High-pressure tectono-metamorphic evolution of mylonites from the Variscan basement of the Northern Apennines, Italy

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Short title

P-T-D path of mylonitic rocks

ABSTRACT

Strain localization within shear zones may partially erase the rock fabric and the metamorphic assemblage(s) that had developed before the mylonitic event. In poly-deformed basements, the loss of information on pre-kinematic phases of mylonites hinders large-scale correlations based on tectono-metamorphic data. In this study, devoted to a relict unit of Variscan basement reworked within the nappe stack of the Northern Apennines (Italy), we investigate the possibility to reconstruct a complete pressure (P) – temperature (T) – deformation (D) path of mylonitic micaschist and amphibolite by integrating microstructural analysis, mineral chemistry and thermodynamic modelling. The micaschist is characterized by a mylonitic fabric with fine-grained K-white mica and chlorite enveloping mica-fishes, quartz, and garnet pseudomorphs. Potassic white mica shows Mg-rich cores and Mg-poor rims. The amphibolite contains green amphibole+ plagioclase+garnet+quartz+ilmenite defining S₁ with a superposed mylonitic fabric localized in decimetre- to centimetre-scale shear zones. Garnet is surrounded by an amphibole+plagioclase corona. Phase diagram calculations provide P-T constraints that are linked to the reconstructed metamorphicdeformational stages. For the first time an early high-pressure stage at > 11 kbar and 510 °C was constrained, followed by a temperature peak at 550-590 °C and 9-10 kbar and a retrograde stage (< 475 °C, < 7 kbar), during which ductile shear zones developed. The inferred clockwise P-T-D path was most likely related to crustal thickening by continentcontinent collision during the Variscan orogeny. A comparison of this P-T-D path with those of other Variscan basement occurrences in the Northern Apennines revealed significant differences. Conversely, a correlation between the tectono-metamorphic evolution of the Variscan basement at Cerreto pass, NE Sardinia and Ligurian Alps was established.

KEYWORDS

Mylonite, *P-T-D* path, high-pressure metamorphism, Northern Apennines, Variscan orogeny.

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1 | INTRODUCTION

The effects of high-strain and re-equilibration occurring in shear zones may obliterate most of the pre-existing minerals and structures in mylonitic rocks. Therefore, the early evolution of such rocks is usually tricky to unravel and this difficulty hampers the reconstruction of a complete metamorphic history. However, a *P-T* path involving early stages of the metamorphic evolution is essential, for instance, to establish correlations among basement units and to reconstruct geodynamic scenarios. The application of thermodynamic modelling, coupled with microstructural observations and mineral composition analyses, to mylonitized rocks was tested here in order to assess if this methodological approach can establish a complete *P-T-D* path, including the pre-mylonitic stages.

The study was carried out on mylonitic medium-grade metapelites and associated amphibolites from the Cerreto pass, belonging to the Variscan basement of the Northern Apennines, a remnant of a southern portion of the Variscan belt (e.g., Franceschelli, Gianelli, Pandeli, & Puxeddu, 2004; Lo Pò & Braga, 2014; Lo Pò, Braga, & Massonne, 2016a; Lo Pò et al., 2016b; Molli, Montanini, & Frank, 2002). To date, only classical geothermobarometry has been used to decipher the metamorphic evolution of these rocks which suffered severe retrogression and shearing (Molli et al., 2002). A combined microstructural-petrological study, including phase diagram calculations, provides new *P-T* constraints for the recognized metamorphic-deformational phases. These calculations result in an improved *P-T-D* path for the Cerreto basement. This path elucidates diverse aspects of the Variscan metamorphism in the Northern Apennines, for instance the occurrence of a high-pressure event. The obtained evolution for the Cerreto basement is compared with the thermobaric history of coeval south-European Variscan units outcropping in the neighborhood in order to establish possible correlations.

2 | GEOLOGICAL FRAMEWORK

The studied samples belong to the Variscan basement of the Northern Apennines (Franceschelli et al., 2004; Ricci, 1968; Vai, 2003), a remnant of Variscan chain in Italy (Figure 1a). The Northern Apennines is a nappe-pile edifice formed after the collision of the European (the Sardinia-Corsica block) and African (the Adria microplate) margins in Oligocene times (Vai & Martini, 2001). This edifice consists of oceanic and continental units (from top to the bottom):

- (1) Ligurian units: ophiolites derived from the oceanic lithosphere of the Western Tethys and their Mesozoic-Cenozoic sedimentary cover (Elter, 1975);
- (2) Tuscan Nappe and external foreland units: a continental Triassic-Tertiary sedimentary sequence detached from its original basement and unaffected by Alpine metamorphism (Bernoulli, 2001; Molli, 2008);
- (3) Tuscan Metamorphic units: Variscan basement and its Triassic-Oligocene cover, belonging to the Adria-derived continental sequence, both metamorphosed during the Alpine orogenic cycle (Franceschelli et al., 2004).

The Variscan basement of the Northern Apennines (Conti, Di Pisa, Gattiglio, & Meccheri, 1993; Franceschelli et al., 2004; Lo Pò & Braga, 2014; Lo Pò et al., 2016a, 2016b) consists of low- to medium-grade metamorphic rocks. It is exposed in the study area at the Cerreto pass, in the Tuscan metamorphic ridge (Punta Bianca, Alpi Apuane, Monti Pisani, Monticiano-Monti Leoni), and on the Elba island. In addition, drilling has detected this basement in the subsurface of Pontremoli and Larderello (Fig. 1b). The Variscan basement in the Larderello subsurface has been subdivided into three tectonic units (Batini, Brogi, Lazzarotto, Liotta, & Pandeli, 2003; Bertini, Casini, Gianelli, & Pandeli, 2006):

- Phyllitic—quartzitic complex: low-grade metasedimentary rocks and metabasite layers, overprinted by the Alpine metamorphism and correlated with the Variscan succession from the Apuane Alps, Monti Pisani and Punta Bianca;
- Micaschist complex: two-mica garnet-bearing albite micaschists with minor amphibolites, which were derived from ocean-floor basalts (OFB), affected by polymetamorphism during the Variscan and Alpine orogeneses;
- Gneiss complex: muscovite-biotite paragneisses with orthogneiss, OFB amphibolite layers and calc-silicate rocks, affected only by Variscan metamorphism.

The Cerreto metamorphic rocks represent the northernmost occurrence of the Variscan basement in the Apennines, and are usually correlated with the micaschist complex of the Larderello subsurface (Pandeli, Gianelli, & Morelli, 2005). They consist of mylonitic micaschists with minor bodies of amphibolites exposed over an area of about 80 hm². The mylonitic fabric is more strongly developed within the micaschists than in the associated amphibolites. The whole micaschist-amphibolite complex occurs as a tectonic slice enclosed in very low grade Triassic quartzite within Late Triassic evaporites and dolomites (Anidriti di Burano Formation). The contact between micaschists and amphibolites is commonly covered by debris. The main foliation in the amphibolites was dated at 328-312 Ma by Ar-Ar on hornblende separates (Molli et al., 2002) confirming that the Cerreto metamorphic rocks were involved in the collisional stage of the South-European Variscides. This amphibolite stage (650°C, 8 kbar) was followed by a retrograde mylonitic stage at 530°C and 4-5 kbar (Molli et al., 2002). In this study, we investigated a micaschist (PC1) and an amphibolite (CER4) from the Cerreto pass and performed thermodynamic modelling on these rocks. PC1 and CER4 crop out at 44° 18' 28'' N, 10° 11' 52'' E and 44° 18' 30'' N, 10° 11' 56'' E, respectively.

3 | ANALYTICAL METHODS

Petrographic observations and microstructural analyses were performed with a polarising optical microscope and a scanning electron microscope Philips 515B at the Dipartimento di Scienze Biologiche, Geologiche ed Ambientali (Università di Bologna). The chemical composition of the minerals in the micaschist PC1 was acquired using a CAMECA SX100 electron microprobe (EMP) equipped with five wavelength dispersive (WD) spectrometers at the Institut für Mineralogie und Kristallchemie (Universität Stuttgart). Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Ba, Cr were analysed in white mica, chlorite, and plagioclase with an acceleration voltage of 15 kV and a beam current of 10-15 nA. Counting times for each element were 20 s at the peak and the background. Synthetic and natural minerals and pure oxides were used as standards. The raw data were corrected using the PaP correction procedure. The errors of the applied method are given by Massonne (2012). X-ray maps (Fe, Mg, Ti, Na) of white mica were prepared using a counting time of 100 ms, a step width of 1 µm, an acceleration voltage of 15 kV and a current of 30 nA. Structural formulae for white mica, chlorite and plagioclase, were calculated with the CalcMin program (Brandelik, 2009). X-ray maps were elaborated with the XMap software (Bernhardt, Massonne, Reinecke, Reinhardt, & Willner, 1995, and updates).

The bulk-rock composition of micaschist PC1 was determined through WD-XRF analysis on a pressed powder pellet using a Philips PW1480 and an Axios-Panalytical spectrometer at the Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna. The sample preparation and the instrumental set-up were reported by Braga and Cinelli (2014). Loss on ignition (L.O.I.) was obtained with standard gravimetric procedures, after heating the powder at 950 °C for 12 hours. The mineral and rock-chemistry of CER4 were taken from Molli et al. (2002).

4 4. Tri fa se po M le fe

4 | PETROGRAPHY AND MICROSTRUCTURAL ANALYSIS

4.1 | Micaschists

The mylonitic micaschists contain pre-kinematic microstructures (Figure 2a,b) and a shearing fabric (Figure 2c,d). Shear bands and mantled porphyroclasts commonly indicate a dextral sense of shear (i.e. top to the NE in present day setting). Only few samples contain garnet porphyroclasts whereas most exhibit garnet pseudomorphed by chlorite (Figure 2e). Muscovite-paragonite-chlorite intergrowths occur at the μ m scale (Figure 2f). Ultramylonitic levels occasionally cut the mylonitic foliation. Accessory minerals are pyrite, epidote, K-feldspar and titanite.

PC1 is a mylonitic micaschist showing garnet pseudomorphs, quartz porphyroclasts and mica-fish (some hundreds of μm long) mantled by a fine-grained (few tens of μm thick) white mica-chlorite mylonitic foliation. The quartz porphyroclasts (some hundreds of μm in diameter) host chlorite and white mica inclusions. Large quartz crystals are surrounded by quartz subgrains with sutured grain boundaries. The recrystallized quartz shows an oblique shape preferred orientation in some domains. The mylonitic foliation is locally crenulated (Figure 2c), or associated with C'-type shear bands. Asymmetric foliation boudins consisting of white mica aggregates are also present. Garnet is totally pseudomorphosed by chlorite (Figure 2e). The modal content of these pseudomorphs is 3 vol. %, determined through image analysis of a thin-section photograph with the JMicroVision 1.2.7 software (http://www.jmicrovision.com/). Feldspar is locally found in the mylonitic foliation. Ilmenite, rutile, titanite, allanite, epidote, pyrite, tourmaline, apatite and zircon are accessory minerals. Ilmenite is xenoblastic and forms fish-shaped crystals and boudins. It contains inclusions of rutile and biotite (Figure 2b). Titanite is oriented parallel to the mylonitic foliation and may form irregular rims around ilmenite (Figure 2b). Epidote has allanite cores.

Based on the occurrence of coarse-grained K-white mica , rutile and biotite inclusions in ilmenite, chlorite inclusions in quartz porphyroclasts, garnet porphyroclasts and ilmenite-fishes, the assemblage K-white mica +biotite+chlorite+quartz+garnet+rutile+ilmenite in PC1 is attributed to a metamorphic event (M_1) predating mylonitization (Figure 2a,b,d,e). Fine-grained K-white mica+ chlorite+quartz+plagioclase+titanite are oriented along the mylonitic foliation. These minerals hence formed by shearing during the syn-kinematic event (M_2) . The same event is also responsible for the development of an oblique foliation in quartz, C'-shear bands, asymmetric foliation boudins and the deformation of pre-kinematic minerals (mica and ilmenite fishes, quartz, garnet and plagioclase porphyroclasts) in the micaschist (Figure 2a-e). Titanite surrounding ilmenite and chlorite replacing garnet also formed during M_2 .

4.2 | Amphibolites

The amphibolites associated with the micaschists are foliated, fine-grained rocks showing a schistosity (S_1) , which is locally crosscut by millimetre- to decimetre-wide mylonitic to ultramylonitic shear zones (Figure 2g).

CER4 contains green amphibole+plagioclase+garnet+quartz+ilmenite+chlorite defining S_1 (M_1). Apatite is an accessory mineral. Garnet occurs as rounded pre-kinematic porphyroclasts with a diameter up to 5 mm. It typically shows an amphibole+plagioclase corona (Figure 2h), and can be partially or totally replaced by chlorite, quartz, amphibole, plagioclase, epidote and titanite (M_2).

5 | ROCK AND MINERAL COMPOSITION 5.1| PC1

The bulk-rock composition (Table 1) is similar to PAAS (Post-Archean Australian Shale; Taylor & McLennan, 1985) and UCC (Upper Continental Crust; McLennan, 2001), except for CaO, which is depleted in PC1 with respect to these mean rock compositions. In the Fe₂O₃/K₂O vs SiO₂/Al₂O₃ diagram (Herron, 1988; not shown), PC1 plots at the wacke-shale boundary.

Pre-kinematic white mica (Ms₁) is potassic and characterized by Mg-rich cores and Mg-poor rims as evident from X-ray mapping (Figure 3a,b). The Mg-rich pre-kinematic K-white mica has Si = 3.17-3.30 atoms per formula unit (apfu), Mg = 0.14-0.22 apfu and Na = 0.04-0.06 apfu. The Mg-poor pre-kinematic K-white mica has Si = 3.03-3.08 apfu, Mg = 0.05-0.08 apfu, Na = 0.15-0.27 apfu. Potassic white mica oriented along the mylonitic foliation (Ms₂) also shows a variable composition with Si = 3.06-3.19 apfu, Mg = 0.06-0.23 apfu, Na = 0.02-0.10 apfu (Figure 4a-c; Table 2). Chlorite from the mylonitic foliation has Si = 5.15-5.93 apfu, Al^{IV} = 2.07-2.85 apfu, Al^{VI} = 2.21-3.34 apfu and XFe=Fe/(Fe+Mg) = 0.50-0.60 (Table 3). Feldspar along the mylonitic foliation is albite (Ab₉₄₋₉₉An₀₋₅Or₀₋₄) with K-feldspar (Ab₀₋₁An₂₋₅Or₉₅₋₉₇) exsolutions (Table 3).

5.2 | CER4

Mineral and bulk compositions of the amphibolite (CER4) are from Molli et al. (2002). The protolith of CER4 was a mafic igneous rock (Molli et al., 2002), according to the projection of bulk-rock major element composition in the (Al+Fe+Ti) vs. (Ca+Mg) diagram of Moine and De La Roche (1968; not shown in Molli et al., 2002, and in this study). We calculated the effective bulk-composition after fractionation of some elements into garnet (Table 1), since zoned minerals are removed from the reacting rock volume during cooling (Stüwe, 1997). The average garnet composition was subtracted from the XRF bulk composition, following the approach of Lo Pò et al. (2016b). For this purpose, the densities of the rock (3.1 g/cm³) and of garnet (4.1 g/cm³) were calculated with PERPLE_X (see below) at *P-T* conditions at which the garnet rim formed (see "Modelling results for amphibole CER4"). The modal content of garnet (3 vol. %) was determined with the JMicroVision 1.2.7 software (see above). The resulting fractionated bulk composition is depleted in Al₂O₃, FeO and enriched in SiO₂, TiO₂, MgO, CaO, Na₂O relative to the unfractionated bulk-rock composition (Table 1). Manganese is totally sequestered in garnet.

The amphibole classification follows the IMA nomenclature (Leake et al., 2004). Amphibole occurring along S_1 (Amph₁) and replacing garnet (Amph₂) is unzoned ferrotschermakite. Si and Al^{IV} in Amph₁ range from 6.28 to 6.30 apfu and from 1.70 to 1.72 apfu, respectively. Amph₂ has Si = 5.98-6.18 apfu and $Al^{IV} = 1.82$ -2.02 apfu. Plagioclase along S_1 (Pl₁) is oligoclase (Ab₈₀An₂₀). Plagioclase in garnet pseudomorphs (Pl₂) is oligoclase-andesine (Ab₆₄₋₈₀An₂₀₋₃₆). Garnet is almandine-rich showing an increase of Fe and a decrease of Mn from core (Alm₅₄Grs₂₃Sps₁₆Prp₄Adr₄) to rim (Alm₅₈Grs₂₃Sps₁₁Prp₅Adr₃).

6 | GEOTHERMOBAROMETRY

6.1 |Isochemical phase diagram calculations

Isochemical phase diagrams (pseudosections) were calculated for micaschist PC1 and amphibolite CER4 with the PERPLE_X program package (Connolly, 1990; Connolly & Petrini, 2002). The considered *P-T* range is 350-600 °C and 2-15 kbar. Silica (only for PC1) and H₂O were considered to be in excess. The pseudosection for micaschist PC1 was calculated in the MnCKNFMASHT system assuming all iron to be totally ferrous because no

Fe³⁺-oxides are present and minerals with significant Fe³⁺ amounts (i.e. epidote) occur in low quantities (< 1 vol. %). The bulk-rock composition was recalculated discarding P_2O_5 and reducing the CaO content by the amount bound to apatite (Table 1). The thermodynamic dataset of Holland and Powell (1998, with the 2002 upgrade), the compensated Redlich Kwong (CORK) fluid equation of state by Holland and Powell (1991, 1998), and the following solid-solution models were used: Pheng(HP) for K-white mica (Holland & Powell, 1998; the maximum paragonite content set to 50 mol.%), Mica(M) for Na-Ca white mica (Massonne, 2010; the maximum muscovite content was set to 50 mol.%), Gt(HP) for garnet (Holland & Powell, 1998), TiBio(HP) for biotite (Powell & Holland, 1999; White, Powell, Holland, & Worley, 2000), Chl(HP) for chlorite (Holland, Baker, & Powell, 1998), feldspar for plagioclase (Fuhrman & Lindsley, 1988), St(HP) for staurolite (Holland & Powell, 1998), and the ideal models (see

http://www.perplex.ethz.ch/PerpleX_solution_model_glossary.html) hCrd for cordierite and IlGkPy for ilmenite. Pure phases are, for instance, titanite, rutile, zoisite, lawsonite, sillimanite and andalusite.

For the thermodynamic modelling of the amphibolite CER4, the XRF composition given by Molli et al. (2002) was used, converting Fe₂O₃^{tot} to FeO^{tot}, reducing CaO according to P₂O₅ in apatite (see above) and eliminating K₂O because of its negligible concentration (Table 1). Two *P-T* pseudosections were calculated, in the MnCNFMASHT and CNFMASHT systems in order to determine the M₁ and M₂ conditions, respectively. The latter was calculated using the fractionated bulk-rock composition in a Mn-free system due to the sequestration of the bulk Mn into garnet. For the calculations based on the amphibolites CER4, the solid-solution models GlTrTsPg (Powell & Holland, 1999) and Act(M) (Massonne & Willner, 2008) for amphibole and Omph(HP) for clinopyroxene (Holland & Powell, 1996) were additionally considered.

The obtained pseudosections were contoured by isopleths for Si in K-white mica and modal amount of garnet (micaschist) and molar fractions of garnet components and anorthite in plagioclase (amphibolite).

6.2 | Modelling results for micaschist PC1

In the pseudosection for micaschist PC1 (Figure 5), K-white mica is present over the entire *P-T* grid. The Na-Ca white mica disappears above 520 °C at 2 kbar and below 5 kbar at 600 °C. Chlorite breaks down above 520 °C, 2 kbar and 580 °C, 15 kbar. Biotite appears at 450 °C, 8 kbar. Garnet occurs above 400 °C, > 11 kbar. Plagioclase is present below 7 kbar and above 380 °C. Rutile disappears below 9 kbar above 525 °C. Ilmenite coexists with rutile at 450 °C, 2 kbar to 500 °C, 9 kbar. Ilmenite replaces rutile above 550 °C below 10 kbar completely. The titanite-out curve is at 380 °C, 2 kbar and 500 °C, 12 kbar. The Si in K-white mica increases with pressure reaching a maximal 3.39 apfu. The isopleth for the maximum measured Si of the Mg-rich pre-kinematic K-white mica (3.30 apfu) plots at pressures above 10 kbar. An early stage of M₁ (prograde stage) can be constrained above 11 kbar and 510 °C by the intersection of this isopleth and the *P-T* boundaries of biotite-bearing, titanite-absent assemblage fields.

The calculated paragenesis, corresponding to the inferred M_1 mineral assemblage (Ms+Chl+ Bt+Grt+Il+Rt+Qtz) except for paragonite, plots at 520-590 °C and 9-10 kbar. The estimated garnet modal quantity (3 vol. %) plots above 500 °C and 8 kbar. The corresponding isomode occurs in the M_1 mineral assemblage field at 550-590 °C and 9-10 kbar, defining the peak stage of the M_1 event.

The P-T conditions of the M_2 event were determined considering isopleths for the Si content of the mylonitic K-white mica (3.06 to 3.19 apfu) and the P-T fields of biotite-absent and garnet-absent mylonitic assemblages. Corresponding intersections occur at < 475 °C and < 7 kbar in the calculated paragenetic fields of chlorite+K-white mica+paragonite+plagioclase+rutile+titanite+ ilmenite (Figure 5).

6.3 | Modelling results for amphibolite CER4

A pseudosection was calculated for the bulk-rock composition of amphibolite CER4 to constrain the P-T conditions of the M_1 event (Figure 6). Calcic-sodic amphibole appears from 370 °C at 2 kbar and 525 °C at 15 kbar. From 525 °C and 9 kbar towards higher temperature and pressure conditions two amphibole types (Na-amphibole and Ca-amphibole) coexist. Chlorite breaks down at 600 °C, 2 kbar and 550 °C, 15 kbar. Plagioclase occurs only below 7 (350 °C) - 13 kbar (600 °C). Garnet is present over almost the entire P-T grid except below 4 kbar at 450-525 °C and below 400 °C. The ilmenite-in curve runs through 450 °C – 2 kbar and 530 °C – 15 kbar. Titanite is stable from 350 to 525 °C. The calculated isopleths corresponding to the analyzed garnet core composition intersects at 530 °C and 5 kbar in the paragenetic field amphibole+plagioclase+garnet+chlorite+ quartz+ilmenite in agreement with the observed M_1 paragenesis. The isopleths representing the garnet rim composition (Alm₅₈Grs₂₃Sps₁₁Prp₅; Molli et al., 2002) intersect at 550 °C and 6 kbar (Figure 6), defining the peak stage of the M_1 event.

The pseudosection calculated for the fractionated bulk-composition (see above) constrains the M₂ conditions (Figure 7). The garnet stability field in the *P-T* pseudosection occurs above 475 °C at 15 kbar and 595 °C at 2 kbar. The Ca-amphibole-in curve is located at 350 °C - 6 kbar and 525 °C - 15 kbar. Towards higher temperatures and lower pressures, Ca-amphibole replaces clinopyroxene. Two coexisting amphibole types (Ca-amphibole and Na-amphibole) are present at high temperatures and high pressures. Chlorite disappears above 525 °C at 10 kbar. Plagioclase breaks down above 7 (350 °C) -13 (600 °C) kbar. Ilmenite occurs above 450 °C, 2 kbar and 550 °C, 15 kbar. Titanite appears only in the 350-525 °C range. Zoisite is present below 550 °C (clinozoisite at < 370 °C) and is here assumed to be equivalent to epidote in the Fe³⁺-free system. The calculated paragenesis corresponding to the observed M₂ (amphibole, plagioclase, epidote, chlorite, titanite, quartz) occurs at 425-525 °C and 3-10 kbar (Figure 8). The minimum anorthite component in Pl₂ (molar fraction of An = 0.2) constrains the maximum pressure of M₂ at 8 kbar.

7 DISCUSSION

7.1 | P-T-D path of the mylonites from the Variscan basement at Cerreto pass

Mylonites from shear zones, albeit forming a limited portion of rock outcrops, are first-order features for understanding plate tectonics (Bercovici & Ricard, 2012). Because of the localization of intense strain, mylonites are considered to have the potential to record metamorphic conditions of syn- to post-shearing (i.e. retrogression) events (Cirrincione, Fazio, Ortolano, Pezzino, & Punturo, 2012). Associated studies on adjacent less deformed/undeformed portions of wall rocks may provides hints on the pre-shearing metamorphic history. Our study indicates that extended portions of *P-T* paths, including pre-shearing stages, can be reconstructed even from mylonites by combining microstructural analysis, mineral-chemistry and thermodynamic modelling. In favourable circumstances, such as the Cerreto Pass mylonites, metamorphic conditions predating and during the mylonitic event are constrained from a small volume of rock at thin-section scale. In our case study, a clockwise *P-T-D* path for micaschist PC1 belonging to the Variscan basement at the Cerreto pass was reconstructed. This path includes two metamorphic events (M₁ and M₂;

Figure 8). In particular, the M_1 event consists of (i) a high-pressure prograde stage (P-T conditions above 11 kbar and 510 °C) recognized by Mg-rich cores in deformed K-white mica grains and a biotite-bearing, titanite-free paragenesis; (ii) a peak temperature stage (550-590 °C at 9-10 kbar), during which the M₁ paragenesis equilibrated. Ilmenite, which is not present in the paragenesis of the prograde stage, formed during the peak stage. The M₂ event occurred during the retrograde stage (below 475 °C and 7 kbar) and is represented by Kwhite mica oriented along the mylonitic foliation and by the absence of garnet and biotite. During the M₂ event, a well-developed mylonitic fabric developed (mylonitic foliation, shear bands, asymmetric foliations boudins, quartz oblique foliation). Paragonite was predicted to be present during the metamorphic evolution of the micaschist, but it was not found in PC1 (Table 4). However, this mineral can be easily overlooked, e.g. because of a very small grain size. Indeed, high-magnification observations with a field emission scanning microscopy on another micaschist from the Cerreto pass (sample PC23) revealed the existence of finegrained paragonite flakes (10-50 µm wide, only a few µm thick; Figure 2f) intergrown with K-white mica. The bulk composition of the paragonite-bearing micaschist PC23 is similar to the bulk composition of PC1. In particular, the Na₂O/(Na₂O+K₂O) ratio in PC23 and PC1 is 0.35 and 0.37, respectively. Although high-magnification observations with a field emission scanning microscopy are not available for PC1, it is conceivable that very fine-grained paragonite may also be present in this sample, in agreement with the pseudosection calculation result. Another apparent discrepancy between the observed M₂ mineral assemblage in micaschist PC1 (K-white mica+chlorite+plagioclase+quartz+titanite) and the predicted paragenesis (K-white mica+chlorite+

plagioclase+quartz+paragonite+titanite+rutile+ilmenite) is the presence of low amounts of ilmenite and rutile (calculated mode for ilmenite and rutile in the retrograde stage is below 1 vol. %; Table 4). Substitutions of Al and F for Ti and O in titanite should extend the *P-T* stability of the titanite solid-solution (Tropper, Manning, & Essene, 2002). However, the calculation presented in this work considers titanite only as a pure ideal phase, with consequences on the titanite stability and its relationships with Ti-bearing minerals.

During the M_1 event, the amphibolite associated with the micaschist records a prograde stage at 530 °C and 5 kbar, followed by peak temperature conditions at 550 °C at 6 kbar (Figure 6). The retrograde paragenesis amphibole+plagioclase+epidote+chlorite+titanite+quartz developed at 425-525 °C and 3-8 kbar (M_2). Although no extended P-T path could be reconstructed for the amphibolite, the obtained P-T conditions for amphibolite CER4 are quite different from those of the micaschist for the M_1 event but compatible for the M_2 event. Thus, the results from the thermodynamic modelling suggest a common retrograde evolution for the two rock types.

The obtained *P-T-D* path (Figure 8) points to a single metamorphic loop experienced by the Cerreto micaschist and amphibolite during the Variscan orogeny. The initial prograde high-pressure stage (> 11 kbar and > 510 °C) testifies a burial to 40 km and more during collision-related thickening of the crust. Peak temperatures of 550-590 °C at 9-10 kbar followed the peak pressure. This suggests that heating by thermal equilibration occurred after the exhumation had already begun (see England & Thompson, 1984). Similar *P-T* paths have been reported from other collisional zones worldwide (e.g., Fiannacca, Lo Pò, Ortolano, Cirrincione, & Pezzino, 2012; Massonne & Calderón, 2008; Massonne & Toulkeridis, 2012; Massonne, 2016; Rötzler, Schumacher, Maresch, & Willner, 1998). The retrograde stage, accompanied by mylonitic deformation, is related to an exhumation process along ductile shear zones. Two tectonic scenarios can be proposed for the recognized retrograde stage in the Cerreto mylonites: (i) a post-Variscan intracontinental strike-slip shearing (Marroni,

Molli, Montanini, & Tribuzio, 1998; Martini, Rau, & Tongiorgi, 1986; Massari, 1986; Matte, 2001; Padovano, Dörr, Elter, & Gerdes, 2014; Padovano et al., 2012; Ricci & Serri, 1975); (ii) a Jurassic rifting stage that preludes the opening of the Western Tethys (Beltrando, Zibra, Montanini, & Tribuzio, 2013; Froitzheim & Manatschal, 1996; Mohn, Manatschal, Müntener, Beltrando, & Masini, 2010; Mohn, Manatschal, Beltrando, Masini, & Kusznir, 2012; Molli et al., 2002; Montanini, Tribuzio, & Anczkiewicz, 2006).

7.2 | **Implications for the pre-Alpine evolution of the Northern Apennine basement** Only three *P-T* paths have so far been presented for the pre-Alpine metamorphism in the Variscan basement of the Northern Apennines: Cerreto pass (Molli et al., 2002, and this work), Larderello (Bertini, Elter, & Talarico, 1994) 73 km SSE of the Cerreto pass, and Pontremoli (Lo Pò et al., 2016b) 25 km WNW of the Cerreto pass.

Molli et al. (2002) investigated the metamorphic evolution of the micaschist complex at Cerreto pass, postulating an early metamorphic event at the garnet-amphibolite or eclogite facies, but did not constrain the pre-peak stage by geothermobarometry. These authors used classical thermobarometry to constrain the peak conditions at 650°C and 8 kbar for the amphibolites and 630°C and 8.5 kbar for the micaschists. These P-T conditions are about 50°C higher and 1 kbar lower than those calculated in this study for micaschist PC1. Considering 2 σ -errors in the range of 5% for the temperature estimate and 10% in the pressure value (Massonne, 2013) determined through thermodynamic modelling, the previous P-T constraints overlap with the thermobaric constraints derived in this study. Since micaschist and amphibolite are deformed together and show the same structural features (e.g. pre-kinematic relicts and mylonitic fabric), we infer that they shared a common metamorphic evolution from at least peak temperature conditions onward. The 40 Ar/ 39 Ar age determined for the amphibolites (328-312 Ma, Molli et al., 2002) record cooling below \approx 500 °C. These ages therefore constrain the inception of the retrograde evolution in the micaschists which occurred at < 475 °C and < 7 kbar (this study).

Bertini et al. (1994) reconstructed the pre-Alpine *P-T* history of the gneiss complex in the Larderello subsurface through classical geothermobarometry and the stability fields of staurolite, muscovite, and alusite and cordierite. These authors estimated peak conditions of 500-600°C and 7 kbar, followed by an isothermal decompression to 2-3.5 kbar at 500-600°C, for the pre-Alpine history. Bertini et al. (1994) interpreted the obtained *P-T* path as related to a fast tectonic exhumation after the Variscan collision. The isothermal decompression stage, invoked by these authors, is different from the retrograde branch (from the peak temperature stage to the retrograde stage) of our *P-T-D* path, that proposes a concomitant diminution of pressure with decreasing temperature. The contrasting retrograde evolution of the two complexes (Figure 9) suggests that they were related to different sectors or units of the former Variscan belt.

The Pontremoli garnet-bearing micaschist underwent a metamorphic evolution characterized by a prograde path starting at 530 °C and 5.5 kbar, a metamorphic peak temperature of 575 °C at 7 kbar (in early Permian times: 293 Ma), subsequent peak pressure of 8 kbar at 520 °C and a retrogression at 475 - 520 °C and 2 - 7 kbar (Lo Pò et al., 2016b). The peak conditions of the Cerreto metamorphic rocks (328-312 Ma) were reached earlier and at different pressures (9-10 kbar *vs.* 7 kbar in the Pontremoli basement; Figure 9). Hence, we propose that Cerreto and Pontremoli basement rocks also belong to distinct tectonic units or sectors of the former South Variscan belt, according to the present day Apenninic tectonic setting which supports their attribution to different crustal segments (i.e. Apenninic palaeotectonic domains; Molli, 2008).

7.3 | Comparison between the Cerreto and neighbouring south-European Variscan units The metamorphic evolution of the Cerreto micaschists resembles the Variscan history of chloritoid schists from the Inner Zone of the Variscan chain of nearby NE Sardinia (Cruciani, Franceschelli, Massonne, Carosi, & Montomoli, 2013). Through the same thermodynamic approach (pseudosections + isopleths of Si content in K-white mica) used in this work, Cruciani et al. (2013) constrained a high-pressure stage (18 kbar at 460-500 °C) before a Barrovian-type metamorphism, the peak temperature of which is 540-570 °C at 7-10 kbar. The P-T estimates and the overall clockwise shape of the P-T path obtained for the Cerreto rocks (HP prograde stage at > 11 kbar and > 510°C and peak temperature of 550-590 °C at 9-10 kbar) are similar to the Sardinian thermobaric trajectory (Cruciani et al., 2013). Both basements also share decreasing pressure conditions during Barrovian metamorphism and diachronous pressure and temperature peaks, distinctive of orogenic belts affected by crustal thickening and exhumation (Cruciani et al., 2013; England & Thompson, 1984). The Variscan basement in the Northern Apennines and NE Sardinia share some other similarities, namely the E-MORB affinity of the amphibolites and the cooling 40Ar/39Ar ages (Carmignani et al., 1994; Molli et al., 2002). Indeed, the Variscan basement of the Inner Zone in Sardinia experienced a transpressive shearing tectonism that developed, for instance, along the Posada-Asinara Line at 325-315 Ma (Carosi, Montomoli, Tiepolo, & Frassi, 2012; Di Vincenzo, Carosi, & Palmeri, 2004; Elter & Pandeli, 2005). This age is consistent with the age determination of 328-312 Ma in the amphibolites from the Cerreto pass, interpreted to record regional metamorphic cooling below about 500° C (Molli et al., 2002). Another analogy is the protolith nature for the metapelitic rocks. According to the Fe₂O₃/K₂O vs. SiO₂/Al₂O₃ diagram by Herron (1988), the chloritoid schists from NE Sardinia developed from immature clastic sediments similarly to the micaschists from the Cerreto pass. Furthermore, both are characterized by Ca-poor bulk rock compositions. Hence, it is conceivable that the metamorphic rocks studied here and from NE Sardinia represent the same geotectonic collisional zone, as suggested by Molli et al. (2002).

In the Inner Zone of the Variscan chain in Sardinia, eclogites enclosed in medium grade metapelites also record a high pressure stage at 13-15 kbar and 610-700 °C (Cortesogno, Gaggero, Oggiano, & Paquette, 2004; Cruciani, Montomoli, Carosi, Franceschelli, & Puxeddu, 2015). Both eclogites and metapelites re-equilibrated under amphibolite-facies conditions during the Variscan collision at 320-315 Ma (Di Vincenzo et al., 2004). The Sardinian medium-grade metapelites and eclogites were correlated with the eclogite-bearing Gneiss-Amphibolite Complex of the Ligurian Alps (Cortesogno et al., 2004). In the Gneiss-Amphibolite Complex, the high-pressure metamorphic overprint of the eclogite relicts occurred at 392-376 Ma, and was followed by an amphibolite-facies reequilibration at 333 ± 7 Ma (Giacomini, Braga, Tiepolo, & Tribuzio, 2007; Fig. 9). Although eclogitic relicts have not been found in the Cerreto basement, the comparable metamorphic evolution of metapelites from the Cerreto Pass, NE Sardinia and Ligurian Alps (high pressure stage followed by an amphibolite-facies overprint) supports the palaeotectonic correlation between the Cerreto basement, the Inner Zone of the Sardinia Variscan belt and the Gneiss-Amphibolite Complex of the Ligurian Alps.

8 | CONCLUSIONS

When pre-kinematic and syn-kinematic minerals occur in the same mylonitic rock, the application of thermodynamic modelling has the potential to reveal the thermobaric conditions occurred before and during the high-strain event that obliterates most of earlier metamorphic stages. The reconstruction of complete polyphase *P-T* evolutions of mylonites

is useful to unravel the tectono-metamorphic history of crystalline basements now dismembered in different domains of orogenic belts.

Micaschists and amphibolites from the Cerreto pass are remnants of the Variscan basement reworked within the Northern Apennine nappe stack. A clockwise *P-T-D* path (prograde, temperature peak and retrograde stages) has been established from analysis of a mylonitic metapelite and amphibolite. A peak pressure in excess of 11 kbar has been determined in the micaschist, showing the first occurrence of a Variscan high pressure event in the Northern Apennines. This event was caused by crustal thickening during the collision of Gondwana and Laurussia. The high-pressure stage was followed by metamorphism at peak temperature of 550-590 °C at 9-10 kbar. The post-peak evolution occurred at 328-312 Ma in micaschist and adjacent amphibolite, which both experienced similar *P-T* conditions. The retrogression stage at < 475 °C, < 7 kbar at the Cerreto pass, responsible for the well-developed mylonitic fabric, is most likely related to the exhumation of Variscan crust along ductile shear zones.

The Variscan basements at Larderello (gneiss complex) and Pontremoli show different metamorphic evolutions suggesting provenances from different units or sectors of the former Variscan belt. In contrast, metamorphic evolution and timing of the Cerreto Variscan basement is similar to those inferred for micaschists from NE Sardinia and Ligurian Alps. This new finding supports a palaeotectonic correlation of these Variscan basement areas.

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FIGURE AND TABLE CAPTIONS

Figure 1

Location of the Northern Apennines in Italy (a) and regional geological framework of the Northern Apennines with the distribution of the Variscan basement in black (b; modified after Lo Pò et al., 2016b).

Figure 2

Petrographic features of the Cerreto metamorphic rocks (a-f refer to micaschists, g-h to amphibolites): (a) external foliation (S_e) surrounding a plagioclase porphyroclast, which exhibits an internal foliation (S_i) (CER7; crossed nicols microphotograph from Molli et al., 2002); (b) rutile in an ilmenite grain surrounded by titanite (PC1; BSE image); (c) folded mylonitic foliation (PC1; BSE image); (d) mica- and ilmenite-fish (PC1; BSE image); (e) fractured and retrogressed garnet porphyroclast (PC1; plane-polarized light

microphotograph); (f) K-white mica+Na white mica+ chlorite intergrowths forming an asymmetric foliation boudin (PC23; BSE image); (g) matrix in amphibolite crosscut by a mylonitic foliation (CER6; plane-polarized light microphotograph from Molli et al., 2002); (h) garnet porphyroclast surrounded by an amphibole+plagioclase corona (CER4; crossed nicols microphotograph).

Figure 3

X-ray maps of K-white mica in PC1 (a) Mg distribution; (b) Na distribution. The colour code scales are related to the counts of specific $K\alpha$ radiation per time unit.

Figure 4

Compositional diagrams for K-white mica in PC1: (a) Fe²⁺+Mg vs. Si; (b) Mg vs. Si; (c) Na vs. Si. Additional analyses not reported in Table 2 are also shown.

Figure 5

P-T pseudosection for PC1 with K-white mica isopleths (expressed in apfu), garnet isomodes (expressed in vol. %) and the selected constraints for the M₁ event (prograde and peak stages) and M₂ event (retrograde stage). The biotite-in curve and the garnet-out curve are marked. Mineral abbreviations are Ms (K-white mica), Chl (chlorite), Pg (Na white mica), Grt (garnet), Bt (biotite), Pl (plagioclase), Kfs (K-feldspar), Ilm (ilmenite), Rt (rutile), Ttn (titanite), Lws (lawsonite), Zo (zoisite), And (andalusite), Sil (sillimanite), St (staurolite), Crd (cordierite).

Figure 6

P-T pseudosection for amphibolite CER4. The M₁ stage is constrained by garnet isopleths. Mineral abbreviations are as in Figure 5, with the addition of Amph (amphibole), Cpx (clinopyroxene), Czo (clinozoisite).

Figure 7

P-T pseudosection for the M_2 stage in amphibolite CER4. The red-coloured paragenesis corresponds to the observed one. Mineral abbreviations are as in Figures 5 and 6. The isopleth related to the maximum anorthite content in Pl_2 is shown.

Figure 8

P-T-D path for the Cerreto micaschists. The table contains a summary of the tectonometamorphic evolution, with the microstructures, the constraining phases and the corresponding P-T estimates. The pink figures mark the P-T constraints in the micaschist.

Figure 9

The Cerreto *P-T* path (red arrow) compared with the thermobaric trajectories proposed for some Variscan segments in the Northern Apennines, Sardinia and Liguria: violet arrows and boxes for the Larderello gneiss complex (Northern Apennines; Bertini et al., 1994); green arrows and boxes for the Cerreto amphibolites (Northern Apennines; Molli et al., 2002); light blue arrow for the Pontremoli micaschist (Northern Apennines; Lo Pò et al., 2016b); black continuous to dashed arrow for the Inner Zone of the Sardinian basement (Cruciani et al., 2013); brown arrow for the eclogites from Savona Crystalline Massif of the Ligurian Alps (Giacomini et al., 2007 and references therein).

Table 1

Bulk-rock composition of PC1 determined through WD-XRF analysis (this work), (unfractionated) CER4 from Molli et al. (2002) and CER4 after garnet fractionation (calculated in this study). Compositions modified for thermodynamic modelling (see text) are also presented.

Table 2

Representative mineral compositions of K-white mica in micaschist PC1. The formula of K-white mica is calculated assuming 42-(Ca+Ba) valencies and 4 H.

Table 3Representative mineral compositions of chlorite and feldspar in micaschist PC1. The structural formula of chlorite is calculated on the basis of 28 oxygen and 16 H, neglecting Na and Ca. The structural formula of plagioclase is based on 8 oxygen.

Table 4

Observed and calculated paragenesis in micaschist PC1 and in amphibolite CER4 related to different metamorphic events. See text for the microstructural position of each mineral.

Table 1

		XRF		The	Thermodynamic modelling				
	PC1	CER	R4	PC1	CER4				
ı	ICI	unfractionated	fractionated	rcı	unfractionated	fractionated			
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %			
SiO_2	67.74	49.49	49.68	70.53	50.99	51.68			
TiO_2	0.85	2.5	2.58	0.89	2.58	2.68			
Al_2O_3	16.9	12.18	11.67	17.6	12.55	12.14			
Fe ₂ O ₃	4.61	17.22	16.58	-	-	-			
FeO	-	-		4.32	15.95	15.51			
MnO	0.05	0.27	0.00	0.06	0.28	-			
MgO	1.53	6.01	6.18	1.59	6.19	6.43			
CaO	0.75	9.44	9.38	0.53	9.20	9.21			
Na ₂ O	1.59	2.19	2.27	1.66	2.26	2.36			
K_2O	2.71	0.31	0.32	2.83	-	-			
P_2O_5	0.18	0.39	0.40	-	-	-			
L.O.I.	3.08	0.94	0.94						
H_2O				in excess	in excess	in excess			
Total	99.99	100.94	100.00	100	100	100			

Table 2

K-white mica									
Prekinematic Mg-rich core			Prekinematic Mg-poor rim			Mylonitic foliation			
Point analyses	Ms11_4	Ms11_5	Ms11_6	Ms08_1	Ms9_2	Ms9_3	Ms10_01	Ms10_02	Ms10_03
SiO ₂	50.13	49.69	50.62	46.40	47.05	46.38	46.39	45.55	45.10
TiO_2	0.30	0.33	0.38	0.14	0.46	0.40	0.37	0.36	0.31
Al_2O_3	31.45	31.33	30.95	34.78	35.45	36.15	33.85	34.50	34.12
FeO	1.64	1.43	1.66	2.15	1.09	0.98	1.87	1.33	1.69
MnO	0.05	-	-	-	-	-	0.04	-	-
MgO	2.04	1.94	2.30	1.10	0.87	0.72	1.19	0.78	0.95
CaO	0.04	0.03	0.01	-	0.03	0.01	0.02	0.01	0.01
Na_2O	0.42	0.39	0.39	0.35	0.92	0.91	0.33	0.43	0.33
K_2O	10.56	10.76	10.46	10.94	10.56	10.35	10.65	10.93	10.60
BaO	0.19	0.20	0.15	0.35	0.24	0.27	0.34	0.25	0.32
Total	96.82	96.11	96.91	96.20	96.67	96.18	95.04	94.13	93.44
Si	3.27	3.27	3.29	3.09	3.09	3.06	3.11	3.09	3.08
Al^{IV}	0.73	0.73	0.71	0.91	0.91	0.94	0.89	0.91	0.92
Ti	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02
Al^{VI}	1.70	1.71	1.67	1.81	1.84	1.87	1.79	1.84	1.82
Fe^{2+}	0.09	0.08	0.09	0.12	0.06	0.05	0.10	0.08	0.10
Mn	0.00	-	-	_	-	-	0.00	-	
Mg	0.20	0.19	0.22	0.11	0.09	0.07	0.12	0.08	0.10
Ca	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.0
Na	0.05	0.05	0.05	0.04	0.12	0.12	0.04	0.06	0.04
K	0.88	0.90	0.87	0.93	0.89	0.87	0.91	0.95	0.93
Ba	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.0

Table 3

		Chl	orite			F	Feldspar		
		Mylonitio	foliation		Myl	onitic folia	ation	Exsolution in p	lagioclase
Point analyses	Chl06_02	Chl06_03	Chl06_04	Chl06_05	P101	Pl06_10	P103	Kfs03	Kfs04
SiO_2	24.20	24.41	23.93	25.67	68.03	68.27	67.94	64.39	65.00
TiO ₂	0.06	0.06	0.07	0.07	0.07	0.00	0.10	0.00	0.00
Al_2O_3	22.05	22.06	22.07	21.85	20.71	20.05	20.97	18.52	18.30
FeO ^{tot}	28.85	28.88	28.87	28.49	-	-	-	-	-
Fe_2O_3	-	-	-	-	0.45	0.09	0.31	0.27	0.28
MnO	0.21	0.23	0.23	0.26	-	-	-	-	-
MgO	12.55	12.89	12.52	12.20	0.00	0.00	0.03	0.00	0.01
CaO	-	-	-	-	0.84	0.67	1.11	0.02	0.00
Na ₂ O	-	-	-	-	11.67	11.59	11.55	0.54	0.31
K_2O	-	-	-	-	0.10	0.07	0.11	16.54	16.39
BaO	-	-	-	-	0.00	0.00	0.00	0.33	0.17
Total	87.91	88.53	87.69	88.54	101.88	100.73	102.12	100.61	100.45
Si	5.19	5.20	5.15	5.43	2.93	2.97	2.92	2.98	3.00
Ti	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Al	5.58	5.54	5.60	5.45	1.05	1.03	1.06	1.01	0.99
Fe ³⁺					0.01	0.00	0.01	0.01	0.01
Fe ^{tot}	5.18	5.14	5.20	5.04	-	-	-	-	-
Mn	0.04	0.04	0.04	0.05	-	-	-	-	-
Mg	4.02	4.09	4.02	3.85	-	-	-	-	-
Ca	-	-	-	-	0.04	0.03	0.05	0.00	-
Na	-	-	-	-	0.98	0.98	0.96	0.05	0.03
K	-	-	-	-	0.01	0.00	0.01	0.98	0.96
Ba	-	-	-	-	-	-	-	-	-
XAn					0.04	0.03	0.05	0.01	0.00
XAb					0.96	0.97	0.94	0.05	0.03
XOr					0.01	0.00	0.01	0.95	0.97

Table 4

		PC1	CER4		
M_1	Observed	Grt+Ms+Bt+Chl+Qtz+Rt+Ilm	Grt+Amph+Pl+Qtz+Ilm+Chl		
	Calculated	Grt+Ms+Bt+Chl+Qtz+Rt+Ilm+Pg	Grt+Amph+Pl+Qtz+Ilm+Chl		
\mathbf{M}_2	Observed	Ms+Chl+Pl+Qtz+Ttn	Amph+Pl+Chl+Qtz+Ep+Ttn		
	Calculated	Ms+Chl+Pl+Qtz+Pg+Ttn+Rt+Ilm	Amph+Pl+Chl+Qtz+Ep+Ttn		

















