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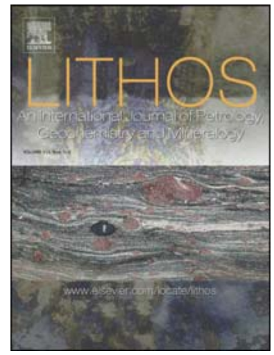

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Basement provenance revealed by U-Pb detrital zircon ages: a tale of African and European heritage in Tuscany, Italy

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Abstract

A new data set of ca. 500 LA-ICP-MS U-Pb detrital zircon ages for six metasedimentary units from the Tuscan basement (Apuan Alps, Monti Pisani, Monticiano-Roccastrada), along with a precise SHRIMP U-Pb crystallization age of a metavolcanic unit (Apuan Alps) have been collected to determine their depositional ages and provenance. These results have been integrated with the recently published ca. 900 U-Pb detrital zircon ages from Elba Island to draw a complete picture of the Paleozoic journey of the Tuscan basement. A major change in the sources supplying sediments to the Tuscan basins is shown to occur during this journey. Detrital zircon ages of early Cambrian to middle Ordovician metasediments mirror those of coeval northern Africa sediments: most samples were sourced in western Africa, while one sample is derived material from central northern Africa. The Tuscan block was therefore located at the peri-Gondwana margin, close to central northern Africa. The prominent mid-Ordovician magmatic arc activity (ca. 460 Ma) at the northern Gondwana margin and its detritus, characterise the zircon age distribution of Ordovician and Silurian volcano-sedimentary rocks, that were therefore generated at the northernmost Gondwana margin during subduction and subsequent initial Paleotethys rifting. The Carboniferous-Permian metasediments are dominated by populations of Ordovician and Variscan-age zircons, with a minor occurrence of Neoarchean and Paleoproterozoic zircons that is best explained by recycling of European Neoproterozoic-Cambrian metasediments. In summary, the main sources supplying the Tuscan basins were located in northern Africa throughout Cambrian-Ordovician times, shifting to the volcanic arc active at the northern Gondwana margin during the middle Ordovician. During Variscan and post-Variscan times, detrital zircon sources were mostly located in European terrains, witnessing the shift of Tuscany from Africa to Europe.

Keywords: Detrital zircon; Provenance; U-Pb dating; Tuscan basement; peri-Gondwana terranes; European terranes

1. Introduction

The evolution of the Apennines fold-and-thrust belt has played a key role in shaping the western Mediterranean area (Fig. 1). In this framework, the Apennine basement in Tuscany has been considered as a fragment of the Variscan European belt that was part of the northern Gondwana margin until it was separated by the opening of the Rheic Ocean in the early Paleozoic and drifted northwards to become part of Europe (e.g. Stampfli et al., 2002a; von Raumer et al., 2002, 2003). Paleozoic sedimentary units of the Tuscan basement and its cover units are exposed in several areas of the northern Apennines (Apuan Alps, Monti Pisani, Monticiano-Roccastrada Ridge and Elba Island - Fig. 1; Franceschelli et al., 2004). In the late Paleozoic, they were located near the Sardinia-Corsica block along the southern part of the Variscan chain (Elter and Pandeli, 2005; and reference therein). On this basis, the metasedimentary sequences of the Tuscan basement have been correlated with the Paleozoic formations of the Variscan chain of Sardinia, based on sedimentary and tectono-metamorphic evidence, and this correlation has been used as a basis for paleogeographic reconstructions (e.g. Bagnoli et al., 1979; Carmignani et al., 1992; Pandeli et al., 2004). However, uncertainties in the stratigraphic age and paleogeographic origin of most units make correlations open to question and severely limit the reconstruction of the Tuscan basement stratigraphic-tectonic evolution.

To overcome these limitations, we have performed ca. 500 new LA-ICP-MS U-Pb detrital zircon age determinations for six metasedimentary units of the mainland Tuscany basement, as well as a precise SHRIMP crystallization age of the igneous protolith of a metavolcanic unit. These data have been integrated with the recently published ca. 900 detrital zircon ages from Tuscan basement in Elba Island (Sirevaag et al., 2016). The resulting age of deposition and provenance of sediments of the Tuscan basement and its cover sequences shed light on both the changing sediment supply from African to European sources throughout the Paleozoic, and the Ordovician magmatic activity, whose sedimentary derivatives are widespread in Europe, representing a valuable stratigraphic and paleogeographic marker.

2. Tectonostratigraphy of the Tuscan domain

The Tuscan basement crops out in tectonic windows in the Apennine Mesozoic units, from the Apuan Alps in the north to the Monticiano-Roccastrada Ridge and the eastern Elba Island in the south (Fig. 1). The

Tuscan basement of both mainland Tuscany and Elba Island is considered as a part of the Adria plate, that was located close to the northern margin of Gondwana until mid-Paleozoic times, before it was separated from Gondwana together with other future Variscan terranes (Stampfli et al., 2002b; von Raumer et al., 2002, 2003) and became part of central Europe. The detrital zircon record of the Tuscan basement has thus to be interpreted in the light of both European and Gondwanan plate tectonics.

Apuan Alps

The Paleozoic basement of the Apuan Alps tectonic window is composed of four formations (Conti et al., 1993; Molli, 2000) whose age of deposition has been mainly inferred by correlation with similar units from Sardinia. These formations are, from bottom to top: (i) the Lower Quartzites-Phyllites, non-fossiliferous siliciclastic turbidites, which have been given either an Ordovician-middle Silurian (Bagnoli et al., 1979) or a late Cambrian-early Ordovician age (Barberi and Giglia, 1965); (ii) the Valle del Giardino metabasites, inter-layered with the Lower Quartzites-Phyllites (Bagnoli et al., 1979; Barberi and Giglia, 1965; Puxeddu et al., 1984); (iii) the Porphyroid unit, a schistose rock rich in quartz and K-feldspar phenocrysts set in a quartz- and white mica-rich matrix, interpreted as metamorphosed rhyolitic volcanic rocks of middle Ordovician age (Barberi and Giglia, 1965; Puxeddu et al., 1984); the Porphyroids are associated with the Porphyritic Schists, derived from their immediate subaerial erosion (Barberi and Giglia, 1965); (iv) the Upper Quartzites-Phyllites, which have been given a late Silurian-Devonian (Bagnoli et al., 1979) or late Ordovician age (Pandeli et al., 2004).

Monti Pisani

The Monti Pisani are located between the basement exposures of the Apuan Alps and Iano (Fig. 1). The metamorphic core of the Monti Pisani is formed by low-grade metamorphic units, including a Paleozoic basement unconformably overlain by an early Permian-Triassic sedimentary cover. The Paleozoic basement includes, from bottom to top: (i) the non-fossiliferous Buti Quartzites-Phyllites, comprising meta-sandstones, phyllites and meta-siltstones which have been given either a Silurian age by correlation with the Porphyritic Schists and Upper Quartzites-Phyllites of the Apuan Alps (Bagnoli et al., 1979), or a late Ordovician age by correlation with the transgressive deposits of Central Sardinia (Pandeli et al., 1994), and (ii) the San Lorenzo Schists, including dominant organic-rich black and silty shales and minor quartzitic meta-sandstones, fine-grained conglomerates and graphitic layers, with a late Carboniferous to early Permian age indicated by the abundant fossil flora (Rau and Tongiorgi, 1984). The basement is overlain by (i) the Permian Asciano Breccias and Conglomerates, consisting of poorly bedded, massive metarudites that include angular fragments of phyllites and meta-siltstones (Rau and Tongiorgi, 1974), and (ii) the late Paleozoic-early Triassic Verrucano cover sequence, made of coarse-grained conglomerates (braided stream deposits), violet schists, fine-grained arenites (meandering stream deposits) and quartzites (Franceschelli et al., 1987; Rau and Tongiorgi, 1974).

Monticiano-Roccastrada

The Monticiano-Roccastrada basement unit crops out in the southern part of the mid-Tuscan ridge (Fig.1), where the Farma River cuts deeply into the Paleozoic and Triassic strata, exposing the Farma Formation that consists of interbedded turbiditic and hemipelagic mudstones. This formation has previously been assigned to the Moscovian stage of the late Carboniferous, but more recent data suggest a mid-late Permian depositional age (Aldinucci et al., 2008a; and references therein).

Elba Island

The provenance and depositional ages of the Tuscan basement of Elba Island have recently been investigated in considerable detail (Sirevaag et al. 2016). The basement units are, from bottom to top: (i) the Porto Azzurro Unit, traditionally considered of middle Paleozoic age, based on correlations with similar units from mainland Tuscany (Barberi et al., 1967; Musumeci et al., 2011; Pandeli et al., 1994; Puxeddu et al., 1984), whereas detrital zircon data indicate an early Paleozoic age (Sirevaag et al., 2016), and (ii) the Porphyroid formation (and its sedimentary …) of the Ortano Unit, commonly correlated with the Porphyroids of the Apuan Alps and the middle Ordovician igneous rocks of Sardinia (Barberi, 1966; Bortolotti et al., 2001; Carmignani et al., 1986), with a well-defined middle-late Ordovician zircon crystallization age that confirms previous correlations (Sirevaag et al., 2016). These basement units are overlain by the Monticiano-Roccastrada Unit, including metasediments thought to be of late Carboniferous to Triassic age (Bortolotti et al., 2001; and references therein) and correlated with the Verrucano sequence from the Monti Pisani (Rau and Tongiorgi, 1974) and southern Tuscany (Bortolotti et al., 2001). Detrital zircon age distributions indicate an early Permian maximum depositional age (Sirevaag et al., 2016).

3. Analytical methods

Seven representative samples from the Tuscan basement and its cover have been investigated (Fig. 1), including: (i) two metasedimentary samples and one metavolcanic rock from the Porphyroid Formation from the Apuan Alps, (ii) three metasedimentary rocks from Monti Pisani, including the Buti Phyllites-Quartzites, San Lorenzo Schists and Violet Schists of the Verrucano sequence, and (iii) one sample from the Farma Formation of the Monticiano-Roccastrada Unit. The six metasedimentary samples were dated by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), while the metavolcanic sample from the Apuan Alps was dated by Sensitive High-Resolution Ion MicroProbe (SHRIMP). Sample descriptions are given in Table 1.

LA-ICP-MS

*Z*ircon grains were separated using conventional mineral separation techniques (Holman-Wilfley shaking table, magnetic and heavy liquid separation) and ca. 250-300 zircons from each sample were handpicked, avoiding metamict grains, and mounted in epoxy. The grain mounts were polished and imaged (Fig. 2, Fig. S1), using a Zeiss Supra 55VP Scanning Electron Microscope (SEM) with cathodoluminescence detector (CL), in order to observe the internal structure prior to the isotopic analyses. U/Pb and Pb/Pb isotopic ratio analyses of zircon grains from metasedimentary rocks were carried out by LA-ICP-MS at the University of Bergen, using a Thermo-Finnigan Element II sector field ICP-MS system coupled with a 193 nm ArF Excimer Resonetics RESOlution M-50 LR laser. The analytical procedure is described in detail in Sirevaag et al. (2016). Laser-induced elemental fractionation and instrumental mass discrimination were corrected by normalisation to the reference zircon Plešovice (337 Ma; Sláma et al., 2008). Two standards, the 91500 zircon (1065 Ma; Wiedenbeck et al., 1995) and the GJ-1 zircon (609 Ma; Jackson et al., 2004), were analysed together with the unknowns. The 91500 zircon standard yielded an age of 1067±4 Ma (n=97, MSWD=0.052) while the GJ-1 standard gave an age of 601±3 Ma (n=57, MSWD=1.7).

The LA-ICP-MS data (Fig. 3) have been filtered in order to provide a robust dataset, excluding analyses with 2σ errors of the measured isotopic ratios >20% and/or a probability of concordance <0.05 (see Appendix A.2). Detrital single-grain ages are reported as concordia ages with corresponding 2σ errors, calculated by Isoplot (version 4.15; Ludwig, 2012). Detection limits have been calculated for each sample, giving the size of the smallest age fraction still detected with 95% confidence (Figs. 3, 4) (Vermeesch, 2004; Andersen, 2005).

SHRIMP

U-Pb zircon dating of the metavolcanic Apuan Alps Porphyroids was carried out using a multi-collector Sensitive High Resolution Ion Microprobe SHRIMP IIe/mc, at the University of Granada (IBERSIMS laboratory). The analytical procedures are described in Williams and Claesson (1987). The primary beam was set to an intensity of about 5 nA with a 120 μm Kohler aperture, generating 17x20 μm elliptical spots on the target. The secondary beam exit slit was fixed at 80 μm with a mass resolution sufficient to resolve Pb ions from molecular interferences (M/ΔM ca. 5000). All calibration procedures were performed on the standards included on the same mounts as the samples. Mass calibration was done on the REG zircon (ca. 2.5 Ga, very high U, Th and common lead content). Every analytical session started by measurement of the SL13 zircon, that was used as a concentration standard (238 ppm U). The TEMORA-1 zircon (416.8±1.1 Ma) was used as an isotope ratio standard and was measured between every four unknowns.

Analyses with a probability of concordance <0.05 and/or >5% 1σ error in isotopic ratios have been excluded. A common concordia age with a 2σ confidence interval is calculated from the SHRIMP analyses for the volcanic protolith (Fig. 4).

4. Geochronological results

The geochronological data for ca. 500 detrital zircons are reported in Supplementary Table S1. Maximum depositional ages are estimated as the weighted mean value of the youngest detrital zircon grains with overlapping 1σ uncertainties (Table 1; Dickinson and Gehrels, 2009; Spencer et al., 2016). Zircon crystals from a metavolcanic rock of the Apuan Alps have been analysed by SHRIMP to precisely determine the protolith crystallization age (Table S2).

Apuan Alps - Lower Quartzites-Phyllites (THHS-05)

Sample THHS-05 consists of very fine-grained sandstone and quartzitic phyllite. The zircon crystals are mainly idiomorphic and elongated. Most grains have sub-rounded to rounded edges, consistent with sedimentary transport. Oscillatory zoning is dominant and is interpreted to represent igneous zircon growth. Sector zoning is observed in some grains with modest elongation. 78 of the 93 analysed grains (84%) passed the data filtering. The majority of the ages fall between ca. 1030 and 500 Ma (94%), with the main peak at ca. 640 Ma and minor peaks at ca. 790 and 915 Ma (Fig. 3). A Neoarchean zircon population of ca. 2610-2540 (5%) is also present. Worthy of mention is a single grain of Paleoproterozoic age (1821±30 Ma). Paleozoic grains are commonly euhedral, while the Paleoproterozoic grains tend to be rounded, suggesting a longer transport history. The weighted mean age of the youngest detrital zircon grains overlapping at the 1σ-level (8%) is early Cambrian. A single younger detrital zircon grain (497±13 Ma) does not overlap within its uncertainties with any other analyses and has thus not been used to calculate the maximum depositional age.

Apuan Alps - Upper Quartzites-Phyllites (THHS-07)

The sample THHS-07 has a silty-sandy grain size and a well-developed foliation. Zircon grains are commonly subhedral to idiomorphic, with a few rounded grains. Many of the grains are fractured, have inclusions or show signs of metamictization. Oscillatory zoning is common, and a few sector-zoned grains are also present. Distinct cores are observed in many grains. Sixty-three of 76 analysed grains (83%) have been used for interpretation (Fig. 3). The youngest and oldest concordant zircon grains have ages of 529±14 Ma and 3285±35 Ma respectively. The major populations are at ca. 1055-850 Ma (41%), and ca. 750-540 Ma (44%). A Neoarchean zircon population of ca. 2600-2530 Ma (5%) and a Paleoproterozoic zircon population of ca. 1980-1865 Ma (8%) are also present, but of minor significance compared with the other populations. Worthy of mention is a single grain of Paleoarchean age (3285±35 Ma), which is the oldest zircon grain from all the analysed Tuscan basement metasediments (Fig. 3). The youngest concordant zircon grains have ages of 539±14 Ma and 529±14 Ma, indicating an early Cambrian maximum depositional age.

Apuan Alps - Porphyroids (THHS-06)

Sample THHS-06 shows a distinct augen texture with large magmatic phenocrysts of quartz, suggesting that the protolith was an ignimbrite (Barberi and Giglia, 1965; Barberi, 1968). Zircon crystals are commonly subhedral with no or minimal rounding, suggesting only short transport. Oscillatory zoning is common and less than 5% of the crystals show distinct cores. Overall, the internal structures and the absence of rounding are consistent with a volcanic protolith that underwent only minimal, if any, sedimentary reworking. SHRIMP analyses of 32 spots on 30 zircons from the Porphyroids were used to precisely define the crystallization age. Five grains (15%) gave discordant ages and were excluded, while three analyses (9%) were rejected due to large errors. Of the remaining grains, four analysed zircon grain cores (12%) have ages ranging from early Ordovician to Paleoproterozoic. The remaining 20 analyses on oscillatory-zoned domains (62%), interpreted as magmatic zircon growth, provided a common concordia age of 457±3 Ma (Fig. 4). This age is interpreted as the crystallization age of the volcanic protolith.

Monti Pisani - Buti Quartzites-Phyllites (THHS-02)

The Buti Quartzites-Phyllites were sampled on Monti Pisani just below the base of the Verrucano sequence. The sample THHS-02 is fine-grained with alternating highly deformed phyllites and quartzites. Zircons are mostly euhedral to subhedral, with prismatic shapes. Most grains (~70%) consist entirely of moderately luminescent zircon with concentric or locally oscillatory zoning. The remaining grains show inherited cores with moderately luminescent overgrowths. Eighty-six of 100 analysed grains (86%) yield concordant ages ranging from 2590 to 540 Ma. About 90% of all the zircon grains are younger than ca. 1010 Ma, with a continuous distribution of ages and main peaks at ca. 615, 755 and 865 Ma. The remaining six zircon ages define two populations at ca. 2590-2425Ma (4%) and ca. 1930-1825 (4%) (Fig. 3). The maximum depositional age, based on the ages of the seven youngest detrital zircon grains with overlapping ages, is late Proterozoic-early Cambrian.

Monti Pisani - San Lorenzo Schists (THHS-10)

Sample THHS-10 is a massive silty sandstone, with thick layers of coarse-grained micaceous sandstones or quartz conglomerates characterising the upper part of the formation, from which the sample was collected. Many zircon grains have distinct cores, typically surrounded by a mantle with oscillatory zoning. Ninety-two grains were analysed, with 66 (71%) of them passing the data filtering. These zircons show a complex polymodal age distribution, spanning from ca. 2530 and 260 Ma (Fig. 3). Most zircon grains (~90%) have ages younger than ca. 1010 Ma, with main populations at ca. 355-260 Ma (52%), 470-435 Ma (19%) and 615-520 Ma (13%). Seven zircon grains give ages scattered from ca. 1010 to 690 Ma, and the remaining five zircons give scattered ages between the Paleoproterozoic and the late Archean (8%). The youngest detrital zircon grains define a middle-late Permian maximum depositional age.

Monti Pisani - Verrucano sequence, Violet Schists (THHS-15)

Sample THHS-15 is made up of violet phyllites and meta-siltstones with thin irregular quartzite layers. Zircon crystals are mostly subhedral and rounded. Most grains are moderately luminescent, with oscillatory or occasionally sector zoning. The remaining grains consist of a core with a discordant, moderately luminescent overgrowth. Sixty-eight of 83 zircon grains (82%) have been used for interpretation. The ages range from ca. 2130 to 265 Ma, with main populations at 320-265 Ma (30%), 485-420 Ma (41%), and 760-500 Ma (22%). A few single grains (~7%) give scattered Proterozoic ages between ca. 2130 and 1105 Ma (Fig. 3). On the basis of the youngest detrital zircon grains we define a middle-late Permian maximum depositional age.

Monticiano-Roccastrada - Farma Formation, meta-turbidite (THHS-11)

Sample THHS-11 (Fig. 2) is a coarse-grained meta-turbidite sampled along the Farma River in southern Tuscany. Zircons are mostly elongated, commonly with oscillatory zoning, thin low-luminescent rims and widespread inclusions. Sixty-five out of 90 analyses (62%) provide reliable data for interpretation. Eighty-three percent of the analyses fall between ca. 645 and 345 Ma. A small population of zircons at ca. 370-345 Ma (6%) defines an early-middle Carboniferous maximum depositional age. Zircon grain ages are continuously distributed from ca. 640 to 445 Ma with a main peak at ca. 480-470 Ma. The remaining analyses (17%) yielded scattered Neoproterozoic to Archean ages, defining a minor population at ca. 2115-1918 Ma (6%). Two Neoarchean and one Mesoarchean ages of ca. 2600-2530 Ma and 2985 Ma are also present (Fig. 3).

5. Depositional age

The actual depositional age is bracketed by the maximum depositional age (Table 1; Fig. 5) based on youngest detrital zircons, and the age of the oldest zircon-generating event known in the area that is not represented in the age spectrum (Fig. 3).

The oldest metasedimentary sequences in the Monti Pisani (Buti Quartzites-Phyllites), Apuan Alps (Lower and Upper Quartzites-Phyllites) and Elba Island (Monte Calamita Formation; Sirevaag et al., 2016) all show an early Cambrian maximum depositional age (Fig. 5). The lack of zircons from middle-late Ordovician volcanism, which are widespread in all the post-Ordovician sediments, is taken as evidence for a depositional age between early Cambrian and middle-late Ordovician times. This age is older than suggested in most previous works (late Ordovician-Silurian-Carboniferous: Barberi and Giglia, 1965; Musumeci et al., 2011; Pandeli et al., 2004; Puxeddu et al., 1984; Rau and Tongiorgi, 1974; Table 1). It also shows both the Upper and Lower Quartzites-Phyllites to be older than the Apuan Alps Porphyroids that geometrically separate them, suggesting a tectonic rather than stratigraphic origin for this arrangement.

The Porphyroids from the Apuan Alps (457±3 Ma) are coeval with the Porphyroids (460±3 Ma) and their erosional products (455-450 Ma) from Elba Island (Sirevaag et al., 2016). These data are in agreement with previous age estimates based on either U-Pb detrital zircon chronological data from

Elba Island (Musumeci et al., 2011) or correlations with the mid-late Ordovician magmatic events of Sardinia, dated at 465±1 Ma (Oggiano et al., 2010; Puxeddu et al., 1984). Indeed, a magmatic flare-up took place in the middle Ordovician at the northern margin of Gondwana and has been interpreted as an Andean-type arc. Later, an early Silurian re-deposition of the final phase of alkaline magmatism of the collapsing convergent margin has been documented in Sardinia (Oggiano et al., 2010) and Elba Island (Sirevaag et al., 2016), but no traces of it are found in mainland Tuscany.

After the Ordovician magmatic event, the oldest maximum depositional age is recorded by the Farma Formation (early Mississippian). The very limited occurrence of Variscan-age zircons, otherwise abundant in Permian deposits (e.g. Monti Pisani, Fig. 3), suggests that the depositional age cannot be significantly younger than the maximum depositional age: the Farma sample records just the earliest Variscan zircon-generating events (Fig. 5). This is slightly older than some previously proposed ages of deposition based on the fossil content (Aldinucci et al., 2008a), whereas it is in agreement with ages proposed on the basis of close similarities of the Farma Formation's tectono-sedimentary framework with the early Carboniferous turbidite sequences of the Carnic Alps, central Sardinia and Calabrian-Peloritan segment (Carmignani et al., 1992; and references therein). These observations support the traditional stratigraphic-geodynamic interpretation as a flysch deposit emplaced in a Variscan foredeep (Lazzarotto et al., 2008; and references therein). Thereafter, between late Carboniferous and early Permian times, the change of the tectonic setting produced a number of small sub-basins (e.g. Catalan Pyrenees, Lodève basin, Central Sardinia, Provence) that typically accommodated continental to shallow-marine epiclastics coupled with volcanic deposits (Aldinucci et al., 2008b; Gretter et al., 2015). These basins record the signature of progressive erosion of the Variscan chain (Pangea break-up) and the late- to post-orogenic Carboniferous to Permian magmatism (Gretter et al., 2015; Stampfli et al., 2013; and reference therein).

After cessation of the Variscan events, the earliest ensialic sediments that accumulated on the developing passive margin of the Adria microplate are represented by the San Lorenzo Schists and the Verrucano succession of Monti Pisani that share a mid-Permian maximum depositional age (Fig. 5) with the Verrucano sequence and the underlying Rio Marina Formation from Elba Island (Sirevaag et al., 2016). These maximum depositional ages correspond to previous biostratigraphic estimates for the San Lorenzo and Rio Marina formations (Pandeli et al., 2008; and references therein), whereas they are somewhat older than mid-late Triassic ages reported for the Verrucano sequence from both areas (Rau and Tongiorgi, 1974). The youngest limit for the actual depositional ages of these units is difficult to constrain on a geochronological basis owing to the lack of significant zircon-generating events after the Variscan orogeny until the mid-late Jurassic oceanic magmatism (Tribuzio et al., 2016). However, the fossil record helps in defining a mid-Permian depositional age for San Lorenzo and Rio Marina formations, and a mid-late Triassic age for the Verrucano sequences.

6. Provenance

Our reconstruction of sediment provenance is based on first assigning a source area to each observed zircon age population, then reconstructing the sample's provenance by combining the zircon populations observed in that sample.

Detrital zircon populations

In every sediment, the zircon population with a prominent peak close to the age of deposition is most likely of quite local derivation. On the other hand, much older populations yield more insights on wide-range provenance, provided their peaks are significant, i.e. not deriving from multiple recycling. The detrital zircon grains from the Tuscan basement are spread over a wide range of ages, from the Archean (ca. 3285 Ma) to the late Paleozoic (ca. 260 Ma), including five significant populations in the Permian-late Mesoproterozoic interval, as well as groups of a few zircons of Paleoproterozoic-Archean age.

The zircon population with ca. 350-260 Ma ages was generated during the Variscan orogenic cycle. Among them, the early-middle Permian zircons (ca. 290-260 Ma) are related to the final stage of magmatism between ca. 290 and 260 Ma (Gaggero et al., 2007; Marocchi et al., 2008). This early Permian magmatism in Sardinia and the southern Alps is linked to the geodynamic shift from Paleotethys subduction to Neotethys opening and reflects the transition from the late Variscan to the Alpine cycle (Gretter et al., 2013; Stampfli and Kozur, 2006; von Raumer et al., 2013).

The middle Ordovician-Silurian zircon population is related to the magmatic flare-up generated by the diachronous process of subduction/slab rollback/Paleotethys opening along the northern margin of Gondwana (Gaggero et al., 2012; Helbing and Tiepolo, 2005; Oggiano et al., 2010; von Raumer et al., 2015). The middle-late Ordovician metavolcanic rocks from Apuan Alps (457±3 Ma) and Elba Island (460±3 Ma; Sirevaag et al., 2016) are coeval with arc volcanism in Sardinia (465±1 Ma; Oggiano et al., 2010), and almost coeval with the slightly older volcanism in Central Iberia (ca. 475, Bea et al., 2010; Montes et al., 2010). The early Silurian component of this population was generated during the final phase of alkaline magmatism of the collapsing convergent margin (Oggiano et al., 2010).

The ca. 700-520 Ma, mostly Ediacaran, large zircon population can be correlated to Pan-African events and represents a long-lived magmatic arc in the eastern sector of the peri-Gondwanan margin (von Raumer et al., 2015) documented in several European areas (e.g. Saxothuringian-Bohemian Massif, Ossa Morena, Iberia, Alpine domains), and terminating with the opening of the Rheic Ocean (Linnemann et al., 2008, 2011).

The ca. 850-750 Ma Cryogenian zircon population has been found as well in Neoproterozoic-Ordovician metasediments from the Arabian-Nubian shield (Linnemann et al., 2011) and from the Saharan Metacraton, with the primary zircons most probably generated in the Congo-Tanzania craton during breakup of Rodinia (Pisarevsky et al., 2003; Zhao et al., 2002). Detrital zircons of such age are also found in Neoproterozoic metasediments from the Volta basin, but recycling of these sediments is ruled out by the lack of ca. 1600-1300 Ma detrital zircons in the Tuscan metasediments (Avigad et al., 2012).

The ca. 1100-900 Ma, Grenville-age, zircon population occurs also in several Neoproterozoic-Ordovician sedimentary basins of the Trans-Saharan belt (Hoggar Shield), the Saharan Metacraton (Libya basin), and the Arabian-Nubian shield (e.g. Avigad et al., 2012; Linnemann et al., 2011; Meinhold et al., 2013). Primary production of zircons could be related to igneous rocks of eastern Chad and the southeastern margin of the Congo and Tanzania cratons (Goodge at al., 2008; Linnemann et al., 2011; Meinhold et al., 2011; Muhongo and Lenoir, 1994), as well as of remote Amazonia, where Grenville-age basement is well known (Meinhold et al., 2013).

The small zircon groups of Paleoproterozoic (ca. 2.2-1.8 Ga) and earliest Proterozoic-Neoarchean age (ca. 2.8-2.4 Ga) have a distribution resembling the age spectra from cratonic areas of the Saharan Metacraton (Abdelsalam et al., 2002; Bea et al., 2011). Finally, Paleoarchean igneous zircon grains occur only in the Leonian orogenic belts of the West Africa Craton (Kröner et al., 2001), while detrital zircons with ages of ca. 3.4-3.2 Ga occur in Neoproterozoic metasediments of the Saxo-Thuringian zone and in eastern Archean terranes of the Sahara Metacraton (Bea et al., 2011; Linnemann et al., 2004). Nevertheless, the scarcity of these very old grains calls for extreme caution in using these zircons as provenance indicators in the next section.

Implication for sediment provenance

The Cambrian-mid Ordovician metasediments from the Apuan Alps, Monti Pisani and Elba Island are all characterized by a prominent Pan-African peak (Fig. 6), along with a distinct Cryogenian population, closely resembling coeval sandstones from Morocco-Algeria (Meinhold et al., 2011, 2013). Thus, a similar provenance from westernmost northern Africa (West African Craton) is inferred for these Tuscan basement units. A notable exception is the Upper Quartzites-Phyllites that have a prominent Grenville-age population and no Cryogenian zircons at all. This feature is most likely linked to a dominant sediment supply from erosion of Neoproterozoic metasediments from the Trans-Saharan belt (Hoggar), the Saharan Metacraton (Libya) or the Arabian-Nubian shield, where the Neoproterozoic collision between East and West Gondwana resulted in uplift and erosion of extensive Grenville-age terrains (e.g. Avigad et al., 2012; Meinhold et al., 2013; Squire et al., 2006). Sediments deposited coevally with the Upper Quartzites-Phyllites are found in southeastern Europe, Libya, and Morocco-Algeria. The SE Europe sediments contain Grenville-age zircons together with ca. 2.2–1.9 Ga zircons (Williams et al., 2012), with the latter not observed in the Upper Quartzites-Phyllites. Cambrian sediments from Libya have a zircon distribution similar to that of the Upper Quartzites-Phyllites, including the ca. 1 Ga population and minor Proterozoic and Archean grains. This could indicate an Amazonian provenance. However, the Cambrian paleogeographic position of Amazonia makes it difficult to transport detritus from Amazonia without mixing it with West African materials (Nance et al., 2008), thus the lack of a significant ca. 2.2-1.9 age peaks in our samples casts some doubt on this interpretation. In summary, Tuscan Cambrian-mid Ordovician basins were collecting sediments from similar source areas located in northern Africa. The larger contribution from central northern Africa to the Upper Quartzites-Phyllites (similarly to Libya) could be related to a lateral supply variation in the Apuan Alps basin(s), or to a time shift of sediment supply in the same basin, as suggested by Meinhold et al. (2011) for Libya basins.

Mid-Ordovician to Silurian metavolcanic and metavolcaniclastic rocks show that the volcanism recorded in the Apuan Alps and Elba Island (457±3 and 460±3 Ma, respectively; Fig. 6) was coeval with mid-Ordovician arc volcanism in Sardinia at 465±1 Ma (Oggiano et al., 2010) and almost coeval with the slightly older volcanism in Central Iberia (Montes et al., 2010). This period of intense magmatic activity is commonly interpreted as the widespread marker of the Rheic ocean subduction underneath the northern Gondwana margin (Gaggero et al., 2012; Helbing and Tiepolo, 2005; Oggiano et al., 2010). This volcanism had a strong impact on both immediate and delayed sediment production. Indeed, late Ordovician and middle Silurian metasediments from Elba Island show a unimodal zircon age distribution, entirely dominated by the Ordovician-Silurian volcanic activity (Oggiano et al., 2010; von Raumer et al., 2015). Furthermore, the mid-Ordovician signal is the most prominent in all the younger metasediments, rivalled only by the Variscan signal in post-Variscan sediments.

Post-Ordovician metasediments are characterised by a scarcity of zircons older than Ordovician, coupled with a different age distribution with respect to the Cambrian metasediments. The ca. 1 Ga and the 850-750 Ma zircon groups are much less pronounced, with more abundant zircons of ca. 2.2-1.8 Ga coupled with the oldest age found in Carboniferous metasediments from southern Tuscan basin (ca. 3.0 Ga). These features mirror those of metasediments from the Trans-Saharan belt, rather than those from eastern Africa or the Saharan Metacraton. Nevertheless, since the Adriatic plate was already separated from Gondwana during the deposition of these African units, these old zircons most likely represent recycled material from other European Variscan blocks. The syn- and post-Variscan metasediments are all characterized by Variscan and Ordovician signals of variable size. The Carboniferous Farma and the Permian Rio Marina formations are dominated by the Ordovician signal, and have prominent Pan-African populations, as well as a minor (Rio Marina) or very minor (Farma) Grenville-age signals. These two samples also share a modest Variscan-age population, suggesting they were deposited at the beginning of the Variscan cycle. In mainland Tuscany, the significance of the Ordovician component is higher in the youngest Verrucano with respect to the San Lorenzo Schists, possibly related to the onset of erosion of intrusive Ordovician rocks. On the other hand, the Verrucano from Elba Island shows a spectrum equivalent to the San Lorenzo Schists, suggesting a potential age of deposition slightly older than the Verrucano from mainland Tuscany. Overall, the syn- and post-Variscan metasediments are dominated by sources from the terranes detached from Gondwana (Ordovician igneous and Variscan crystalline rocks), so that the minor components of Pan-African and Grenville-age were likely derived from recycling of African detritus through European terrains.

7. Conclusions

The new U-Pb detrital zircon ages from the Tuscan mainland and Elba Island provide the first compelling evidence for the location and migration of the Tuscany block during the Paleozoic. Metasediments deposited from early Cambrian to middle Ordovician times mirror the age distributions of Morocco-Algeria basins, suggesting common western African sources. The different signature found for one Apuan Alps sample reflects the difference reported for coeval sediments of easternmost (Libya) versus central (Morocco-Algeria) northern Africa. These results indicate that the Tuscan block was part of the peri-Gondwana margin, likely close to the central-eastern northern Africa. The unimodal age distribution of Ordovician and Silurian volcano-sedimentary rocks reflects the massive mid-Ordovician volcanism (ca. 460 Ma) at the northern Gondwana margin. Following this momentous event, the sediment supply from African sources became very minor during the Carboniferous-Permian and thereafter. The syn- and post-Variscan metasediments are indeed dominated by detritus from the terranes detached from Gondwana (Ordovician igneous and Variscan crystalline rocks), along with minor components of Pan-African and Grenville-age that are likely derived from recycling of African detritus through European terrains. Overall, the main sources supplying the Tuscan Paleozoic basins were located in northern Africa during Cambrian-early Ordovician times and on the active peri-Gondwana magmatic arc during the middle-late Ordovician. During Variscan and post-Variscan times, detrital zircon sources were mostly located in European terrains, witnessing the shift of Tuscany from Africa to Europe.

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Figure Captions

Fig. 1. A: Present-day location of pre-Mesozoic basement areas of the Alps (orange), the Apennines (red) and the Variscan terrains (light brown; Neubauer, 2014). African Precambrian basement and Cambrian basins are also included (modified after Van Hinsbergen et al., 2011; Linnemann et al., 2011). Abbreviation of key localities: Aq-Aquitaine; Arm-Armorica; AS-Arabian Shield; Ca-Cantabrian terrane; CIb-Central Iberia; Co-Corsica; EAAO-East African-Antarctic Orogen; MC-French Central Massif; MS-Meseta; NS-Nubian Shield; OM-Ossa Morena; Py-Pyrenees; Sa-Sardinia; Si-Sicilian-Apulian basement; Sx-Saxothuringia; TS-Trans-Saharan belt; Tu-Tuscany; WL-West Asturian-Leonese zone. **B:** Overview map of Paleozoic formations in the northern Apennines, showing also the locations of the studied samples (modified after Franceschelli et al., 2004).

Fig. 2. Cathodoluminescence (SEM-CL) images of zircon crystals, selected to show the full range of obtained ages, from the Archean (THHS-07) to the late Paleozoic (THHS-10). For more complete image sets, see Supplementary Figure S1.

Fig. 3. Histograms and probability density plots of the U-Pb detrital zircon ages for metasediments from the Apuan Alps (Upper and Lower Quartzites-Phyllites), Monti Pisani Unit (Verrucano sequence and San Lorenzo Schists), and Monticiano-Roccastrada Unit (Farma Formation). Only grains with probability of concordance >0.05 and 2σ errors of the measured isotope ratios <20% are shown. n=number of zircon grains. The complete U-Pb data set is reported in Supplementary Table S1.

Fig. 4. Concordia diagram of SHRIMP U-Pb ages of the Apuan Alps Porphyroids. Twenty analyses yielded a common concordia age of 457±3 Ma (red ellipse). Inset: cathodoluminescence (SEM-CL) images of representative zircon grains from this sample.

Fig. 5. Schematic chart showing the inferred depositional ages of the Tuscan basement units in the framework of the main Paleozoic geodynamic events. Grey boxes: the lowermost boundary indicates the maximum depositional ages based on LA-ICP-MS U-Pb detrital zircon ages of the (meta)sedimentary rock; vertical extent indicates the possible time span for the deposition (see text for discussion). Red boxes: SIMS/SHRIMP U-Pb igneous crystallization ages of the metavolcanic rocks. Data from Elba Island from Sirevaag et al. (2016). Geodynamic events from literature (e.g. Nance et al., 2012; von Raumer and Stampfli, 2008; Oggiano et al., 2010; Gretter et al., 2015).

Fig. 6. Upper part: probability density plots reporting all the U-Pb detrital zircon ages from the studied samples. The samples are grouped according to their age of deposition and combined into one probability density curve when comparable. The vertical red bar shows the age of metavolcanic rocks from the Apuan Alps (this study) and Ortano Unit (Elba Island; Sirevaag et al., 2016). Lower part: igneous-metamorphic ages (black bars) and detrital zircon ages (grey bars) of potential source areas from pre-Cambrian African basement and Neoproterozoic-Cambrian sediments: WAC=West African Craton; TS=Trans-Saharan belt; SM=Saharan Metacraton; CTC=Congo-Tanzania Craton; ANS=Arabian-Nubian Shield; Sx=Saxothuringian-Boemian Massif; Ly=Libya Basin; Mo=Morocco Basin; VB=Volta Basin; ROP=Rheic Ocean subduction and Paleotethys opening; V=Variscan Basement (e.g. Linnemann et al., 2004; Linnemann et al., 2011; Meinhold et al., 2011, 2013; Pratt et al., 2015; Oggiano et al., 2010).

Table Caption

Table 1. The maximum depositional ages represent the oldest possible age of sedimentation, based on the youngest detrital zircons. The actual depositional age could be somewhat younger. See text for discussion.

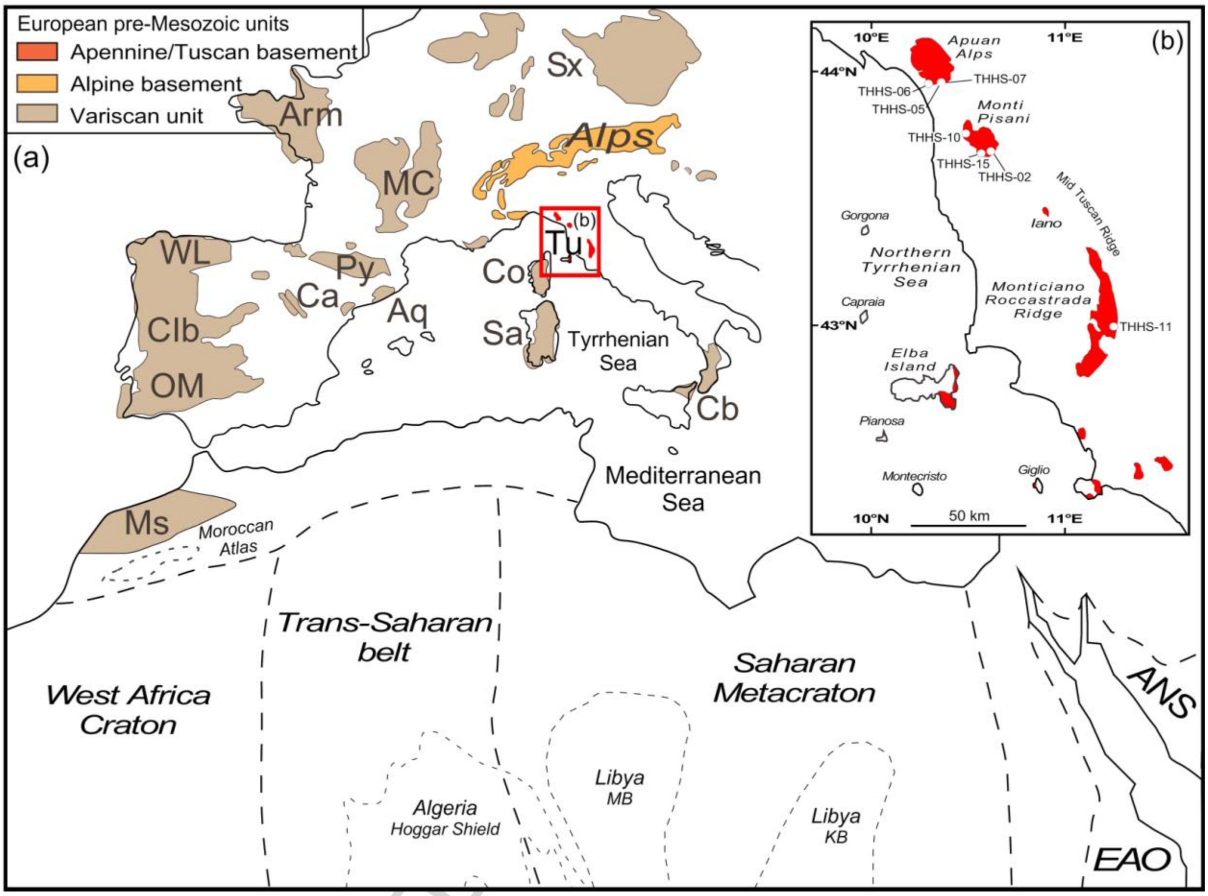
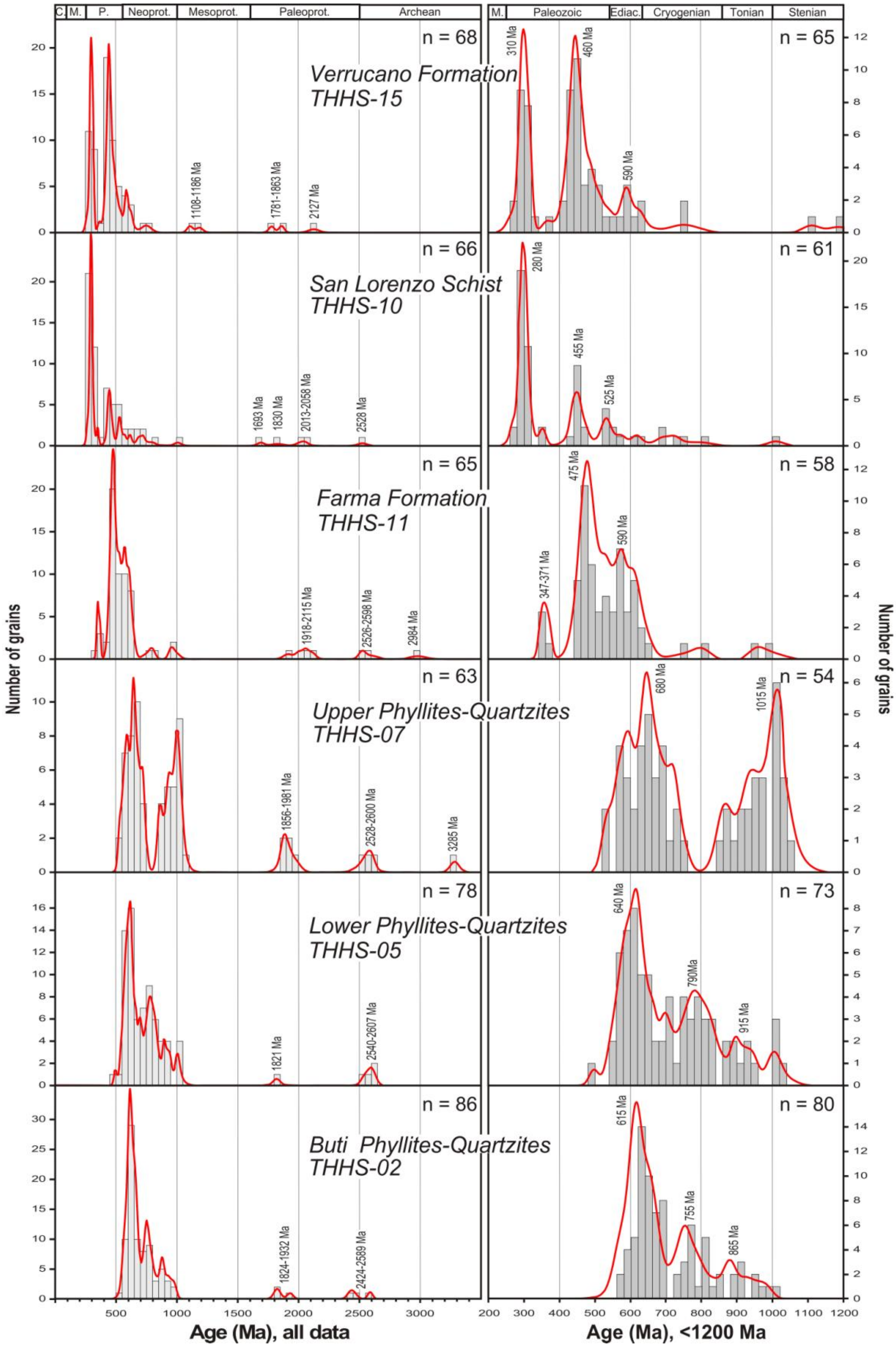

European pre-Mesozoic units
Apennine/Tuscan basement
Alpine basement
Variscan unit
(a)
Arm
Sx
MC
Alps
WL
Py
Ca
CIb
OM
Aq
Co
Tu
(b)
Sa
Tyrrhenian Sea
Cb
Mediterranean Sea
Ms
Moroccan Atlas
Trans-Saharan belt
West Africa Craton
Saharan Metacraton
Algeria
Hoggar Shield
Libya
MB
Libya
KB
ANS
EAO
10°E
11°E
44°N
43°N
10°N
Apuan Alps
THHS-07
THHS-06
THHS-05
Monti Pisani
THHS-10
THHS-15
THHS-02
Mid Tuscan Ridge
Gorgona
Iano
Northern Tyrrhenian Sea
Monticiano Roccastrada Ridge
Capraia
THHS-11
Elba Island
Pianosa
Montecristo
Giglio
50 km

Figure 1


THHS-10/003
THHS-10/059
THHS-10/015
THHS-11/039
263±24 Ma
291±13 Ma
353±17 Ma
355±19 Ma
THHS-15/060
THHS-06/027
THHS-06/032
THHS-11/033
448±19 Ma
449±28 Ma
452±25 Ma
453±32 Ma
THHS-05/017
THHS-05/014
THHS-02/020
THHS-11/032
529±37 Ma
579±29 Ma
608±26 Ma
624±26 Ma
THHS-05/089
THHS-10/061
THHS-15/016
THHS-07/003
1005±40 Ma
2016±66 Ma
2127±87 Ma
3285±71 Ma
100 μm

Figure 2



C. M. P. Neoprot. Mesoprot. Paleoprot. Archean
M. Paleozoic Ediac. Cryogenian Tonian Stenian
Verrucano Formation
THHS-15
n = 68
n = 65
1108-1186 Ma
1781-1863 Ma
2127 Ma
310 Ma
460 Ma
590 Ma
San Lorenzo Schist
THHS-10
n = 66
n = 61
1693 Ma
1830 Ma
2013-2058 Ma
2528 Ma
280 Ma
455 Ma
525 Ma
Farma Formation
THHS-11
n = 65
n = 58
1918-2115 Ma
2526-2598 Ma
2984 Ma
475 Ma
590 Ma
347-371 Ma
Upper Phyllites-Quartzites
THHS-07
n = 63
n = 54
1856-1981 Ma
2528-2600 Ma
3285 Ma
680 Ma
1015 Ma
Lower Phyllites-Quartzites
THHS-05
n = 78
n = 73
1821 Ma
2540-2607 Ma
640 Ma
790Ma
915 Ma
Buti Phyllites-Quartzites
THHS-02
n = 86
n = 80
1824-1932 Ma
2424-2589 Ma
615 Ma
755 Ma
865 Ma
Number of grains
Number of grains
Age (Ma), all data
Age (Ma), <1200 Ma

Figure 3

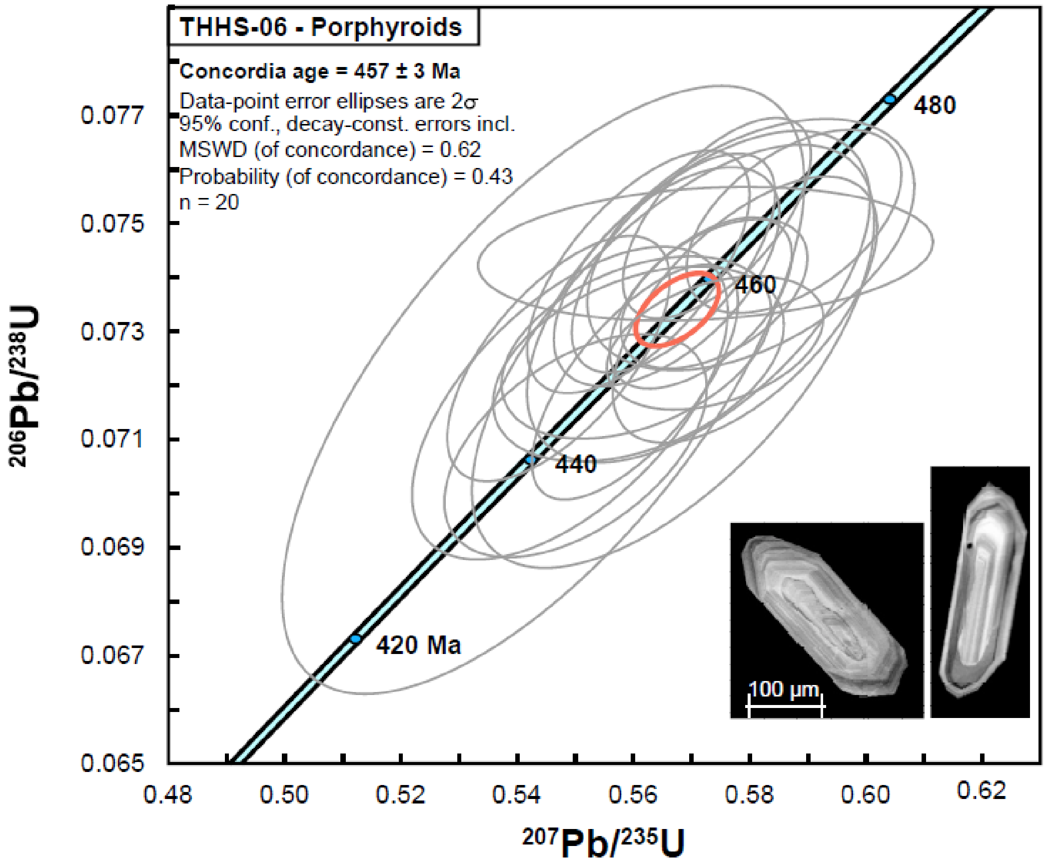

THHS-06 - Porphyroids
Concordia age = 457 ± 3 Ma
Data-point error ellipses are 2σ
95% conf., decay-const. errors incl.
MSWD (of concordance) = 0.62
Probability (of concordance) = 0.43
n = 20
480
460
440
420 Ma
100 µm
0.077
0.075
0.073
0.071
0.069
0.067
0.065
0.48
0.50
0.52
0.54
0.56
0.58
0.60
0.62
206Pb/238U
207Pb/235U

Figure 4

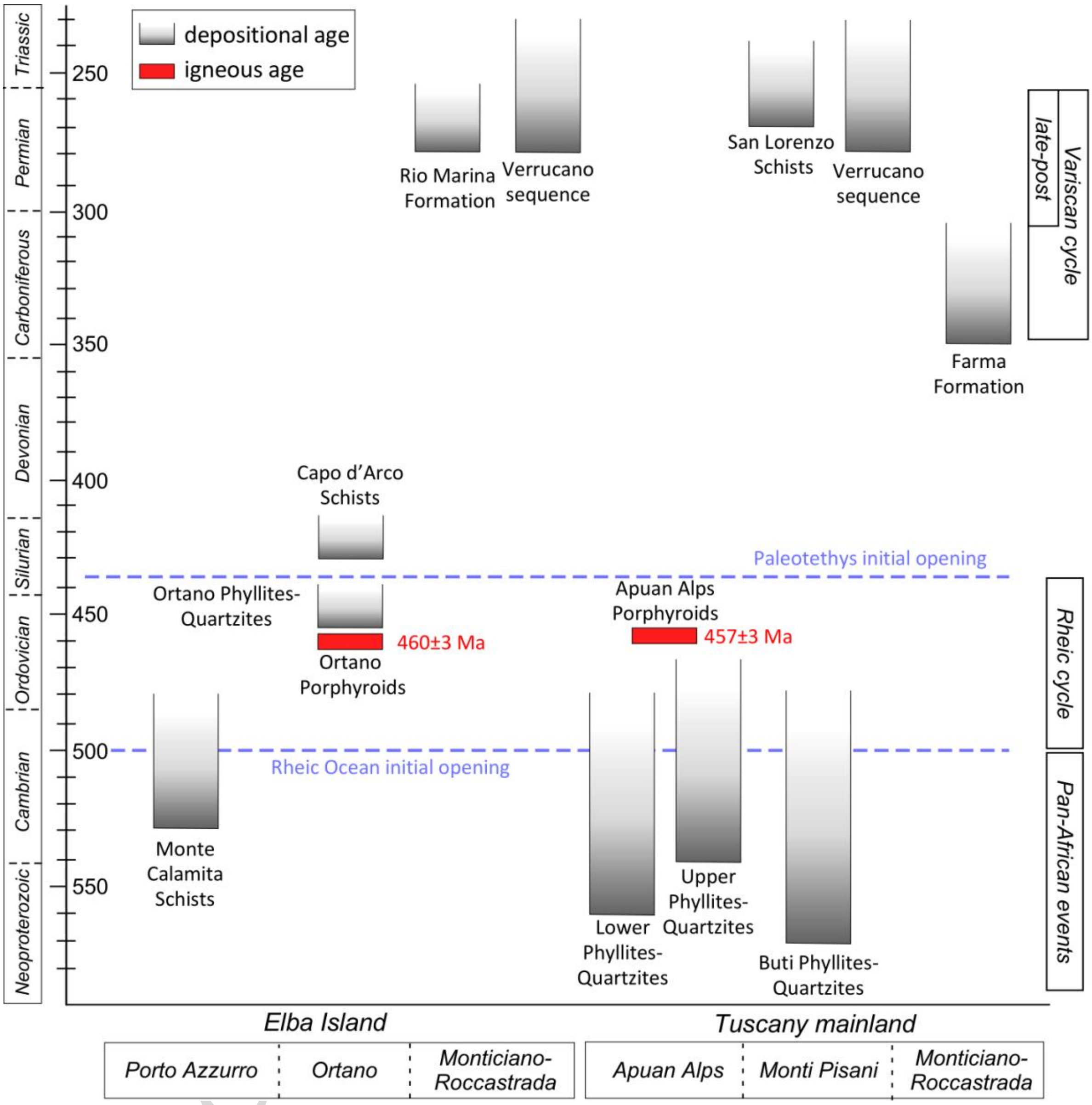

depositional age
igneous age
Triassic
Permian
Carboniferous
Devonian
Silurian
Ordovician
Cambrian
Neoproterozoic
250
300
350
400
450
500
550
Rio Marina Formation
Verrucano sequence
San Lorenzo Schists
Verrucano sequence
Farma Formation
late-post
Variscan cycle
Capo d'Arco Schists
Paleotethys initial opening
Ortano Phyllites-Quartzites
460±3 Ma
Ortano Porphyroids
Apuan Alps Porphyroids
457±3 Ma
Rheic cycle
Rheic Ocean initial opening
Monte Calamita Schists
Lower Phyllites-Quartzites
Upper Phyllites-Quartzites
Buti Phyllites-Quartzites
Pan-African events
Elba Island
Tuscany mainland
Porto Azzurro
Ortano
Monticiano-Roccastrada
Apuan Alps
Monti Pisani
Monticiano-Roccastrada

Figure 5

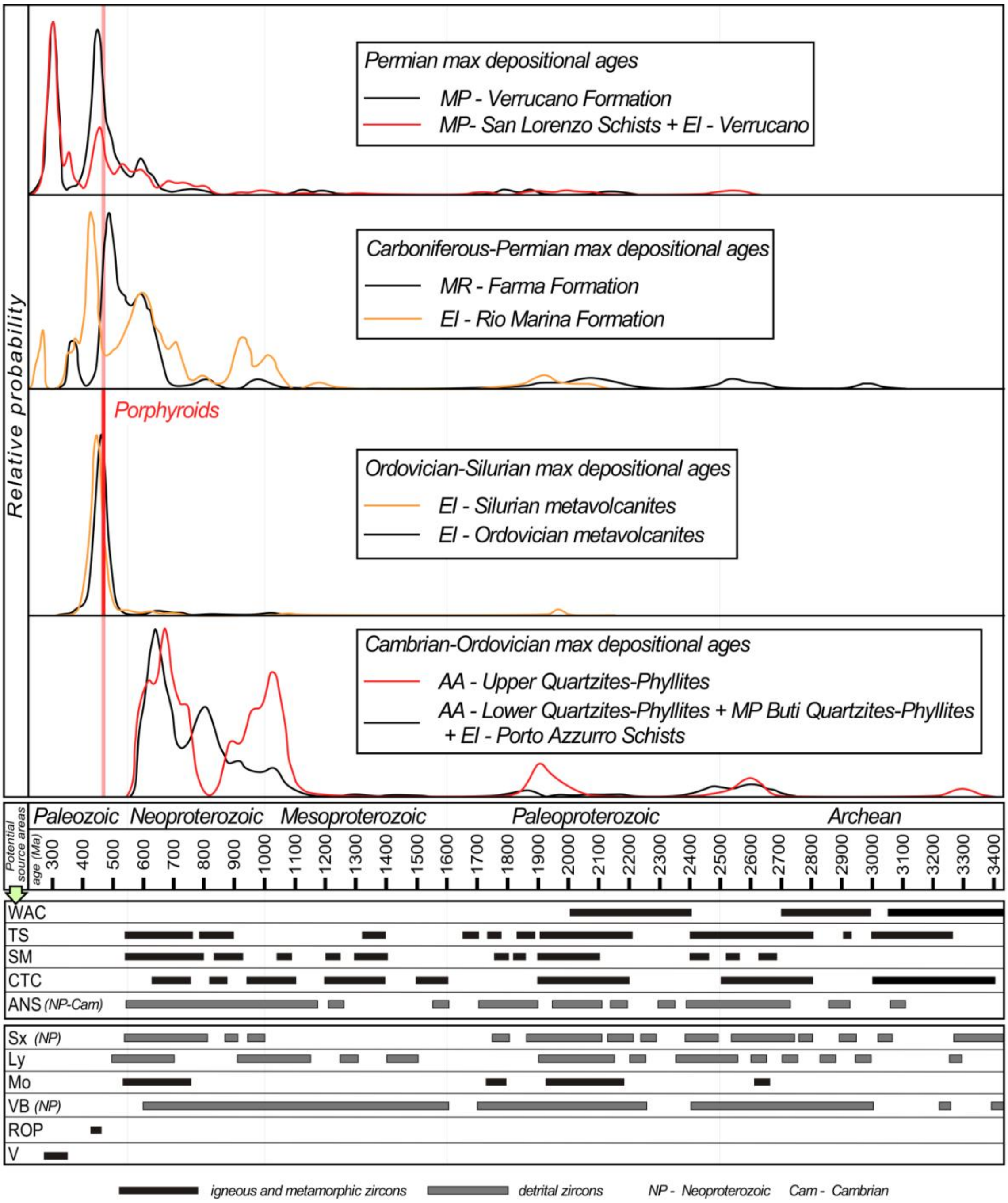
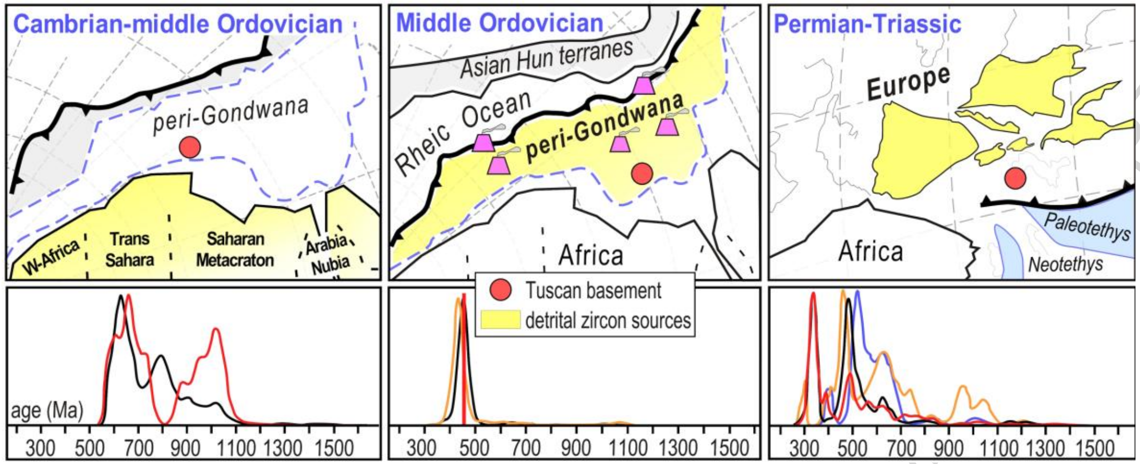

Relative probability
Permian max depositional ages
MP - Verrucano Formation
MP- San Lorenzo Schists + EI - Verrucano
Carboniferous-Permian max depositional ages
MR - Farma Formation
EI - Rio Marina Formation
Porphyroids
Ordovician-Silurian max depositional ages
EI - Silurian metavolcanites
EI - Ordovician metavolcanites
Cambrian-Ordovician max depositional ages
AA - Upper Quartzites-Phyllites
AA - Lower Quartzites-Phyllites + MP Buti Quartzites-Phyllites + EI - Porto Azzurro Schists
Paleozoic Neoproterozoic Mesoproterozoic Paleoproterozoic Archean
Potential source areas
age (Ma)
300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400
WAC
TS
SM
CTC
ANS (NP-Cam)
Sx (NP)
Ly
Mo
VB (NP)
ROP
V
igneous and metamorphic zircons
detrital zircons
NP - Neoproterozoic
Cam - Cambrian

Figure 6

Table 1. Summary of sample information and deposition age

Geographical area	Formation	Lithotype	Petrographic features	Samples GPS location	Stratigraphically inferred deposition age: age	Stratigraphically inferred deposition age: reference	Actual age of deposition (max depositional age)*
Monticiano-Roccastrada	Farma	meta-turbidite	Highly deformed, grain size from silty to sandy, calcite veins; Qtz+Ms±Chl±Cal±Ab(±Kfs)	THHS-11 N43°04'50" E11°16'50"	mid-late Permian late Carboniferous	Aldinucci et al., 2008a Pasini and Vai, 1997 Bagnoli et al., 1979	early-middle Carboniferous (ca. 350 Ma)
Monti Pisani	Verrucano	violet schists	Well foliated, phyllitic/silty; Qtz+Ms	THHS-15 N43°43'42" E10°31'56"	middle Triassic	Rau and Tongiorgi, 1974 Franceschelli et al., 1987	middle Permian-middle Triassic (ca. 280 Ma)
	San Lorenzo Schists	sandstone	Grey/yellow/brownish sandstone, two sets of joints, dm-scaled poor foliation, quartz veins; Qtz+Ms±Chl	THHS-10 N43°47'36" E10°28'16"	late Carboniferous-early Permian	Pandeli et al., 2004	middle Permian-middle Triassic (ca. 270 Ma)
	Buti Phyllites-Quartzites	phyllites	Well foliated, fine-grained, varying from quartzitic to phyllitic; lighter and darker coloured varieties; Qtz+Ms±Chl(±Bt)	THHS-02 N43°43'58" E10°34'03"	late Ordovician Silurian	Pandeli et al., 1994 Bagnoli et al., 1979	early Cambrian - middle Ordovician (ca. 570 Ma)
Apuan Alps	Porphyroids	porphyroids-porphyritic schists	withe/greyish, Kfs surrounded by Qtz+Ms±Ab±Kfs	THHS-06 N44°01'17" E10°17'13"	Permian early-middle Carboniferous Silurian middle Ordovician	Barberi, 1965 Vai, 1978 Bagnoli et al., 1979 Puxeddu et al., 1984	mid-late Ordovician (457±3 Ma)
	Upper Phyllites-Quartzites	phyllitic quartzites	Light coloured, fine-grained alternating sandstone and silt levels. Qtz veins and mesoscale folding; Qtz+Ms±Chl±Cal(±Tur)	THHS-07 N44°01'17" E10°17'13"	late Ordovician late Silurian-Devonian	Pandeli et al., 2004 Bagnoli et al., 1979	early Cambrian-middle Ordovician (ca. 540 Ma)
	Lower Phyllites-Quartzites	phyllites	Coarse-grained phyllitic quartzite, grey colour, sub-mm foliation; mainly Qtz alternating with a more mica-rich lithotype. Qtz+Ms+Chl+Ab(±Tur)	THHS-05 N44°01'49" E10°15'41"	Ordovician-middle Silurian late Cambrian-early Ordovician	Bagnoli et al., 1979 Puxeddu et al., 1984	early Cambrian-middle Ordovician (ca. 560 Ma)

*Age of deposition and maximum depositional age: see text for discussions



Graphical abstract

Research highlights

1. Detrital zircon ages define depositional age and provenance of Tuscan basement

2. Three main depositional events: early Cambrian, mid-Ordovician, late Paleozoic

3. Sediment sources shift from Africa to Europe after mid-Ordovician magmatism