



Extreme isotopic variation documents extensional tectonics in arc magmas from Methana, Greece

M.A. Elburg^{a,b,*}, I. Smet^b, P. Van den haute^b, F. Vanhaecke^c, M. Klaver^{d,e}, T. Andersen^{a,f}

^a Department of Geology, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa

^b Department of Geology, Ghent University, Krijgslaan 281 – S8, Gent BE9000, Belgium

^c Department of Analytical Chemistry, Ghent University, Gent BE9000, Belgium

^d Department of Geology and Geochemistry, Vrije Universiteit, De Boelelaan 1085, Amsterdam 1081 HV, the Netherlands

^e School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Bristol BS8 1RJ, United Kingdom

^f Department of Geosciences, University of Oslo, PO Box 1047, Blindern N-0316, Norway

ARTICLE INFO

Article history:

Received 22 April 2018

Accepted 24 August 2018

Available online 31 August 2018

Keywords:

Subduction

Aegean Arc

Crustal contamination

Radiogenic isotopes

Extension

ABSTRACT

New Sr-Nd-Hf-Pb isotope data for volcanic rocks from the peninsula of Methana (South Aegean Active Volcanic Arc, Greece) show a wide variation, and more 'enriched' isotopic signatures (e.g. elevated $^{87}\text{Sr}/^{86}\text{Sr}$ at 0.705–0.709) than those of other active Aegean volcanic centres, all located on thinner crust. The data set is best explained by polybaric AFC processes, with contaminants similar to country rocks and xenoliths, showing moderately high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and with isotopically more evolved lower crust, similar to the pre-Alpine Ios basement. Pb isotope ratios show some minor influence of assimilation of fluid-altered volcanic cumulates. Intermediate lava domes with mafic enclaves were formed during periods of compression, whereas an extensional period saw the deposition of explosive products of bimodal composition, with the more felsic deposits showing the most pronounced influence of crustal assimilation. The latter likely represent stalled magmas from an earlier compressional period, which were remobilised and flushed out by ascending mafic magmas during extension. Recognition of these volcanological, geochemical and isotopic characteristics of deposits associated with extensional tectonics in a modern arc will enable us to use these criteria to infer paleo-tectonics from older volcanic deposits.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The role of regional tectonics in the style of volcanism and the composition of the erupted products at convergent plate margins has been increasingly recognised in recent years (Defant, 1992; Elburg et al., 2004; Shinjo, 1999; Straub and Zellmer, 2012; Zellmer, 2009). The effects are most noticeable in complicated convergent settings, such as near-collisional situations, where the arrival of small continental fragments at the trench influences the stress regime of the arc as whole. The Aegean arc is such a system, and for this study we concentrate on the volcanic peninsula of Methana (Greece; Fig. 1). Methana is a nominally active volcano in the westernmost part of the South Aegean Volcanic Arc, with a magmatic record extending from the mid-Pliocene to 230 BCE (Pe-Piper and Piper, 2013). It is a typical continental arc volcano, consisting of mainly intermediate to felsic lava domes and minor explosive magmatic deposits, emplaced upon a basement that consists of Mesozoic limestones, with minor siliciclastic and mélange-type rocks (Dietrich and Gaitanakis, 1995). Since the reconnaissance-style

analyses of Sr isotope ratios of the lavas that were performed during the 1970's (Pe-Piper, 1975), it has been known that the magmatic system of Methana has seen a greater influence of crustal materials than the presently active Aegean volcanoes of Santorini and Nisyros, and this has been confirmed by more recent data (e.g. Elburg et al., 2014; Woelki et al., 2018). The style of magmatic activity on Methana, and the eruption rates, have been argued to have been strongly influenced by regional tectonics (Pe-Piper and Piper, 2013). This also affected the major and trace element geochemistry of the erupted products. For instance, the most primitive magmas erupted during a period of strike-slip faulting that provided crustal-scale pathways for magma transport to the surface (Pe-Piper and Piper, 2013). In this scenario, the magmas erupted during this strike-slip event would also be the least contaminated, as they would have had less opportunity to interact with the country rocks. This idea, however, has not been tested with systematic isotopic investigations, and the present paper will redress this omission.

The obtained whole rock major and trace element and Sr-Nd-Hf-Pb isotopic data for the various igneous units, including their mafic enclaves, as well as country rocks and xenoliths, will be used to assess the identity of potential assimilants, and the processes that led to the wide range of geochemical and isotopic variation observed in the

* Corresponding author.

E-mail address: marlinae@uj.ac.za (M.A. Elburg).

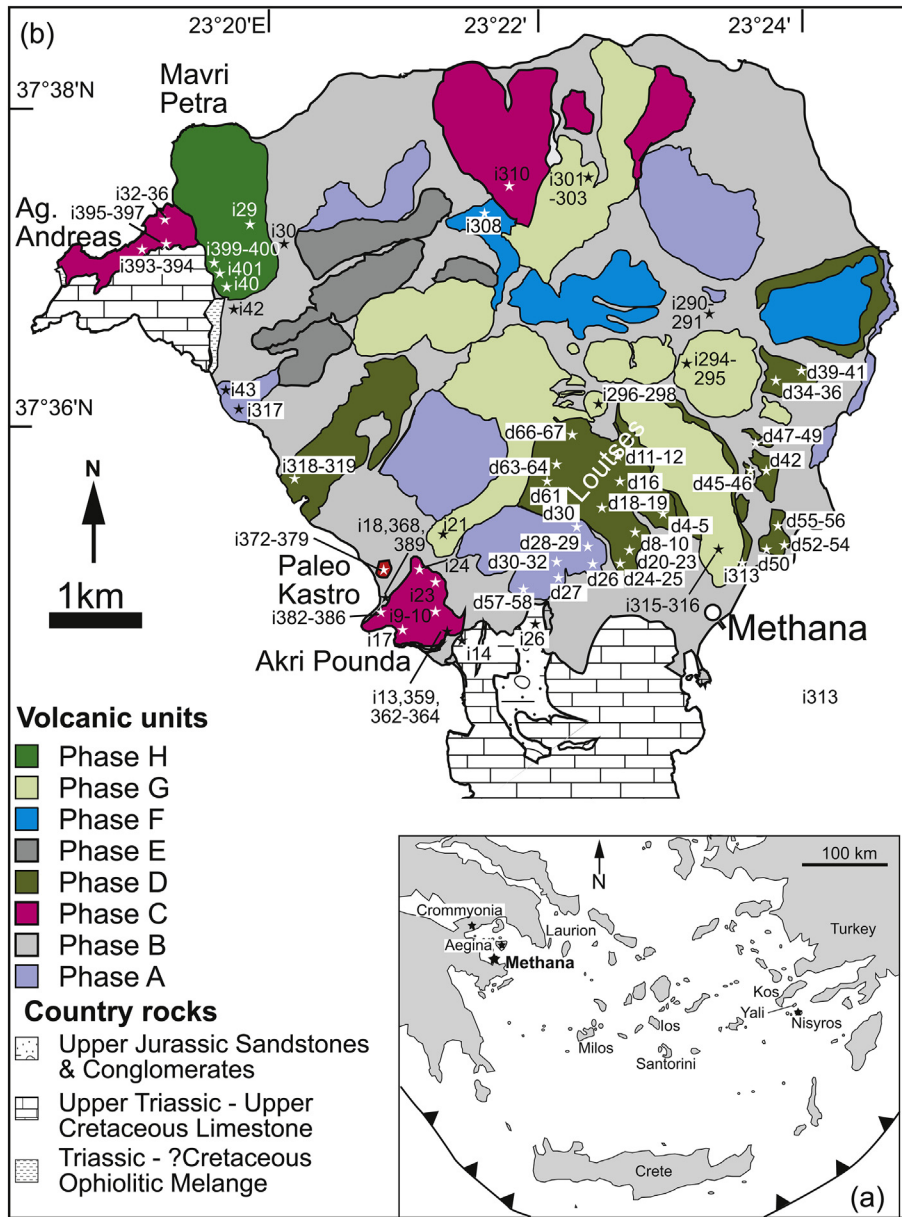


Fig. 1. (a) Overview map of the Aegean area; b: Geological map of Methana after Pe-Piper and Piper (2013) and Dietrich and Gaitanakis (1995) with samples indicated. Sample pre-fix abbreviations: d = DPM; i = IM.

volcanic products of Methana volcano. We will show that the wide geochemical variation is dominantly a result of assimilation of a variety of crustal rocks, with the most extensive range seen in the explosive deposits that surfaced during a period of extensional tectonics.

2. Geological setting

The South Aegean Active Volcanic Arc is the present-day manifestation of the long-lived convergence system between Africa and Europe, which has been active since the Jurassic (Van Hinsbergen et al., 2005). Convergence between the two continents has been accommodated by subduction, nappe stacking and periodic back-stepping of the volcanic arc, which resulted in the present-day volcanic arc being located on continental crust that originated from the East-African (Keay and Lister, 2002; Van Hinsbergen et al., 2005) and ‘Amazonian’ (South American: Zlatkin et al., 2014) cratons. Slab roll-back in a southward direction has been ongoing since the Oligocene and was responsible for the formation of the Aegean Sea (Jolivet et al., 2015).

The active South Aegean Volcanic Arc extends from the Saronic Gulf centres of Methana and Aegina in the west, through Milos and Santorini to Yali-Nisyros in the east (Fig. 1). On the Greek mainland, west of the Saronic Gulf, the Crommyonia volcanic centres were active around 4 and 2.5 Ma. The volcanic centre of Methana is situated on the Pelagonian Unit (Pe-Piper and Piper, 2002) that forms the upper nappe of the Internal Hellenides, of which the exposed rocks are dominated by Mesozoic limestones, and which is thought to be underlain by the pre-Alpine (perhaps even pre-Variscan) basement of the Cycladic Blueschist Unit, as exposed on, for instance, Ios and Sikinos (Mizera and Behrmann, 2015). The area was already part of a magmatic arc during the Miocene, and granitoids with ages between 11 and 17 Ma (Bolhar et al., 2010) are common on the Cycladic islands (e.g. Naxos) and mainland Greece (e.g. Laurion). They are likely also present in the basement underlying the present-day volcanic arc (e.g. Skarpelis and Kyriakopoulos, 1992). The thickness of the crust under the Saronic Gulf has been estimated to be 30 km based on the tomographic work of Karagianni et al. (2005), which is thicker than underneath the

other Aegean volcanic centres such as Santorini (20 km) and Nisyros (25 km).

The tectonic evolution of the Saronic Gulf has been summarized most recently by Pe-Piper and Piper (2013), who also presented absolute and relative ages for the different volcanic units on the peninsula. They defined three main periods in the tectonic evolution of Methana, whereby the first period (around 3.5 Ma) saw the emplacement of volcanic domes along N–S faults (volcanic phase A; Fig. 1b). These oldest volcanic deposits were partially eroded to yield the volcanoclastic ‘apron’ assigned to Phase B. Volcanic phases C to E (early-middle Pleistocene, ca. 1.5–0.5 Ma) coincided with enhanced uplift and active NE–SW strike-slip faulting. Uplift accelerated around 0.38 Ma, giving rise to steep normal faults, and associated voluminous eruptions of volcanic phase F and G. Volcanic phase H, comprising the most recent, historic activity, occurred during the waning stages of this regime.

3. Analytical techniques

A detailed description of the analytical techniques is given in supplementary material S1, which also gives data on international standards.

All analyses were performed on agate-milled samples, with major elements being determined by ICP-OES after Li-borate fusion-assisted dissolution, and trace elements by ICP-MS after HF-HNO₃ dissolution in capped teflon vials. Reported Zr concentrations are from ICP-OES analyses, as only the flux-assisted dissolution procedure assures that all zircon is dissolved. Sr, Nd and Pb isotopic measurements were performed, using a Thermo-Scientific Neptune at Ghent University, on the same splits as those used for preparing the solutions for trace element analysis, after isolation of the elements of interest. Hf isotopes were measured using a Thermo-Scientific Neptune at the Vrije Universiteit Amsterdam on low- and high-pressure (for zircon-bearing samples) dissolutions, after isolation of Hf from its matrix. During the course of the analyses, international standards gave results within the uncertainty of their accepted values (e.g. BHVO-2 ($\pm 2SD$): $^{87}\text{Sr}/^{86}\text{Sr} = 0.705020 \pm 0.000013$; $^{143}\text{Nd}/^{144}\text{Nd} = 0.512975 \pm 0.000024$; $^{176}\text{Hf}/^{177}\text{Hf} = 0.283096 \pm 0.000018$; JB-2: $^{206}\text{Pb}/^{204}\text{Pb} = 18.345 \pm 0.01$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.564 \pm 0.01$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.287 \pm 0.02$).

Zircons were separated using heavy liquids and, after cathodoluminescence imaging, analysed for their Hf isotope ratios by LA-MC-ICPMS (Nu Plasma combined with NWR-213 ablation system) at the Department of Geosciences of the University of Oslo, following the procedures described by Elburg et al. (2013). A few spots were ablated for U–Pb dating with the same set-up to see whether a numerical age could be determined with the set-up used. The results indicated that the age was <5 Ma, but no attempt at further quantification was made because of the lack of suitable standards.

4. Distribution and petrography of volcanic rocks

We follow the newly established volcanic stratigraphy from Pe-Piper and Piper (2013) for the description and interpretation of our data, ranging from the domes of Phase A at the base (ca. 3.5 Ma) through to

the historic eruption of Phase H at Mavri Petra. Sample locations are given in Fig. 1b, and in supplementary material S2. Apart from the igneous rocks, samples of country rocks and xenoliths were also obtained to assess their role as crustal contaminants. Apart from Phase C, which also hosts explosive deposits, all volcanic phases are dominated by effusive volcanic products. In our description below, we first focus on the effusive deposits, and then on the Phase C deposits.

The effusive deposits occur mainly in the shape of lava domes and flows. Mafic enclaves are common (Fig. 2a,b), although their volume percentage, shapes and sizes are variable. The groundmass of the lavas typically consists of very fine-grained plagioclase, pyroxenes \pm hornblende. Most lavas are crystal-rich, with plagioclase (showing polysynthetic twinning, oscillatory zoning and sieve-textured zones) occurring as a common constituent. The lavas are generally hornblende- and sometimes also biotite-bearing, but most deposits also contain lavas that are poor in hydroxyl-bearing minerals. In many samples, the hornblende is partially to wholly replaced by opacite (Fig. 3a), and in the hornblende-poor samples, some larger aggregates can be recognised as pseudomorphs after hornblende or biotite, but they are wholly replaced by hydroxyl-free minerals. Disequilibrium textures are common in the hornblende-rich rocks: resorbed quartz crystals can be observed occasionally mantled by small clinopyroxene crystals and occurring in the same sample as olivine crystals, olivine crystals with Cr-spinel inclusions may be overgrown by hornblende or clinopyroxene and biotite may be rimmed by hornblende or fine-grained pyroxene. Orthopyroxene, clinopyroxene and Fe-Ti-oxides occur in most samples. Plagioclase, hornblende or biotite commonly contain inclusions of apatite, and occasionally also of zircon (Fig. 3d). Cathodoluminescence imaging shows that the zircons exhibit oscillatory zoning (Fig. 3i, j), sometimes superimposed on sector zoning; no core-rim structures were observed in any of the zircons.

Enclaves typically show mineralogical coherence with their host rock in terms of the abundance of hydroxyl-bearing minerals. Their crystal size is variable, and smaller enclaves typically contain crystals with higher aspect ratios but larger crystals, similar to those seen in the host rock, also occur (Fig. 3e). Glass is more common in the enclaves than in the host rocks, and many enclaves have a vesicular texture.

Phase C is the only one to contain appreciable pyroclastic deposits in addition to lava flows. There are minor pumice lapilli beds near Akri Pounda (Fig. 1b), originating from a pyroclastic fall, consisting of 85–95% of juvenile, well-sorted, typically light grey pumice fragments between 1 and 6 cm in size. Lithics are typically oxidised lava blocks, similar to those found in the earlier Phase A and B deposits. The pumice is rich in glass and its crystal cargo is dominated by plagioclase, orthopyroxene and Fe-Ti-oxide; olivine (Fig. 3c), clinopyroxene, quartz and hydroxyl-bearing minerals are rare. However, some intergrowths of plagioclase and orthopyroxene appear to be pseudomorphs, likely after hornblende. Phase C lavas and pyroclastic density current deposits are found near Akri Pounda and Agios Andreas, and consist of coarser and more mafic material than the fallout deposits, which they overlie. Plagioclase and clinopyroxene dominate the mineralogy, with olivine, sometimes as skeletal crystals, as the third most abundant phase (Fig.

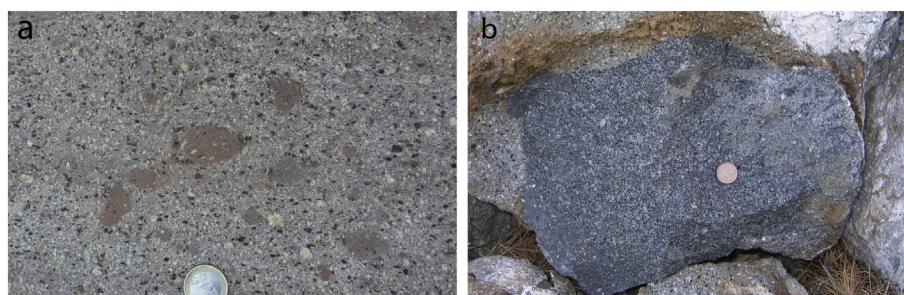


Fig. 2. Variable textures and sizes of enclaves in lavas from Phase D (a) and Phase H (b).

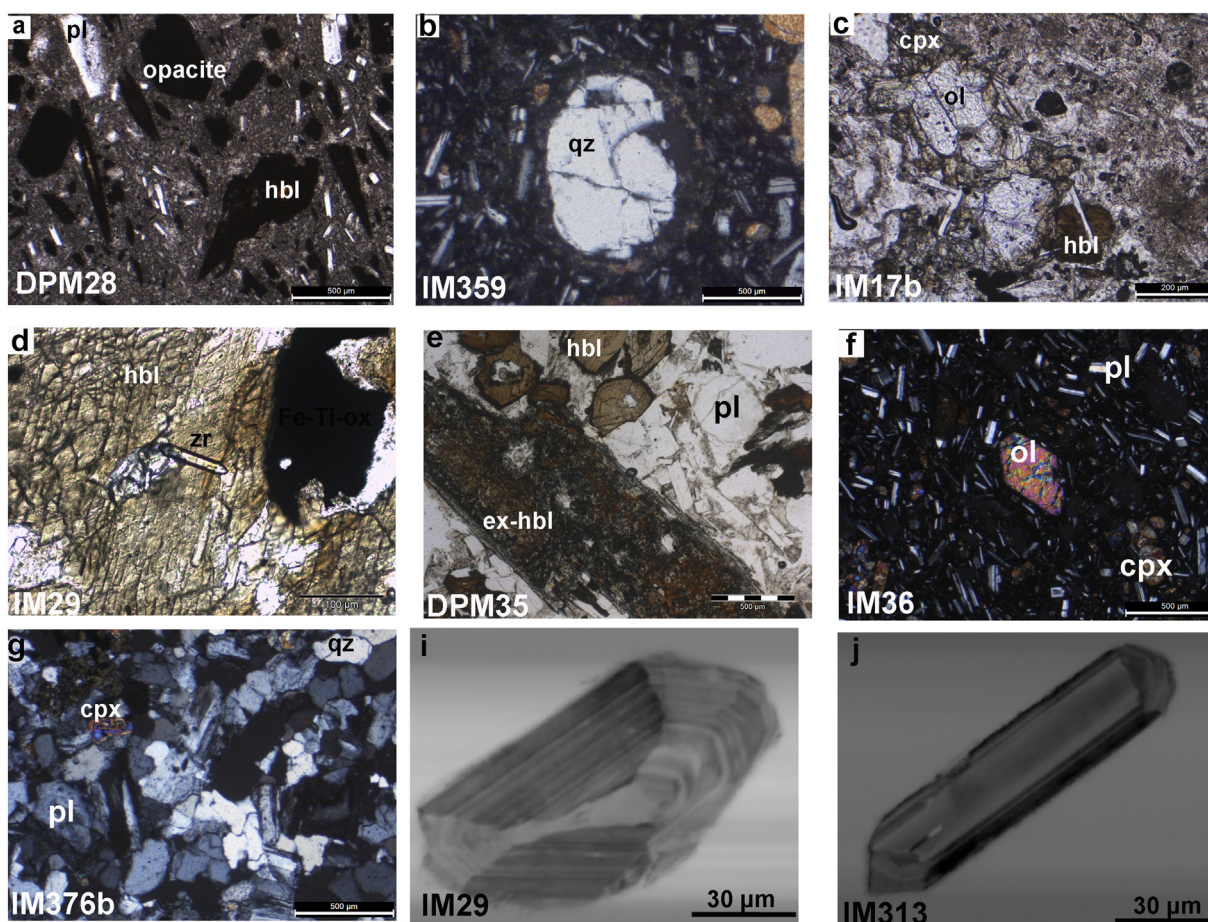


Fig. 3. Thin section (a–g) and cathodoluminescence (h–i) images. PPL = plane polarised light; XPL = crossed polars. a: host rock sample DPM28 from Unit A with plagioclase and hornblende, which is almost completely replaced by opacite (PPL); b: scoriaceous sample IM359 from the mafic deposits of Unit C, showing a rounded quartz crystal rimmed by fine-grained pyroxenes (XPL); c: dacitic pumice sample IM17b from Unit C, with a xenocryst of olivine, mantled by clinopyroxene and hornblende (PPL); d: host rock sample IM29 from Phase H with euhedral zircon enclosed in a large crystal of hornblende (PPL); e: enclave sample DPM35 from Phase D, with a large hornblende crystal, now partially altered to opacite in a matrix of smaller plagioclase and hornblende (PPL); f: sample IM36 from the mafic Agios Andreas lavas of Phase C, showing the typical mineralogy of olivine, clinopyroxene and plagioclase (XPL); g: holocrystalline enclave IM376 with plagioclase, quartz and clinopyroxene (XPL); i and j: typical zircon crystals in samples IM29 (Phase H) and IM313 (Phase D) respectively.

3f). These are the same minerals as those found in the Phase C lava flows, particularly at Palaeo Kastro. Several samples from the density current deposits contain quartz, mantled by clinopyroxene (Fig. 3b). Anhydrous pseudomorphs after larger crystals of hornblende and biotite are scarce.

Within one of the Phase C lavas at Palaeo Kastro, a holocrystalline, phaneritic igneous enclave (sample IM376) was found, contrasting in texture with the common porphyritic enclaves. It consists of a more coarse-grained tonalitic part (plagioclase, quartz, clinopyroxene pseudomorphs of hornblende; Fig. 3g), which is separated by a quartz vein from a finer-grained dioritic part (plagioclase, clinopyroxene, partially pseudomorphosed hornblende). The two parts were analysed separately.

Sampled country rocks comprise Mesozoic limestones and sandstones. Xenoliths are uncommon within the volcanic deposits, and consist mainly of limestones and calcareous sandstones, comparable to the country rocks.

5. Geochemistry

Our approach to sampling was not geared towards a representative selection proportional to the volume of the eruptive products. We tested compositional variability in a single volcanic phase by more dense sampling of Phase D, where we collected 41 samples out of the total of 98 igneous samples. As sampling has been carried out prior to

the new volcanic stratigraphy of Pe-Piper and Piper (2013), we failed to sample their Phase E, and Phase F is only represented by a single sample. As we concentrate on the isotopic composition of the magmas, data from previous studies (Dietrich et al., 1988; Francalanci et al., 2005; Pe-Piper, 1975), which do not report complete Sr–Nd–Hf–Pb isotopic data, have not been used. All geochemical data are given in Supplementary Materials S3–6.

5.1. Major and trace elements

Our analysed samples vary in silica content between 50 and 68 wt%. The more mafic samples (<57 wt% SiO₂) are represented by the enclaves, the Phase C lavas and pyroclastic flow deposits and a few samples from Phase B. Analyses with <54 wt% SiO₂ comprise enclaves only. The densely sampled Phase D deposits span the full range in silica content, from enclave DPM36 at 50.5 to host rock DPM42 at 60.1 wt% SiO₂. MgO concentrations vary between 8 and 1 wt% (Fig. 4a), with Mg# (molar MgO/(MgO + FeO*)) ranging between 69 and 42. Scatter is pronounced in all variation diagrams, making it hard to argue for curved or inflected differentiation trends. TiO₂ concentrations show a rather monotonous decrease from 0.9 to 0.4 wt% with increasing SiO₂ content (Fig. 4b), whereas K₂O continuously increases from 0.9 to 2.7 wt% (Fig. 4c), which corresponds to the medium-K trend of Gill (1981). The two parts of the holocrystalline enclave IM376 stand out

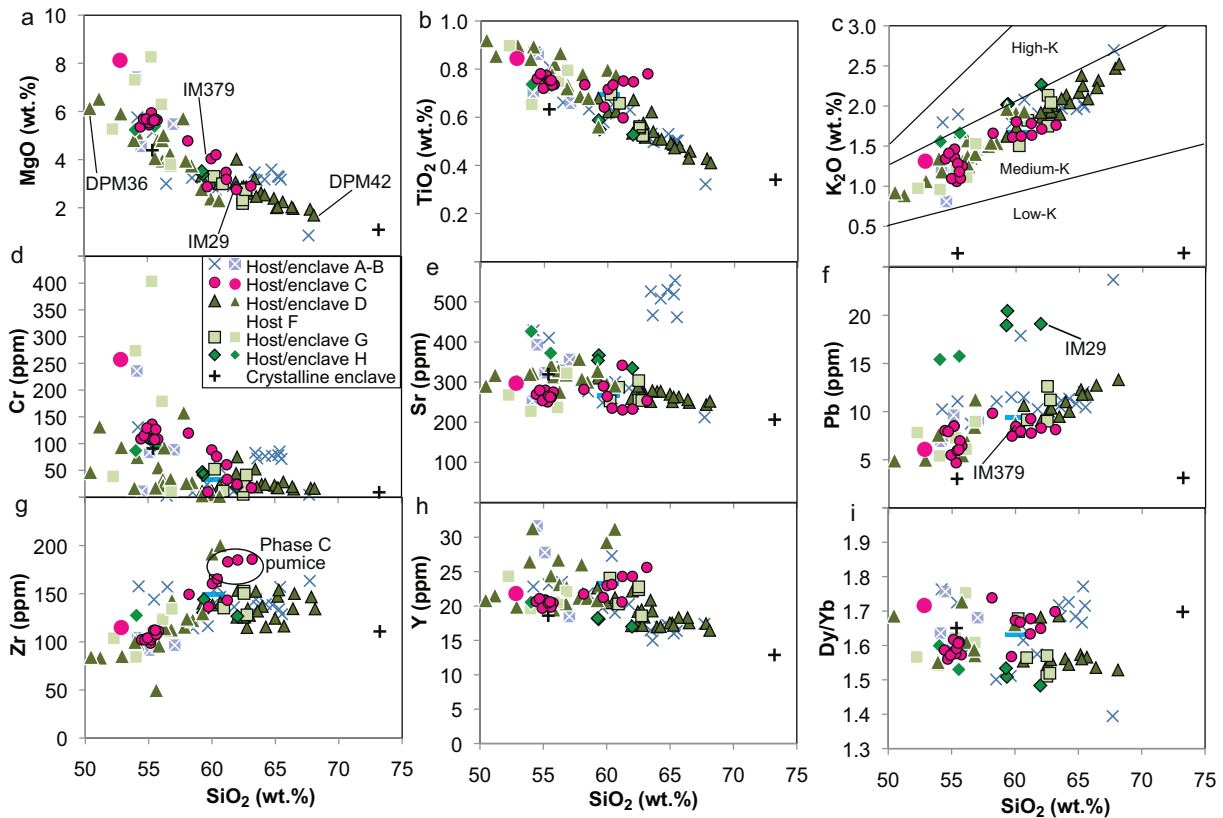


Fig. 4. Harker variation diagrams for igneous samples. Major element oxides in weight percent and trace elements in ppm. Fields in K_2O diagram after Gill (1981). Individual samples of which the isotopic characteristics are referred to in the text have been indicated with their sample names.

with respect to their very low potassium content. Apart from a single low-Ca sample in Phase B, all analyses show an aluminium saturation index (molar $Al_2O_3/(Na_2O + K_2O + CaO)$) of <1 . In terms of FeO^*/MgO ratios, Methana defines a typical calc-alkaline (Miyashiro, 1974) or low-Fe (Arculus, 2003) trend, and it classifies as being calcic in the MALI classification of Frost et al. (2001).

For Methana as a whole, scatter is even more pronounced for trace elements when compared to major elements, especially for the compatible elements such as Cr and Ni: at an SiO_2 content around 54 wt%, Cr varies between 400 and 20 ppm (Fig. 4d). However, the basaltic andesites of Phase C are noticeably more homogeneous than enclaves at the same silica content. Using MgO or Mg# on the x-axes gives some reduction of scatter for the compatible (but not for the incompatible) trace elements, but the Phase C products remain more homogeneous. Some of the Phase A samples stand out in having elevated contents of some compatible elements (Cr 80, Ni 50 ppm) at ca. 65 wt% SiO_2 . These samples also have significantly elevated Sr contents (ca. 500 vs 300 ppm; Fig. 4e). Other characteristics that stand out are high Rb, Be and especially Cs, U and Pb (Fig. 4f) contents for the youngest (Phase H) volcanics and enclaves, although K_2O (Fig. 4c) and Th are only marginally higher than the main trend. Most trace elements display the expected compatible (Cr, Ni, Sc, Co) or incompatible (Rb, Cs, Be, Ba, Nb, light rare earth elements (LREE)) behaviour with increasing SiO_2 contents, but Zr concentrations show an inflection at 60 wt% SiO_2 (Fig. 4g), whereas Y (Fig. 4h) and the middle to heavy rare earth elements generally decrease. Sr (Fig. 4e) and Eu show a scattered, marginally decreasing trend with increasing SiO_2 content. Ratios of MREE/HREE such as Dy/Yb are very scattered (Fig. 4i) but have a tendency to decrease with increasing SiO_2 content, apart from the data for Phase C, which show a clear increase in Dy/Yb ratios (as well as Y contents).

Rare earth element patterns all show clear LREE over HREE enrichment (Fig. 5), with typically a slightly concave-upward shape for the

MREE-HREE patterns (apart from phase C). All samples show a negative Eu anomaly, but this is more pronounced for the more felsic samples. Primitive mantle-normalised trace element diagrams (Fig. 6) show the expected hallmarks of subduction-related magmas, with negative Nb—Ta and Ti anomalies, and a positive one for K and Pb. Nearly all samples also have a negative Ba anomaly. The mafic-intermediate samples show a positive Sr anomaly.

5.2. Radiogenic isotope ratios

In terms of radiogenic isotope ratios, most of the data form a broad concave trend between $^{87}Sr/^{86}Sr = 0.7055$ at $^{143}Nd/^{144}Nd = 0.51266$ and $^{87}Sr/^{86}Sr = 0.7093$ at $^{143}Nd/^{144}Nd = 0.51224$ (Fig. 7a), but the high-Sr samples from Phase A are displaced towards lower $^{87}Sr/^{86}Sr$ (0.7050) relative to the main array, and the Phase H samples appear to have high $^{143}Nd/^{144}Nd$ for their Sr isotope ratios. The holocrystalline enclave IM376 is virtually indistinguishable from its host rock with regards to Sr and Nd isotopic ratios. Local limestones have $^{87}Sr/^{86}Sr$ of 0.707–0.708 (Fig. 7b), typically with Nd contents too low to determine their Nd isotope signature. More siliciclastic country rocks and xenoliths within some of the volcanic deposits extend the array to slightly more ‘crustal’ values than the volcanics, with values for $^{87}Sr/^{86}Sr = 0.710$ at $^{143}Nd/^{144}Nd = 0.51221$ (Fig. 7a).

Generally the values for $^{87}Sr/^{86}Sr$ (Fig. 7c) and $^{143}Nd/^{144}Nd$ become gradually more ‘crustal’ with increasing differentiation. The Phase C pumice, however, exhibits abnormally high $^{87}Sr/^{86}Sr$ and low $^{143}Nd/^{144}Nd$ ratios when comparing its SiO_2 and MgO content and its Mg#, to comparable samples from the other units. Even for samples from a single eruptive phase, the correlation between Sr or Nd isotope ratios and fractionation indices is poor. For the whole data set, the negative correlation between Nb content and Nd isotopic composition (Fig.

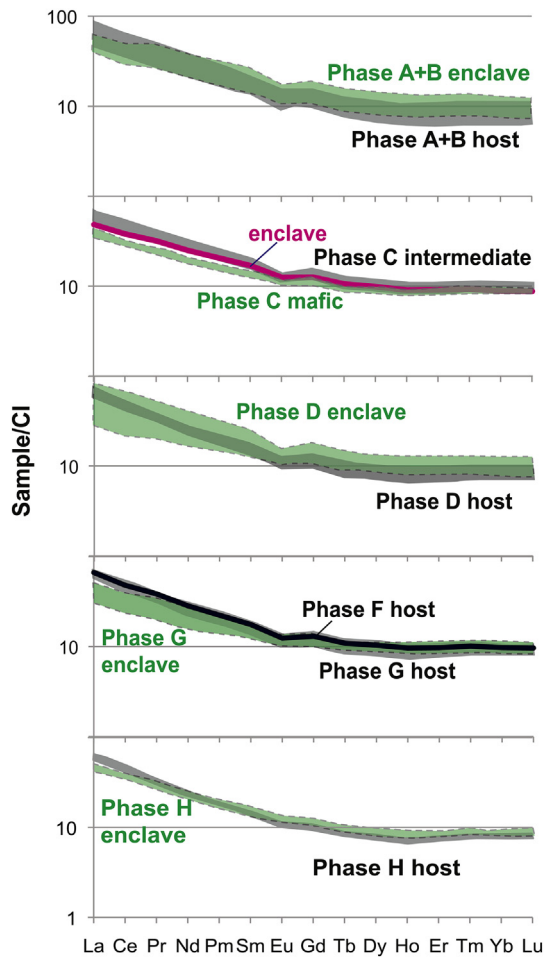


Fig. 5. Normalised rare earth element diagrams for the different volcanic host rocks and their enclaves. Normalising factors from Evensen et al. (1978).

7d) shows the highest correlation coefficient ($r^2 = 0.41$) for an element (or elemental ratio) and a radiogenic isotope ratio.

Our slightly more restricted set of Hf isotopic data shows a positive correlation with Nd isotope ratios (Fig. 7e). There is some scatter, but there is no clear distinction between the samples from different phases. Most volcanic samples fall towards the high Hf side of the terrestrial array of Vervoort et al. (2011), especially at the higher end ($\epsilon\text{Nd} > -2$) of the array. One of the calc-silicate xenoliths found in the Phase C pumice airfall shows the clearest offset from the terrestrial array.

Pb isotope ratios show a poor correlation (Fig. 7f, g). Data for some volcanic phases are better clustered than for others, but these are samples that were derived from a restricted geographical area and the spatial distribution of the samples appears to be the most important parameter with respect to the Pb isotope ratios. Both parts of holocrystalline enclave IM376 (see inset in Fig. 7f, g) have ratios of $^{207}\text{Pb}/^{204}\text{Pb}$ (15.55) and $^{208}\text{Pb}/^{204}\text{Pb}$ (38.3) that are significantly lower than those of the volcanic samples (>15.67 and >38.7 respectively). The Phase C basaltic andesite sampled in the vicinity of the xenolith, IM379, has the lowest Pb isotope ratios of all the volcanic samples. Three samples from Phase A and B, also taken along the west coast of the peninsula, bridge the isotopic gap between the phase C sample and the rest of the Pb isotopic data array. Trends of Pb isotope ratios against $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ are scattered (Fig. 9b), but the Phase C pumice with the most crustal Sr and Nd isotope ratios has the highest Pb isotope ratios. There are no obvious correlations when Pb isotope ratios are plotted against differentiation indices, or ratios of trace elements with contrasting aqueous mobility (e.g. Pb/Ce, Sr/Y or Th/U; not shown).

For five samples, 20 to 80 zircons per sample were analysed for their Hf isotope ratios by LA-MC-ICPMS in order to assess their variability (e.g. Rojas-Agramonte et al., 2017) and their similarity to the Hf isotope whole rock analyses (Fig. 7h). The limited amount of material analysed with LA-MC-ICPMS and the correction for interfering ions cause larger uncertainties on the measured ratio for each zircon spot analysis compared to whole rock solution analyses, thereby giving a greater uncertainty for the average Hf isotopic ratio for the zircons compared to the whole rock analyses. However, the standard deviation of the laser ablation $^{176}\text{Hf}/^{177}\text{Hf}$ analyses for the zircon population from each sample can be compared to that for zircon reference materials such as the Mud Tank or Temora-2 zircon (around 0.008% during the course of the LA-MC-ICPMS analyses). The data for the five unknowns show a somewhat larger standard deviation, between 0.009 and 0.013%, indicating that the population is relatively homogeneous. Considering the uncertainties, the average Hf isotopic composition for the population of zircons from each of the five samples are very similar.

Taking the uncertainty of the LA-MC-ICPMS measurements into account, the Hf isotope ratios of the zircons are similar to the ratio of the whole rock for the samples with 60–65 wt% SiO_2 , but only in the case of the Phase A sample with 64 wt% SiO_2 (DPM28) are the values of the zircons as well as the high- and low-pressure dissolution of the whole rock equal within analytical uncertainty. For the other two intermediate samples (IM29 and IM313 from Phase H and Phase D respectively), the zircons have slightly lower Hf isotope values than the HP dissolution, which in turn is lower than the LP dissolution. In the case of the zircons found in a Phase C basaltic-andesite (IM36, with 55 wt% SiO_2) the zircons' $^{176}\text{Hf}/^{177}\text{Hf}$ (0.282739 ± 38) is markedly lower than for the host rock; this distinction is more marked for the low-pressure (0.282896) than the high-pressure dissolution (0.282868) of the host rock, indicating that the zircons have a more 'crustal' signature (lower $^{176}\text{Hf}/^{177}\text{Hf}$) than their host. The systematics are opposite for the phase D sample with 68 wt% SiO_2 (DPM42), where the zircons have an average higher Hf isotope ratio than the host rocks; also here, the HP dissolution of the host rock is closer to that of the zircons than the LP dissolution.

6. Discussion

6.1. Mixing and assimilation

Field and petrographic evidence (presence of enclaves, ubiquitous mineralogical disequilibrium textures; Fig. 3b,c) shows that magma mingling and magma mixing were important processes in the petrogenesis of the Methana lavas, and this is supported by, for instance, the lack of inflection points on the Harker diagrams of TiO_2 and Y (Fig. 4b,h). Magma mixing was likely accompanied by the selective entrainment of certain minerals to explain excess scatter in the Harker variation diagrams, as has also been mentioned by previous workers (Pe-Piper and Piper, 2013). Besides, the different phases may also have had different primary magmas, as exemplified by the elevated Pb concentrations of the Phase H deposits. Ignoring the complications of different primary magmas, fractionation and selective entrainment of minerals for the moment, we will first assess the broad trends seen in the radiogenic isotope data in order to identify end members and constrain the processes that yielded these trends, refining the models proposed by Elburg et al. (2014). Parameters for the simple mixing and Assimilation-Fractional Crystallisation (AFC; DePaolo, 1981) models can be found in Table 1. For the AFC models, bulk distribution coefficients were taken as 0.3 for Nd, 0.001 for Th and 1.7 for Sr except for the high pressure (HP) AFC model, where it was 0.1. These values are based on the general trends seen in the variation diagrams, and are in broad agreement with the observed mineral assemblages (olivine, clinopyroxene, orthopyroxene, plagioclase, hornblende).

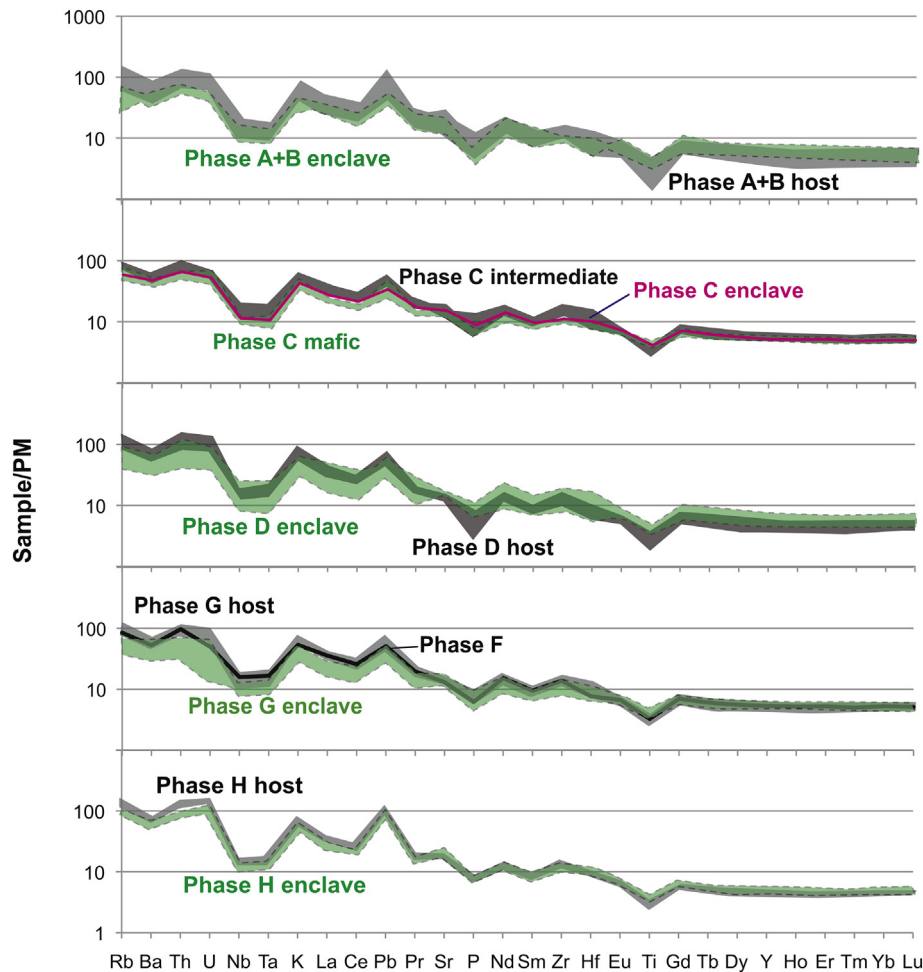


Fig. 6. Normalised trace element diagrams. Normalising factors from Palme and O'Neill (2014).

6.1.1. Exploring evolved end members

The majority of the Sr and Nd isotopic data can be explained by simple mixing between the two isotopically extreme samples from the Phase C deposits (Fig. 7a), namely the basaltic andesites with relatively low Sr isotope ratios (0.7057) and high Nd isotope ratios (0.51260), and the most isotopically evolved pumice ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7093$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.51224$). This yields a mixing line on which the majority of the samples fall. The isotopically most primitive samples are similar to those analysed by Woelki et al. (2018), and the reader is referred to this publication for an in-depth discussion on the primary magma to the Methana volcanics.

Evidence for mixing of a geochemically and isotopically more evolved magma with the basaltic andesites comes from petrographic data (Fig. 3b, c), as well as from the observation that zircons with a much lower Hf isotope ratio than the whole rock were found within mafic sample IM36 (Fig. 7h). The relative isotopic homogeneity of this zircon population, combined with the petrographic observations of the elongated euhedral shape of the zircons (Fig. 3d), the CL-imaging that shows magmatic oscillatory zoning without any core-rim structure (Fig. 3i, j), and the maximum age of 5 Ma, shows that these zircons are unlikely to be xenocrysts derived from the country rocks. Although a simple mixing line satisfactorily models most of the Methana samples within Sr–Nd (and also Hf) isotopic space, scatter in diagrams of Sr–Nd–Hf isotope ratios against an index of fractionation indicates that this cannot be the whole story. For instance, the isotopically most evolved pumice samples of Phase C are not the most evolved in terms of SiO_2 (Fig. 7c) or incompatible trace elements. We will use Th as an index of fractionation (Fig. 8a), as Pe-Piper and Piper (2013)

noticed a correlation between the concentration of Th and the volume percentage of enclaves in the deposits, and suggested that Th could trace the role of AFC (Assimilation + Fractional Crystallisation) processes. In this model, the repeated input of less fractionated magma (now represented by the enclaves) would provide the thermal energy necessary for assimilation.

The first thing the $^{143}\text{Nd}/^{144}\text{Nd}$ versus Th diagram (Fig. 8a) shows is that the interpretation of the Phase C products representing simple mixing between two end members is not quite accurate, as the isotopically most primitive basaltic andesites from Agios Andreas in the north (to which zircon-bearing sample IM36 belongs) have a higher Th content than the basaltic andesites from Akri Pounda in the south, which have slightly lower $^{143}\text{Nd}/^{144}\text{Nd}$. The latter seem to form a mixing line (curve i in Fig. 8a) with the Akri Pounda pumice samples, whereas the former lie on a mixing trend (curve ii in Fig. 8a) with the Palaeo Kastro andesites at higher Th contents. The high-Th end of the trend can be extended to the field for the Miocene granitoids, but these are unlikely to be the material directly involved in the physical mixing process: The zircons from those intrusives have present-day $^{176}\text{Hf}/^{177}\text{Hf}$ values dominantly between 0.2822 and 0.2826 (Bolhar et al., 2012), and are thus significantly less radiogenic than the values for zircons from the Methana samples (0.28265–0.28285).

Phase D sample DPM42 has among the highest Th contents at intermediate $^{143}\text{Nd}/^{144}\text{Nd}$; although Phase H sample IM29 has equally high Th contents, it isn't as evolved in terms of SiO_2 content (62 vs 68 wt%), and also has a higher $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. Sample IM29 falls close to the isotopically less evolved Aegean Miocene granitoids (from Samos and Kos; Altherr and Siebel, 2002) in this diagram, but it is very different

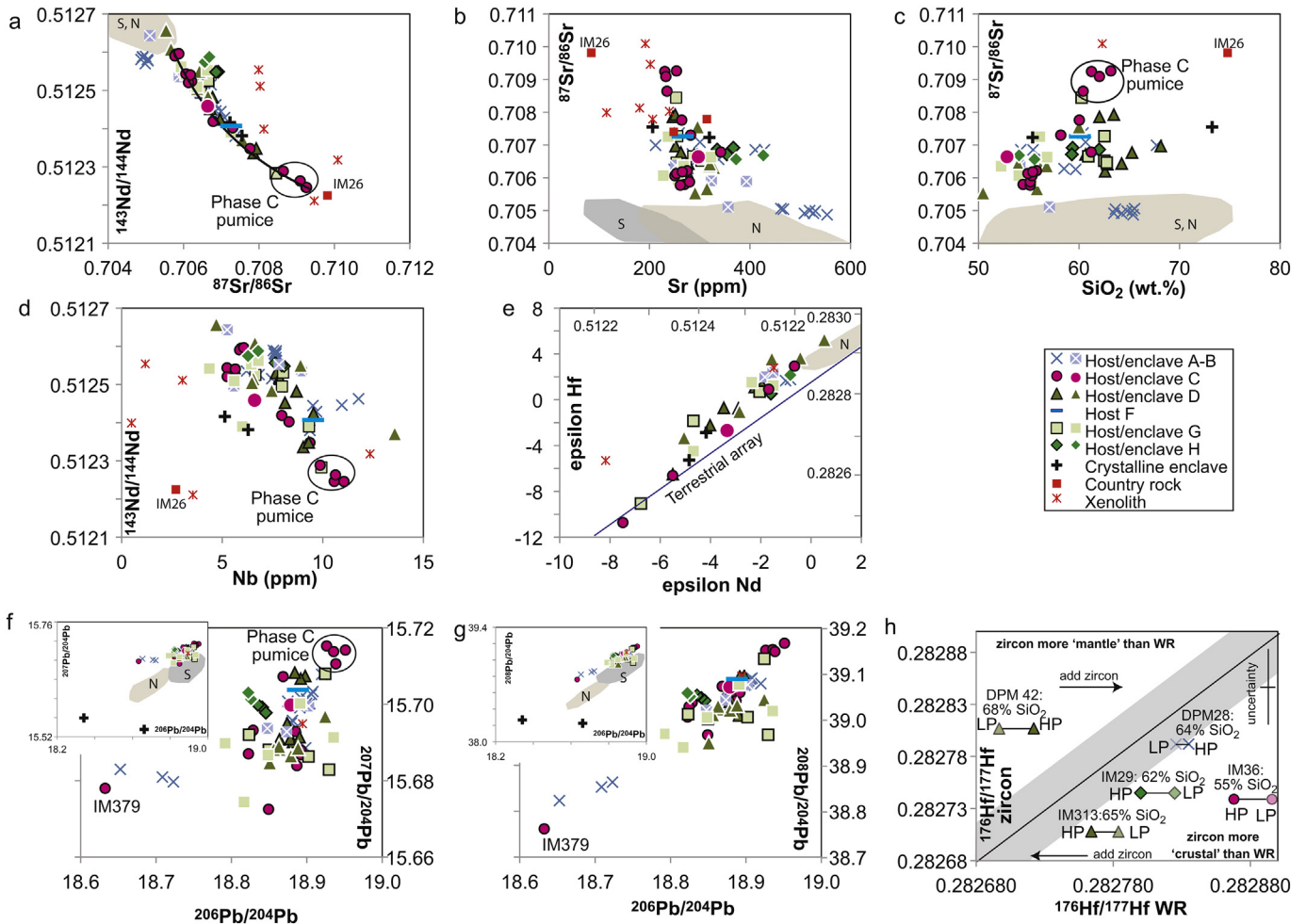


Fig. 7. Bivariate diagrams relating to radiogenic isotope ratios. Fields shown are for Santorini (S) and Nisyros (N) from the authors' data compilation. a: $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ (note that limestones cannot be shown because Nd contents are too low to determine their isotopic composition) with curve showing simple mixing for the Phase C deposits (see Table 1 for end members); b: $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr concentration; c: $^{87}\text{Sr}/^{86}\text{Sr}$ versus SiO_2 ; d: $^{143}\text{Nd}/^{144}\text{Nd}$ versus Nb; e: whole rock epsilon Hf versus epsilon Nd, with the terrestrial array after Vervoort et al. (2011); f: $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, with inset to show the outlying holocrystalline enclave; g: $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, with inset to show the outlying holocrystalline enclave; h: average LA-MC-ICPMS $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of zircon versus whole rock values, for both high-pressure (HP; dark colours) and low pressure (LP; light colours) dissolutions. The grey field around the equal-Hf-isotope line shows the uncertainty of the laser-ablation analyses. The 'add zircon' arrows indicate the way in which the whole rock Hf isotopic signature changes by adding zircon.

in its Sr content (330 vs 450–2000 ppm, not shown). Although a simple-mixing curve between the most mafic (DPM36) and most felsic (DPM42) Phase D samples could explain some of the observed variability in Methana, it does not explain how DPM42 obtained its isotopic characteristics in the first place. Sample DPM42 is also characterised by zircons that are isotopically more primitive (high $^{176}\text{Hf}/^{177}\text{Hf}$ ratio) than the whole rock composition. This implies that crustal contamination occurred after the onset of zircon crystallisation, which could argue for the operation of AFC-type processes to explain the isotopic characteristics of the evolved end members.

We modelled this AFC process by taking calc-silicate country rock IM26 (Upper Jurassic calcareous sandstone) as the crustal end member and Phase D enclave DPM36 as the more primitive melt. This yields a satisfactory fit (curve i in Fig. 8b) for sample DPM42, but only with a high parameter R (rate of assimilation: fractionation) of 0.8, and a remaining melt fraction of slightly <60 wt%, meaning that >30% of host rock would need to be assimilated. This high amount of assimilation is mainly a reflection of the very low Th and Nd contents of this crustal end member. If a pelitic, rather than calc-silicate, xenolith (IM362) is taken, the obtained AFC curve is similar, but the amount of assimilated material is reduced to 13%. The curve can be shifted upward (curve ii in Fig. 8b) to pass through sample IM29 by adjusting the R parameter downward to ca. 0.4 (for IM26 as an assimilant) or 0.25 (for IM362).

With this lower rate of assimilation, the amount of melt remaining would be smaller; this is contrary to what is observed for the SiO_2 content of Phase H sample IM29 (62 wt%) versus Phase D sample DPM42 (68 wt%). It is therefore more likely that Phase H belongs to a different magmatic series, with inherently higher Th contents, rather than being related to the Phase D deposits by a different rate of assimilation to crystallisation (see further discussion in section 6.1.4).

Returning to the very 'crustal' Sr-Nd-Hf isotopic characteristics of the Phase C pumices, it would be possible to explain these by a large degree of remelting of some Miocene granitoid and mixing with small amounts of the basaltic andesitic melt. However, this interpretation is not supported by the very moderate contents in the rhyodacites of elements such as K, Rb and Ba (Fig. 8c), which are significantly enriched in all the Miocene granitoids. As these are incompatible elements, AFC-type processes would provide an even worse fit to the data than simple mixing.

The very crustal Sr-Nd-Hf isotopic characteristics of the Phase C pumice end member are best explained by assimilation with material similar to that of the Ios basement, with a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.5119 (Klaver et al., 2016). Depending on whether the primitive end member is assumed to be enclave DPM36 (curve iii in Fig. 8b), or a hypothetical composition with a higher $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.5127 (curve iv), the pumice can be modelled by an R value of 0.8 or 0.4 respectively, and a total

Table 1
Mixing end members for curves in Figs. 7 and 8.

	Curve	$^{143}\text{Nd}/^{144}\text{Nd}$	Nd (ppm)	Th	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppm)	R
Phase C mixing	Fig. 7a						
Primitive		0.51265	12		0.7055	300	
Evolved		0.51224	22		0.7093	250	
	Fig. 8a i						
Primitive		0.5126	12	4			
Evolved		0.5122	22	7			
	Fig. 8a ii						
Primitive		0.5126	12	5			
Evolved		0.5122	22	10			
	Fig. 8a iii						
Primitive		0.51266	12	3			
Evolved		0.51242	17	11			
	Fig. 8a iv						
Primitive		0.51266	12	3			
Evolved		0.51255	16	11			
	Fig. 8b i						
Phase D AFC		0.51266	12	3			
Assimilant		0.51222	6	2			0.8
	Fig. 8b ii						
Phase H AFC		0.51266	12	3			
Assimilant		0.51222	6	2			0.4
	Fig. 8b iii						
Phase C AFC		0.51266	12	3			
Assimilant		0.5119	48	15			0.8
	Fig. 8b iv						
Phase C AFC		0.5127	9	1	0.7055	350	0.4
Primitive 2		0.5119	48	15	0.743	100	
Assimilant							
Methana HP AFC	Fig. 8d	0.5129	9		0.7035	300	0.3
Primitive							
Assimilant		0.5122	30		0.725	100	

Bulk distribution coefficients were taken as 0.3 for Nd, 0.001 for Th and 1.7 for Sr except for the high pressure (HP) model, where it was 0.1. R = ratio assimilation / fractionation (for AFC models).

amount of assimilation of 5 and 13%. This also fits the Sr isotope data (not shown) if the assimilant has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio around 0.74 and a Sr concentration of 100 ppm, which has indeed been measured for the Ios basement (Buettner et al., 2005; Klaver et al., 2016).

In conclusion, the isotopic and trace element data can be explained by the assimilation of material similar to entrained xenoliths for the evolved but isotopically less extreme end members of Phase D and H. However, this explanation does not hold for the very 'crustal' isotopic

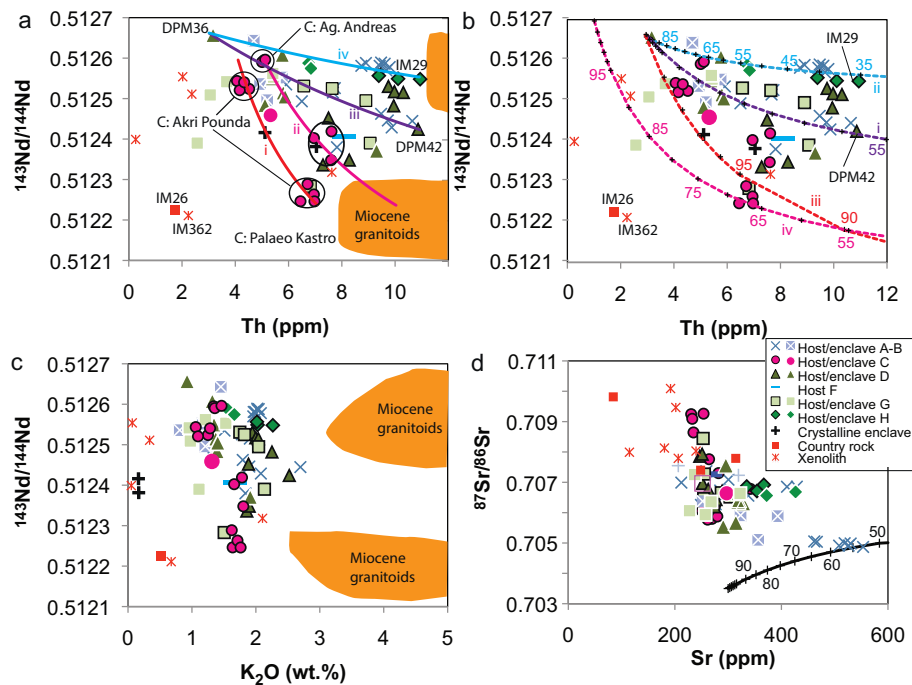


Fig. 8. a: $^{143}\text{Nd}/^{144}\text{Nd}$ versus Th concentrations with curves showing simple mixing models (see Table 1 for end members); b: as a, but with AFC models; c: $^{143}\text{Nd}/^{144}\text{Nd}$ versus K_2O concentration to show unsuitability of Miocene granitoids as mixing end members; d: $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr concentration illustrating high pressure AFC model for the high-Sr Phase A samples.

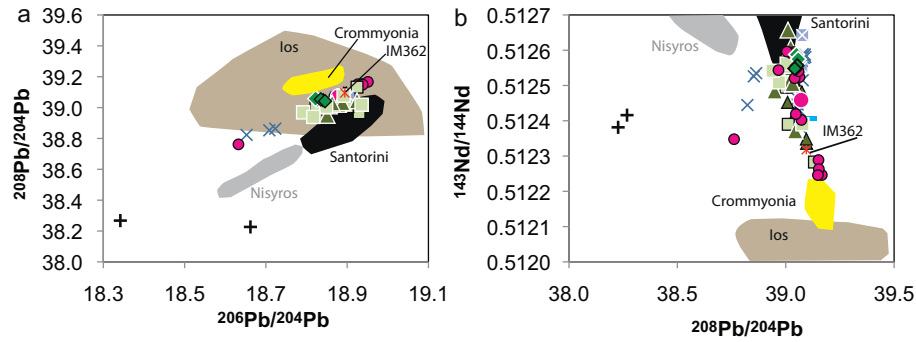


Fig. 9. Isotope diagrams showing potential contamination by los basement and an unknown unradiogenic Pb end member. a: $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$; b: $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$.

signature of the Phase C pumice sample, for which an isotopically more extreme contaminant similar to the los basement is needed. The observed isotopic arrays are mainly a result of physical mixing between isotopically primitive mafic magmas and the more evolved magmas that obtained their chemical and isotopic characteristics as a result of AFC processes. However, when elemental data are taken into account (e.g. Fig. 8a), it is obvious that variable primary magmas may be involved as well, which will be explored further below in Section 6.1.4.

6.1.2. Pb isotopic constraints: los basement and localised fluid

Arguments for the involvement of an assimilant similar to the los basement rocks can also be made on the basis of the Pb isotopic signature. The majority of samples from los are characterised by having high $^{208}\text{Pb}/^{204}\text{Pb}$ ratios relative to their $^{206}\text{Pb}/^{204}\text{Pb}$, reflecting high time-integrated Th/U ratios (Klaver et al., 2016). The $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the Methana samples (Figs. 7f, 9a) are higher than those of Santorini and Nisyros, but lower than the field for Crommyonia (Soens, 2015). The Phase C pumice is again an end member in the data set, with the highest $^{206,7,8}\text{Pb}/^{204}\text{Pb}$ ratios. However, one of the Phase C samples, an andesite from Palaeo Kastro, which is the host to the dioritic-tonalitic crystalline enclave, is significantly offset in Pb isotopic space towards the low Pb isotopic ratios of this enclave. A slightly less pronounced offset is also seen for two Phase A and one Phase B samples. The most obvious factor that these samples have in common is that they were taken near the west coast of the peninsula. However, there are also samples from the same area that do not display this offset. In Pb–Nd isotopic space (Fig. 9b), these aberrant samples give the impression that only the Pb isotopic signature was lowered to offset them from the main array. The crystalline enclave itself would make a very inefficient contaminant, as its Pb content (ca. 3 ppm) is lower than for any of the juvenile samples (> 5 ppm). It appears more likely that some of the juvenile samples were affected by the same, perhaps fluid-related, contaminant that affected the Pb isotopic composition of the crystalline enclave. The isotopic signature of this Pb contaminant suggest a source with only moderate time-integrated U + Th/Pb ratios, not dissimilar to Mid-Ocean Ridge Basalt. The location of this source is as yet unclear, but it

could potentially be related to a mafic rock type such as the sliver of ophiolitic mélangé exposed on the NW side of the peninsula (Dietrich and Gaitanakis, 1995). The mode of contamination could be by assimilation of fluid-altered volcanic cumulates, which would be difficult to detect in other geochemical parameters.

6.1.3. High-Sr Phase A samples

Some of the phase A host rocks, derived from two flows near the village of Loutsés, have notably lower Sr isotopic ratios and higher Sr concentrations than the other rocks, and fall outside of the main data trend in many diagrams (Fig. 7a, b). This group of samples is also unusual in having high MgO, Cr and Ni contents (Fig. 4a, d) for their SiO₂ contents of 65 wt%, which is likely related to the presence of olivine and clinopyroxene, overgrown by hornblende, observed in the samples.

One of the samples from this group (DPM28) was analysed for its Hf isotopic characteristics by LP and HP whole rock dissolution as well as for the individual zircon crystals, and gave no detectable differences between these analyses. Therefore, the higher compatible element contents could reflect entrainment of clinopyroxene and olivine cumulates, as these minerals would contribute negligibly to the Hf budget. Further characteristics of these samples are moderately low Y contents, similar to Phase D samples of the same silica content, but significantly higher Dy/Yb ratios than most Phase D samples. Low Dy/Yb ratios are typical for melts that underwent amphibole fractionation (Davidson et al., 2007), which has been argued to have been an important process for the Methana lavas (Elburg et al., 2014), whereas a low Y content in combination with high Dy/Yb ratios points towards a role for garnet fractionation. Therefore, the high-Sr samples may document a phase of fractionation at higher pressure during which plagioclase was not stable, and hence Sr would have been an incompatible element. This can be modelled with a primitive magma with Sr and Nd isotopic compositions as primitive as 0.7035 and 0.5129 respectively, and only 300 ppm Sr in this mafic magma, which increases to the observed ca. 500 ppm during the high pressure phase of AFC, using an los-style assimilant (Fig. 8d, Table 1). The slight increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with decreasing Sr concentrations within this group is likely related to

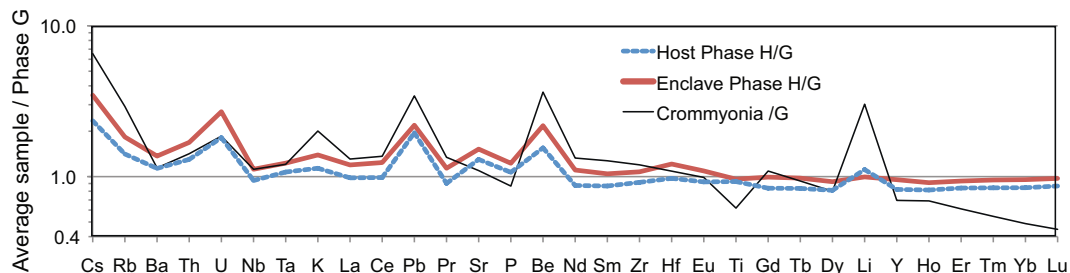


Fig. 10. Trace element diagram, normalised over Phase G deposits, to show the enrichments of Phase H, resembling those of Crommyonia samples from Soens (2015).

a subsequent phase of fractionation where plagioclase was crystallising. Alternatively, these samples could have been derived from a different primary magma with higher Sr concentrations, making crustal contamination less visible in the Sr isotope signature.

6.1.4. Phase H

Both the host rock and the enclaves of Phase G and Phase H are similar in their silica and MgO content, and the differences in their trace element concentrations can thus be illustrated by a normalised trace element diagram (Fig. 10) without the need to correct for differences in degree of fractionation. Here the average of the Phase H host rocks is normalised over the average of the Phase G host rocks, and the same for the enclaves. This shows that the Phase H enclaves and host rocks both show clear enrichments in certain elements compared to their Phase G equivalents, with $Cs > U > Pb = Be > Rb > Th > Sr > Ba = K$. For the other elements, apparent enrichments and depletions fall within the standard deviation of the corresponding averages. Since the most incompatible elements are not those that are the most enriched, smaller degrees of partial melting of an invariant source cannot be the main cause for the distinctions between Phase G and H. Some of the enriched elements are considered to be ‘fluid mobile’ (Cs, U, Pb), but other elements that show equal enrichments, such as Be and to a lesser extent Th, are considered fluid immobile (Ryan and Chauvel, 2014), whereas still other fluid-mobile elements such as Li do not show significant enrichment. The lack of enrichment in the latter element could be related to amphibole fractionation. However, the other discrepancies are more difficult to explain if we would want to invoke a fluid component, for instance derived from the subducted slab. The observed enrichments are broadly similar to those seen in the (significantly more felsic) Crommyonia volcanics (Soens, 2015), which appear to show the most pronounced imprint of assimilation of Ios-like material based on their low Nd isotope ratios (Fig. 9b). Clearly, the Phase H volcanics have significantly higher Nd isotopic ratios than the Crommyonia volcanics, but they do trend towards the Crommyonia field in terms of Pb isotopic composition (Fig. 9a). Remarkably, the Phase H enclaves are

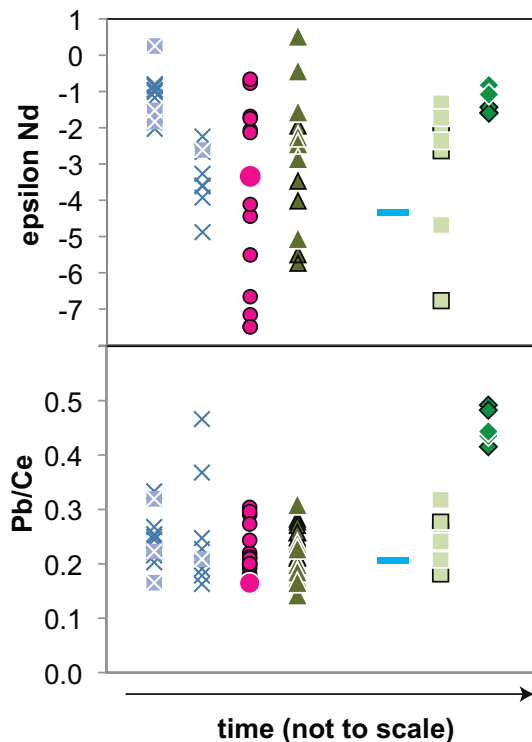


Fig. 11. Epsilon Nd and Ce/Pb ratios of the various igneous units, arranged in temporal order. No unidirectional temporal trend can be seen.

actually more similar to the Crommyonia volcanics than the host rocks in terms of Pb isotopic composition. This could potentially be related to two consecutive phases of assimilation, first with an Ios-like contaminant followed by a contaminant more similar to xenolith IM362 for the host rocks. However, we have not been able to find assimilants of which the whole rock composition matches the pattern seen in Fig. 10 in our own data set, nor in the Ios basement samples analysed by Klaver (2016) or among the Miocene granitoids published by Altherr and Siebel (2002). Perhaps selective assimilation of a partial melt of any of these rock types, with a specific residual phase such as rutile or allanite, could explain the patterns. However, our lack of knowledge of either the likely assimilant(s) or the processes involved does not permit more detailed modelling.

6.2. Geochemistry versus time and the relationship with tectonics

The data presented here do not show any clear unidirectional progression with time in the geochemistry of the magmas (Fig. 11), with the oldest and youngest deposits (Phase A vs H) having similar and, for Methana, relatively high Nd isotope ratios (epsilon Nd 0 to -2). Although the youngest volcanic phase (Phase H) appears quite distinct in terms of its geochemical signature, as discussed above, it does not represent the culmination of a progressive enrichment trend through time, as samples from Phase G and phase D cannot be distinguished from each other in terms of their incompatible trace element signature.

The changes in tectonic regime, documented by Pe-Piper and Piper (2013), mainly appear to affect the Phase C deposits, interpreted to have erupted during the onset of strike-slip faulting. These deposits also stand out from the others from a volcanological point of view, with their higher content of explosive products (air fall pumice and pyroclastic flow deposits). The air fall pumice deposits were erupted at the start of Phase C, and contain samples with the most crustal Sr and Nd isotopic signatures, even though they are not the most felsic ones (60–63 wt% SiO₂). The basaltic-andesitic lava flows and pyroclastic flow deposits are among the most mafic (ca. 55 wt% SiO₂) and isotopically most primitive on the island. They represent the only eruptive phase during which mafic magmas formed their own deposits; other mafic rocks are only found as enclaves within more evolved flows. This fits in with the idea that the faulting taking place during phase C facilitated magma ascent and eruption of these mafic magmas. During periods of compression, magmas stalled at intermediate depths and suffered ‘rheological death’ as a result of hornblende crystallisation. They could only erupt after being remobilised by a pulse of more mafic magma, which we now find as enclaves within the intermediate-felsic deposits (Elburg et al., 2014; Fig. 12).

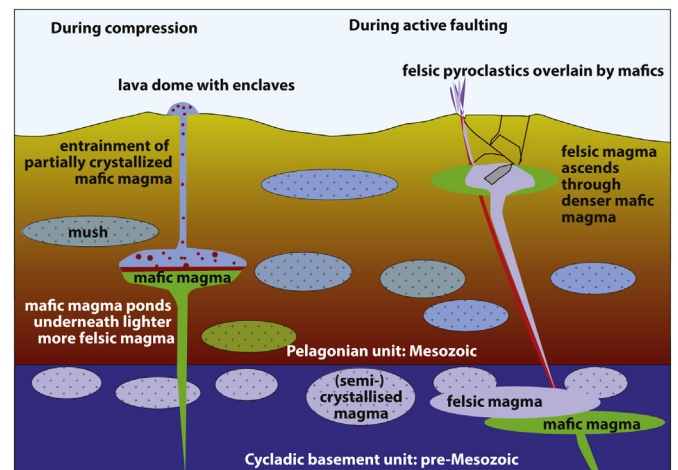


Fig. 12. Cartoon illustrating the envisaged magmatic development during compressional (left) and extensional (right) phases, after Eichelberger et al. (2000).

The eruption of the isotopically most evolved magmas during this period of extension is somewhat surprising, as it seems more logical that lavas would experience higher degrees of crustal contamination as a result of hindered ascent during periods of compression. The presence of olivine in some of the pumice samples, combined with the fact that their pyroclastic fall deposits are directly overlain by pyroclastic density current deposits containing juvenile basaltic-andesite clasts, of which some contain quartz, suggests that the two contrasting magmas formed part of a single eruptive phase. Contrasting with the case of mafic enclaves within a more felsic host rock, this semi-simultaneous eruption of contrasting magmas could have been initiated by felsic magma entering a magma chamber filled with mafic magma (Eichelberger et al., 2000; Fig. 12). The pumice samples are also somewhat different from other samples at similar SiO₂ contents and fall on the low-Sr, high-Y and high-Dy/Yb side of the data set. Although higher Y contents can be associated with a dry fractionation series (with pyroxene rather than amphibole as the main ferromagnesian phase), the offset from the main array is too small to invoke a significant role for this process: a typical hornblende-poor fractionation series such as seen on the island of Santorini contains twice as much Y at 60–65 wt% SiO₂ (Elburg et al., 2014) as the rather modest 25 ppm seen in the Phase C pumice. The presence of pseudomorphs of plagioclase and pyroxene, presumably after hornblende, supports the idea of amphibole fractionation, but the higher Dy/Yb ratios of these deposits could possibly indicate a minor role for garnet fractionation. Taken together, the trace element and isotopic data may be explained by a prolonged period of AFC-type processes in a magma chamber located at a deeper crustal level, with host rocks more similar to the Ios basement than to the exposed Mesozoic country rocks and the entrained xenoliths.

This idea of prolonged storage is supported by the age gap between the Phase A (ca. 3.5 Ma) and Phase C deposits (ca. 1.4 Ma) (Pe-Piper and Piper, 2013): The Phase C pumice deposits represent the first evidence of renewed magmatic activity, and could represent magmas that were arrested in the deeper crust during the waning stages of Phase A. During solidification, they had ample opportunity to ingest the country rocks. The renewed magmatic activity during Phase C brought mafic magma in contact with these solidified intrusions, which were remelted, and followed the same pathway to the surface as the more mafic magmas, eventually erupting coevally. Hence, it seems that during times of extension, we clearly see the effects of mafic-felsic interaction at a deep crustal level, giving rise to explosive activity, whereas during a compressional regime, effusive igneous activity only documents the processes that are taking place at a shallow level in the crust (Fig. 12). Although deeper assimilation also happens during compressional stages, the results thereof never make it to the Earth's surface, but may be forming granitoids that only become exposed after uplift and erosion.

7. Conclusions

The volcanic deposits of Methana peninsula show a wide variation in their geochemical and isotopic characteristics and contain the most 'crustal' rock types of the active South Aegean Volcanic Arc in terms of Sr-Nd-Hf composition, trending towards the values for the extinct, more evolved centres of Crommyonia. In combination with the high ^{207.8}Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb isotopic compositions, the data point towards an important role for assimilation of crustal rocks similar to those of the Cycladic Basement of Ios, although these are nowhere exposed on Methana. Assimilation of Mesozoic rocks, as exposed on Methana and entrained as xenoliths, is likely to also have played a role. Assimilation thus took place at different crustal levels, and some of the deeper stages of evolution may also have influenced the crystallising mineral assemblages, with plagioclase-free fractionation resulting in high Sr concentrations in some of the older samples. There is no temporal geochemical trend in the volcanic deposits, although the youngest samples show unusual enrichments of some elements, of which the source cannot be determined with certainty.

The period of extension, during which the Phase C deposits erupted (Pe-Piper and Piper, 2013), had an important effect on the igneous products, which were explosive, rather than effusive, and contain isotopically more primitive mafic rocks as well as pumice with the most 'crustal' isotopic signature. The latter likely obtained their signature by stalling of the magma at deeper crustal levels during an earlier tectonic compressional phase, where they assimilated Ios-type crust. They were remobilised by mafic magmas during the extensional period, and followed the same path towards higher crustal levels. Their emplacement took place explosively, forming deposits that are more similar to those seen on the island of Santorini, of which the crust is in a permanent state of extension (Feuillet, 2013), than to the typical lava domes of Methana. However, the chemical and isotopic composition of the Methana pumice deposits is very different from those of Santorini, as the Santorini magmas evolved by predominantly shallow-level fractionation of pyroxene, rather than amphibole, leading to Y enrichment in the more differentiated products. Moreover, even the most evolved Santorini lavas typically have less crustal Sr-Nd-Hf isotopic compositions than the most primitive Methana products. Both characteristics are likely related to the thickness of the crust which is much thinner under Santorini (20 km) than under Methana (30 km) (Karagianni et al., 2005).

The case of Methana clearly shows how the geochemical and isotopic characteristics of a subduction-related volcano may vary in accordance with regional changes in tectonic regime. The ability to recognise these characteristics and their relationship to the tectonic conditions in a modern arc will enable us to use geochemical data of igneous rocks from the earlier geological record to make inferences about their palaeotectonic setting.

Acknowledgments

This research formed part of Smet's PhD work, who was funded by a BOF bursary; research costs were borne by FWO grants G.0585.06N, G.0669.06 and 1509007N. Hf isotopic analyses were performed at the Vrije Universiteit Amsterdam funded by TransNational Access project 079-TNA3 of Europlanet. Laboratory work was assisted by Mr. Kris Latruwe (Ghent), Mr. Richard Smeets (Amsterdam) and Ms. Siri Simonsen (Oslo). Thin sections were prepared by Mr. Jan Jurceka. Olga Zlatkin and Robert Bolhar are thanked for their constructive reviews.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lithos.2018.08.029>.

References

- Altherr, R., Siebel, W., 2002. I-type plutonism in a continental back-arc setting: Miocene granitoids and monzonites from the central Aegean Sea, Greece. *Contributions to Mineralogy and Petrology* 143, 397–415.
- Arculus, R.J., 2003. Use and Abuse of the Terms Calcalkaline and Calcalkalic. *Journal of Petrology* 44, 929–935.
- Bolhar, R., Ring, U., Allen, C.M., 2010. An integrated zircon geochronological and geochemical investigation into the Miocene plutonic evolution of the Cyclades, Aegean Sea, Greece: Part 1: Geochronology. *Contributions to Mineralogy and Petrology* <https://doi.org/10.1007/200410-200010-200504-200414>.
- Bolhar, R., Ring, U., Kemp, A.I.S., Whitehouse, M.J., Weaver, S.D., Woodhead, J.D., Uysal, I.T., Turnbull, R., 2012. An integrated zircon geochronological and geochemical investigation into the Miocene plutonic evolution of the Cyclades, Aegean Sea, Greece: part 2—geochemistry. *Contributions to Mineralogy and Petrology* 164, 915–933.
- Buettner, A., Kleinhanns, I.C., Rufer, D., Hunziker, J.C., Villa, I.M., 2005. Magma generation at the easternmost section of the Hellenic arc: Hf, Nd, Pb and Sr isotope geochemistry of Nisyros and Yali volcanoes (Greece). *Lithos* 83, 29–46.
- Davidson, J., Turner, S., Handley, H., Macpherson, C., Dosseto, A., 2007. Amphibole "sponge" in arc crust? *Geology* 35, 787–790.
- Defant, M.J., 1992. The geochemistry of young volcanism throughout western Panama and southeastern Costa Rica: an overview. *Journal - Geological Society (London)* 149, 569–579.
- DePaolo, D., 1981. Trace element and isotopic effects of combined wallrock assimilation and fractional crystallisation. *Earth and Planetary Science Letters* 53, 189–202.

- Dietrich, V., Gaitanakis, P., 1995. Geological Map of Methana Peninsula (Greece). ETH, Zürich, Switzerland.
- Dietrich, V.J., Mercogli, I., Oberhänsli, R., 1988. Dazite, High-Alumina-Basalte und Andesite als Produkte amphiboldomierter Differentiation (Aegina und Methana, Ägäischer Inselbogen). *Schweizerische Mineralogische und Petrographische Mitteilungen* 68, 21–39.
- Eichelberger, J.C., Chertkoff, D.G., Dreher, S.T., Nye, C.J., 2000. Magmas in collision: Re-thinking chemical zonation in silicic magmas. *Geology* 28, 603–606.
- Elburg, M.A., van Bergen, M.J., Foden, J.D., 2004. Subducted upper and lower continental crust contributes to magmatism in the collision sector of the Sunda-Banda arc, Indonesia. *Geology* 32, 41–44.
- Elburg, M.A., Andersen, T., Bons, P.D., Simonsen, S.L., Weisheit, A., 2013. New constraints on Phanerozoic magmatic and hydrothermal events in the Mt Painter Province, South Australia. *Gondwana Research* 24, 700–712.
- Elburg, M.A., Smet, I., De Pelsmaeker, E., 2014. Influence of source materials and fractionating assemblage on magmatism along the Aegean Arc, and implications for crustal growth. In: Zellmer, G., Straub, S., Gómez-Tuena, A. (Eds.), *Orogenic Andesites and Crustal Growth*. Geological Society, London.
- Evensen, N.M., Hamilton, P.J., O'Nions, R.K., 1978. Rare-earth abundances in chondritic meteorites. *Geochimica et Cosmochimica Acta* 42, 1199–1212.
- Feuillet, N., 2013. The 2011–2012 unrest at Santorini rift: Stress interaction between active faulting and volcanism. *Geophysical Research Letters* 40, 3532–3537.
- Francalanci, L., Vougioukalakis, G.E., Perini, G., Manetti, P., 2005. A West-East Traverse along the magmatism of the south Aegean volcanic arc in the light of volcanological, chemical and isotope data. In: Fytikas, M., Vougioukalakis, G.E. (Eds.), *South Aegean Active Volcanic Arc: Present Knowledge and Future Perspectives*, pp. 65–111.
- Frost, B.R., Barnes, C.G., Collins, W.J., Arculus, R.J., Ellis, D.J., Frost, C.D., 2001. A geochemical classification for granitic rocks. *Journal of Petrology* 42, 2033–2048.
- Gill, J.B., 1981. *Orogenic andesites and plate tectonics*. Springer-Verlag.
- Jolivet, L., Menant, A., Sternai, P., Rabillard, A., Arbaret, L., Augier, R., Laurent, V., Beaudoin, A., Grasemann, B., Huet, B., Labrousse, L., Le Pourhiet, L., 2015. The geological signature of a slab tear below the Aegean. *Tectonophysics* 659, 166–182.
- Karagianni, E.E., Papazachos, C.B., Panagiotopoulos, D.G., Suhadolc, P., Vuan, A., Panza, G.F., 2005. Shear velocity structure in the Aegean area obtained by inversion of Rayleigh waves. *Geophysical Journal International* 160, 127–143.
- Keay, S., Lister, G., 2002. African provenance for the metasediments and metaigneous rocks of the Cyclades, Aegean Sea, Greece. *Geology* 30, 235–238.
- Klaver, M., 2016. Dynamics of magma generation and differentiation in the central-eastern Aegean arc. Faculty of Earth and Life Sciences. Free University Amsterdam, Amsterdam, p. 213.
- Klaver, M., Carey, S., Nomikou, P., Smet, I., Godelitsas, A., Vroon, P.Z., 2016. A distinct source and differentiation history for Kolumbo submarine volcano, Santorini volcanic field, Aegean arc. *Geochemistry, Geophysics, Geosystems* 17. <https://doi.org/10.1002/2016GC006398>.
- Miyashiro, A., 1974. Volcanic rock series in island arcs and active continental margins. *American Journal of Science* 274, 321–355.
- Mizera, M., Behrmann, J.H., 2015. Strain and flow in the metamorphic core complex of Ios Island (Cyclades, Greece). *International Journal of Earth Sciences* 105, 2097–2110.
- Palme, H., O'Neill, H.S.C., 2014. Cosmochemical estimates of mantle composition. In: Carlson, R.W. (Ed.), *Treatise on Geochemistry*. Vol. 3. Elsevier, New York, pp. 1–39 The Mantle and Core.
- Pe-Piper, G., 1975. Strontium isotope ratios in volcanic rocks from the northwestern part of the Hellenic Arc. *Chemical Geology* 15, 53–60.
- Pe-Piper, G., Piper, D.J.W., 2002. The igneous rocks of Greece: The anatomy of an orogen. Gebrüder Borntraeger, Berlin, p. 573.
- Pe-Piper, G., Piper, D.J.W., 2013. The effect of changing regional tectonics on an arc volcano: Methana, Greece. *Journal of Volcanology and Geothermal Research* 260, 146–163.
- Rojas-Agramonte, Y., Williams, I., Arculus, R., Kröner, A., García-Casco, A., Lázaro, C., Buhre, S., Wong, J., Geng, H., Echeverría, C.M., Jeffries, T., Xie, H., Mertz-Kraus, R., 2017. Ancient xenocrystic zircon in young volcanic rocks of the southern Lesser Antilles island arc. *Lithos* 290–291, 228–252.
- Ryan, J.G., Chauvel, C., 2014. The Subduction-Zone Filter and the Impact of Recycled Materials on the Evolution of the Mantle. pp. 479–508.
- Shinjo, R., 1999. Geochemistry of high Mg andesites and the tectonic evolution of the Okinawa Trough-Ryukyu arc system. *Chemical Geology* 157, 69–88.
- Skarpelis, N., Kyriakopoulos, K., 1992. Occurrence and ⁴⁰Ar/³⁹Ar dating of a granite in Thera (Santorini, Greece). *Geologische Rundschau* 81, 729–735.
- Soens, B., 2015. Petrology and geochemistry of the Crommyonia volcanic rocks north of the Saronic Gulf, Greece. Department of Geology. Ghent University, Ghent, Belgium, p. 201.
- Straub, S.M., Zellmer, G.F., 2012. Volcanic arcs as archives of plate tectonic change. *Gondwana Research* 21, 495–516.
- Van Hinsbergen, D.J.J., Hafkenschied, E., Spakman, W., Meulenkamp, J.E., Wortel, R., 2005. Nappe stacking resulting from subduction of oceanic and continental lithosphere below Greece. *Geology* 33, 325–328.
- Vervoort, J.D., Plank, T., Prytulak, J., 2011. The Hf–Nd isotopic composition of marine sediments. *Geochimica et Cosmochimica Acta* 75, 5903–5926.
- Woelki, D., Haase, K.M., Schoenhofen, M.V., Beier, C., Regelous, M., Krumm, S.H., Günther, T., 2018. Evidence for melting of subducting carbonate-rich sediments in the western Aegean Arc. *Chemical Geology* 483, 463–473.
- Zellmer, G.F., 2009. Petrogenesis of Sr-rich adakitic rocks at volcanic arcs: insights from global variations of eruptive style with plate convergence rates and surface heat flux. *Journal of the Geological Society* 166, 725–734.
- Zlatkin, O., Avigad, D., Gerdes, A., 2014. Peri-Amazonian provenance of the Proto-Pelagonian basement (Greece), from zircon U–Pb geochronology and Lu–Hf isotopic geochemistry. *Lithos* 184–187, 379–392.