain, a clear interpretation of the tectonic setting of deformation of the IL units is also crucial to depict the bigger geodynamic picture of the Alps-Apennine system. The Western Alps, located west of the IL units, include ocean-derived units with a clear, undoubted subduction-related metamorphic imprint and are classically interpreted as formed through subduction, accretion at different structural levels, and subsequent exhumation into the Alpine wedge (Federico et al., 2015; Sanità et al., 2022a; Seno et al., 2005). Deciphering whether the

Statement of significance

We have quantified the *P*–*T* conditions recorded in the Loco subunit (Internal Ligurian units) cropping out in an area East of Passo della Forcella (GE, Northern Apennine, Italy). This unit was buried at depth corresponding to blueschists facies conditions during the Alpine orogeny. The reconstruction of the *P*–*T* path of the Loco subunit permitted to better constrain the tectonic evolution of this sector of the Northern Apennine

IL units show a subduction signature is necessary to discriminate between a geodynamic picture that interprets these units as geodynamically separated from the Western Alps of Liguria, or as part of the same Alpine accretionary wedge (Bortolotti et al., 2001; Castellarin & Cantelli, 2010; Schmid et al., 2017).

We have performed a detailed study to quantify the *P-T* conditions of the deep-sea pelagic deposits covering the ophiolite

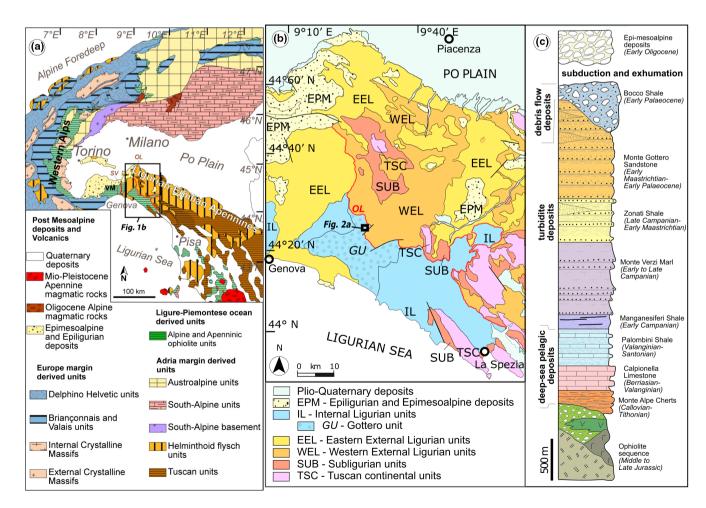


FIGURE 1 Regional setting of the Northern Apennines belt. (a) Tectonic setting of the Northern Apennine and Alps. OL, Ottone-Levanto line; SV, Sestri Voltaggio line; VM, Voltri Massif. Location of (b) is also shown; (b) sketch map of Northern Apennine in the area between Piacenza, Genova and La Spezia. The study area (Figure 2a) is indicated by the black square; (c) stratigraphic log of IL units.

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sequence. The *P-T* conditions of the samples were estimated by combining different methods based on the dependency of mineral composition on pressure and temperature. The results are discussed to discriminate the different interpretations proposed for the tectonic setting of the IL units during the subduction event.

2 | GEOLOGICAL OVERVIEW OF THE IL UNITS

The IL units crop out extensively in the Ligurian–Emilian sector of the Northern Apennines between two main, north–south trending strike-slip fault systems: the Sestri–Voltaggio line to the west and Ottone–Levanto line to the east (Figure 1b). The Sestri–Voltaggio line juxtaposes the IL units with the Voltri Massif, a stack of eclogite-facies metamorphic ophiolite-bearing units belonging to the Alpine belt (e.g., Capponi et al., 2016). The Ottone–Levanto line represents the boundary with the External Ligurian units (Marroni et al., 2019), representative of the ocean–continent transition to the Adria margin of the Ligure–Piemontese basin (e.g., Elter et al., 1991).

The IL units are characterized by all or part of the same oceanic sequence (Principi et al., 2004 and quoted references), whose reconstructed stratigraphy (Figure 1c) includes at its base a 800-900 m-thick ophiolitic section that formed in the Middle to Late Jurassic in an ultra-slow spreading ridge (Sanfilippo & Tribuzio, 2011 and quoted references). The ophiolite shows a transition to deep-sea pelagic deposits represented by Monte Alpe cherts (Callovian-Tithonian), Calpionella Limestone (Berriasian-Valanginian) and Palombini Shale (Valanginian-Santonian). The Palombini Shale is the most represented deposit of the IL units, cropping out ubiquitously in all the different IL units. It consists of CaCO3-free shales alternating with layers of metalimestones and metasilstones. The Palombini Shale grades upward into a turbidite complex that includes the Early Campanian Manganesiferi Shale, the Early to Late Campanian Monte Verzi Marl, the Late Campanian-Early Maastrichtian Zonati Shale and the Early Maastrichtian-Early Palaeocene Monte Gottero Sandstone (Marroni & Perilli, 1990). The turbidite formations are all interpreted as belonging to a complex turbidite fan system that includes mixed siliciclastic-carbonatic and siliciclastic turbidites supplied by the European continental margin (Fonnesu et al., 2018 and guoted references). The youngest deposits of the succession are represented by Early Palaeocene debris flow deposits (Festa et al., 2021 and quoted references). The transition from pelagic deposits to turbidites up to debris flow deposits reflects the trenchward motion of a portion of the oceanic lithosphere (Marroni & Pandolfi, 2001).

The most complete sedimentary succession is preserved in the Gottero unit. Its complex and long-lived tectono-metamorphic history achieved during the closure of the Ligure-Piemontese oceanic basin have been described in detail by Marroni and Pandolfi (1996), Marroni et al. (2004) and Meneghini et al. (2007). This deformation path includes two folding phases, respectively referred to as D1 and D2 phases, each subdivided into several sub-phases. The same deformation history has been identified in all the other IL

units (e.g., Hoogerduijn Strating & Van Wamel, 1989; Marroni & Meccheri, 1993; Molli, 1996). In this context, the D2 phase has been interpreted as exhumation up to the surface of the IL units, and the D1 phase is regarded as the main deformation event that affected these units during the development of the metamorphic peak.

The IL units tectonic stack is unconformably topped by Early Oligocene conglomerates (Di Biase et al., 1997) bearing deformed clasts derived from the IL units, whose deformation structures and microstructures can be related to the above-described deformation history. This allows to date the deformation path as pre-Early Oligocene.

3 | METHODS

We have estimated the *P-T* conditions of samples from the Palombini Shale Fm. collected in the more deformed portion of the Gottero unit, i.e., the Loco subunit, in an area located East of Passo della Forcella (Figure 2a,b; Marroni et al., 2019).

Microstructural analyses were performed on ten samples of Palombini Shales Fm., to select those in which the dynamic recrystallization of chlorite and white mica during the D1 phase is better expressed. *P* and *T* conditions of the D1 phase were estimated on the base of the local equilibrium of these two mineral phases through multi-equilibrium approach (i.e., Chlorite-quartz-water, Phengite-quartz-water and Chlorite-Phengite-quartz-water methods). The different thermobarometric methods were applied on chlorite and phengite sampled within the S1 foliation of the two samples from Loco subunit (ULI13 and ULI14) after their standardization (see De Andrade et al., 2006). The calculations were performed fixing variables such as Fe³⁺, water activity and structural water in phengite (see Data S1). The different methods were performed independently and then the results were merged to obtain a best fit of *P* and *T* estimates. Results were then compared with classical geobarometer and geothermometers.

Raman Spectroscopy of Carbonaceous Material (RSCM) were also performed on selected samples of Palombini Shales Fm. to quantitatively estimate the peak metamorphic temperatures (see Data S1).

4 | MATERIALS AND RESULTS

We have estimated the *P-T* conditions of samples from the Palombini Shale Fm. focusing on the paragenesis grown along the S1 axial-plane foliation developed during the D1 phase, that is the most pervasive in the field and is associated to the metamorphic peak reached in each IL unit (Marroni et al., 2004; Meneghini et al., 2007). The S1 foliation represent the axial plane foliation of strongly non-cylindrical, isoclinal F1 folds with thickened hinges, boudinaged limbs, and northwestward facing. In the shales, the S1 axial-plane foliation is a continuous and penetrative slaty cleavage characterized by synkinematic recrystallization.

Three samples (ULI12, ULI13, and ULI14) were selected from coarse to medium silt-sized layers in the Palombini Shale Fm.

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(Figure 2c). They consist of flakes of detrital muscovite (up to 70 μm in diameter), chlorite (30-50 μm), quartz (20-30 μm), albite (10-20 μm), and minor titanite (5-10 μm), all packed in a phyllosilicate-bearing matrix (<10 µm, Figures 2b,c). A metamorphic paragenesis of $Chl + Phg + Qz + Ab \pm KFsp \pm Cal$ grown along the S1 foliation has been recognized in all samples, with recrystallized domains not

exceeding 5-10 µm thickness (Figures 2c,d). Carbonaceous material occurs in neoblastic agglomerates and veins (Figure 2c).

Chlorites grown along the S1 foliation are Al-rich and Si-poor, with Al content ranging from 2.70 to 3.90 atoms per formula unit (a.p.f.u.) and Si content never exceeding 2.75 a.p.f.u. (Figure 3). The composition of chlorite crystals in the microdomains in which

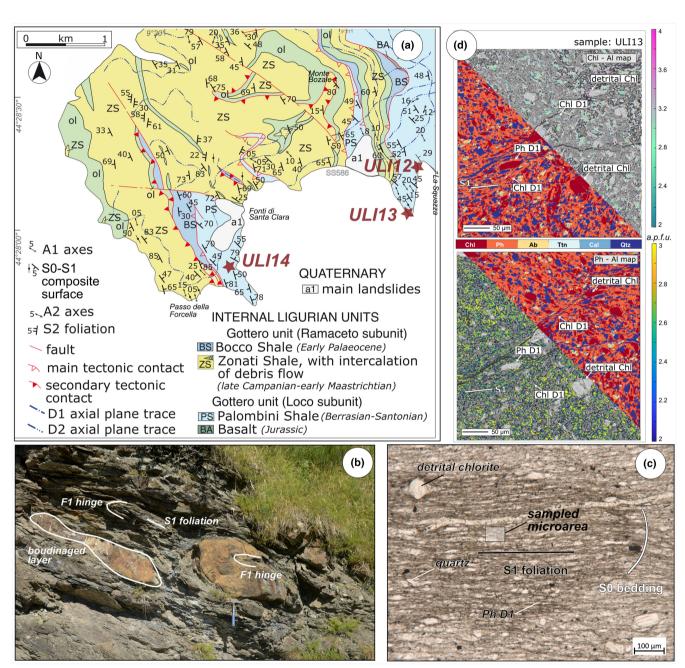


FIGURE 2 Map- to micro-scale features of the Palombini Shale studied in this work, (a) Geological map of the area east of Passo della Forcella (redrawn from Marroni et al., 2019). The map highlights the complicate structural setting where the Ramaceto and Loco subunits are associated during the last stage of the D1 phase and folded together during the D2 phase. The sampled areas are indicated by violet stars; (b) an example of the Palombini Shale outcrop from the study area. The main deformation structures that characterize the D1 phase are emphasized; (c) S1 foliation observed at the optical microscope (sample ULI14, cross-polarized light). The microdomain sampling for EPMA analyses of (c) is provided in the box: (d) Back-scattered images obtained with the microprobe showing chlorite and phengite distribution on the sample ULI13. Rendering and schematization were done with XMapTools (Lanari et al., 2014) re-elaborating the WDS intensity maps: the sketched portions of chlorite and phengite Al-maps consist in masks, where the six mineral phases occurring in the microareas are represented by different colours (the relative legend is provided in the bar between the two maps).

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chlorite is grown together with phengite varies very little along the amesite-sudoite solid solution (Figure 3).

Phengite grown along the S1 foliation is Si-rich and Na-poor (i.e., <0.01 a.p.f.u.). In all studied samples, Si-content ranges between 3.00 and 3.50 a.p.f.u. with a modal value of 3.20 a.p.f.u. (Figure 3),

whereas the K in phengite mainly ranges from 0.65 to 0.85 a.p.f.u. (Figure 3). Despite different trends shown by the samples, all of them show an affinity with the muscovite end-member (Figure 3). ULI14 shows a symmetric distribution around the muscovite vertex and ULI13 is characterized by a great dispersion between muscovite

diagrams showing the compositions of the chlorite and phengite of the samples ULI13 and ULI14. The position of each colored ellipse in the diagrams is that of the average value calculated on 15 spot analysis. Rainbow spots in the small ternary diagrams indicate the distribution of all the spot analysis acquired from the compositional map. Yellow triangles and di/triochtaedral (DT) and Tschermak (TK) substitutions reported in the ternary diagrams are taken from Vidal and Parra (2000, see Data S1).

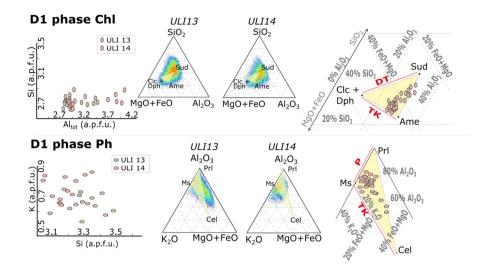


TABLE 1 Examples of mineral chemistry of Chl-Ph couples selected along the S1 foliation of metapelites of the Loco subunit.

Sample Analyse	ULI13						ULI14					
	Couple 1		Couple 2		Couple 3		Couple 1		Couple 2		Couple 3	
	Chl37	Ph5	Chl51	Ph10	Chl86	Ph96	Chl22	Ph22	Chl77	Ph54	Chl98	Ph11
Wt%												
SiO ₂	25.68	48.76	26.90	47.63	25.60	48.70	30.43	52.66	26.62	56.61	26.62	52.66
TiO ₂	-	0.85	-	-	0.06	0.28	-	-	-	0.22	-	-
Al_2O_3	30.47	35.12	26.11	35.12	22.17	31.33	36.35	33.00	27.96	28.74	25.16	33.00
FeO	20.60	4.73	35.02	4.73	29.35	5.58	3.98	1.70	27.86	3.40	23.88	1.70
MnO	-	-	-	-	0.07	0.04	-	-	-	-	-	-
MgO	8.37	1.94	3.35	1.94	11.13	2.32	17.97	2.26	4.49	-	13.48	1.51
CaO	0.09	-	0.17	0.13	0.04	0.04	-	-	-	-	-	0.07
Na ₂ O	-	-	-	-	-	0.35	-	0.75	-	-	-	0.75
K ₂ O	0.85	8.40	0.12	9.73	0.02	7.44	1.54	8.07	-	10.55	0.47	8.69
Tot.	86.06	99.80	91.67	99.28	88.44	96.08	90.27	98.44	86.95	99.52	89.61	98.38
Cations												
Si	2.65	3.10	2.80	3.07	2.72	3.22	2.73	3.32	2.81	3.58	2.70	3.34
Ti	-	0,04	-	-	0.01	0.01	-	-	-	0.0.1	-	-
Al	3.70	2.63	3.20	2,67	2.78	2.44	3.84	2.45	3.48	2.14	3.01	2.46
Fe ²⁺	1.78		3.05		2.61		0.30		2.50		2.03	
Fe _{tot}		0.25		0.26		0.31		0.09		0.18		0.09
Mn	-	-	-	-	0.01	-	-	-	-	-	-	-
Mg	1.29	0.18	0.52	0.19	1.76	0.23	2.40	0.21	0.71	-	2.04	0.14
Ca	0.01	-	0.02	0.01	0.01	-	-	-	-	-	-	-
Na	-	-	-	-	-	0.04	-	0.09	-	-	-	0.09
K	0.11	0.68	0.02	0.80	-	0.63	0.18	0.65	-	0.85	0.06	0.70
sum ox	14	11	14	11	14	11	14	11	14	11	14	11

Note: -= below detection limit.

and celadonite end-members derived from the strong variability in Al content of this sample (see map of Figure 3).

Pressure and temperature conditions were estimated combining different methods, starting from a compositional analysis and mineral chemistry definition. Spot analyses and quantitative maps of compositions were acquired with the electron probe micro-analyser (EPMA), following the procedure of De Andrade et al. (2006); Table 1.

A range of temperature were calculated for all the samples with the chlorite-quartz-water method (Vidal et al., 2006) fixing water activity and a starting pressure value (see Data S1). The starting pressure was chosen by selecting the value that gives the largest convergence of single analyses having the same XFe $^{3+}$ (=Fe $^{3+}$ /Fe $_{\rm tot}$), which is a pressure dependent parameter (e.g., Munoz et al., 2006). Temperature ranges obtained for the chlorites growing along the S1 foliation are 180–310 (±30)°C for ULI13 and 240–310 (±30)°C for ULI14 (Figure 4).

The pressure conditions were estimated by the phengite-quartz-water method (Dubacq et al., 2010). The equilibrium conditions are represented with a line in the P-T diagram (Figure 5) along which the interlayer water content (XH $_2$ O) varies (see Data S1). The optimized range of temperature used were those obtained with the chlorite-quartz-water method for each sample (see above). Pressure ranges calculated for the phengites grown along the S1 foliation are 0.5-0.8 (± 0.2) GPa for ULI13 and 0.6-1.1 (± 0.2) GPa for ULI14. The equilibrium conditions of chlorite-phengite pairs in the S1 foliation of the samples were estimated with the Vidal and Parra (2000) multi-equilibrium approach (see Data S1). Equilibrium P-T ranges

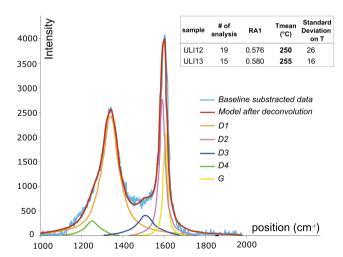


FIGURE 4 Representative Raman spectra of carbonaceous material from sample ULI13. The spectra were deconvoluted following the method of Lahfid et al. (2010). Observed data, the modeled spectrum after deconvolution and the five Lorentzian bands are shown. In the table below, the estimated final peak temperatures with error, and the RA1 ratio calculated from the area below the five Lorentzian bands (RA1=[D1+D4]/[D1+D2+D3+D4+G]), are shown for the analysed samples (see Data S1 for details on the deconvolution method).

estimated for the analysed samples are 230–300°C and 0.6–0.7 GPa for ULI13 and 260–280°C and 0.8–0.9 GPa for ULI14.

Peak metamorphic temperatures were quantitatively estimated also using Raman Spectroscopy of Carbonaceous Material on two of the selected samples (RSCM, Lahfid et al., 2010). To perform RSCM geothermometry analyses (Figure 4, see also Data S1), transparent crystals of calcite and, occasionally, other calcsilicates were selected in the metasiltites of two of the selected samples. For each sample, ca. 15 to 20 spectra were routinely recorded to smooth out the inner structural heterogeneity of carbonaceous material within samples, and then processed and converted into temperature. The spectra were deconvoluted following the method of Lahfid et al. (2010). Estimated average Tmax is 250 (\pm 26)°C for ULI12 and 255 (\pm 16)°C for UII13.

5 | DISCUSSION & CONCLUSION

The *T* conditions of the metamorphic peak estimated in this study with different methods are coherent with those reported in previous studies where the *T* is regarded as ranging from 230 to 300°C (Ellero et al., 2001; Leoni et al., 1996; Reinhardt, 1991; Venturelli & Frey, 1977). The *P* conditions in the range from 0.6 to 0.9 GPa are the first quantitative geobaric estimates for the IL units, and are crucial to reconstruct a *P-T* gradient. The data indicate that the metamorphic peak has been acquired at about 20–30 km in a setting characterized by a geothermal gradient of about 10–12°C/km.

The resulting geothermal gradient is not coherent with the interpretation of the IL units as remnants of a trapped crust lying above the subduction zone, as in this case the ophiolites escape subduction-related metamorphism and are deformed only during continental collision (e.g., Brown, 2007 and quoted references), thus in a geothermal gradient warmer than what is estimated in this study. Similarly, a deformation of the IL units in a transpressional zone is also unlikely.

The estimated "cold" geothermal gradient instead supports the hypothesis of a deformation of the IL units in a subduction zone. Particularly, these metamorphic conditions and the structural features of the D1 phase, i.e., the isoclinal folds and the foliation, are coherent with a transfer of a fragment of oceanic lithosphere at the base of an accretionary wedge by a process of coherent underplating (sensu Moore & Sample, 1986) as proposed by Marroni and Pandolfi (1996) Marroni et al. (2004, 2017) and Meneghini et al. (2007).

The IL units as part of a pre-Oligocene subduction system allows us to discuss their evolution in the bigger context of the Alps-Apennine system and geodynamic evolution. The Western Alps, located west of the IL units, feature several ophiolite-bearing units, from the westernmost Moglio-Testico unit (Sanità et al., 2022a), through the Montenotte unit (Federico et al., 2015; Seno et al., 2005) to the Voltri Massif west of the IL units, with a clear subduction-related metamorphic signature, proving their building during subduction, accretion at different structural levels, and subsequent exhumation into

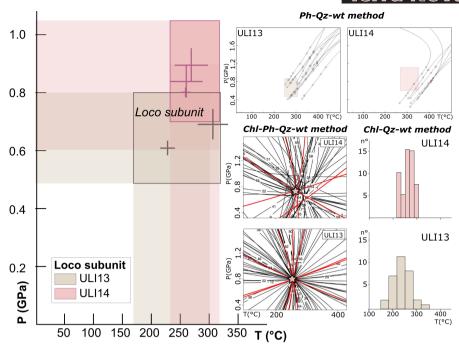


FIGURE 5 Results of the analytical methods employed (chlorite-quartz-water, phengite-quartz-water and chlorite-Phengite-quartz-water multiequilibrium methods) for the study of the samples ULI13 and ULI14. The colored boxes in the main *P/T* space represent the *P-T* equilibrium stability of the chlorite-phengite couples, tracked using the results of the chlorite-quartz-water method (histograms) and of the phengite-quartz-water of Dubacq et al., 2010 (lines with circles). Black circles along the colored lines indicate the activity of the water (aH₂O). Given the presence of calcite, water activity was set to 0.8 for all the samples (e.g., Di Rosa et al., 2020; Sanità et al., 2022b). Crosses indicate the *P-T* equilibria conditions of a single representative chlorite-phengite couple estimated with the Chlorite-Phengite-quartz-water multiequilibrium approach (Vidal & Parra, 2000). The dimension of the crosses is proportional to the energy required to obtain the equilibrium (biggest crosses require higher energy). Equilibrium tolerance was set to 1000 J. Details about the reactions related to these chlorite-phengite couples are reported in the small *P-T* diagrams. In red the six equilibria used for modeling are marked. They are: (4) – 4 Clinochlore +4 Daphnite – 5 Fe-Amesite +5 Mg-Amesite; (29) 14 alpha-Quartz – 4 Daphnite +5 Fe-Amesite +3 Mg-Amesite – 6 Sudoite +8 water; (34) – 10 Mg-Celadonite +15 alpha-Quartz – 2 Daphnite +10 Fe-Celadonite +2 Mg-Amesite – 4 Pyrophyllite + Sudoite; (53) 75 alpha-Quartz – 2 Clinochlore +2 Daphnite – 10 Fe-Celadonite +10 Muscovite – 20 Pyrophyllite +5 Sudoite; (7) – 5 Mg-Celadonite + Clinochlore +4 Daphnite – 5 Fe-Amesite +5 Muscovite; (64) 2 Fe-Amesite – 8 Fe-Celadonite +13 Mg-Amesite +8 Muscovite +14 Pyrophyllite – 26 Sudoite +30 water.

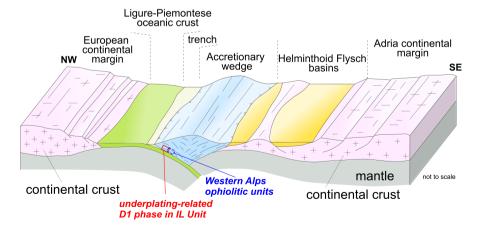


FIGURE 6 3D sketch illustrating the geodynamic setting of the Ligure-Piemontese oceanic basin during Late Cretaceous subduction based on the reconstruction of Bracciali et al., 2007 (see main text to compare this reconstruction with the different ones proposed in literature). Red box indicates the position of the Loco subunit during the D1 phase deformation within the Alpine wedge. The inferred position of the ophiolite-bearing units of Western Alps (e.g., Montenotte and Moglio-Testico units and Voltri Massif, see main text) in the same wedge is shown with the blue box.

the Alpine wedge. The lack of a clear subduction imprint for the IL units has resulted in an interpretation of them as geodynamically separated from the Western Alps of Liguria, and considered instead as the westernmost sector of the Northern Apennine, not involved in the Alpine subduction evolution (Bortolotti et al., 2001; Castellarin & Cantelli, 2010; Schmid et al., 2017).

Following the evidence provided in this study of a blueschists facies metamorphism in the Palombini Shale of the easternmost IL units, coupled with a deformation style unambiguously interpreted as coherent with a subduction setting (e.g., Shreve & Cloos, 1986) we then propose a geodynamic model where the IL units were subducted and accreted at much shallower depths at the base of the same pre-Oligocene Alpine accretionary wedge where the deeper, higher pressure oceanic units of the Western Ligurian Alps were developed their structures. The proposed model is shown in the 3D, not to scale reconstruction of Figure 6 and it is worthy to compare it with the alternative models proposed in literature, such as fig. 4 of Principi & Treves, 1984; fig. 9 of Principi & Treves, 1984, fig. 8 of Hoogerduijn Strating, 1994, and fig. 15 of Nirta et al., 2005.

The proposed model supports then the hypothesis of a unique, pre-Early Oligocene orogenic system for the Alpine belt and the westernmost sector of the Northern Apennine belt.

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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 can be found online in the Supporting Information section at the end of this article.

Data S1

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