New insights on the Petrology of submarine volcanics from the Western Pontine Archipelago (Tyrrhenian Sea, Italy)

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Commentato [RB1]: The title has been changed according to the Reviewer #1 indication

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Abstract

The Pontine Islands form a volcanic archipelago in the Tyrrhenian Sea. It consists of two edifices, the islands of Ponza, Palmarola and Zannone and the islands of Ventotene and Santo Stefano, respectively. The Archipelago developed during two main volcanic cycles in the Plio-Pleistocene: 1) the Pliocene episode erupted subalkaline, silica-rich volcanic units, which constitute the dominant products in the western edifice (Ponza and Zannone Islands); 2) the Pleistocene episode erupted more alkaline products, represented by evolved rocks (trachytes to peralkaline rhyolites) in the islands of Ponza and Palmarola and by basic to intermediate rocks in the eastern edifice (Ventotene and Santo Stefano Islands). In this paper we present new geochemical and petrological data from submarine rock samples collected in two oceanographic cruises and a scuba diving survey. The main result is the recovery of relatively undifferentiated lithotypes that provide further insights on the magmatic spectrum existing in the Pontine Archipelago, allowing modelling of the whole suite of rocks by fractional crystallization processes. New major and trace element data and thermodynamic constrains (by the software PELE) indicate the existence of three distinct

evolutionary trends corresponding to a HK calcalkaline series in the Pliocene, followed by a transitional and then by a shoshonite series in the Pleistocene. In particular, the transitional series, so far overlooked in the literature, is required in order to explain the genesis of several peralkaline felsic rocks recognized in the Archipelago. On the whole, the new geochemical data *i)* confirm the orogenic signature of the suites, *ii)* allow to rule out an anatectic origin for both subalkaline and peralkaline rhyolites and *iii)* indicate highly heterogeneous mantle sources, due to crustal components variously recycled in the mantle via subduction.

Keywords: Western Pontine Islands; submarine volcanic rocks; subduction-related magmas; fractional crystallization modelling; orogenic environment.

1. Introduction

In the study of volcanic archipelagos or islands marine geology offers an essential contribution to the reconstruction of the character and evolution of the volcanism. Despite intrinsic difficulties in sampling, the definition of the extents and characters of submarine volcanics at a regional scale leads to a better comprehension of the structure of volcanic edifices that are for the most part submerged and cannot be fully defined by studying only the subaerial, often more recent, counterpart. These considerations are valid for the volcanism of the Pontine Archipelago (Tyrrhenian Sea, Italy) that has been previously interpreted only on the basis of subaerial samples, mainly consisting of a limited distribution of lithologies. The gap of knowledge has been filled in the framework of the CARG (Geological cartography; Geological Survey of Italy-ISPRA) and MaGIC (Marine Geohazard along the Italian Coasts; http://www.magicproject.it) projects, which included the exploration of the seafloor surrounding the western Pontine Archipelago. In particular, scientific marine cruises provided new bathymetric and morphological maps and the collection of the new submarine samples that are reported in this paper.

The Plio-Quaternary volcanic activity that caused the built up of the Pontine Islands is strictly related to the geodynamic processes involved in the opening of the Tyrrhenian Sea. At present, the most accepted model to account for the tectono-magmatic setting of the Tyrrhenian basin and its eastern margin is based on the evolutionary stages of a subduction process. Subduction began during the Eocene with the northwest-dipping subduction of Mesozoic oceanic lithosphere. This was followed by continental collision and sinking of the Adria microblock under the European plate (Beccaluva et al., 1987; 2005; Carminati et al., 1998; Faccenna et al., 2004; Lustrino et al., 2009). In this framework, the opening of the Tyrrhenian Sea can be interpreted as result of back-arc extensional activity, which mainly occurred during the late Miocene-Pliocene and continued in the Quaternary (e.g., Peccerillo, 1999; Lustrino, 2000), linked to an increased steepening of the subducted lithosphere, which led to extensional deformations in the eastern margin of the upper plate. These extensional phases, which acted in different ways in the northern and southern Tyrrhenian domains are associated to the wide range of magmatic products emplaced during the Plio-Quaternary (Doglioni et al., 1999; Argnani and Savelli, 1999; Savelli, 2000; Beccaluva et al., 1987; 2005).

In particular, the five volcanic islands forming the Pontine Archipelago made up of a western and an eastern volcanic edifice, were built during two eruptive cycles (e.g., Barberi et al., 1967; Bellucci et al., 1999). The first cycle developed during Pliocene with the emplacement of rhyolites, which constitute the dominant products in Ponza and Zannone islands in the western volcanic edifice. The second cycle developed during Pleistocene with the emplacement of evolved more alkaline to peralkaline products (trachytes to rhyolites) in the south-eastern part of Ponza and Palmarola Islands (western volcanic edifice) and with the eruption of more mafic products (basalts to trachytes) in the eastern volcanic edifice comprising the islands of Ventotene and Santo Stefano (Conte and Dolfi, 2002; Cadoux et al., 2005; Paone, 2013).

The Pliocene rhyolitic units have been related, in terms of age and serial affinity, to the Pliocene calcalkaline volcanism of the Tyrrhenian Sea (Argnani and Savelli, 1999), as well as to some products of the Tuscan magmatic Province (TMP, Pinarelli et al., 1989 and reference therein; Conte and Dolfi, 2002; Cadoux et al., 2005). The products of the Pleistocene cycle, cropping out in the western islands of Ponza and Palmarola have been considered as the first episode of K-alkaline magmatism, which successively developed southeastward in the eastern Pontine Islands and more in general in the Roman Magmatic Province (RMP) including the Campanian Region (e.g. Ischia and Procida Islands and the Phlegrean fields -Vesuvius area; e.g., Beccaluva et al., 1991). Geochemical features among and within rock series of RMP were generally interpreted to represent a subduction-related affinity (Conte and Savelli, 1994; Conticelli et al., 2002; De Astis et al., 2004; Cadoux et al., 2005; Avanzinelli et al., 2009) and most authors explain the observed compositional heterogeneity by the variable influence of crust-derived (subduction-related) components (Mazzeo et al., 2014 and references therein). In this scenario, further complexity is probably given by disequilibrium melting of composite (veined) mantle sources, as proposed by Gaeta et al. (2016).

Commentato [RB2]: Reviewer #1. Lines 127-134. In the discussion of different magma sources for western Pontine and Campanian volcanism, the reference to the Roman Magmatic Province, to which neither the Pontine nor the Campania provinces belong, should be better explained.
An introductory sentence explaining the general framework of the volcanism in central Italy has been added. In this new sentence, we stated that the volcanism in the Pontine can be considered the incipit of the K-alkaline volcanism, that subsequently developed widely in the Roman Magmatic Province defined (by Washington 1906) as the large region of potassium-rich volcanism, extending from southern Tuscany to the Campania area.

In this work we present new geochemical and geochronological data on volcanic products sampled during the investigation of submarine portions of the western Pontine islands. For the first time, relatively undifferentiated rocks were recovered offshore whereas similar lithologies were not recognized by earlier studies based only on products from subaerial outcrops. The new findings allow us to better refine the petrogenesis of different magma series of the Pontine Islands, using fractional crystallization models that link the new relatively undifferentiated compositions to those of the more abundant evolved rocks.

Commentato [RB3]: Reviewer #1. Lines 142-143. Misleading - quoted discussion is totally missing in the paper. This possibly has repercussions on the title (See discussion and conclusions). Coherently with the change of the title, the last sentence of the introduction has been deleted.

2. Geological setting

The Pontine Archipelago consists of five major volcanic islands divided into two groups related to two distinct volcanic edifices: Ponza, Palmarola and Zannone on the northwest and Ventotene and S. Stefano to the southeast (Fig.1). A small volcanic body, i.e., La Botte rock representing the neck of an eroded volcanic vent, is also present at ca 12 km east from the western edifice (Fig. 1).

On the whole the Islands form a 30 km-long chain, running parallel to the central sector of the Eastern Tyrrhenian Margin, about 30 km offshore the coast between the Circeo Promontory and the Gulf of Gaeta (Central Italy). This location roughly corresponds to the boundary between Central and Southern Apennines onland (De Rita et al., 1986; Bruno et al., 2000). The islands lie on a basement deeply affected by the Plio-Pleistocene extensional deformations which was reconstructed on the basis of seismic data (Zitellini et al., 1984; Marani et al., 1986; Marani and Zitellini, 1986) and structural analysis (De Rita et al., 1986; Malinverno and Ryan, 1986). The extensional tectonics gave rise to: a) a very steep NW-SE trending continental slope; b) a NE-SW elongated structural high, dividing two major areas of sedimentation, i.e. the Palmarola and Ventotene intra-slope basins; c) an intense magmatic activity developed from late Pliocene to late Pleistocene (Barberi et al., 1967; Cadoux et al., 2005 and references therein) that caused the building of the whole Archipelago.

The western islands are located on the Ponza-Zannone structural high, forming a NE-SW ridge that separates the Palmarola and Ventotene basins. On the Ponza-Zannone high Pliocene volcanic products were erupted from fissure vents. The eastern edifice on the contrary is a large strato-volcano, emplaced at the center of the subsiding Ventotene basin and bounded southward by NW-SE regional tectonic structures (Marani and Gamberi, 2004).

Commentato [RB4]: Reviewer #1. Lines 170-174. Not clear
The structural setting where the western and the eastern Pontine Islands are located, has been better clarified, as required by the reviewer.

2.1. Western volcanic edifice

In the *western islands* volcanism developed diachronously in a complex volcanic edifice in both submarine and subaerial environment (De Rita et al., 1986). In these islands, the Pliocene volcanic cycle (4.2-2.9 Ma; Cadoux et al., 2005) produced a large effusion of rhyolite lava from extensional fissures. This activity was characterized by the emplacement of lava domes, dykes and hyaloclastites in a submarine environment, which gave rise to most part of Ponza Island. At Zannone, acidic volcanic domes and lava flows of chemical composition similar to that of Ponza Pliocene volcanites were emplaced in a subaerial environment on a substrate made up of sedimentary and metamorphic units, which are locally exposed (De Rita et al., 1986). The absolute age of rhyolites outcropping at Zannone is unknown as the pervasive hydrothermal alteration affecting the rocks prevented chronological investigations. However, the chemical similarity with the Ponza rhyolites, as well as the morphological and lithological linkage between Ponza and Zannone (Conte et al., 2015) suggest an almost coeval extrusion of magma in the two islands.

In the isle of Palmarola, although field observations suggest onset of volcanism in the Pliocene (Carrara et al., 1986; Vezzoli, 1999), K-Ar datings provided by Cadoux et al. (2005) indicated an Early Pleistocene age (1.64-1.52 Ma) during which Palmarola was entirely built owing to the emplacement of a large, submarine hyaloclastite unit, subsequently intruded by domes of alkali-rhyolitic composition. This event marks the beginning of the Pleistocene volcanic activity in the Western Islands, resumed after a pause of about 1.5 Ma.

The Pleistocene activity progressed with the local emission of comendite lava (1.2 Ma, Savelli, 1987) and with the emplacement of trachytic products (i.e., M.te Guardia lava dome) in the southern part of Ponza (1.2-0.9 Ma; Savelli, 1987; Bellucci et al., 1999; Cadoux et al., 2005), where the resumption of volcanism coincides with the transition from a submarine to a subaerial environment. This is indicated by explosive activity due to hydromagmatic events (from small centers fed by trachytic magma) and two major pyroclastic explosions (pumice flow events; Bellucci et al., 1997, 1999; Vezzoli, 1988) carrying juvenile lava clasts and syenitic blocks (Barberi et al., 1967; Savelli, 1987; Conte and Dolfi, 2002). The final phase of the Ponza volcanic activity is represented by several trachytic islets forming relicts of a system of necks and dykes, emplaced offshore SE Ponza. Among these, Le Formiche shoals have been dated at 0.9 Ma (Bellucci et al., 1999). Moreover, trachytic and one phonolitic lava (the latter also representing a new finding among submarine sampling) also crops out at the neck of La Botte rock (Fig. 1), i.e. the small emerged summit of a volcano dated 1.2 Ma (Savelli, 1987), which represents the link with the eastern Pontine volcanism.

2.2. Eastern volcanic edifice

Commentato [RB5]: The paragraph concerning the "eastern volcanic edifice" has been simplified eliminating some inconsistencies, as required by Reviewer #1.

The *eastern Pontine islands* (Ventotene and S. Stefano) are the emerged portions of the caldera rim of a large strato-volcano rising about 700 m from the sea-floor (Barberi et al., 1967; Metrich et al., 1988; Bellucci et al., 1999; Casalbore et al., 2014). The two islands belong to the same volcanic edifice (Ventotene volcano) and display a similar chronological sequence of the outcropping units, which were erupted during the 0.9 and 0.1 Ma time span (Metrich et al., 1988; Bellucci et al., 1999). The Ventotene volcano was initially characterized by effusive activity followed by a huge explosive phase, which ended with the caldera formation. Pre-caldera lava sequence, emplaced on a volcaniclastic

Commentato [RB6]: Reviewer #2. 0.5 Ma or 0.2 Ma? In line 231 after 0.53 Ma is cited the same paper of Bellucci et al., 1999. What date should be considered?
The paragraph concerning the "eastern volcanic edifice" has been simplified eliminating some inconsistencies and the dates have been corrected.

substrate, is about 100 m thick and comprises a number of trachybasaltic lava flows, with two episodes of quiescence.

The composition of the volcaniclastic products ranges from latitic to trachytic and phonolitic, although juvenile lava clasts of basaltic composition (Congi, 2001) occur within the main pyroclastic units.

3. Sampling and analytical methods

The marine area offshore the western Pontine archipelago was investigated through seafloor sampling and bathymetric investigation in the years 2001 and 2006 (c/o "Martino" and "S. Silverio" aboard National Research Council R/V Urania). Eleven dredge samples were collected along the Pontine continental slope and close to La Botte rock (Fig. 2).

Forty rock samples were collected in shallow-water (Fig. 2), offshore the western islands by scuba diving during marine investigations carried out for geological mapping purposes (CARG Project, Geological Survey of Italy-ISPRA), on rocky outcrops identified by bathymetric data.

Sampling sites and microscopic features of samples from the different surveys are reported in Appendix Table A.1

The shallow-water submarine samples mainly come from rocky shoals at depths less than 30-40 m (Ponza-Zannone ridge, the western and south-eastern sides of Ponza, the northern and southern part of Palmarola). The recovery of volcanic samples from depth greater than 50 m was scarce (some rocky shoals south of Ponza, SW Palmarola and near La Botte rock) since the rocky substrate is extensively covered by encrusting algae and corals hindering rock dredging. Deep-water submarine samples were dredged on morphological reliefs of the Pontine continental slope (down to about 3400 m water depth) (Fig. 2).

Major (including the Loss On Ignition, LOI) and trace elements were measured on selected samples by ICP-AES and ICP-MS, respectively, at Activation laboratories, Ancaster, Canada. Details on the chemical analysis methods can be found at the site: http://www.actlabs.com.

Mineral phases and glass were analysed by a 4-spectrometer Cameca SX50 electron microprobe with an accelerating voltage of 15 keV and 15 nÅ beam current at C.N.R.-Istituto di Geologia Ambientale e Geoingegneria (IGAG) laboratory of Rome, using the ZAF correction procedure. A focused beam was used for all minerals, whereas a 10 μm broad beam was used for glasses to minimize volatilization of sodium.

To perform ^{40}Ar/^{39}Ar dating, three selected samples were crushed and biotite crystals (size fraction of 250–300 μm) were separated using heavy liquids (bromoform). Aliquots of biotite, which at the scale of optical microscopy resulted unaffected by the presence, even minimal, of chlorite intergrowth were irradiated for two hours at the TRIGA nuclear reactor in the Applied Nuclear Energy Laboratory of the University of Pavia. The neutron flux was monitored with the biotite standard FCT-3 (age of 27.95 Ma - Baksi et al., 1996). Irradiated aliquots were analyzed by step-heating technique with infrared laser (wavelength 1064 μm) defocused to ~ 2 μm, at the ^{40}Ar/^{39}Ar dating laboratory, C.N.R.- Istituto di Geoscienze e Georisorse (IGG) of Pisa. More details on analytical procedures are described in Di Vincenzo et al. (2003, 2004). The analytical results are presented in Table A.3, with errors expressed as 2σ.

Sr and Nd isotopic compositions were determined at the CNR-IGG of Pisa on rock powders leached in hot 6.2 M HCl for 45 min and rinsed several times in ultraclean water. Measurements were obtained by a Finnigan MAT 262 V multi-collector mass-spectrometer following separation of Sr and Nd by conventional ion-exchange procedures. Measured ^{87}Sr/^{86}Sr ratios were normalized to ^{86}Sr/^{88}Sr = 0.1194, ^{143}Nd/^{144}Nd ratios to ^{146}Nd/^{144}Nd =

Commentato [RB7]: Reviewer #2. In table several samples have LOI higher than 3 and some of them have LOI ca. 4. These samples are altered and I would not use for classification, particularly in the TAS diagram, where major elements are recalculated on anhydrous basis.
The effect of alteration processes on the presented geochemical analyses has been taken into consideration and discussed in chapter 3.

Commentato [RB8]: The part of the text dealing with the Ar/Ar method has been synthesized, as required by the Reviewer #1.

Commentato [RB9]: Reviewer #2. I am not an expert on this field, however, two among the dated samples have high LOI. If they are altered, as it seems, I am not convinced about using the biotite for dating.
Some additional details have been included to explain that in these samples biotite was fresh and suitable for Ar-Ar dating.

0.7219. Further correction was not necessary, as during the collection of isotopic data, replicate analyses of the Sr SRM-NIST 987 ($SrCO_3$) isotopic standard gave an average $^{87}Sr/^{86}Sr$ value of 0.710253 ± 13 (2σ, N = 30), whereas the Nd isotopic standard JNdi-1 (Tanaka et al., 2000) gave an average $^{143}Nd/^{144}Nd$ value of 0.512098 ± 8 (2σ, N = 25) that are close to the values notionally accepted. The external reproducibility 2σ is calculated according to Goldstein et al. (2003).

Commentato [CP10]: Reviewer 2#. Authors should write if the measured ratios, particularly Nd ratios, have been normalized for the Standards. Furthermore, are the authors sure that leaching was enough for removing alteration in the shallow and deep water samples. Some authors preferred to analyze minerals instead of bulk rocks (see Brown et al., 2014, Contrib. Min. Petr.), or performing a strong leaching, several times, to attempt to reduced the effect of alteration.
In the revised text we have specified that correction of Sr-Nd isotopes was not necessary because during the analytical sessions the standards yield values closely approaching those notionally accepted in the literature.

4. Rock description and classification

Most shallow-water submarine samples display massive and homogeneous microstructures similar to those of the rhyolitic lava domes and dikes in Ponza and Palmarola Islands. Lava samples collected in the SE sector of Ponza, near Le Formiche shoals and La Botte rocks resemble those of M.te Guardia lava unit described by Conte and Dolfi (2002). The main petrographic features of the studied samples and related chemical analyses are presented in the Tables A.1-A.2.

These rocks invariably preserve the typical magmatic textures and seem minimally affected by sea-water interactions that would promote pervasive formation of secondary minerals such as serpentine (on olivine), chlorite and actinolite (on pyroxenes) and epidotes together with a marked albitizitation of plagioclase that are not observed.

Commentato [CP11]: Reviewer #2. See previous comment on the possibility to erroneously interpret the obtained trends is samples are altered. TAS: I would not include samples with high LOI. They may cause erroneous interpretation.
On the basis of what explained at the first sentences of this section of the revised text, we think that the reported compositions are not significantly affected by secondary processes.

The presented analyses reflect the magmatic character of the rocks and, in spite of the relatively high LOI values, the effects of secondary interactions with sea water seem to be irrelevant on the major element budget. In fact, immobile elements such as titanium show a restricted range of variation, and the significant TiO_2 enrichment observed in palagonitization processes induced by seawater (see discussion provided by Staudigel and Hart, 1983) are not observed at all.

Coherently, the presented analyses display correlation of the main oxides that would not be expected in samples significantly altered by seawater. This evidence suggests, as already proposed by Cadoux et al. (2005), that most of the fluid content of the rocks from the Pontine Islands is juvenile and not linked to secondary processes. Similar high LOI content (sometimes > 5 %) have been observed in other suites of rocks from circum-Mediterranean volcanic districts in which seawater alteration has not been envisaged (Beccaluva et al., 2013). Analogously, the trace elements are characterized by a relatively regular distribution and by the lack of scattered patterns that would be expected in rocks significantly affected by seawater interactions.

The samples plot in the Total Alkalis vs. Silica (TAS; Le Maitre et al., 1989; Fig. 3a) and SiO_2 vs. K_2O (Peccerillo and Taylor, 1976¸ Fig. 3b) diagrams mainly in the field of the subalkaline (high-potassium calcalkaline, HKCA), and K-alkaline (shoshonite) magma series partially overlapping the compositions of volcanites outcropping in the western islands.

The *shallow water submarine samples* (hereon "offshore" samples, Fig. 2) recovered between the Ponza and Zannone Islands mostly consist of subalkaline rhyolites, whereas those sampled SE of Ponza, near Le Formiche and La Botte rocks (Fig. 2) are trachytes. This shows the close similarity between the subaerial and submarine substrate in this sector of the Archipelago. On the contrary, samples offshore the island of Palmarola show a wider compositional variability with respect to the lithologies cropping out on land. These samples consist of highly evolved and nearly peralkaline rhyolites (see 4.2 section) similar to those exposed in the island but also include new findings represented by: *i*) nearly peralkaline trachytes and *ii*) an association of subalkaline trachytes, trachydacites and rhyolites cropping out in the south-west area (Fig. 2 and Fig. 3).

Commentato [RB12]: Reviewer #1. Lines 326-328. The “nearly peralkaline trachytes” similar to those on the islands are then included in the new findings. Please clarify.
The finding of new lithotypes have been better specified.

The *deep water submarine samples* (hereon DWS) are clasts of lavas or massive–lava blocks. Those of subalkaline composition include a prevalence of rhyolites but also subordinate basalts and andesites. DWS of alkaline composition are mostly classified as trachytes; however, a relatively undifferentiated sample of latite (i.e. a trachyandesite having $Na_2O/K_2O<2$) composition was also found (Fig. 3a) as well as a sample of phonolitic composition recovered near La Botte rock (Fig. 3a and Fig. 2).

5. Petrography and Petrochemistry

5.1. Subalkaline rock type

The andesites reported in this study represent the first finding of less evolved subalkaline rocks recognized in the western Pontine Archipelago. From the petrographic point of view they are not homogeneous and display different textures. Sample DS11BISB (Fig. 4a), is a typical porphyritic, weakly glomeroporphyritic andesite (Table A.1). Plagioclase phenocrysts (An_{62-90}) are usually oscillatory and patchy zoned or display sieve textures. Abundant orthopyroxene (Wo_3, En_{63}, Fs_{34}) and subordinate clinopyroxene (Wo_{39-43}, En_{41}, Fs_{16-20}) phenocrysts are also present. Olivine is occasional, while Fe-Ti oxides occur both as microphenocrysts (ilmenite) and microlithes in the groundmass (Ti-magnetite). In the intergranular groundmass the interstices between plagioclase microlites are occupied by grains of pyroxene and iron-titanium oxides.

Sample DS15B is a nearly aphanitic andesite, with phenocryst content lower than 5% by volume (Fig. 4b; Table A.1). Phenocrysts are represented only by plagioclase (An_{76-80}) displaying peculiar coronas at their border (Fig. 4b). Microphenocrysts of plagioclase (An_{70}, on average), clinopyroxene (Wo_{41}, En_{40}, Fs_{19}, on average), orthopyroxene (Wo_3, En_{61}, Fs_{36}, on average) and oxides (Ti-magnetite) also display reabsorbed shapes and reaction/overgrown rims. In the intersertal matrix, the interstices between plagioclase and opaque grains are occupied by glass of rhyolite compositions (Fig. 3a; Tab. A.2).

The subalkaline trachyte, trachydacite and rhyolite samples collected offshore (SW of Palmarola), and some of the subalkaline rhyolites from deep water setting are porphyric (porphyritic index, P.I. $\geq$15 vol %) with phenocryst assemblage dominated by sieve textured plagioclase (An$_{37-67}$) and minor amount of idiomorphic biotite, horneblende and rare potassium feldspar (Or$_{67}$). Other subalkaline rhyolites from deep water setting are SiO_2-rich (SiO_2>71 wt%) and almost aphyric (P.I. $\leq$5 vol %), with the rare phenocrysts consisting of homogeneous alkali feldspars (Or$_{73}$, on average). Taken as a whole, the petrographic and chemical features of differentiated samples are comparable to those reported for the analogous subaerial lithologies (Conte and Dolfi, 2002; Cadoux et al., 2005), although the occurrence of submarine trachytes and trachydacites enlarge the compositional field of subalkaline lithotypes towards less evolved compositions.

Commentato [RB13]: Reviewer #1. Lines 385-386. Unclear-rewrite.
The phrase has been rewritten.

In the SiO_2-K_2O diagram (Peccerillo and Taylor, 1976; Fig. 3b), all the subalkaline rocks roughly belong to High-K calcalkaline rock series (HKCA) and are characterized by a similar Na_2O/K_2O ratio (0.7, on average) and a metaluminous character (ASI ~ 1; Table A.2). In representative Harker diagrams (Fig. 5), these subalkaline rocks define rough trends of decreasing Al_2O_3, CaO, MgO and increasing K_2O at increasing silica content.

Commentato [CP14]: Reviewer #2. For the samples characterized by high LOI the ratio between these elements can be influenced by alkali loss.
On the basis of what explained at the first sentences of section “Rock description and classification”, we think that the reported compositions are not significantly affected by secondary processes. we think that the reported compositions are not significantly affected by secondary processes.

In the incompatible trace-element patterns (Fig. 6), these rock types display an "orogenic" imprint, being characterized by significant P, Ti, Nb-Ta negative anomalies and by enrichments of large ionic radius elements (LILE - Rb, Th, U, K) and light rare earth (LREE - La, Ce), compared to high field strength elements (HFSE) and heavy rare earths.

5.2. Transitional and K-alkaline rock-types

The DWS basalt (TD4B) shows a weakly vesicular structure and a seriate and weakly glomeroporphyritic texture (Figs. 4 c, d; Table A.1). The phenocryst assemblage consists of plagioclase, minor clinopyroxene and scarce olivine; the intersertal groundmass is made up of prevailing plagioclase, subordinate clinopyroxene and Fe-Ti oxides, plus scarce amount of glass. Although plagioclase appears early in the crystallization sequence, this sample is discriminated from the basic rocks of HKCA series by the significant absence of orthopyroxene. Whole rock geochemical data indicate that the TD4B basalt has low SiO_2 content (46.9 wt%) coupled with a relatively high Na_2O/K_2O ratio (1.6) that in the TAS diagram plots close to the subalkaline and alkaline series discrimination line, exhibiting a “transitional” (mildly alkaline) character. It shows analogies with the composition of the basalts recovered in the site 651 of the Leg107, i.e. from a zone of the Vavilov basin where basaltic rocks have an age of ca 2Ma (Beccaluva et al., 1990).

The latite DS74V sampled by deep-water dredging also belongs to this transitional series. It contains phenocrysts of alkali-feldspar, plagioclase, green clinopyroxene, minor biotite and magnetite set in a light-coloured glass matrix. To the same transitional series are linked the nearly peralkaline trachytes and rhyolites recovered in both a deep water setting and in shallow water, mostly offshore Palmarola Island. These are among the most evolved rocks of the whole Pontine Archipelago (Fig. 3a) and include highly evolved trachytes and rhyolites characterized by aphanitic to weakly porphyritic textures, in which the main phenocryst phase (never exceeding 10% by volume) is represented by a sodium-alkali feldspar (Or_{30-42}) (Table A.1). Such samples closely resemble the highly evolved trachytes (ST trachyte in Conte and Dolfi, 2002) and the peralkaline rhyolites cropping out on shore at Palmarola and SE Ponza Island (Conte and Dolfi, 2002; Cadoux et al., 2005). It is important to note that the trachytes found in association with peralkaline rhyolites in the

Commentato [CP15]: Reviewer #2. This sample has LOI ca. 5 when recalculated SiO_2 increases more than the other less abundant oxides.
We understand the perplexity of the Reviewer. TD4B has ca 4.8 of LOI. However, it is the only basic sample pertaining to this series and is characterized by distinctive petrographic feature strongly indicating that it is not an HKCA or a K-alkaline product. We don't see petrographic evidence of pervasive alteration (no serpentine, chlorite, epidote, calcite, sulphates) and we therefore think that its geochemical peculiarity really reflects the magmatic character and is not related to secondary processes.

submarine substrate offshore Palmarola Island, represent the first recovery of highly-evolved trachytes recognized as lavas. On shore, similar rocks were only recognized as xenoliths included in less evolved trachytes at Ponza (Conte and Dolfi, 2002). These highly differentiated alkaline trachytes and rhyolites attain consistently high Na_2O/K_2O ratios, which mark the change towards nearly peralkaline character (0.9 <AI <1; Table A.2). In the trace-elements distribution patterns, such nearly peralkaline rocks are characterized by comparatively lower LILE/HFSE and LREE/HFSE ratios, with respect to alkaline trachytes (Fig. 6b), and by the lack of Ta negative anomaly and a very discrete Nb negative anomaly. Moreover, the strong negative anomalies in K, Ba, Sr (and Eu) reflect the protracted fractionation of feldspars..

Other samples collected from both deep and shallow water settings are trachytes (TAS classification, Fig. 3a) which, according to the K_2O-SiO_2 diagram (Peccerillo and Taylor, 1976; Fig. 3b), belong to the shoshonite rock-series (Fig. 3b). All these trachytes consist of porphyritic lavas characterized by the presence of alkali-feldspar phenocrysts (Or_{48-44}), subordinate clinopyroxene (augite, Wo_{47} En_{39} Fe_{14}, on average) and scarce biotite within a pilotassic-textured groundmass composed of feldspar ± opaques ± mafic microlithes (Table A.1). Due to the lack of modal plagioclase they are classified as alkali-trachytes (Innocenti et al., 1999) and closely resemble trachytes outcropping in the SE sector of the Ponza Island (named light trachyte, LT, in Conte and Dolfi, 2002).

Finally, the deep-water phonolite sample (D29), collected offshore La Botte rock seems to be an end-member of the suite which, although characterized by higher alkalinity, show petrographic similarities with the more abundant alkaline trachytes. It is characterized by phenocrysts of alkali-feldspar (5-10 vol%, Or_{56-60}) and accessory biotite and clinopyroxene, set in a light-coloured pilotassic-textured matrix. In the Harker diagrams of Fig. 5, the

Commentato [CP16]: Reviewer 2#. This sample has LOI ca. 5. It is true, but in our view is important to emphasize its existence because it is the unique sample of this lithology in the western Pontine.

submarine trachytes and the phonolite of the shoshonite series plot near the fields of their subaerial counterparts.

In the incompatible trace element patterns, all these rocks show orogenic signatures similar to those described above for the subalkaline rock-types (Fig. 6). However, with respect to subalkaline types, most of them are characterized by higher absolute concentration of most of trace-elements, by less pronounced troughs in HFSE (mostly Nb and Ta) and more pronounced troughs of Sr and Ba, which indicate a higher degree of feldspar fractionation.

6. Thermodynamic modelling of magma evolution

The new samples analyzed in this study are important to investigate the genesis of the volcanism in the Pontine Archipelago and to test previous hypotheses, which gave different emphasis to distinct petrogenetic processes, such as crystal fractionation from mantle-derived basic magmas (Conte and Dolfi, 2002) and partial melting at crustal levels (i.e. anatexis; Paone, 2013)

Commentato [RB17]: This part has been rewritten as required by the Reviewer #1.

The new samples presented in this study, including scarcely differentiated products appear crucial to confute/test petrogenetic hypotheses that propose the anatectic origin of both calcalkaline and peralkaline rhyolites (Paone, 2013). For this reason, both the new results obtained from the new submarine samples and data retrieved from the literature have been critically revaluated using a thermodynamically based fractional crystallization model (PELE; Boudreau, 1999; See supplementary Figs. 1 and 2) with the approach described by Natali et al. (2011, 2013).

The andesite DS15B properly corrected by addition of 10 % of olivine (Fo 88), approaches the composition proposed for “primary” andesites in subduction related magmatic arcs delineated by the world-wide compilation of Kelemen et al. (2014). This computed melt could represent a suitable parental composition for the subalkaline (H-K calcalkaline) series

Commentato [CP18]: Reviewer 2#. Line 499. LOI>3
See previous comments.

of the Pontine archipelago. Starting from this initial composition, various theoretical Liquid Lines of Descent (LLD) were calculated by PELE and compared with the real rhyolite compositions observed in the studied area. Best fit was obtained for a pressure of 0.2 GPa at the QFM oxygen fugacity buffer. According to the model olivine crystallization occurred at 1230 °C and was followed by plagioclase (pl) at 1055 °C, clinopyroxene (cpx) at 1000 °C, magnetite (mt) at 990 °C, apatite (ap) at 980 °C, orthopyroxene (opx) at 950 °C, ilmenite (ilm) at 900 °C, alkali feldspar (af) at 740 °C. The resulting LLD (Supplementary Fig. 1a) was controlled by removal of: 12% ol, 35% pl, 5% mt, 4% cpx, 4% opx, 2% ap, 1% ilm, 3% af, ultimately leading at 700 °C to a residual liquid fraction (F) of 34% with rhyolitic composition closely comparable with those observed. The existence of such a differentiation processes is corroborated by the mentioned observation of glass having rhyolite composition in the andesite DS15B. The modelling reasonably fits also the incompatible trace element distribution (Supplementary Fig. 1b).

Modelling by PELE of the basalt TD4B gives a significantly different LLD (Supplementary Fig. 2a), which evolves toward peralkaline felsic compositions. Best fit was obtained at pressure of 0.3 GPa and oxygen fugacity buffered to the QFM. According to the model ol crystallization occurred at 1280°C, followed by pl at 1190°C, cpx at 1160°C, mt at 1040°C, ap at 1020 °C ilm at 1010 °C and finally af at 870°C. The relative LLD was controlled by removal of: 19% ol, 47% pl, 12% cpx, 3% mt, 1% ilm, 4% ap, 6% af, leading first to residual peralkaline trachyte (F=17%, at 850 °C) and finally to peralkaline rhyolite compositions (F= 9%, at 700 °C). Results show analogies with what observed in the modelling of other suites of magmas worldwide (e.g., Peccerillo et al., 2003, 2007; Natali et al., 2011; Renna et al., 2013), which invariably show that the attainment of peralkaline compositions necessarily requires, as a precursor, a parental melt having a transitional character. Trace element modelling indicates that to fit the entire spectrum of observed

Commentato [CP19]: Reviewer 2#. Line 499. LOI>3
See previous comments.

Commentato [RB20]: The references have been added as required by the Reviewer #1.

compositions it is necessary to change the input parameters and in particular the H_2O content, to take into consideration the reciprocal stability field of plagioclase and clinopyroxene (Supplementary Fig. 2b). We note that the relatively undifferentiated latite DS74V lies on the trend joining the transitional basalt to peralkaline compositions.

As concerns the third, and more potassic (shoshonite) series, in agreement with what previously suggested (Fedele et al., 2003; Paone, 2013), we consider for thermo-chemical modelling a primitive starting composition taken from known shoshonitic basalts of Ventotene. Accordingly, considering the sample AVT23 (D'Antonio et al., 1999) as a parental melt, modelling by PELE gives a LLD (Supplementary Fig. 2a) which evolves toward trachyte compositions. Best fit was obtained at a pressure of 0.15 GPa and oxygen fugacity buffered to the QFM; according to the model ol crystallization occurred at 1140 °C, closely followed by cotectic crystallization of cpx and pl at 1130 °C, mt at 1030 °C, ap at 940 and finally af at 830 °C. The relative LLD was controlled by removal of: 9% ol, 41% pl, 20% cpx, 6% mt, 2% ap, 2% af, leading to residual trachyte (F=23%, at 810 °C), which is also characterized by trace element distribution comparable with that of the observed rocks (Supplementary Fig. 2c).

Note that some samples having trachyte compositions in the TAS diagram of Supplementary Fig. 2a plot in an intermediate position between the two modelled LLD, and could be either ascribed to the transitional or to the shoshonite trends, or - to be more precise -would require a further fractionation trend. The same consideration arises from the observed phonolite composition (D29) that to be properly modelled would require a more K-alkaline (silica under-saturated) parental melt.

In synthesis, the entire spectrum of the Pontine magmas recall (at least) three distinct magmatic series having parental melts characterized by slightly different silica-saturation, that ultimately led to totally distinct differentiated products along well separated LLD.

7. Sr-Nd isotope geochemistry

The wide range of isotopic compositions recorded in the studied rocks could be, at least in part, attributed to interactions with seawater. However, the trace element diagrams highlighted the lack of scattered anomalies, thus suggesting that the studied rocks preserved their pristine geochemical budget. Samples have been preliminary leached with 6.2M HCl, a procedure that according to Nobre Silva et al. (2010) is efficient to remove the isotopic signature of "secondary" processes in submarine volcanic rocks, leaving the pristine magmatic isotopic signature. The rock-types of the HKCA series sampled from the SW Palmarola offshore display a narrow range of Sr-Nd isotopic compositions (^{87}Sr/^{86}Sr 0.71063-0.71076 and ^{143}Nd/^{144}Nd 0.51215-0.51218, respectively), approaching, although with slightly lower ^{143}Nd/^{144}Nd ratios, isotopic compositions of the coeval, pliocenic subaerial HKCA rhyolites cropping out in Ponza Island (Fig. 7). Among the less evolved lithologies of this series, one andesite closely resembles the Sr-Nd isotopic features of the more evolved rocks, whereas the second one (DS11BISB) displays ^{87}Sr/^{86}Sr the more radiogenic values of the whole series (Fig. 7). This observation demonstrates that the extremely radiogenic Sr (and unradiogenic Nd) isotopic values of this series were characteristic of the parental melts and do not relate to crustal contamination during magma ascent toward the surface. This statement is obvious considering that these andesites contain more Sr (380-450 ppm) than the crustal rock of the circum-Tyrrhenian area (usually less than 100 ppm; Mazzeo et al., 2014) and that they tend be similar or even more radiogenic than the associated rhyolites. According to recent papers, extreme isotopic values can be obtained directly by partial melting of highly metasomatized mantle sources related to subduction processes (Mazzeo et al., 2014; Gaeta et al., 2016).

The DWS transitional basalt TD4B and latite DS74V display significantly lower ^{87}Sr/^{86}Sr (0.70593-0.70787) and higher ^{143}Nd/^{144}Nd (0.51241-0.51253) respect to HKCA rocks,

Commentato [RB21]: We revised and clarified the whole section according to the reviewer suggestions, with particular regard to the possible effect of crustal contamination processa s required Reviewer #1.

Commentato [RB22]: Reviewer #1. Line 566. 400ppm is similar to 450ppm. Have the authors verified that no modifications in the isotope composition are produced in magmas from the CA series by crustal contamination?
We modified this sentence specifying (according to the recent paper by Mazzeo et al., 2014) that most metasedimentary rocks that should be present in the local upper crust contain less than 100 ppm of Sr. The slight isotopic variation observed in the CA series cannot be ascribed to crustal contamination because one of the andesites has Sr isotope composition more radiogenic that the evolved rocks!

Commentato [CP23]: Reviewer #2. On this argument authors may found some information in Gaeta et al., 2016 (Lithos).
This paper has been cited.

providing the fingerprint of an independent transitional series that has been already envisaged by the described thermo-chemical modelling.

The very high Sr isotopic compositions of the peralkaline rhyolites ($^{87}Sr/^{86}Sr$ up to 0.71217) can be attained with very low amount of crustal contamination during magma ascent toward the surface (less than 1 % of contamination with the crustal basement; Mazzeo et al., 2014). This is due to the negligible Sr content of such differentiated rocks for which any contribution from assimilated crust would favor a drastic increase of $^{87}Sr/^{86}Sr$ in the melt.

Commentato [CP24]: Reviewer #2. Samples from this series are those displaying the largest isotopic variation.
We explained in the revised text that peralkaline rhyolites having very low amount of Sr (about 10 ppm) are extremely sensitive to crustal contamination. We did a mass balance calculation specifying that less than 1% of assimilation of crustal rocks of the basement is enough to explain the observed isotopic variations.

Within alkaline rocks, the primitive Ventotene basalt assumed as parental melt of this series has respectively lower and higher $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ (0.70709 and 0.51242; D'Antonio et al., 1999) than the more evolved submarine products. Indeed, among the latter the trachytic submarine samples from Le Formiche and La Botte rocks display $^{87}Sr/^{86}Sr$ in the range of 0.70898-0.709668 and $^{143}Nd/^{144}Nd$ ratios of 0.51227 (Fig. 7). These isotopic values approach the range of subaerial trachytes ($^{87}Sr/^{86}Sr$ 0.70850-0.70881; $^{143}Nd/^{144}Nd$, 0.51236-0.51237) and imply 2-3% of crustal contamination with the rocks of the basement (Mazzeo et al., 2014), during magma ascent toward the surface.

Commentato [CP25]: Reviewer #2. This trend could either due to alteration. Leaching is not always able to remove alteration and samples result enriched in radiogenic Sr. Furthermore, the same trend could be due to source enrichement by slab derived fluids and melts (Eg. D'Antonio et al. 2007; Mazzeo et al., 2014).
At begin of section 7 we added a sentence which explains that the preliminary leaching of the samples is considered efficient to remove any effect of alteration processes, as demonstrated by Nobre Silva et al. (2010). The final sentence of the chapter states that in our view most of the observed variations are related to metasomatic fluids/melts that affected the mantle sources, citing the pertinent paper of D'Antonio et al. (2007).
Reviewer #2.. Crustal contamination should able to modify both isotope ratios. However, authors could try to madel such a process in order to verify their hypothesis.
Considering that the Nd isotopic ratio is relatively constant in the studied suites of rocks we decided to test the extent of crustal contamination taking into consideration only the Sr isotopes. Results indicate the extent of crustal contamination is invariably low (less than 2-3).

In any case, in the whole suite of rocks from the Pontine Archipelago (and surrounding regions), the significant lack of isotopic values corresponding to those observed in “anorogenic” magmas of the surrounding areas (Wilson and Bianchini, 1998; Bianchini et al., 2008), invariably demonstrates that the magmas in both volcanic cycles of the Pontine archipelago had an orogenic signature. Accordingly, the radiogenic Sr isotopic composition and unradiogenic Nd isotopic composition were influenced by recycling - via subduction - of crustal components that forms fluids and/or melts that metsomatized the mantle sources (D'Antonio et al., 2007 and references therein).

8. Geochronology

Commentato [RB26]: Reviewer #1. Short, 6 lines of description. There is no mention of why these 3 samples were chosen - this should be added here. It would emphasize the new recognition of Pliocene lavas from Palmarola Island and probably correlate and date the small Pliocene outcrop on the island itself.
In the revised text we explained why these particular samples from the Palmarola surroundings were chosen for geochronology analyses. In particular, the aim was to verify if the compositional analogies with the Pliocene products from Ponza were coupled with a comparable age. The criteria of selection took into consideration the presence of a phase suitable for dating (biotite) and its freshness. Moreover, the three samples are representative of three distinct compositions. The section has been implemented with a sentence that discusses the importance of the new data for the debate concerning the age of volcanism in Palmarola. We also clarified meaning of the small Pliocene outcrop.

Commentato [CP27]: Reviewer #2. Two of the dated samples have high LOI. Is the biotite fine for dating such samples?
It is now specified that dating has been carried out on fresh biotite.

$^{40}Ar/^{39}Ar$ dating has been performed on fresh biotite from three submarine rocks sampled in the SW Palmarola offshore, where an association of volcanites of HKCA series, similar to the Pliocene rhyolites from Ponza and Zannone area have been found for the first time. The three samples are representative of the subalkaline trachytes, trachydacites and rhyolites found in the area. $^{40}Ar/^{39}Ar$ dating was performed to test if a chronological link exists between these subalkaline offshore volcanites and those of Ponza-Zannone. The values reported in the Appendix Table A.3 show that $^{40}Ar/^{39}Ar$ ages for subalkaline trachyte S31 and trachydacite S27 are concordant being, respectively, 3.86±0.05 Ma and 3.88±0.06 Ma. The rhyolite S49 appears slightly older (4.01±0.06 Ma). On the whole these new data fit the age range of 2.9-4.2 Ma recorded in HKCA Pliocene rhyolites of Ponza (Savelli, 1987; Cadoux et al., 2005).

These findings are an important contribute to the debate concerning the age of the volcanism in Palmarola Island that has been attributed to both Pliocene and Pleistocene age by De Rita et al. (1986) and Vezzoli (1999) and entirely to Pleistocene age by Codoux et al. (2005). The new data demonstrate that Pliocene rocks occur in the submarine substrate of Palmarola. These rocks are analogous to the Pliocene rocks of Ponza, both from the petrological and geochronological point of view.

9. Discussion

Commentato [RB28]: The Discussion has been reorganized as required Reviewer#1.

The petrographic-geochemical characterization of submarine rocks sampled in the area surrounding the western Pontine Islands provides new constraints on the age, distribution and composition of the Pontine Archipelago magmatism.

Key results are the finding, in the SW sector offshore the Palmarola Island, of HKCA rocks that are similar to those outcropping in the islands of Ponza and Zannone. $^{40}Ar/^{39}Ar$

geochronology performed on three of these samples indicates a possible temporal link, confirming a common Pliocenic age; this result is relevant for the general volcanological setting of Western Pontine, since Palmarola was previously known to be constituted only by Pleistocene products (Cadoux et al., 2005). Moreover, these new evidences, together with the identification of HKCA products on the Pontine continental slope and the occurrence of similar products in the Campanian Plain boreholes (e.g. Barbieri et al., 1979; Albini et al., 1980), significantly extends the distribution of calcalkaline magmatism in the southern Tyhrrenian area. In addition, the finding of a phonolite, sampled for the first time near La Botte rock, establishes a correlation with the magmatism of the eastern islands, where this rock type is common.

Of particular relevance is the recovery of scarcely evolved rock-types thought to be the primitive/intermediate lithologies representing parental compositions for the more evolved rock types. The occurrence of a spectrum of rocks ranging from basic to variously evolved felsic types supports the early petrogenetic hypothesis of Conte and Dolfi (2002) relating the highly evolved HKCA and peralkaline rhyolites to high degrees of crystal fractionation starting from less evolved magmas. The new data confirm the existence of two independent rock series, HKCA and shoshonitic that are demonstrated by LLD modelling, which link parental melts to evolved lithotypes. We also propose the existence of a third series, so far overlooked in the literature, necessary to explain the petrogenesis of peralkaline differentiates which cannot be linked genetically to the above mentioned series. Models demonstrate that the genesis of the peralkaline silicic melts is due to protracted feldspars-dominated fractionation starting from parental melts that are transitional basalts, confirming the inferences of many other studies (e.g., Peccerillo et al. 2003; White et al. 2009; Renna et al., 2013). This transitional series is particularly represented in the Island of Palmarola

Commentato [RB29]: Reviewer #1. Apart from Piocene outcrop.
In the "Geological setting" chapter we clarified that the "Pliocene outcrop" was a submarine sedimentary deposit useful for stratigraphic reconstrution and not a volcanic outcrop.

that was previously considered exclusively formed by extremely differentiated K-alkaline rocks (Conte et al., 2015).

The crucial role of crystal fractionation as the predominant process, and the minor role of anatexis and/or significant crustal contamination is confirmed by the isotopic fingerprint of the analyzed rock samples. For example, similar Sr-Nd isotope ratios in the HKCA andesites and rhyolites are a feature that links them to common magma sources, which were metasomatized by subduction-related fluids. A further evidence for the predominant role of fractional crystallization is provided by the composition of interstitial glass found in the andesites that approaches the composition of the evolved rhyolites (Fig. 3a, b).

As concerns the transitional series, in spite of a wide isotopic range, we demonstrated that the main differentiation processes is provided by crystal fractionation. The extremely low Sr contents (as low as 10 ppm) and high Rb/Sr of peralkaline lavas cannot be attained by the assimilation of the crustal rocks of the circum-Tyrrhenian basement. In fact, at such low levels of Sr, contributions from assimilated crust > 1% would favor a drastic increase of Sr content and $^{87}Sr/^{86}Sr$ in the melt.

Commentato [RB30]: Reviewer #1. Author should verify this by modelling assimilation+fractional crystallization. However, if there is no assimilation feldspar and the host matrix should be in isotopic equilibrium.
We agree with the reviewer, as it would be very interesting to compare Sr-Nd isotope ratio of whole rock with those of separated minerals. This could be the aim of a future development of the research on the Pontine volcanism.

The existence of the transitional series does not imply a shift toward an intra-plate geodynamic setting because occurrences of peralkaline rhyolites have been recorded in other subduction-related volcanic contexts (Smith et al., 1977; Morra et al., 1994). In contrast to the trace element distribution of the HKCA and shoshonitic rock series, which display clear orogenic signature, the evolved rocks of the transitional series mimic an intraplate-like fingerprint (Fig. 7; Conte and Savelli, 1994; Cadoux et al., 2005). However, tectono-magmatic interpretations based on trace element distribution of evolved magmatic rocks are largely inappropriate; this is particularly true for extremely differentiated peralkaline rocks. Indeed, apart from the important role of feldspar removal, the absolute trace-element abundances in these melts may largely depend on the fractionation of minerals that selectively incorporate specific trace elements. In this light, Peccerillo et al. (2003, 2007 and references therein) and Marks et al. (2004 and references therein) demonstrated that trace element partition coefficients are strongly influenced by phases abundance and relationship during alkaline-peralkaline magma evolution. These authors showed that the removal of mafic minerals (specifically amphibole and clinopyroxene) control the LREE/HREE ratio and also the concentrations of HFSE in evolving magmas. These authors also showed that HFSE partitioning appears to be mainly related to changes in the crystal site parameters of host clinopyroxene and amphibole crystals, which vary from Ca–Mg-dominated members to Na–Fe^{3+} dominated members during peralkaline magma evolution (cfr. Conte and Dolfi, 2002). This may explain the different enrichment of HSFE during the magma evolution leading to peralkaline compositions. Moreover, in late stages of crystallization of peralkaline magmas massive feldspar removal induces a progressive increase of all the elements except than those incorporated by the feldspar (Ba, Sr, Eu^{2+}), inducing the peculiar trends of the studied differentiated peralkaline rocks (Fig. 6). Furthermore, in addition to extreme fractional crystallization, the influx of F-rich fluids may act to greatly modify the composition of peralkaline rhyolitic magmas as attested by the presence of F-bearing phases (i.e., arfvedsonite, annite) in erupted products (Conte and Dolfi, 2002; Mbowou et al., 2012).

Commentato [RB31]: This part has been semplified, as required Reviewer #1.

Of note, the shift from calcalkaline to variable K-alkaline rock series recorded in the Pontine Islands has been also observed in several other volcanic districts of the circum-Tyrrhenian region (Beccaluva et al., 2005, 2013; Conticelli et al., 2009a, 2009b, 2015; Mazzeo et al., 2014) and largely reflects the compositional variability of sources, due to progressively more marked metasomatic events following sediment recycling within the upper mantle via subduction. The evolution of orogenic arc volcanism from calcalkaline (s.l.) up to shoshonite products is generally ascribed to the mode of subduction, which becomes progressively steeper in the advanced stages of convergence (Beccaluva et al., 2013), with potassic products becoming preponderant in the late collisional stages. The extensional tectonics occurring in the southern Tyrrhenian domain induced the collapse of crustal blocks that prevented an easy magma ascent. Further petrological evolution and mode of volcanic emplacement were controlled by the tectonic stresses occurring in the upper plate, as proposed worldwide in other study-cases (Bursik, 2009; Gudmundsson, 2012; Chaussard and Amelung 2014). In fact, the regional tectonics occurring in the southern Tyrrhenian domain induced the collapse of crustal blocks that favored the evolution of deep-sourced dykes, sheets and sills in crustal magma chambers, where (especially in the western sector of the Archipelago) basic magmas were forced to pond and stagnate. This ultimately resulted in widespread differentiation processes generating the felsic rocks observed in the western Pontine Islands that were invariably erupted by fissure vents.

Commentato [RB32]: Some inferences originally reported in the conclusions have been moved in the chapter "Discussion" and properly implemented as suggested Reviewer #1.

10. Conclusions

Commentato [RB33]: Some inferences originally reported in the conclusions have been moved in the chapter "Discussion" and properly implemented and the mention to the importance of physical parameters during magma evolution has been removed as it is out of scope, as suggested Reviewer #1.

This paper reports the findings of an extensive underwater investigation carried out offshore the Pontine Archipelago. Analyses of new offshore samples provide new geochemical data that, integrated with those from the literature, do not fit interpretations which relate the genesis of the Pontine magmas either to pervasive anatectic processes, or to hypotheses which propose a significant change of the geodynamic setting during the Plio-Pleistocene period. The most striking features resulting from this study can be summarized as follow:

1) in the relatively small tectonic environment of the Pontine Archipelago and surroundings (up to the Campanian Region), both Pliocene and Pleistocene volcanic products are

representative of orogenic magmas emplaced in a subduction context, with metasomatized mantle sources conforming to those of converging continental margin basalts;

2) basic rocks with slightly different compositions, in terms of alkali-silica ratio and potassic character, were the precursors of three series of Pontine magmas having HKCA , transitional and shoshonitic affinities. The differentiation of these parental melts led ultimately to totally different evolved (felsic) lithotypes.

This would mean that, in the Pontine Archipelago, starting from parental magmas having small differences in major element compositions and common orogenic signatures (a spectrum of basalts straddling the subalkaline–alkaline boundary), differentiation processes gave rise to distinct evolved rocks characterized by diverse phases relationship and relative proportions which, in turn, produced different trace element distribution patterns in the more evolved rocks. In particular, the discovery of a transitional series allows to explain the petrogenesis of the peralkaline rhyolites of Ponza and Palmarola, the genesis of which was very debated in the literature (Conte and Dolfi, 2002; Cadoux et al., 2005).

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Figure captions

Fig. 1. Location of the Pontine Archipelago, (central Tyrrhenian Sea). The black rectangle indicates the study area. Eastern Pontine Islands (Ventotene and S. Stefano) are also reported along with other important volcanic edifices of neighboring areas: Alban Hills, Roccamonfina, Phlegrean Fields, Ischia Island.

Fig. 2. Shaded relief map and bathymetry of the study area with location of seafloor samples.

Fig. 3. Classification diagrams of submarine volcanic rocks of Pontine archipelago: (a) Total alkalis vs. silica (TAS; Le Maître et al., 1989); (b) K_2O vs. silica (Peccerillo and Taylor, 1976). Alkaline/subalkaline limit in (a) is after Irvine and Baragar (1971). Major elements analyses recalculated on a volatile-free basis. In the diagrams subaerial volcanic rocks from Ponza and Palmarola Islands (Conte and Dolfi, 2002) and from Ventotene Island (D'Antonio et al.,1999; Congi, 2001), are also reported. HKCA: High-Potassium Calcakaline; T: Transitional; SHO: Shoshonite; DWS: Deep water samples; TH: Tholeiite.

Fig. 4. Cross-polarized photographs of thin sections showing the textures and mineralogy of deep water calcalkaline andesites DS11BISB (a) and DS15B (b) and of transitional basalt TD4B (c, d).

Fig. 5. Harker diagrams for submarine volcanic rocks of the Pontine archipelago and surrounding areas. Data sources and abbreviations as in Figure 3.

Fig. 6. Spider diagrams for submarine volcanic rocks of Pontine archipelago normalized to primitive mantle (Sun and McDonough, 1989). (a) High-K calcalkaline rock series; (b) transitional rocks and c) shoshonite series rocks. Abbreviations as in Figure 3.

Fig. 7. $^{87}Sr/^{86}Sr$ vs $^{143}Nd/^{144}Nd$ diagram for submarine volcanic rocks of Pontine Archipelago. Others data sources and abbreviations as in Figure 3.