1. Introduction

In situ U-Pb dating combined with SEM images on zircon crystals represent a powerful tool to reconstruct metamorphic and magmatic evolution of basements recording a long and complex geological history [1-3].

The development of high spatial and mass resolution microprobes (e.g., LA-ICP-MS, SIMS, SHRIMP) allows in-situ measurements of U–Pb ages in micro domains smaller than 30-50 microns [4, 5].

The growth of zircon crystals, evidenced by their internal microtextures, can be easily revealed by SEM imaging by Cathodoluminescence (CL) and Variable Pressure Secondary Electrons (VPSE) detectors on separated grains or in situ within a polished thin rock section [6,4,7].

Therefore it is possible to date different domains of single crystals, which may record magmatic or metamorphic events of the rock’s geological history [8,4]. In acidic magmatic rocks abundant zircon crystals provide precise age data about magma emplacement and origin of source indicating the geodynamic context and the pertinence of terranes forming the continental crust.

As regards the metamorphic context, zircon can potentially preserves multiple stages of metamorphic records owing its highly refractory nature, high closure temperature and slow diffusion rate of Pb, thus it is an ideal mineral for U-Pb dating of poly-metamorphic rocks [9,10]. In addition, in situ analyses of trace elements such as rare earth elements (REE) in zircon and between zircon and coexisting minerals is useful to decipher the REE behavior and
mineral chemistry during metamorphism and to determine metamorphic P-T conditions [8,11,12]. In particular, garnet is one of the most important rock-forming minerals in high-grade metamorphic rocks since it can be also used to constrain metamorphic conditions if its composition is combined with that of other major minerals such as pyroxene and amphibole [13,14]. Relatively to REE partition in metamorphic rocks garnet, pyroxene, amphibole and zircon being competitors for REE partition, represent a useful tool to outline continental crust evolution.

In this paper we present the geochronological and chemistry data collected in the last ten years in Calabria and Peloritani sectors of Italy, utilizing the new analytical techniques, useful to reconstruct the magmatic and metamorphic history of a key sector of the South European Variscan Belt in the peri-Mediterranean area.

Metaigneous and metasedimentary rocks of the Calabria-Peloritani Terrane (Southern Italy) represent a particularity in the South Mediterranean area being connected to Alpine chain (Northern Italy) through sedimentary Apennines Chain. They represent sectors of Variscan upper, intermediate and lower continental crust sutured by a thick layer of Carboniferous-Permian granitoids overlapped on Alpine oceanic crust units. Only rocks forming intermediate and deep crust levels of the continental crust were considered in this review. These rock types preserve memory of Precambrian to Permian geological events and in some cases up to Mesozoic times. The available geochronological data [15-24] together with CL and VPSE imaging and the REE-U-Th distribution in the zircon domains helped to depict the geological history through: (1) the emplacement ages of the protoliths of metaigneous rocks, (2) the contribution of the Neoproterozoic-Early Cambrian anatectic melts to produce the protoliths of Variscan metaigneous rocks, (3) the sedimentation ages of the protoliths of the metasedimentary rocks; (5) the P-T-t path of the Variscan metamorphism. In the following, an extensive and detailed description of utilized analytical techniques was presented together with the realized geological deductions relatively to Calabria-Peloritani Terrane.

2. Analytical techniques

2.1. Sample preparation

The U-Pb age data were obtained on zircons directly separated from samples or on polished thin rock sections. In the last case, in situ analyses allow to evaluate the micro-domains in which the zircon grew or was resetted. Separated zircon crystals were selected from 50-125 μm and 125–250 μm fractions extracted from about 5-10 kg of each rock sample. Crushing, heavy liquids, a Carpco and a Frantz magnetic separators have been used for mineral separation. The clearest, crack-and inclusion-free zircon grains were handpicked under binocular microscope and finally mounted in epoxy resin (Fig.1).

Only in the case of SIMS analyses, selected crystals were mounted together with chips of zircon standards (Fig.1), whereas for LA-ICP-MS analyses external standards were used. Grains were
then polished to half their thickness to expose internal structures. In the case of selected zircons in thin section, they are chosen also for their peculiar structural site.

2.2. Zircon imaging

All crystals were inspected under transmitted light and by SEM (Scanning Electron Microscope) in order to investigate their morphology and collect high-resolution images unravelling the internal microstructures. The first observations on zircon crystals were realized by BSED (Back-Scattered Electron Detector), in order to examine morphologic characters and the possible presence of inclusions of other minerals.

The high-resolution images of internal zoning patterns of zircons were realized by CL (Cathodoluminescence) and by VPSE (Variable Pressure Secondary Electrons) detectors, the last used in high vacuum conditions. Operating conditions were an accelerating voltage of 15 kV with a beam current of 20 nA for CL images and 100 nA for VPSE images. The images obtained by two different detectors (CL and VPSE, Fig.2) are almost completely overlapping [25,26].

The most suitable location of the spots for U-Pb analyses was then selected. Zircon grains were also inspected after the isotopic and chemical analyses in order to define the precise spot location with respect to internal microstructures (Fig.3).

2.3. In situ U-Pb data acquisition on zircon crystals

U-Pb age data on zircons were performed by LA-ICP-MS, SIMS and SHRIMP techniques. Three techniques produce comparable results with equally accurate U-Pb zircon ages [5,27,17]. However, LA-ICP-MS technique is generally preferred for the greater simplicity of use, the faster data capture (ca 4 minutes per analysis versus ca 30 minutes per SIMS and SHRIMP analysis; see [5]) and because it allows a complete acquisition of trace element composition in selected zircon domains.
2.3.1. LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry)

LA-ICP-MS U-Pb data on zircons (17,18,7,22,21,20,24) were performed at the CNR-Istituto di Geoscienze e Georisorse (Pavia, Italy) using a 193 nm ArF excimer laser ablation microprobe (Geo-Las200Q-Microlas) coupled to a magnetic sector high resolution-ICP-MS (Element I from Thermo Finnigan).

Figure 2. The same zircon crystal investigated by Cathodoluminescence Detector (CLD) and Variable Pressure Secondary Electrons Detector (VPSED). With the permission of Acquafredda and Fiore (2005).

Figure 3. Images of the same zircon crystal obtained by BSE (a) and VPSE detectors (b). In (a) the craters left by microprobe are clearly visible.
The analyses were carried out in single spot mode and with a spot size of approximately 20 μm. The laser was operated with 5 Hz of frequency and 12Jcm\(^{-2}\) of fluence. Sixty seconds of background signal and at least 30 s of ablation signal were acquired. The signals of masses \(^{202}\)Hg, \(^{204}\)Pb+Hg, \(^{206}\)Pb, \(^{207}\)Pb, \(^{208}\)Pb, \(^{232}\)Th and \(^{238}\)U were acquired in magnetic scan mode. \(^{235}\)U is calculated from \(^{238}\)U on the basis of the ratio \(^{238}\)U/\(^{235}\)U=137.88. The 202 and 204 masses were collected in order to monitor the presence of common Pb in zircon. In particular, the signal of \(^{202}\)Hg was acquired to correct the isobaric interference of \(^{204}\)Hg on \(^{204}\)Pb [28]. The relatively high Hg background, however, hampers the detection of low \(^{204}\)Pb signals and, as a consequence, also the calculation of small common Pb contribution. Generally, the analysed zircons showed signals of 204 mass elements, which were indistinguishable from the background; thus no common Pb correction was applied (more analytical details in [29]).

All fractionation effects involving Pb/U ratios (e.g. mass bias and laser induced fractionation) were corrected by using the external zircon standard 91,500 (1,065 Ma [30]). The same spot size and integration intervals were considered on both standard and studied zircons. During each analytical run reference zircon 02123 (295 Ma [31]) was analysed together with unknowns for quality control. Data reduction was carried out through the GLITTER software package [32]. Time resolved signals were carefully inspected to detect perturbation of the signal related to cracks or mixed age domains that were avoided in the integration intervals.

Within the same analytical run, the uncertainty associated to the reproducibility of the external standards was propagated to each analysis (see Horstwood et al. 2003) and after this procedure each age determination is considered as accurate within a quoted uncertainty.

Correlation coefficients for the \(^{206}\)Pb/\(^{238}\)U and \(^{207}\)Pb/\(^{235}\)U data point uncertainties are calculated simply as a ratio of the two uncertainties [33].

LA-ICP-MS technique also permits a complete acquisition of trace element composition in specific zircon domains. In this case a dedicated configuration of the machine couples a Nd:YAG laser working at 266 nm with a quadrupole ICP mass spectrometer type DRCe from Perkin Elmer.

For trace element determination the laser was operated at a repetition rate of 10 Hz, with pulse energy of about 0.01 mJ and an ablation spot of about 25 μm in size. NBS NIST-610 and SiO\(_2\) were adopted as external and internal standard, respectively. Data reduction was carried out through the GLITTER software package [32].

Minimum detection limits at 99% confidence level were <10-5 ppm for the most of the elements. Precision and accuracy were assessed on the BCR-2 USGS reference glass and are more than 6% relative.

2.3.2. SIMS (Secondary Ion Mass Spectrometry)

SIMS data [16,17] were collected using the Cameca IMS-1270 ion microprobe (CRPG-CNRS, Nancy, France). Primary O2– ion beam was accelerated at 13 kV with an intensity that ranged between 5 and 20 nA and focused on a 20–25 μm diameter area, providing
a mean secondary ions yield of 25cps/nA/ppm. Each spot was analysed for 18 min, after a presputtering of 2 min. An empirical relationship between UO+/U+ and Pb+/U+ was defined from all the measurements performed on the standard parts of each sample mount in order to determine the relative sensitivity factor for Pb and U used for samples [34]. Also in this case zircon 91,500 (1,065 Ma, [30]) is the reference standard. Correction for common lead was made measuring the 204 Pb amount. The common lead composition was calculated at \( ^{207}\text{Pb}/^{206}\text{Pb} \) measured ages, using Stacey and Kramers model [35]. The \( ^{206}\text{Pb}/^{204}\text{Pb} \) ratios range in most case from 3,000 to more than 50,000, and thus the common Pb composition chosen for correction is not highly critical. Further information on instrumental conditions and data reduction procedures are found in [36]. Errors include the analytical statistical error, the error associated with the common lead correction and the systematic error associated with the U/Pb calibration procedure [36]. As regards the ion microprobe analyses we used \( ^{206}\text{Pb}/^{238}\text{U} \) ages for all the data instead of \( ^{207}\text{Pb}/^{235}\text{U} \) ages, which are more sensitive to common lead contribution, being the \( ^{207}\text{Pb} \) ion signal about ten times lower than the \( ^{206}\text{Pb} \) ion signal [36].

2.3.3. SHRIMP (Sensitive High Resolution Ion MicroProbe)

SHRIMP data were collected [19,23] using procedures based on those described by [37]. A 2.5 nA, 10 kV primary beam of O2 ions was focused to a probe of c. 25 μm diameter. Positive secondary ions were extracted from the sample at 10 kV, and the atomic and molecular species of interest analysed at c. 5000 mass resolution using a single ETP electron multiplier and peak switching. The Pb isotopic composition was measured directly, without correction for the small mass dependent mass-fractionation (c. 0.25% per a.m.u.). Interelement fractionation was corrected using the TEMORA II reference zircon, using a Pb/U-UO/U power law calibration equation [38]. The uncertainty in the Pb/U calibration was 0.46%. Pb, U and Th concentrations were measured relative to SL13 reference zircon. Common Pb corrections were very small (most<0.3 ppm total Pb), so all were made assuming that the common Pb was all laboratory contamination of Broken Hill galena Pb composition (\( ^{204}\text{Pb}/^{206}\text{Pb}=0.0625, ^{207}\text{Pb}/^{206}\text{Pb}=0.962, ^{208}\text{Pb}/^{206}\text{Pb}=2.23; [39] \)). Corrections for the plots and isotopic data table were made using \( ^{204}\text{Pb} \). Corrections for the calculation of mean \( ^{206}\text{Pb}/^{238}\text{U} \) ages used \( ^{206}\text{Pb} \), assuming the analyses to be concordant. Ages were calculated using the constants recommended by the IUGS Subcommission on Geochronology [40].

All collected data were traited by the software package Isoplot/Ex3.00 [41]. This software was used for the concordia test and the probability of concordance calculation, performed for each analytical spot from \( ^{206}\text{Pb}/^{238}\text{U} \) and \( ^{207}\text{Pb}/^{235}\text{U} \) ratios. The Isoplot/Ex3.00 software was also used to construct Concordia, possible discordia lines and probability density plots and to calculate the mean concordia ages for data clusters defined on the basis of: (i) statistical significance, (ii) the visual appearance on the Concordia plot, (iii) the peak distribution along the probability density plot, and (iv) the correspondence with specific internal microstructures of zircon.
3. Geological setting of case study

The Calabria-Peloritani Terrane (CPT) represents an “exotic terrane” formed by a Pre-Mesozoic basement consisting of different tectonic units affected by Variscan metamorphism and stacked during the Alpine orogenesis [42-43]. It carries the crystalline Massifs of Calabria (Sila, Serre and Aspromonte) and Peloritani Mountains in Sicily (Fig.4).

In the following, we describe the geological and petrological features of the four considered tectonic units representing portions of middle and lower continental crust. Many samples from the different rock types in each unit were considered with the aim to reconstruct and date the geological events recorded by zircon grains. The mineralogical composition of the all cited samples and their relative spectrum of U-Pb zircon ages are reported in Table 1. Their exact localization is indicated in Fig.4.

Four tectonic units were considered along the CPT from North to South (Fig. 4):

The Mandatoriccio Complex outcropping in Sila Massif represents intermediate continental crust and consists mainly of metapelites, meta-arenites, acidic metavolcanites and metabasites with rare intercalations of marbles and orthogneisses crosscutted by abundant aplite and pegmatite veins [44-46]. Metasediments show a static porphyroblastic growth mainly of biotite, garnet, andalusite, staurolite and muscovite [46-48]. Recently, clockwise P–T paths have been constrained for siliciclastic metasediments of this complex. Peak-metamorphic conditions of ca. 590 °C and 0.35 GPa are reported for the lower structural levels of the Mandatoriccio Complex and they were reached at 299 Ma (U-Th-Pb ages in monazite, [46]) during Variscan post-orogenic extension.

The Castagna Unit outcropping in the central part of Calabria, consists of paragneisses, micaschists, augen gneisses, Variscan granitoids and minor amphibolites, quartzites, calc-silicate rocks and marbles [49,50]. It includes metamorphic rocks equilibrated under greenschist to amphibolite facies conditions in Variscan times and reworked by Alpine tectonics [49,46,18].

The Sila Unit occupies wide areas in Sila and Serre Massifs. In the Serre the section of Variscan crust consists, from the bottom to the top of: i) 7-8 km thick lower crustal rocks, ii) an about 10 km-thick “layer” of granitoids [51] emplaced ~300 Ma ago (U-Pb conventional zircon data, [51,52]), and iii) amphibolite to sub-greenschist facies metamorphic rocks of the upper crust. The geochronological features of the lower portion recording Variscan amphibolite-granulite facies metamorphism and representing a fragment of deep crust were considered. This section includes from the bottom: a) felsic and mafic granulites with rare meta-peridotites and metapelites, b) migmatitic metapelites with interleaved metabasites, rare marbles and augen gneisses. The metabasic rocks from the lower part of the section together with the augen gneisses from the upper part of the section bear memory of pre-Variscan magmatism (Table 1).

The Aspromonte-Peloritani Unit (APU) outcrops in Southern Calabria and Eastern Sicily (Fig. 4); it consists of augen gneisses, micaschists, biotite paragneisses with minor amphibi-
olites and marbles. A pre-Variscan origin of protoliths of augen gneisses at 543-545 Ma was suggested by spot U-Pb zircon ages [16,23,53]. According to [23] the timing of high-grade metamorphism accompanied by partial melting in paragneisses, was synchronous (at 545 Ma) with the intrusion of protoliths of augen gneisses. The metamorphic rocks are diffusely intruded by late-Variscan peraluminous granitoids [54-57,19], sometimes affected by Alpine metamorphism. P–T estimates for the Variscan tectono-metamorphic evolution indicate T around 650–675°C and P of about 0.4–0.5 GPa [58,59]. The evolution of the APU provides crustal thickening during early-middle Variscan collisional stages, followed by crustal thinning, granitoid intrusion and unroofing during late-Variscan extensional stages [43].

The collected data in Southern Italy give constraints about the complex magmatic and metamorphic history of South European Variscan Chain in the peri-Mediterranean area. Magmatic and metamorphic events are recorded in the considered rocks from Late-Neoproterozoic-early Cambrian to Permian times. In the following, the geological history is punctually depicted.

**Figure 4.** – Geological sketch map of CPT with the indication of considered samples in four different structural units.
Table 1 – U-Pb concordant data on zircon in the studied rocks from CPT continental crust

| Sila Unit | MINERALOGICAL COMPOSITIONS | INHERITED AGES | NEOPROTEROZOIC-CAMBRIAN MAGMATISM | ORDOVICIAN-SILURIAN AGES | DEVONIAN-LOWER PERMIAN AGES | POST LOWER PERMIAN AGES |
|-----------|---------------------------|----------------|----------------------------------|-------------------------|-----------------------------|------------------------|
| GO 100 augen gneiss (Micheletti et al., 2007) [16] | Qtz+Kfs+Pl+Br/-Ms+/Grt+/Sil | 2302±19, 2404±92, 1760±46, 752±6, 617±23, 575±4, 572±6, 571±4 | 552±9, 545±4, 539±7, 537±4 | 494±14, 462±7 | 377±5 | 282±5 (n=4) 263±8, 231±5 |
| MFS 3 metagabbro (Micheletti et al., 2008) [17] | Pl+Amph=Opx+Cpx | 584±24, 506±21 | 453±19 | 377±5 | 282±5 (n=4) 263±8, 231±5 |
| Tur 3 restitic metagreywacke (Micheletti et al., 2008) [17] | Grt+Pl+Opx+Amph+Br | 595±12 | 483±9 | 325±9, 316±9, 308±9, 297±4 (n=4), 273±8 | 257±7 |
| GO 102 migmaitic metapelite (Micheletti et al., 2008) [17] | Qtz+Pl+Kfs+Sil+Br+Grt+/-Crd | | | 395±8 | 280±2 (n=18) |
| Tur 17 felsic granulite (Micheletti et al., 2008) [17] | Qtz+Pl+Kfs=Grt+/-Bt | 394±14 | 286±4 (n=8) |
| Tur 49 meta-quartz-diorite (Fornelli et al., 2011a) [7] | Pl+Opx+Cpx=Amph | 744±20 | 574±18 | 457±13, 438±13 | 380±11 |
| Tur 52 metabasite interleaved with felsic granulites (Fornelli et al., 2011a) [7] | Opx=Pl+Br | 593±14, 564±17 | 483±2, 46±2, 45±1, 41±4, 37±1 (n=3) | 340±7 (n=2) | 321±3 (n=9) | 300±3 (n=6) 279±9, 277±7 |
| Tur 46 metabasite interleaved with migmatitic metapelites (Fornelli et al., 2011a) [7] | Opx+Pl+Br+Amph | 609±29 | 537±15, 505±11 | 382±9 | 318±5 (n=2) | 303±4 (n=4) | 294±5 (n=3) 279±10 |
| Tur 37b Quartz-monzodiorite dike (Fornelli et al., 2011a) [7] | Kfs+Br=Opx=Cpx+Qtz | | | | 368±11, 367±9 | 323±5 (n=3) |
| Tur 76A mafic granulite (Muschitiello, 2012) [24] | Pl+Opx+Grt=Amph+Bt | 466±15, 43±15 | 34±4, 29±9, 29±6, 28±9, 27±9 | 357±11, 33±30 (n=8) |
| Grt3 mafic granulite (Fornelli et al., 2014) [22] | Pl+Grt+Bt=Opx+Qtz=Kfs | | | | | |

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| Castagna Unit          | MINERALOGICAL COMPOSITIONS     | INHERITED AGES | NEOPROTEROZOIC-CAMBRIAN MAGMATISM | ORDOVICIAN-LOWER PERMIAN AGES | DEVONIAN-LOWER PERMIAN AGES | POST LOWER PERMIAN AGES |
|------------------------|--------------------------------|----------------|-----------------------------------|-------------------------------|----------------------------|--------------------------|
| GO 8 augen gneiss      | Qtz+Kfs+Pl+Bt+/-Ms             | 221±63, 748±6, 62±15, 58±5 | 562±5, 565±5, 58±5, 547±4, 543±4, 54±2, 54±1 | 65±2, 55±16 | 56±16, 54±16 |                                   |
| GO 35 augen gneiss     | Qtz+Kfs+Pl+Bt+/-Ms             | 206±32, 58±31, 63±16 | 55±16 | 55±16, 54±16 |                                   |
| GO 39 fine leucocratic leucocratic gneiss | Qtz+Kfs+Pl+Ms+/-Bt | 858±17, 632±15, 63±16 | 533±11 (n=4) | 473±14, 459±10, 41±3 | 30±2, 30±2, 29±1, 28±1, 27±4, 27±1, 26±6, 25±11 |
| GO 95 fine grained leucocratic gneiss | Qtz+Pl+/-Ms+/-Kfs+/-Bt | 801±19, 633±14 | 547±3 (n=4), 521±12, 509±14, 50±12, 49±14 | 452±13, 437±10, 425±11 | 345±9 | 297±6, 291±8, 279±8, 278±7 | 268±8 |
| GO 82 mylonitic pegmatite | Qtz+Kfs+Pl+Ms+/-Bt |                                                   |                                     |                                 |                                       |

| Mandatoriccio Complex  | MINERALOGICAL COMPOSITIONS     | INHERITED AGES | NEOPROTEROZOIC-CAMBRIAN MAGMATISM | ORDOVICIAN-LOWER PERMIAN AGES | DEVONIAN-LOWER PERMIAN AGES | POST LOWER PERMIAN AGES |
|------------------------|--------------------------------|----------------|-----------------------------------|-------------------------------|----------------------------|--------------------------|
| LL61b2 mica schist     | Bt+Grt+And+St+Ms/-Crd+/-Sil   | 250±43 - 60±42 | 587±14 - 511±13 (n=8) | 885±310 - 428±30 (n=8) |                                       |                           |
Table 1. U-Pb concordant data on zircon in the studied rocks from CPT continental crust

| Aspromonte-Peloritani Unit | MINERALOGICAL COMPOSITIONS | INHERITED AGES | NEOPROTEROZOIC-CAMBRIAN MAGMATISM | ORDOVICIAN-SILURIAN AGES | DEVONIAN-LOWER PERMIAN AGES | POST LOWER PERMIAN AGES |
|---------------------------|-----------------------------|----------------|-----------------------------------|-------------------------|-----------------------------|-------------------------|
| CALABRIA                  |                             |                |                                   |                         |                             |                         |
| ADR 5 augen gneiss        | Qtz+Kfs+Pl+Bt+/-Ms          | 917±26, 614±10, 613±11, 597±10, 586a10 | 577±10, 568±10, 566±13, 550±16, 527±12 |                         |                             |                         |
| (Micheletti et al., 2007) |                             |                |                                   |                         |                             |                         |
| ADR 18 augen gneiss       | Qtz+Kfs+Pl+Bt+/-Ms          | 623±18, 617±17, 565±16 | 548±16, 531±15, 526±15, 522±15 | 446±13 |                         |                         |
| (Micheletti et al., 2007) |                             |                |                                   |                         |                             |                         |
| AS5 amphybolite           | Hbl+Pl/-Bt/-Qtz            | 2457±45, 2447±45, 2223±21, 2081±11, 997±22, 935±22 | 566±14, 548±14, 517±15 | 391±10, 365±11, 324±13, 279±12 | 259±11, 288±11, 252±10, 247±10 |                         |
| (Grande, 2009)            |                             |                |                                   |                         |                             |                         |
| VSG-1 leucogranodiorite   | Pl+Qtz+Kfs+Ms+/Sil         | 355±8 - 536±8 | 456±21 | 300±24 (n=12) |                         |                         |
| (Fiannacca et al., 2008)  |                             | 654±18, 614±7 | (n=7) |                             |                         |                         |
| PELORITANI                |                             |                |                                   |                         |                             |                         |
| FIU-11 augen gneiss       | Qtz+Kfs+Pl+/Ms+/Sil        | 324±13 - 607±5 | 578±10 - 516±6 |                             |                         |                         |
| (Williams et al., 2012)   |                             | (n=13) | (n=11) |                             |                         |                         |
| MV-15 augen gneiss        | Kfs+Qtz+Pl+/Ms+/-Ms        | 2435±9 - 634±14 | 549±5 - 528±7 |                             |                         |                         |
| (Williams et al., 2012)   |                             | (n=12) | (n=10) |                             |                         |                         |
| FIU-7 paragneiss          | Qtz+Pl+/-Grt+//-Sil       | 2672±9 - 611±6 | 366±15 - 535±4 |                             |                         |                         |
| (Williams et al., 2012)   |                             | (n=46) | (n=10) |                             |                         |                         |
| GC-5 trondhjemite         | Pl+Qtz+Kfs+Ms+/Sil        | 244±14, 630±18 | 491±12 | 324±2, 314±4 (n=9) | 309±2 |                         |
| (Fiannacca et al., 2008)  |                             |                 |                             |                             |                         |                         |
| Lower Domain              |                             |                |                                   |                         |                             |                         |
| PELORITANI                |                             |                |                                   |                         |                             |                         |
| Ta-Pu1-2-3; Ta-Cs; Tao    | Qtz+Pl Kfs+Grt+Ms+//-Chl   | 2013±1, 114±10 |                             |                             |                         |                         |
| Felsic porphyroids and    |                             |                |                             |                             |                         |                         |
| andesites                 | (Trombetta et al., 2004)   | [15] | ID-TIMS data |                             |                         |                         |

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3.1. Geological reconstructions inferred from U-Pb spot data

3.1.1. Recognizable Gondwana pertinence

Memory of the magmatic Proterozoic events widely occurs in the rocks of the Calabria-Peloritani Terrane as inherited ages preserved in detrital zircons or xenocrystic cores surrounded by younger overgrowths (Fig. 5).

[Image: CL images of zircons showing detritic characters (a-b-c-d) and xenocrystic cores (e-f). Note the younger overgrowths in e and f.]

Figure 5. CL images of zircons showing detritic characters (a-b-c-d) and xenocrystic cores (e-f). Note the younger overgrowths in e and f.

The zircon ages revealed in the different rock-types of the described units are detailed in the following:

- Metagranitoids (augen gneisses) belonging to Aspromonte-Peloritani, Castagna and Sila Units having Fortunian-Ediacaran protoliths (Table 1) preserve inherited zircon ages covering a time span of 2500-1760 Ma and 917-610 Ma [16,18]. In addition, they show Sm-Nd model ages ranging from 1700 to 1500 Ma [16];

- Granulite facies metabasic rocks of the Sila Unit record two Neoproterozoic inherited age (744±20 Ma and 609±29 Ma) despite their magmatic mantle origin in the Neoproterozoic-Cambrian times [7];

- Metasediments from the lower and upper crust of the Sila Unit preserve memory of old events at 2500, 2300, 2000 and 1900 Ma obtained as upper intercepts of U-Pb discordia lines (isotopic dilution method in [60,61]). Furthermore they show Nd model ages of 1500 Ma [60] and 1350 Ma [61];
Amphibole bearing-micaschists from Mandatoriccio Unit preserve xenocrystic cores old up to 2562±44 Ma [20];

Amphibole bearing-gneisses from Aspromonte-Peloritani Unit preserve inherited ages from 2500 Ma to 706 Ma [21];

In Eastern Sicily ortho-and para-gneisses belonging to APU show clusters of Proterozoic ages around 2400-2700 Ma, 900-1100 Ma and 540-850 Ma and some ages at 3200, 1800 and 1600 Ma were also obtained [23].

Still in Eastern Sicily (Lower domain) Ordovician porphyroids preserve inherited ages at 1512 Ma and 1380 Ma (upper intercepts of U-Pb discordia lines; ID-TIMS analyses in [15]). Meta-andesites associated with these porphyroids contain older zircons dated at 2015 and 1150 Ma [15].

The inherited zircon age patterns in Calabria rocks indicate Gondwana domain pertinence. In particular, the similarities in age and chemistry of the protoliths of Calabria augen gneisses with the acidic magmatites from Anti-Atlas Moroccan domain point to a source derived from a reworking of the West African Craton (WAC) [48] showing similarities with other European Cadomian terranes [62-66]. In fact, analogous inherited age patterns occur in other sectors of European Variscides [63]: Southern British Islands, Armorica Massif and Massif Central in France, Bradant Massif (Belgium), Iberian Massif (Spain and Portugal) and Bohemian Massifs (Czech Republic). The distribution of these ages suggests Cadomian pertinence with West African Craton affinity. According to [23], the inherited zircon age patterns in the augen gneisses and paragneisses from Aspromonte-Peloritani Unit in the Sicily bear evidence, on the whole, of East African provenance owing to age cluster in the range 900-1100 Ma revealed in this area. These authors evidence strong similarities between Sicily terranes and those of other areas in the Eastern Mediterranean region as Southern Israel, Jordan and Arabia and suggest an East African provenance as several pieces of basements in Mediterranean area, like Turkey, Greece, Sardinia and Cyclades [23]. Considering the whole set of inherited zircon ages in Calabria and Sicily, we can suggest that a both East and West African provenance was effective in Southern Italy as happened in other Mediterranean areas where pre-Variscan basements, starting with Neoproterozoic, are considered as derived from both East and West Gondwanan cratonic sources [67,68]. The presence of detritic components having West and East African origin was revealed by inherited zircon ages acquired with different techniques in many samples from different domains of Calabria and Sicily terrains, revealing the effectiveness of U-Pb zircon data.

### 3.1.2. Neoproterozoic-Cambrian bimodal magmatism

In situ U-Pb dating performed in metagneous rocks on zircon crystals showing euhedral morphology and a typical undisturbed oscillatory zoning [69] (Fig. 6) has evidenced a widespread Neoproterozoic-Cambrian bimodal magmatism in an older basement of Calabria-Peloritani Terrane. Evidences of basic and acidic magmatism are diffused in Calabria from Sila Massif up to Sicily (Fig. 4) in metabasic rocks, augen gneisses, fine-grained leucocratic gneisses and amphibolites (Table 1, [16-18,7,23,21]).
Zircons from 2 samples of metagabbro and from 2 samples of metabasites interbedded with felsic granulites and migmatitic metapelites of the lower crust of the Serre Massif belonging to Sila Unit were dated [17,7]. In all samples domains dated 564-593 Ma (n=4) showing magmatic oscillatory zoning and high Th/U ratio (0.16-0.19) are present (Fig. 6). These domains
show fractionated REE patterns interpreted as formed in absence of garnet considered as Variscan metamorphic phase [7,70]. On this basis a magmatic origin of the zircons indicating the age of protoliths in the time range 564-593 Ma was suggested [17,7]. So, a basic magmatism in Calabria occurred in Neoproterozoic times in an older basement, as happened in many of the so-called “Cadomian blocks” widespread from Western Alps to Turkey [71].

This basic magmatism records tholeiitic and calc-alkaline affinities and, due to the association with a thick pile of metasediments, seems to be connected with a (mature?) magmatic arc in orogenic context [72].

Zircon grains from seven samples of biotitic augen gneisses and two samples of fine-grained leuocratic gneisses coming from the Aspromonte-Peloritani (4 samples), Sila (1 sample) and Castagna (4 samples) Units in Calabria [16,18] and Eastern Sicily [23] are considered. These gneisses are intimately associated with metasediments affected by Variscan metamorphism, but their zircon domains do not bear memory of this event, preserving only Pre-Cambrian/Silurian ages [16,18,23]. Only one sample (GO39, Table 1) preserves Devonian-Lower Permian ages interpreted as resetted ages due to thermal input of fluids released by Late-Variscan plutonites [18].

In the Calabria augen and fine grained leuocratic gneisses, the majority of the concordant ages forms a statistically significant cluster averaging at $543 \text{ Ma}$ (n=20 ages from 562 to 532 Ma) mainly related to euhedral crystals without discontinuity between core and rim having U contents ranging from 659 to 241 ppm and Th/U ratios mostly comprised between 0.2 and 0.5; one domain analysed for REEs produces a highly fractionated pattern and a distinct negative Eu anomaly [18] interpreted as primary magmatic characters according to [73] or as recrystallized domains with memory of primary magmatic zircons [74]. The moderate variability and the high values of Th/U ratios seem to be more compatible with precipitation from a hybrid magma precursor of the augen gneisses [75] having mantle and crustal origin. Discordia lines with lower intercepts comprised between 562 Ma and 526 Ma have been also calculated considering the discordant data [16].

The augen gneisses from Peloritani Mountains contain zircon grains giving ages around 545 Ma including two kinds of zircon domains having U contents of 320-940 ppm (Th/U=0.08-0.23) and 40-470 ppm (Th/U=0.12-2.32) interpreted as suggestive of magmatic and detritic origin, respectively [23]. On this basis [23] suggest that the protoliths of augen gneisses were the hosting metasediments in which similar ages were detected.

This acidic magmatic activity dated around 543-545 Ma seems to be diffused in the Calabria-Peloritani basement successively than basic magmatism described above.

Chemistry of the augen gneiss indicates that their protoliths derived from shoshonitic to high-K calc-alkaline granitoids related to a post-collisional stage [16, 76], probably at the transition from compressional to extensional tectonics or even after the tectonic collapse of an intracontinental orogen [75]. The emplacement age obtained from the protoliths of all granitic gneisses in CPT and their geochemical affinity share similarities with the granitoids widespread at the Northern edge of the West African Craton, especially in Morocco [77-79], Algerian Tuareg Shield [80] and Mauritania [81]. In fact, voluminous high-K calc-alkaline plutonism charac-
terize the final stages of Panafrican orogeny in Northern margin of the West African Craton as well as in almost all the Cadomian Units along the present Alpine-Mediterranean mountain belts [81,82]. In the period 605–530 Ma, acidic magmatism was diffused at the transition from an active (compressive-transtensive) to a passive (extensional) continental margin with extension and development of foreland basins [83].

It is noteworthy that acidic and basic magmatism of Neoproterozoic-Lower Cambrian times, in Calabria-Peloritani Terrane, is diachronous being mafic magmatic activity 20-40 Ma older than the acidic one [16-18,7]; both magmatic activity monitored the tectonic evolution of Panafrican orogen from compressional to collapse stages [72].

3.1.3. Ordovician–Silurian tectono-thermal activity

Ordovician-Silurian ages (data ranging from 494±14 to 413±9 Ma) have been recorded in augen gneisses, fine-grained leucocratic gneisses and granulite-facies metabasites from Calabria (Table 1) [16-18, 7, 24]. In these rock-types the Ordovician-Silurian ages represent clusters connected to a recrystallization event being the protoliths Neoproterozoic-Cambrian in origin. These ages were measured on cores displaying irregular and patchy microstructures sometimes strongly luminescent (Fig. 7 a-b) or on overgrowths surrounding older cores (Fig. 7 c-d). Owing to the textural features of zircons, the Ordovician-Silurian ages seem related to a tectono-thermal event as an effect of recrystallization (see [84,85]) producing an isotope resetting at that time.

One sample of augen gneiss (sample GO100, Table 1) from Sila Unit interleaved with the migmatitic metapelites shows two Ordovician ages at 494±14 Ma and 462±7 Ma as a Rb-Sr isochron at 450±20 Ma determined in migmatitic metapelites [86]. In addition Ordovician–Silurian detritic population of zircon occurs in the Mandatoriccio micaschists in Mandatoriccio Complex (sample LL61b2, Table 1). In Peloritani Mountains an intermediate-acidic magmatism in Ordovician times was revealed by [15] analysing zircons with magmatic textures from porphyroids and meta-andesites dated at ca. 456–452 Ma.

A look at the European Variscan Chains in which Ordovician-Silurian ages have been detected reveals that from Iberian Massifs to Carpathians several acidic and mafic products are related to a diffusely Ordovician magmatic activity [68]. According to [67,68,71] rifting phases in the Early and Middle Palaeozoic prepared the opening of basins separating the future Variscan
basement from Gondwana. If a tectono-metamorphic phase was responsible of magmatic activity in Ordovician-Silurian times recorded in Variscan fragments of European Chain, then also the U-Pb zircon ages determined in Calabria-Peloritani rocks can be referred to the same phase. Nevertheless, it cannot be excluded that these ages might result from rejuvenation due to the opening of U–Pb radiogenic system with partial loss of Pb during the Variscan metamorphism [16,18]. Alternatively, according to the model proposed by [87], these ages can be related to an Eo-Variscan activity started in Silurian-Ordovician times.

3.1.4. Variscan orogenesis (Devonian-Lower Permian times)

The investigated basement forming continental crust units of Calabria and Sicily was affected by Variscan metamorphism and magmatism [88,42] as shown by Rb-Sr and Sm-Nd isotopic geochronology [89,61]. U-Pb zircon age data can be utilized to evidence these geological processes realized under high temperature conditions; in fact zircon has very high closure temperature for U-Th-Pb isotopic system (>900°C in [90-92]) then only high-T metamorphic and magmatic conditions can be monitored through U-Pb zircon data. Zircons of amphibolitic facies paragneisses and micaschists from Mandatoriccio Complex in Calabria [20] and from Aspromonte-Peloritani Unit in Sicily [23], respectively, do not evidence Variscan ages owing to their low temperature metamorphic conditions (around 500-650°C; [20,93]). Zircon is inefficient in these rock types to record geological events under low temperature conditions. This fact is confirmed in the augen gneisses from Castagna and Aspromonte-Peloritani Units (low-medium grade Variscan metamorphism) where ages younger than ~413 Ma in Calabria [16] and ~516 Ma in the Sicily [23] were not detected.

Zircons from these rock types record domains with oscillatory zoning generated by dissolution/re-precipitation or crystallization in presence of melts [85,94] together with lobate structurless grey or luminescent rims invading older cores (metamorphic re-crystallization in [6]) (Fig. 8). The evaluation of zircon textural features on which spot ages were determined constrains step by step the Variscan metamorphic trajectory of the lower crust of the Sila Unit. Distinct U-Pb zircon age clusters were determined (Table 1): i) a few ages from 380 Ma to 347 Ma; ii) 13 data points around 347-340 Ma; iii) 23 zircon ages clustering at 320 Ma; iv) 31 ages around 300 Ma; v) several ages in the range 270-280 Ma.

Considering the P-T evolution of the lower crust of the Sila Unit representing a fragment of Variscan continental crust, the revealed cluster ages were interpreted in the following [95]:

a. The ages from 380 Ma to 347 Ma indicate phases of crustal thickening during the prograde metamorphism from amphibolite to granulite facies;

b. The cluster at 347 Ma represents the metamorphic peak at T=880°C and P=1.1 GPa under granulite facies conditions in the lower part of the continental crust section;
c. The age peaks at 320, 300 and 280 Ma (Table 1; Fig. 8) date the decompression phases. In particular, the cluster at 320 Ma in the granulites coincide with the age of basic Variscan magmatism determined on zircons of a quartz-monzodioritic dike dated at 323 Ma (sample Tur37b, Table 1, Fig. 9a). The first decompression stage was accompanied by partial melting in the hosted rocks as shown by zircon domains with oscillatory zoning crystallized by partial melt (Fig. 8). The age peak at about 300 Ma dates a further decompression phase and probably the end of anatexis in the granulites as testified by successive homogeneous and luminescent rims of zircons with ages around 280 Ma in which the Variscan cycle stopped [7].

![Figure 8. VPSED images of selected Variscan zircons. See the oscillatory zoning domains surrounded or invaded by lobate structurless grey or luminescent rims. Scale bar: 50 μm.](image)

During the crustal thinning and decompression, emplacement of huge Late-Variscan calc-alkaline granitoids occurred: 1) between the upper and lower crustal portions of the Sila Unit (Fig. 4) at about 300 Ma ago as showed by Rb-Sr isotopic ages [52] and U-Pb zircon ages in granodorities and tonalities of the Serre batholite [96], 2) in the Castagna Unit as showed by U-Pb dating of zircons in a pegmatitic dike (sample GO82, Table 1, Fig. 9b) and 3) in CPU as showed by U-Pb zircon ages from peraluminous magmatites [19] (Table 1).

The geological evolution of the continental crust in Calabria was detailed utilizing the precious textures of zircons and the U-Pb zircon data; the reconstructed scenario is confirmed by the comparison with similar metamorphic evolution of other lower crust fragments from the South European Variscides cropping out in the West Mediterranean areas [97-101].
A limitation of the U-Pb spot analyses on zircon is the spot size; in fact the augen gneisses interleaved with the migmatitic metasediments of the lower crust of the Serre (Calabria) show a thin recrystallized rim clearly shown by the cathodoluminescent images but undatable for the small size. Speculatively, these thin rims have been interpreted as formed during the Variscan metamorphism by [16], but their precise ages are not known.

3.1.5. Post lower Permian events

Few and scattered zircon ages comprised between 268±8 Ma and 231±5 Ma [72] (Table 1, Fig. 10) were measured in the granulites of the Sila Unit and in metamorphites and magmatites of the Castagna Unit. These ages have been interpreted as effect of a recrystallization event assisted by fluids [16,18,7]. A comparison with Variscan basements from Corsica [100] and Western Alps as the Ivrea zone [102,103] show similar cluster ages interpreted as precursor signals of the opening of the Tethys Ocean. An analogous interpretation can be adopted for the Calabria rock types associated to domains formed during the opening of Tethys Ocean. However, it can not be excluded that these ages in Calabria might be connected to opening of U-Pb isotopic system of zircon due to Alpine tectonism [18], in fact the studied rocks belong to tectonic units stacked during the construction of Alpine chain and are affected by Alpine shear zones [49,46].
4. Conclusions

The reconstruction of the pressure-temperature-time (P-T-t) evolution of crustal sections is fundamental to understanding many tectonic processes. This task, particularly difficult in the case of polymetamorphic rocks, requires the combination of metamorphic petrology and geochronology of different mineral phases that potentially can record more than one geological event. Zircon has been largely used for this role in high-grade terrains because its U-Pb system is able to retain the memory of polyphase evolution even at relatively high temperatures for its highly refractory nature, high closure temperature and slow Pb diffusion rate. Zircon is an ideal mineral for U–Pb dating of poly-metamorphic rocks [90,104-106,8,107-113]. In addition, the precise and accurate dating of the retrograde metamorphism is crucial for understanding the exhumation history of the ancient metamorphic basements. Obviously, spot U-Pb zircon data in magmatites formed under high temperature conditions, constrains the timing of magma emplacement and bring light on the geological context in which the magmatism explicated.

The case study presented in this paper shows as in situ zircon dating linked with determined P-T conditions could constrain the evolution of the Calabria-Peloritani Terrane, a crucial fragment of Southern European Variscan Belt.

In the last ten years the advances in analytical capabilities have permitted in-situ investigation of complex zircon grains that allow us to reconstruct the geological history from Neoproterozoic-Cambrian to post Permian times in Southern Italy. In Fig.11 a histogram and a probability density curve of the U-Pb spot zircon ages collected in CPT are reported showing the large number of determinations in a wide time interval from Archean to Triassic ages.

The collected data are interpreted as suggestive of: (1) Neoproterozoic detrital input from cratonic areas of Gondwana testified by inherited zircons; (2) diachronic bimodal basic and acidic magmatism between 570 and 526 Ma, relative to an active tectonic margin setting; (3) rifting and opening of Ordovician-Silurian basins signed by consistent cluster ages around 450 Ma corresponding to acidic and intermediate volcanic activity (porphyroids and meta-andesites in Peloritani Mountains); 4) Variscan granulite facies metamorphism and pervasive partial melting in deep crustal rocks of the Sila Unit; 5) precursor signals of the Tethys evolution showed by post Permian zircon domains.
Figure 11. Histogram and probability density curve for U-Pb concordant data on zircon (n=491) from CPT (Tab.1). References: [7, 15-24].

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