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DIEGO PIERUCCIONI ⁽¹⁾, SIMONE VEZZONI ⁽¹⁾, MAURIZIO PETRELLI ⁽²⁾⁽³⁾

A PETROGRAPHIC AND U-PB GEOCHRONOLOGICAL APPROACH TO THE RECONSTRUCTION OF THE PRE-ALPINE HISTORY OF ALPI APUANE (TUSCANY)

Abstract - D. PIERUCCIONI, S. VEZZONI, M. PETRELLI, *A petrographic and U-Pb geochronological approach to the reconstruction of the pre-Alpine history of Alpi Apuane (Tuscany).*

The Paleozoic basement of the Northern Apennines is formed by a metasedimentary and metavolcanic sequence whose age was established mostly through correlations with Paleozoic formations of Sardinia. Only a few geochronological data are currently available and this lack of data poses some limitations to an accurate reconstruction of the pre-Triassic geological evolution of this area. In order to fill this gap, petrographical and U-Pb zircon geochronological data collected on three selected samples belonging to the “*Filladi Inferiori*” Fm and the “*Porfiroidi e Scisti Porfirici*” Fm are reported. The new data: i) agree with previous depositional ages reported for the “*Filladi Inferiori*” Fm; ii) stress the occurrence of a possible Permian hydrothermal alteration; and iii) indicate that some outcrops mapped as belonging to the “*Porfiroidi e Scisti Porfirici*” Fm are metaparaconglomerate having an Ediacaran maximum depositional age possible related to the Ordovician eo-Caledonian unconformity event.

Keywords - Paleozoic basement, hydrothermal alteration, U-Pb zircon geochronology, Apuan Alps.

Riassunto - D. PIERUCCIONI, S. VEZZONI, M. PETRELLI, *Un approccio petrografico e geocronologico U-Pb per la ricostruzione della storia pre-Alpina delle Alpi Apuane (Toscana).*

Il basamento Paleozoico dell'Appennino settentrionale è formato da sequenze meta-sedimentarie e meta-vulcaniche la cui età è stata stabilita in maniera indiretta, principalmente attraverso correlazioni con le formazioni paleozoiche della Sardegna. Ad oggi esistono pochi dati geocronologici, che limitano una accurata ricostruzione dell'evoluzione geologica pre-Triassica dell'area. Per cercare di colmare questa lacuna, sono stati raccolti dati petrografici e geocronologici U-Pb su zirconi di tre campioni appartenenti alle formazioni delle “*Filladi Inferiori*” e “*Porfiroidi e Scisti Porfirici*”. I nuovi dati i) concordano con l'età deposizionale conosciuta per la formazione delle “*Filladi Inferiori*”; ii) sottolineano la presenza di un'alterazione idrotermale di probabile età Permiana; e iii) evidenziano che alcuni affioramenti ritenuti appartenenti alla formazione dei “*Porfiroidi e Scisti Porfirici*” sono invece meta-paraconglomerati con una età massima di deposizione Ediacariana forse ricollegabili all'evento Ordoviciano di discordanza eo-Caledoniana.

Parole chiave - Basamento paleozoico, alterazione idrotermale, geocronologia U-Pb su zircone, Alpi Apuane.

INTRODUCTION

The Paleozoic basement of the Northern Apennines is discontinuously exposed in the Middle Tuscan Ridge, a geomorphological feature ranging from the Alpi Apuane to Monte Argentario, and constitutes the stratigraphic base of the Meso-Cenozoic succession belonging to the Tuscan domain of the Adria continental margin. Several authors have attributed the Paleozoic sequences of the Northern Apennines to the southern part of the Variscan chain (Bagnoli *et al.*, 1979; Vai & Cocozza, 1986; Di Pisa *et al.*, 1988; Sassi & Zanferrari, 1989; Padovano *et al.*, 2012 and reference therein) that were located, in the Paleozoic tectonic frame, along the Northern Gondwana margin (e.g. Stampfli *et al.*, 2002; Stampfli & Borel, 2002; von Raumer *et al.*, 2013). The knowledge of these sequences is still fragmentary and their ages are mainly based on correlation with similar lithologies in the Variscan chain of Sardinia (Bagnoli *et al.*, 1979; Di Pisa *et al.*, 1988; Gattiglio *et al.*, 1989). The relative and absolute ages have been established only for some formations based on their fossiliferous content (Vai, 1972; Bagnoli & Tongiorgi, 1979 and reference therein), and on U-Pb zircon dating (Paoli *et al.*, 2017; Vezzoni *et al.*, 2018). This lack of data poses serious limitations to the accurate reconstruction of the pre-Triassic geological evolution of the Paleozoic basement of the Northern Apennines.

The aim of this paper is to present new petrographical and geochronological data collected on three selected samples from the Paleozoic basement of the Alpi Apuane, in the framework of a wider study involving the genesis and structural setting of ore deposits from the southern Alpi Apuane.

1. GEOLOGICAL OUTLINE OF ALPI APUANE

1.1. Geological background

The Northern Apennines is a fold-and-thrust-belt formed during the Tertiary continental collision

(1) Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126, Pisa, Italy. Corresponding author e-mail: vezzoni@dst.unipi.it

(2) Dipartimento di Fisica e Geologia, Università di Perugia, Piazza dell'Università, I-06123 Perugia, Italy.

(3) Istituto Nazionale di Fisica Nucleare, Sezione di Perugia, Via Alessandro Pascoli 23c, I-06123 Perugia, Italy.

between Corsica-Sardinia microplate and Adria continental margin (Boccaletti *et al.*, 1971; Carmignani *et al.*, 1995; Bortolotti *et al.*, 2001; Molli, 2008 and reference therein). The Alpi Apuane (NW Tuscany) is the widest tectonic window in the Northern Apennines where the deepest levels (Tuscan Metamorphic Units) of the belt are exposed. Two major tectono-metamorphic units are typically distinguished: the Massa Unit and the Apuane Unit. The Massa Unit is well exposed in the westernmost part of the Alpi Apuane and consists of a Paleozoic basement (mainly phyllites and metavolcanites) and an Upper Permian–Upper Triassic sedimentary succession (e.g., Ciarapica & Passeri, 1982; Patacca *et al.*, 2011). The Apuane Unit includes a litho-stratigraphic sequence made up of a Paleozoic basement (Gattiglio *et al.*, 1989; Conti *et al.*, 1993; Pandeli *et al.*, 1994) intruded by post-Variscan magmatic rocks (“*Fornovolasco Metarhyolite*” Fm; Pieruccioni *et al.*, 2018; Vezzoni *et al.*, 2018), unconformably overlain by an Upper Triassic–Oligocene metasedimentary succession. The deformation structures within the Apuane Unit may be related to Oligocene – early Miocene mid-crustal underplating and antiformal stacking (D1 event according to Carmignani & Kligfield, 1990) and include a main axial-plane foliation of up to km-scale isoclinal folds associated with a regionally NE-oriented stretching lineation (Carmignani *et al.*, 1978; Molli, 2008). The D1 structures were reworked by different generations of folds and high-strain zones, related to a syn-contractional exhumation of the metamorphic unit in the inner portion of the northern Apenninic wedge (D2 structures in Carmignani & Kligfield, 1990; Molli *et al.*, 2018b and references therein).

Available P-T-t data for the Alpi Apuane metamorphism are summarized in Molli *et al.* (2000, 2002, 2018a), Molli & Vaselli (2006), Fellin *et al.* (2007), and references therein. According to these authors, the peak metamorphic conditions reached by Massa Unit are between 0.6–0.8 GPa and 420–500°C, and Apuane Unit are roughly related to 0.4–0.6 GPa and 350–450°C. The early deformation D1 were achieved during early Miocene at 27–20 Ma (Kligfield *et al.*, 1986), whereas syn-metamorphic D2 structures developed at temperatures higher than 250°C and predated cooling at 11 Ma, according to zircon fission-track ages of Fellin *et al.* (2007).

1.2. The pre-Alpine succession of the Alpi Apuane

The southern Alpi Apuane, from M. Corchia to Valdicastello Carducci (Fig. 1), represent one of the Northern Apennines portions where the most complete pre-Alpine succession crops out. Part of this area is known in the geological literature as “Stazzemese Slice Region”, “Stazzemese Parauthocton” or “Fornovolas-

co-Panie Unit” (e.g., Massa, 2007 and references therein), characterized by a complex structural architecture (e.g., Conti *et al.*, 2012a; Molli *et al.*, 2018a).

The Alpi Apuane Paleozoic succession experienced two main tectono-metamorphic events (Variscan and Alpine; Conti *et al.*, 1991a; Franceschelli *et al.*, 2004) and it is classically described as a Lower Cambrian – Devonian litho-stratigraphic succession. Actually, the recognized informal stratigraphic units are briefly described, from bottom to top: i) “*Filladi Inferiori*” Fm; ii) “*Porfiroidi e Scisti Porfirici*” Fm; iii) “*Quarziti e Filladi Superiori*” Fm; iv) “*Graphitic phyllites and Orthoceras-bearing dolostone*” Fm; v) “*Calcschist*” Fm.

The “*Filladi Inferiori*” Fm is made up of light to dark grey quartzite, dark grey and/or grey-greenish phyllitic quartzite and phyllite, interpreted as a metamorphic product of an original alternance of quartzitic sandstone and pelite (Barberi & Giglia, 1965; Tucci, 1980). The top of this formation is locally marked by the presence of a discontinuous level of matrix-supported metamorphic paraconglomerate that contains quartzitic pebbles in a quartzitic-feldspathic matrix (Conti *et al.*, 1993). A Cambrian-early Ordovician depositional age was proposed on correlation with Sardinia succession (Bagnoli *et al.*, 1979; Gattiglio *et al.*, 1989; Conti *et al.*, 1993), recently confirmed by LA-ICP-MS U-Pb zircon data (Paoli *et al.*, 2017).

The “*Porfiroidi e Scisti Porfirici*” Fm represents the main metavolcanic products characterized by relict of the primary porphyritic texture and well-developed schistosity (Barberi & Giglia, 1965; Conti *et al.*, 1991a). This formation is classically divided into two main facies: i) porphyroids; ii) porphyritic schists. The porphyroids were interpreted as primary felsic metavolcanic rocks while the porphyritic schists as the arkosic to orthoquartzitic terrigenous sediments derived from erosion of the porphyroids under sub-aerial conditions (Barberi & Giglia, 1965; Tucci, 1980; Puxeddu *et al.*, 1984). The porphyroids were recently dated to middle-late Ordovician (457 ± 3 Ma; Paoli *et al.*, 2017), in agreement with the previous correlation with the Sardinia porphyroids (Gattiglio *et al.*, 1989; Conti *et al.*, 1991b) dated at 465 ± 1 Ma (Oggiano *et al.*, 2010) and 448 ± 5 Ma (Cruciani *et al.*, 2013). Other metavolcanic rocks are represented by small volume bodies of greenish and grey-greenish basaltic rocks (Valle del Giardino metabasites) that occurred as metric- to decametric-size lenses mainly embedded in the “*Filladi Inferiori*” Fm (Barberi & Giglia, 1965; Bagnoli *et al.*, 1979; Gianelli & Puxeddu, 1979; Conti *et al.*, 1988, 1993). Conti *et al.* (1993) assigned them to a late to post-Ordovician magmatism even if they do not exclude the possibility of younger ages.

The “*Quarziti e Filladi Superiori*” Fm are metagreywackes, phyllitic quartzites and phyllites, that were probably derived from the erosion of the pre-existing

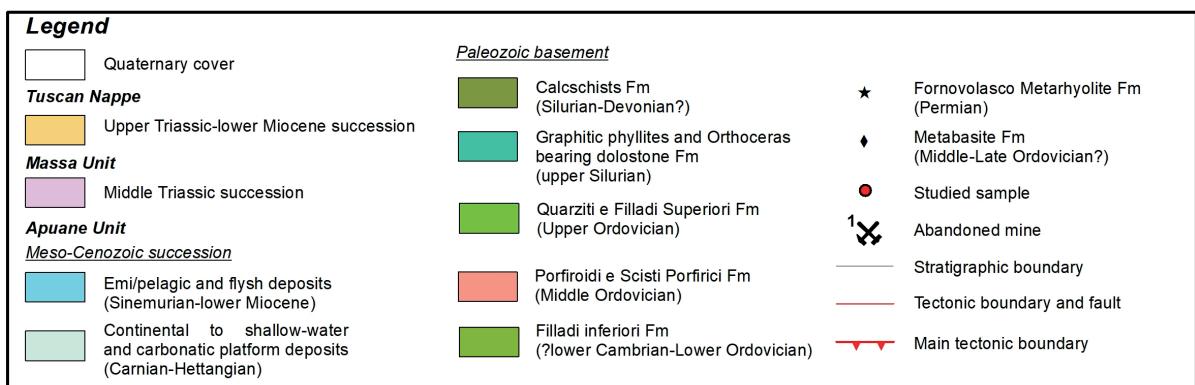
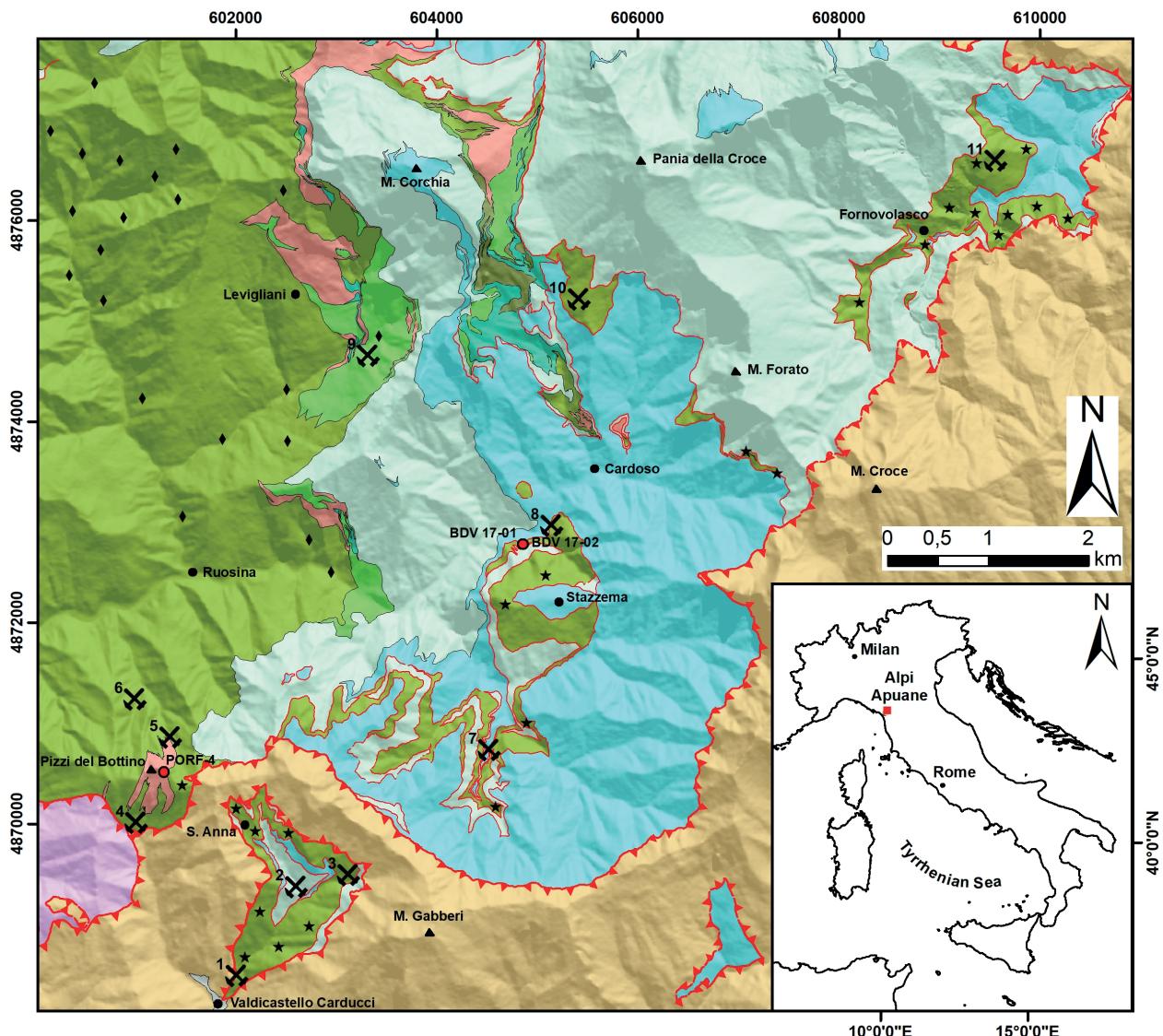


Fig. 1 - Simplified geological map of the southern Alpi Apuane (modified after Carmignani *et al.*, 2000 and Vezzoni *et al.*, 2018) with particular attention to Paleozoic formations (datum: WGS84; projection UTM32N). Red circles indicate the sample locations (see also Tab. 1). Main abandoned mines: i) Pb-Zn(-Ag) ore: (1-Pollone; 4-Argentiera di S. Anna; 5-La Rocca; 6-Bottino; 10-La Tana); ii) Cu-Au ore: (2-Buca dell'Angina); iii) Tl-rich pyrite, baryte, and Fe-oxides ore: (1-Pollone; 3-Monte Arsiccio; 4-Argentiera di S. Anna; 7-Canale della Radice – Farnocchia; 8-Buca della Vena; 10-La Tana; 11-Fornovolasco); iv) Hg ore: (9-Levigliani).

acidic to intermediate volcanites (Barberi & Giglia, 1965) and for this reason are attributed to Upper Ordovician based on correlation with Sardinia succession (Gattiglio *et al.*, 1989; Conti *et al.*, 1991b; Pandeli *et al.*, 1994). Paoli *et al.*, (2017) assigned an early Cambrian – middle Ordovician depositional age, similar to the “*Filladi Inferiori*” Fm, due to the absence of zircon from middle-late Ordovician volcanism which are widespread in all the post-Ordovician sediments.

The “*Graphitic phyllites and Orthoceras-bearing dolostone*” Fm represents a very discontinuous and thin level of black, locally quartzitic, phyllites with several thin layers of dolomitic metalimestone and calcschist (Barberi & Giglia, 1965; Gattiglio & Meccheri, 1987). An Upper Silurian age is assigned on the basis of fossil content (Meneghini, 1880, 1881; Zaccagna, 1932; Gorhani, 1933; Vai, 1972; Bagnoli & Tongiorgi, 1979).

Finally, the “*Calcschist*” Fm are Silurian-Devonian? dolomitic metalimestones (Bagnoli & Tongiorgi, 1979; Gattiglio & Meccheri, 1987; Gattiglio *et al.*, 1989; Pandeli *et al.*, 1994) with thin layers of greenish and bright chlorite-rich and carbonate phyllite.

In addition, a metamorphic magmatic rock was reported, embedded in the “*Filladi Inferiori*” Fm, and spatially associated with the southern Alpi Apuane orebodies (Fig. 1). This intrusive rock shows granular to porphyritic texture with local tourmaline spots up to some cm in size (“Tormalinolite” in Pandeli *et al.*, 2004; “Fornovolasco Metarhyolite” Fm in Pieruccioni *et al.*, 2018; Vezzoni *et al.*, 2018). Vezzoni *et al.* (2018) on the basis of LA-ICP-MS U-Pb zircon dating suggest a Permian age for this formation.

2. METHODS

Three samples of the pre-Alpine basement have been collected in the south-eastern part of the Alpi Apuane (Fig. 1). The samples belong to “*Filladi Inferiori*” (BDV-17-01 and BDV-17-02) and “*Porfroidi e Scisti Porfirici*” (PORF-4) formations (according to the available geological maps; Carmignani *et al.*, 2000; Conti *et al.*, 2010, 2012b). The samples were collected near the Pb-Zn(-Ag) orebodies (e.g., Argentiera di S. Anna, La Rocca, Bottino mines) and Tl-rich pyrite, baryte and Fe-oxides orebodies (Buca della Vena mine; Fig. 1). The petrographic features of the rock samples were investigated by optical microscopy and geochronological data were obtained by U-Pb LA-ICP-MS zircon analyses. About 10 kg of each sample was crushed and sieved, and zircon crystals were concentrated from the 90–250 µm grain size interval using standard separation techniques and, finally, hand-picking. Zircon crystals for each sample were embedded in epoxy resin, ground to expose approximately mid-section of crystals, and finally polished with 0.25 µm alumini-

na paste. The occurrence of inclusions, cores and/or rims and compositional zoning in zircon crystals were investigated using a SEM-cathodoluminescence (SEM-CL). The SEM Philips XL 30 operating at 20 kV accelerating voltage and 5 µm beam diameter at the Dipartimento di Scienze della Terra, Università di Pisa was used.

The U-Pb LA-ICP-MS analyses were performed at the Dipartimento di Fisica e Geologia, Università di Perugia using an iCAPQ Thermo Fisher Scientific, quadrupole-based, ICP-MS coupled to a G2 Teledyne Photon Machine ArF (193 nm) LA system. Uranium-Pb zircon analyses were calibrated with the international reference material zircon 91500 using a spot size of 25 µm and the Plešovice zircon had been used as quality control (Sláma *et al.*, 2008). Raw signal counts and their ratios were carefully monitored in order to exclude from age calculations portions that may be contaminated by inclusions and/or spurious peaks. Complex signals that may represent multiple ages had been carefully inspected to avoid misleading interpretations of the profiles. Data reduction was performed by the VizualAge protocol (Petrus & Kamber, 2012). Net background-corrected count rates for each isotope were used for calculation (for further details, Petrelli *et al.*, 2016). The analytical data were treated using the Isoplot Excel toolkit (Ludwig, 2003) and the $^{206}\text{Pb}/^{238}\text{U}$ ages were used for probability plots.

3. RESULTS

3.1. Petrographic data

BDV 17-01

The sample BDV 17-01 was collected in the “*Filladi Inferiori*” Fm which crops out in the SW part of Buca della Vena mine (Bassoli level - 364 m a.m.s.l.), north of the Stazzema village (Fig. 1; Tab. 1). The sample is a dark grey and grey-greenish fine-grained phyllitic quartzite (Fig. 2A) with granoblastic levels of quartz ± feldspars ± carbonates ± opaque minerals ± carbonaceous materials interlayered with lepidoblastic fine-grained levels of white mica ± carbonaceous materials ± chlorite (Fig. 3A).

BDV 17-02

The sample BDV 17-02 was collected in the “*Filladi Inferiori*” Fm close to the pyrite, baryte and Fe-oxides orebody exploited in the SW part of Buca della Vena mine (Bassoli level - 364 m a.m.s.l.; Fig. 1; Tab. 1). The sample is a whitish fine-grained quartzitic phyllite (Fig. 2B) consisting by granoblastic levels, mainly formed by quartz with minor feldspars, and lepidoblastic layers of white mica. The rock is characterized by abundant pyrite and porphyroclasts of tourmaline, that can form tourmaline-rich levels and pods (Fig. 3B,C).

Table 1 - Details of the samples studied in this work.

Sample	Locality	UTM-E (m) ¹	UTM-N (m) ¹	Elevation (m a.m.s.l.)	Texture	Main mineralogy	Maximum depositional age
BDV 17-01	Buca della Vena mine, Stazzema, Lucca	604626	4872484	364 ²	Phyllitic quartzite	Qtz, Wmca, Chl, Cb, Cm, Fsp	Late Neoproterozoic (ca. 600 Ma)
BDV 17-02	Buca della Vena mine, Stazzema, Lucca	604745	4872499	364 ²	Quartzitic phyllite with porphyroblast of tourmaline	Qtz, Wmca, Chl, Fsp, Tur, Py	Late Neoproterozoic (ca. 560 Ma)
PORF-4	Pizzi del Bottino, Stazzema, Lucca	601385	4870555	863	Matrix-supported polygenic metaconglomerate	Qtz, Wmca, Chl, Fsp	Late Neoproterozoic (ca. 570 Ma)

Abbreviations: Cb, carbonate minerals; Chl, chlorite; Cm, carbonaceous material; Fsp, feldspar; Py, pyrite; Qtz, quartz; Tur, tourmaline; Wmca, white mica; a.m.s.l., above mean sea level.

¹Coordinate system: WGS84-UTM32N

²Elevation of the Bassoli level – Buca della Vena mine

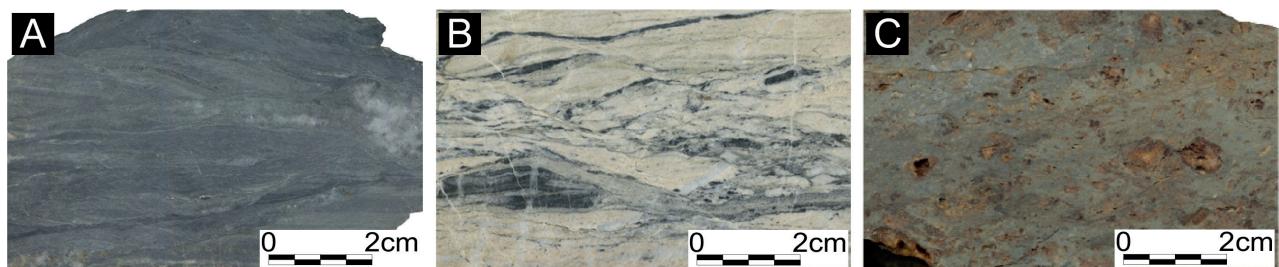


Fig. 2 - Macroscopic features of the investigated samples. A. Fine-grained phyllitic quartzite (BDV 17-01); B. Pyrite and tourmaline-rich whitish quartzitic phyllite (BDV 17-02); C. Metamorphic paraconglomerate (PORF-4).

PORF-4

The sample PORF-4 was collected at Pizzi del Bottino at NW of S. Anna village, in one of the largest outcrops of "Porfiroidi e Scisti Porfirici" Fm of the southern Alpi Apuane (Fig. 1; Tab. 1). The sample is a matrix-supported polygenic metamorphic paraconglomerate whose clasts have dimensions ranging from mm to about 3 cm, and metapsammitic/phyllitic matrix (Fig. 2C). The clasts include mono- and poly-crystalline aggregates of quartz, mono-crystalline aggregates of feldspars (up to 1 mm), lithic grains mainly represented by quartzite, phyllite (quartz ± white mica ± chlorite) with a relict foliation, and possible felsic magmatic rocks (feldspars + quartz ± chlorite ± opaque minerals). The matrix is formed by white mica + quartz ± chlorite ± opaque minerals. The rock has a well-developed S1 foliation wrapping the clasts (Fig. 3D,E,F).

3.2. U-Pb zircon geochronology

BDV 17-01

We selected 27 zircon crystals with generally sub-rounded edges, consistent with sedimentary transport. The grains are rarely fractured, and some grains contain inclusions. Usually, zircon crystals are charac-

terized by complex internal structures. The oscillatory zoning is common but, sometimes, they have a faint aspect (Fig. 4A).

A total of 32 LA spots on 21 zircon crystals gave 22 U-Pb concordant ages (ca. 69%) used for interpretation (Tab. 2, available as online supplementary material). The youngest $^{206}\text{Pb}/^{238}\text{U}$ concordant age is 599 ± 14 Ma (Ediacaran), that can be considered the maximum depositional age. The majority of the ages are below ca. 1054 Ma (ca. 82%), with minor Paleoproterozoic populations with peaks distributed at 1600 Ma, 1850 Ma and Neoarchean population with a peak at 2650 Ma (Fig. 4A).

BDV 17-02

The BDV 17-02 sample provided very rare and small (usually with length < 100 μm) zircon crystals although the starting mass material (ca. 10 kg) and the separation techniques were the same for all the samples. For this reason, we have selected and mounted in epoxy resin all the separated zircon crystals. The crystals have strongly rounded edges and generally fractured, consistent with a long transport history. Zircon crystals show complex internal structures, with common oscillatory zoning, faint oscillatory zoning, and cores (Fig. 4B).

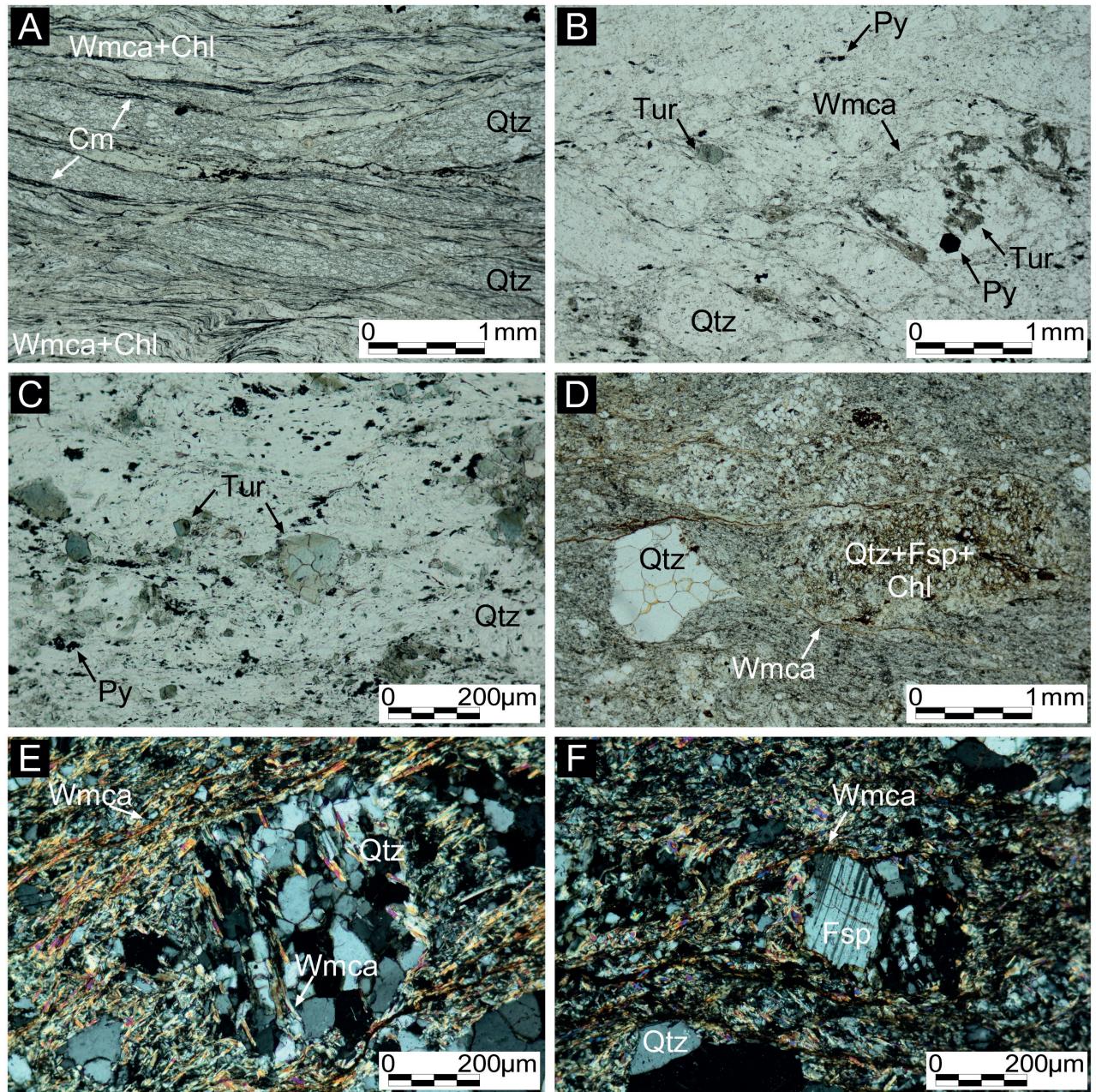


Fig. 3 - Petrographic features of the analyzed samples. A. Texture of BDV 17-01, showing granuloblastic texture; B., C. Tourmaline porphyroclasts in a fine-grained foliated matrix (BDV 17-02); D. Textural features of matrix-supported metaconglomerate and E., F. particular of the clasts wrapping by foliation (PORF-4). Mineral abbreviation: Chl, chlorite; Cm, carbonaceous materials; Fsp, feldspar; Py, pyrite; Qtz, quartz; Tur, tourmaline; Wmca, white mica.

A total of 19 LA spots on 12 zircon crystals gave 16 U-Pb concordant ages (ca. 84%) used for interpretation (Tab. 2, available as online supplementary material). The 6 youngest $^{206}\text{Pb}/^{238}\text{U}$ concordant ages are comprised between 561 ± 10 to 594 ± 11 Ma, indicating an upper Neoproterozoic age (Ediacaran) as the oldest limit for the deposition. The majority of

the concordant ages are below ca. 874 Ma (ca. 62%), with very minor Paleoproterozoic populations, with peaks distributed at 1750-2000 Ma and 2400-2500 Ma, and Neoarchean population with a peak at 2650 Ma (Fig. 4B).

Fig. 4 - Probability density plots of LA-ICP-MS zircon concordant ages and SEM-CL zircon images for the samples (A.) BDV 17-01, (B.) BDV 17-02 and (C.) PORF-4.

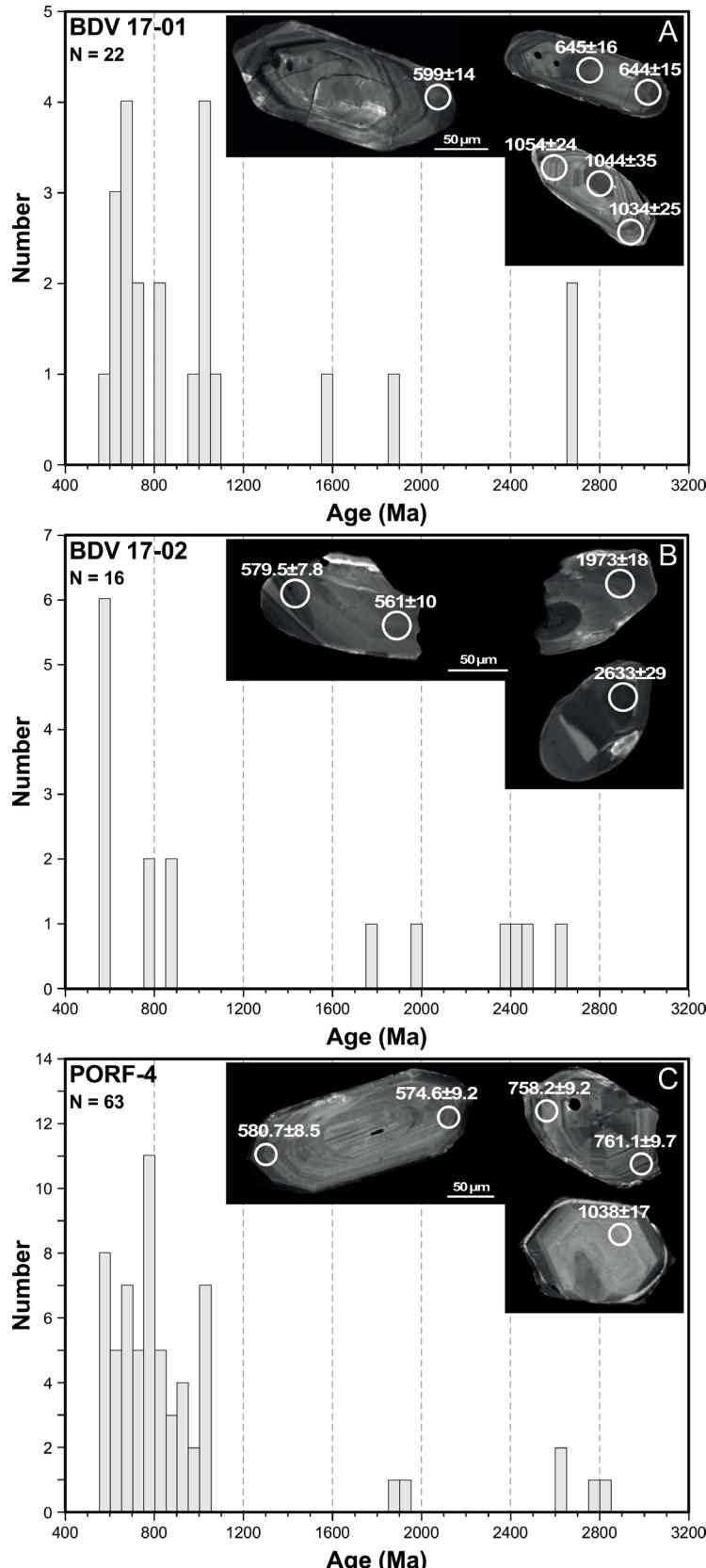
PORF-4

The sample PORF-4 provided the largest number of zircon crystals and we have selected and mounted in epoxy resin 101 crystals. The crystals have generally sub-rounded to rounded edges, suggesting a sedimentary nature in agreement with the petrographic observations. Few of the grains are fractured, and some grains contain fluid- or mineral- inclusions. Some zircon crystals have cores with oscillatory zoning rims, although complex internal structures are common (Fig. 4C).

A total of 74 LA spots on 53 zircon crystals gave 63 U-Pb concordant ages (ca. 85%) used for interpretation (Tab. 2, available as online supplementary material). The 8 youngest $^{206}\text{Pb}/^{238}\text{U}$ concordant ages are comprised between 572.6 ± 5.6 to 588.3 ± 9.1 Ma, indicating an Ediacaran maximum depositional age. The majority of the concordant ages are below ca. 1038 Ma (ca. 90%), with very minor Paleoproterozoic populations, with peaks distributed at 1850–1950 Ma and 2650, and Neoarchean population with a peak at 2800 Ma (Fig. 4C).

4. DISCUSSION

The classical subdivision of the pre-Alpine formations of the Alpi Apuane is based on: i) petrographic features (e.g., Bonatti, 1938; Barberi & Giglia, 1965); ii) fossiliferous content (Meneghini, 1880, 1881; Zaccagna 1932; Gortani, 1933; Vai, 1972; Bagnoli & Tongiorgi, 1979); iii) geometric relationships between the stratigraphic units (Gattiglio *et al.*, 1989; Conti *et al.*, 1991b; Pandeli *et al.*, 1994); iv) comparison with the Paleozoic rocks of the southeastern Sardinia (Bagnoli *et al.*, 1979; Di Pisa *et al.*, 1988; Gattiglio *et al.*, 1989); v) geochemical features (Puxeddu *et al.*, 1984; Verrucchi *et al.*, 1994), while the geochronological data are scarce. Only recently, Paoli *et al.* (2017) reported an early Cambrian – early Ordovician sedimentation age for the “*Filladi Inferiori*” Fm and indicated a middle-late Ordovician age for the “*Porfiroidi e Scisti Porfirici*” Fm mag-



matic event. Moreover, these authors discussed the attribution on Upper Ordovician (Gattiglio *et al.*, 1989; Conti *et al.*, 1991b) for the “*Quarziti e Filladi Superiori*” Fm. Finally, Pieruccioni *et al.* (2018) and Vezzoni *et al.* (2018) have found the occurrence of Permian magmatic rocks (“*Fornovolasco Metarhyolite*” Fm) which in some outcrops was interpreted as a product of the Ordovician magmatism (e.g., S. Anna in Carmignani *et al.*, 1975; Fornovolasco in Pandeli *et al.*, 2004), Silurian-Devonian magmatism (e.g., Orberger, 1985) or a Tertiary and/or Quaternary magmatic event (e.g., S. Anna in Conti *et al.*, 2010; 2012a; 2012b).

4.1. New constraints on pre-Alpine basement

The BDV 17-01 and BDV 17-02 represent part of the internal lithological variability of the “*Filladi Inferiori*” Fm. The BDV 17-01 sample is a typical phyllitic quartzite with minor graphitic levels similar to the sample analyzed by Paoli *et al.* (2017), whereas the BDV 17-02 sample is a tourmaline-rich quartztic phyllite with pyrite, which has never been dated by a geochronological method. The maximum depositional age is Ediacaran similar for both samples (Fig. 4). The lack of younger zircon, and, in particular of Ordovician zircon (the age of the main magmatic event recorded in the Alpi Apuane basement; “*Porfiroidi e Scisti Porfirici*” Fm), which are widespread in all the post-Ordovician sediments (as reported in Paoli *et al.*, 2017), allow us to restrict the depositional age between the Ediacaran and the Middle Ordovician. The inferred depositional age for “*Filladi Inferiori*” Fm partly confirms the literature interpretation (e.g., Barberi & Giglia, 1965; Conti *et al.*, 1993) and the histograms and probability density plots are similar to the sample reported by Paoli *et al.* (2017) with detrital zircon ages mainly younger than ca. 1000 Ma, with very minor contribution from oldest sources. The density probability plot and the maximum depositional age of the tourmaline-rich quartztic phyllite must be considered the same of the “*Filladi Inferiori*” Fm, discharging the hypothesis of a younger depositional age (Ciarapica & Zaninetti, 1983; Ciarapica *et al.*, 1985).

The sample PORF-4 have a sedimentary protolith with clasts of polygenic origins (e.g., quartzite and schist; Fig. 2C, 3D,E,F) and zircon crystals with sub-rounded to rounded edges, suggesting a long transport history (Fig. 4C). The U-Pb LA-ICP-MS zircon ages are spread over a wide range, from Neoarchean (ca. 2800 Ma) to Ediacaran (ca. 570-580 Ma) and lack ages from Ordovician times, similar to “*Filladi Inferiori*” Fm (Fig. 4C). Therefore, the PORF-4 sample is not a metavolcanic product of the Middle Ordovician magmatic cycle, but it is a metamorphic paraconglomerate with an Ediacaran maximum depositional age. Nature and paleogeographic significance are unknown, however, Gattiglio

et al. (1989) and Conti *et al.* (1993) described similar rock at the top of the “*Filladi Inferiori*” Fm. Conti *et al.* (1993) suggested a similarity with some conglomerate in Sardinia related to “eo-Caledonian tectonic movements” associated to important unconformity (“Discordanza Sarda” and “Discordanza Sarrabese; Martini *et al.*, 1991; Carmignani *et al.*, 2001 and reference therein). Thus, the PORF-4 sample could represent the preserved clastic unconformity horizon interposed between the “*Filladi Inferiori*” Fm and the “*Porfiroidi e Scisti Porfirici*” Fm, likely related to a “Caledonian event”. However, further studies will be needed for a correct establishment of the origin of this paraconglomerate.

4.2. Tourmaline occurrence in the *Filladi Inferiori* Fm

Tourmaline-rich rocks are well known in the southern Alpi Apuane and are the host-rocks of the Pb-Zn-(Ag) (e.g., Benvenuti *et al.*, 1989) and the Tl-rich pyrite, baryte and Fe-oxides orebodies (e.g., D’Orazio *et al.*, 2017). The strictly spatial association was already known to the miners, and they used the tourmaline-rich rocks as an empirical prospecting tool for orebodies. The origin and age of tourmaline and tourmalinite are still debated and several hypotheses were proposed: i) magmatic-hydrothermal related to a hypothetical buried granitic body during the Alpine orogenesis (e.g., Carmignani *et al.*, 1975); ii) Triassic mineralization connected to the late Ladinian magmatic cycle (e.g., Ciarapica & Zaninetti, 1983; Ciarapica *et al.*, 1985; Benvenuti *et al.*, 1986); iii) pre-Alpine (Paleozoic?) episode of boron and metal concentration in a sedimentary-exhalative environment (e.g., Orberger *et al.*, 1986; Benvenuti *et al.*, 1989; Pandeli *et al.*, 2004). In this work, we report the first geochronological data on these whitish tourmaline- and pyrite-rich rocks. Some authors identify part of these peculiar rocks with the name of “*Fornovolasco schists*” (e.g., Ciarapica & Zaninetti, 1983; Ciarapica *et al.*, 1985), and assigned them a pre-Norian depositional age never confirmed by geochronological data. On the contrary, other authors correlate them with the “*Filladi Inferiori*” and “*Porfiroidi e Scisti Porfirici*” Fms intensely tourmalinized during the Paleozoic (e.g., Orberger *et al.*, 1985; Benvenuti *et al.*, 1989; Cavaretti *et al.*, 1992; Pandeli *et al.*, 2004) or Tertiary (e.g., Carmignani *et al.*, 1975) hydrothermal event.

The zircon population shows a comparable pattern of the “*Filladi Inferiori*” Fm attesting a similar sediment provenance. However, the different intra-unit petrographic features (e.g., the presence of tourmaline and pyrite) must be clarified. Cavaretti *et al.* (1989; 1992) and Benvenuti *et al.* (1989) hypothesized a pre-Alpine (Paleozoic?) hydrothermal event that produced tour-

malinization of the Paleozoic basement. Pandeli et al. (2004), D’Orazio et al. (2017) and, subsequently, Vezzoni et al. (2018) have refined this scenario, suggesting a genetic link with the Permian magmatism, the only tourmaline-bearing magmatic rock of the Alpi Apuane. It is well known as tourmaline-bearing intrusive rocks can produce tourmaline-quartz hydrothermal veins and masses in the shallow crust (e.g., Dini et al., 2008; Jiang et al., 2008; Zucchi et al., 2017) sometimes associated with massive sulfide orebodies (e.g., Palmer & Slack, 1989; Leach et al., 2005). The appearance of tourmaline in the sedimentary succession is restricted to clasts in the “*Verruca*” Fm (Ladinian – lower Carnian; e.g., Rau & Tongiorgi, 1974; Cavarella et al., 1992; Pandeli, 2002) and in the “*Vinca*” Fm (Upper Carnian – lower Norian; e.g., Cavarella et al., 1992; Pieruccioni et al., 2018) while it is rarely described as accessory mineral in the pre-Permian sedimentary and magmatic rocks (e.g., Barberi & Giglia, 1965; Pandeli, 2002). These evidences suggest that tourmalinite were exposed during the Triassic attesting a pre-Carnian tourmalinization event. In this scenario, we consider that the tourmaline-rich rocks are the product of hydrothermal alteration on “*Filladi Inferiori*” Fm, probably related to the Permian magmatic event. The actual petrographic features of the tourmaline-rich rocks, as the sample BDV 17-02, were acquired during a complex geological history, that could be summarized in the following main events: i) deposition of the sediment (Ediacaran-Middle Ordovician?); ii) metamorphism during Variscan orogenesis; iii) hydrothermal alteration (Permian?); iv) metamorphism during Alpine orogenesis.

5. CONCLUSIONS

The present work underlines a long and complex geological history recorded by the pre-Alpine basement, through a petrographic and geochronological study on the two main formations of Alpi Apuane (“*Filladi Inferiori*” and “*Porfiroidi e Scisti Porfirici*” Fms).

In summary, the following conclusions can be drawn on our study:

- i) the zircon geochronology of BDV 17-01 and BDV 17-02 samples (“*Filladi Inferiori*” Fm.) indicates a depositional age between Ediacaran and Middle Ordovician. Furthermore, this work reports the first geochronological data on the tourmaline-rich rocks (BDV 17-02) which cannot be interpreted as a younger litho-stratigraphic unit, as proposed by Ciarapica & Zaninetti (1983) and Ciarapica et al. (1985), but instead, an example of Permian hydrothermal alteration product on the “*Filladi Inferiori*” Fm;
- ii) the sample PORF-4 is a metamorphic paraconglomerate with an inferred depositional age between Ediacaran and Middle Ordovician?, similar to “*Filladi*

Inferiori” Fm. So, the previously attribution to the Ordovician magmatic event (e.g., Carmignani et al., 2000; Conti et al., 2010; 2012a; 2012b) cannot be supported for this sample.

In conclusion, the present work unravel that the integrated petrographic and geochronological approach is essential to improve the Alpi Apuane geological map and to reconstruct the geological history of the pre-Alpine basement.

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Palazzo Roncioni - Lungarno Mediceo, 16, I-56127 Pisa
info@edizioniets.com - www.edizioniets.com
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