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Generation of arc rhyodacites through cumulate-melt reactions in a deep crustal hot zone: evidence from Nisyros volcano

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ABSTRACT

The generation of continental crust of intermediate composition occurs predominantly in convergent margin settings, yet the mechanisms by which felsic, calc-alkaline arc magmas are generated remain poorly understood. Magma mixing appears to be a common process in voluminous intermediate arc rocks but the composition of the felsic mixing endmember is typically obscured by the mixing process. We investigate a suite of porphyritic (rhyo)dacitic magmas (65–72 wt.% SiO2) from Nisyros, a young stratovolcano in the Aegean arc, Greece. These magmas are not affected by shallow process such as hybridisation or crystal-melt segregation and thus offer a valuable insight into the origin of felsic melts at convergent margins. We find that the Nisyros (rhyo)dacites form through a reaction in which earlier-formed wehrlite cumulates in the deep arc crust react with melts to form amphibole. This implies that melt major element compositions are effectively buffered by a low-variance mineral assemblage to follow this peritectic boundary such that the silica content of melts extracted from the deep crustal hot zone is controlled by the amount of amphibole crystallised. The resorption of cumulates is pivotal in imparting a distinct trace element signature that is decoupled from major element systematics. For example, high compatible element contents and a strong amphibole signature (low Y and Dy/Yb) cannot be captured by simple crystallisation models and require cumulate resorption. Variable radiogenic isotope systematics indicate minor crustal contamination although assimilation is not proportional to silica content and hence not a main driving force behind the generation of felsic melts. Instead, the Nisyros (rhyo)dacites formed through melt-cumulate reaction processes prior to emplacement as mush bodies at shallow depth and partial eruption. Magma mixing only becomes an important process in the youngest unit on Nisyros. On a global scale, peritectic boundary melts are rarely sampled in the whole rock or melt inclusion record. Conversely, peritectic boundary melts do form a suitable felsic mixing endmember for the generation of voluminous “monotonous intermediate” magmas.

Highlights

- Nisyros (rhyo)dacites are unhybridized melts extracted from a cumulate mush
- The peritectic crystallisation of amphibole buffers the composition of the melts
- High compatible element contents emphasize the role of cumulate resorption
- Crustal melting is not required to generate rhyolitic melts
- Peritectic melts are a common global endmember in the monotonous intermediates
Keywords: magma differentiation; calc-alkaline (rhyo)dacites; amphibole; melt-cumulate reaction; Nisyros; Aegean arc

1. Introduction

Rocks of intermediate composition (andesites and dacites; 57-68 wt.% SiO$_2$) comprise a significant proportion of the extrusive products of continental and mature oceanic arc volcanoes worldwide and are a key component of subduction zone volcanism (e.g., Gill, 1981; Reubi and Blundy, 2009). The strong compositional similarity between arc andesites and the bulk continental crust (e.g., Rudnick, 1995) suggests that the Earth’s crust has predominantly formed and evolved at convergent margins. This, in combination with the significant hazards posed by andesitic and dacitic volcanic eruptions and their association with mineral deposits, warrants a clear understanding of the petrogenesis of andesites. Despite decades of research, this is still an unresolved issue and a wide variety of models have been proposed for the generation of intermediate and silicic arc rocks (e.g., Eichelberger, 1975; Gill, 1981; Hildreth and Moorbath, 1988; Annen et al., 2006; Kent, 2014; Lee and Bachmann, 2014; Adam et al., 2016; Blum-Oeste and Wörner, 2016; Blatter et al., 2017; Müntener and Ulmer, 2018). Given the wide textural and compositional variability of intermediate arc rocks, it is unlikely that any single process is dominant. Hence, we will consider the petrogenesis of a subset of global intermediate arc rocks: hybrid, porphyritic andesites and dacites. These magmas are a common and voluminous component of mature arc volcanoes, for instance, the Cascades, Lesser Antilles and Andean arcs and have been responsible for some of the largest volcanic eruptions of the 20th century (e.g., Mount St. Helens, USA, 1980-1986 and Soufrière Hills, Montserrat, 1995-present). The main characteristic of mature arc magmas is the abundant textural and compositional evidence for magma mixing and mingling, most prominently reflected in bimodal distributions of melt inclusion and amphibole compositions (e.g., Reubi and Blundy, 2009; Kent, 2014). In addition, hybrid andesites commonly have a geochemical signature reflecting amphibole fractionation, irrespective of the presence of amphibole as a phenocryst phase (Davidson et al., 2007). The hybridised nature of these intermediate arc rocks, however, tends to obscure the compositions of mixing components (Blum-Oeste and Wörner, 2016). Quenched mafic enclaves can help constrain the composition of the mafic component, but the nature of the felsic component often remains elusive. Here we present a case-study of Nisyros volcano, Aegean arc, to elucidate the petrogenesis of felsic melts that constitute the dominant component of hybrid arc andesites and dacites. Despite its relatively young age, Nisyros has erupted a wide range of magma compositions that show a temporal transition from tholeiitic andesites to porphyritic, calc-alkaline (rhyo)dacites that lack evidence for extensive hybridisation. Thus, Nisyros offers a unique opportunity to investigate the generation of increasingly felsic melts beneath an embryonic arc stratovolcano, of the type typically buried beneath voluminous hybrid andesites and dacites in more mature volcanoes.

2. Geological background
Nisyros is an island volcano that is part of the Kos-Nisyros-Yali volcanic centre at the eastern edge of the Aegean volcanic arc, Greece. Nisyros is a circular island (~8 km diameter) with a central caldera partly filled with rhyodacitic domes (Figure 1) and is built on thinned continental crust (~27 km). Following the cataclysmic Kos Plateau Tuff (KPT) eruption at 161 ka (Smith et al., 1996), the locus of volcanism shifted southward and construction of Nisyros began upon distal KPT deposits and non-volcanic basement. Apart from a small exposure of pillow lavas, all volcanic deposits on Nisyros are inferred to postdate the KPT eruption as the KPT was found immediately overlying non-volcanic basement in drill cores inside Nisyros’ caldera (Volentik et al., 2005 and references therein). The style of volcanism changed gradually from effusive and mildly explosive to larger Plinian eruptions and the emplacement of viscous lava flows and domes. Based on petrographic features, Klaver et al. (2017) divided the eruptive products into two distinct suites: a phenocryst-poor andesite (LPA) and a phenocryst-rich rhyodacite (HPRD) suite. The LPA suite comprises (basaltic-)andesites and rare dacites with low crystal contents (<10 vol.% on average in the andesites). In contrast, the HPRD suite represents porphyritic rhyodacites that display abundant evidence for magma mingling, including the presence of quenched mafic enclaves and reversely zoned crystals (e.g., Braschi et al., 2014). The rhyodacites have a common texture and mineral assemblage dominated by plagioclase, orthopyroxene, Fe-Ti-oxides and minor clinopyroxene. Amphibole has not been found as a phenocryst phase, despite the clear geochemical signature for residual amphibole in the HPRD suite (e.g., Buettner et al., 2005; Zellmer and Turner, 2007; Bachmann et al., 2012). In addition, the HPRD suite hosts a wide variety of plutonic xenoliths. Several of these cumulate fragments record a high-pressure crystallisation trend of hydrous primitive melts, ranging from (hornblende-)wehrlite to plagioclase-hornblendites (Klaver et al., 2017). Hornblende forms at the expense of clinopyroxene in these cumulates and the role of this reaction in generating the (rhyo)dacites is explored in this study.

### 3. Analytical techniques

A representative suite of 39 whole rock samples spanning the entire subaerial volcanic history of Nisyros was analysed for major element, trace element and Sr-Nd-Hf-Pb isotope composition. Major element data for 20 of these samples were reported together with mineral major- and trace element compositions in Klaver et al. (2017), whereas trace element and Nd-Pb isotope data for 11 samples have been previously published in Klaver et al. (2016). Here we provide the complete geochemical dataset for our Nisyros samples, supplemented with two samples of the KPT. Analytical techniques are given in detail in the Supplementary Material. Briefly, major element concentrations were measured by X-ray fluorescence spectroscopy (XRF) on fused glass beads. Sample powders were digested in PTFE bombs after which trace element concentrations were measured by inductively-coupled plasma mass spectrometry (ICPMS) using USGS reference material BHVO-2 as calibration standard. Strontium, Nd and Hf isotope compositions were separated and measured using conventional techniques. Lead isotope composition was measured by thermal ionization mass spectrometry (TIMS) using a 207Pb/204Pb double spike to correct for instrumental mass fractionation. Results for samples and NIST and USGS reference materials are listed in the Supplementary Material.
4. Results

Nisyros eruptive products are medium- to high-K, calc-alkaline and tholeiitic basaltic andesites to rhyodacites with a trace element signature characteristic of subduction zone volcanic rocks (Figure 2; Vanderkluysen et al., 2005). The HPRD suite comprises dacites to rhyodacites (65-72 wt.% SiO₂) with a common petrography. For this reason, these samples are collectively referred to as “(rhyo)dacites” except when either dacites or rhyodacites are specifically addressed. Mafic enclaves and LPA basaltic andesites show significant variation in trace element abundances and isotopic composition (Figures 2 and 3) that is partly inherited from the heterogeneous Aegean mantle wedge (Klaver et al., 2016) and also reflects variable hybridisation with (rhyo)dacite host melts (Braschi et al., 2012). The more evolved samples (andesites to rhyodacites) are more homogeneous but show systematic differences between the two suites. On the basis of the large available whole rock dataset, it is evident that the Nisyros eruptive products do not describe a single liquid line of descent. Major element trends show marked inflections and gaps that correspond to the difference between LPA and HPRD units. The LPA suite shows a fairly well-constrained liquid line of descent; HPRD enclaves and (rhyo)dacites fall off this trend. In particular, HPRD (rhyo)dacites have systematically higher MgO, CaO and Cr contents than the most evolved LPA samples. This was first observed by Wyers and Barton (1989), who were unable to successfully model a relation between the LPA andesites and HPRD rhyodacites through fractional crystallisation. Moreover, isotopic systematics reveal that both the LPA and HPRD suite show evidence for open-system differentiation yet define distinct evolution trends (Figure 3). Hence, the petrographic and mineralogical dichotomy between the LPA and HPRD suite (Klaver et al., 2017) is mirrored in their whole rock geochemistry.

The HPRD (rhyo)dacites have a porphyritic texture and show little within-suite variation in mineral assemblages and crystal content (Wyers and Barton, 1989; Klaver et al., 2017). Still, they can be subdivided into three groups on the basis of geochemical composition, eruption age and vent location (Figures 1-3). The key characteristics of the three groups, referred to as HPRD-1 to -3, are summarised in Table 1. Although the Argos lava flow (Figure 1) is geochemically similar to the HPRD rhyodacites, it lacks the characteristic porphyritic texture and is therefore not considered in the subsequent discussion. Interestingly, the Kos Plateau Tuff (KPT) lies on an extension of the geochemical trends defined by the HPRD groups. Within each group, samples show limited variability and have a homogeneous isotopic composition. Conversely, the variation between the three groups is significant (Figure 3). A defining characteristic of the HPRD suite is the relatively constant FeO*/MgO and aluminium saturation index (ASI) across a range in SiO₂ contents from 65 to 72 wt.% (Figure 4), which contrast with the LPA suite that evolves to peraluminous, tholeiitic dacites (Figure 4).

5. Discussion

5.1. Discrete melt batches in the HPRD suite

The HPRD suite displays abundant petrographic evidence for magma mingling, such as the presence of quenched mafic enclaves and crystal transfer from mafic enclaves to host lavas and vice versa (Braschi et al.,
2014; Klaver et al., 2017). From the combined geochemical data shown in Figures 2-4, however, it is evident that the dacitic HPRD-1 and -2 units are not simply the result of mixing between a rhyodacitic melt (HPRD-3) and (basaltic-)andesites in the LPA suite or HPRD enclaves: Cr contents and FeO*/MgO are relatively constant in the HPRD suite and in particular V-Y and isotopic systematics exclude any combination of mixing between primitive and evolved melts (Wyers and Barton, 1989; Vanderkluysen et al., 2005). Only the youngest volcanic products, the Profitis Ilias domes, show clear geochemical evidence for magma mixing. This unit (subgroup HPRD-3b) consistently defines a mixing relationship between an evolved melt similar to the HPRD-3a rhyodacites and mafic enclaves (Braschi et al., 2012). As such, the Profitis Ilias domes can be considered as hybrid rocks formed by mixing 20-40 % of basaltic andesite into a rhyodacitic reservoir. This clearly contrasts with HPRD-1 and -2 that do not show evidence for hybridisation, as is particularly evident in FeO*/MgO relationships: hybrid melts (HPRD-3b) have significantly lower FeO*/MgO than the other HPRD dacites (Figure 4). Hence, magma mixing is restricted to the youngest domes; the presence of quenched mafic enclaves in the older HPRD units reflects magma mingling without significant hybridisation.

An alternative process capable of linking the three HPRD groups is crystal-melt segregation (e.g., Bachmann et al., 2012; Lee and Morton, 2015), whereby the groups represent phenocryst-richer or -poorer fractions of the same shallow mush reservoir with bulk rhyodacitic composition. Although phenocryst accumulation in the HPRD dacites agrees with the relatively constant FeO*/MgO and ASI, it is at odds with trace element systematics as illustrated in Figure 5. The HPRD suite has a common phenocryst assemblage of plagioclase, orthopyroxene, Fe-Ti-oxides and minor clinopyroxene. Plagioclase (An$_{30-40}$) is the most abundant phenocryst phase and controls the Ba budget of the phenocryst assemblage. Given the high Ba contents of plagioclase phenocrysts in equilibrium with their glass matrix (600-800 ppm Ba in plagioclase at a glass Ba content of 800-900 ppm; Tomlinson et al., 2012; Braschi et al., 2014; Klaver et al., 2017), crystal-melt segregation would be expected to produce relatively high Ba in crystal-rich fractions. This is not observed in the HPRD groups: Ba is positively correlated with incompatible Rb and the dacitic HPRD groups do not fall on a mixing line with plagioclase phenocrysts. Even in the case of Ba-poor crystal extracts, crystal-melt segregation requires crystal contents of 50-70 % for the HPRD dacites, which differs significantly from the observed 20-30 % (Table 1). In fact, crystal contents are higher in the more silicic HPRD units rather than lower. In contrast, a mixing model between average Upper Pumice glass (Tomlinson et al., 2012) and HPRD plagioclase phenocrysts suggests that the Nikia lava flow (HPRD-3a) is a mixture of 30-40 % crystals and 60-70 % glass, consistent with the observed crystallinity of these rhyodacites (Figure 5). This suggests that the porphyritic (rhyo)dacites have not been affected by significant removal or accumulation of phenocrysts and that their bulk compositions approximate melt compositions. Another argument against crystal-liquid segregation is the more pronounced geochemical amphibole-signature in the rhyodacites compared to the dacites, which is hard to explain through crystal accumulation in the absence of amphibole phenocrysts. The significance of the amphibole signature in the HPRD suite is discussed below.

To summarise, the HPRD (rhyo)dacites, except the youngest Profitis Ilias domes: 1) cannot be related to the LPA suite through closed-system crystal fractionation; 2) are not hybrid rocks formed through magma mixing; 3) are not the result of crystal-liquid segregation in a shallow mush reservoir; 4) show relatively little
geochemical variation within each group; and 5) are erupted from different vents. Taken together, this suggests
that the three HPRD groups represent discrete melt batches that were largely unaffected by subsequent
magma mixing or crystal fractionation. Excluding these processes allows us to investigate directly the
petrogenetic processes responsible for the generation of these dacitic to rhyodacitic liquids.

5.2. HPRD (rhyo)dacites as peritectic boundary liquids

5.2.1. Major element constraints

The HPRD (rhyo)dacites acquired their porphyritic texture through degassing-induced crystallisation of
ascending, crystal-poor melts generated at deeper crustal levels (Klaver et al., 2017). Polybaric evolution
explains the decoupling between textural and geochemical characteristics of porphyritic arc magmas (Annen et
al., 2006; Smith, 2014), such as the paradoxical absence of amphibole phenocrysts in magmas that show a clear
geochemical signature of residual amphibole (Davidson et al., 2007). Such decoupling has previously been
proposed for Nisyros by Wyers and Barton (1989), Buettner et al. (2005), Zellmer and Turner (2007) and
Bachmann et al. (2012). Experimental studies suggest that the generation of felsic melts at middle- to lower
crustal pressures is primarily achieved through crystal fractionation (e.g., Nandedkar et al., 2014; Melekhova et
al., 2015; Blatter et al., 2017; Ulmer et al., 2018). Liquids and crystal residues produced in these experiments
match the composition of arc rhyodacites and cumulates, respectively (Müntener and Ulmer, 2018). Although
crystallisation is the likely driving force of differentiation, it does not capture the pronounced evidence for
open-system differentiation recorded in arc xenoliths (e.g., Smith, 2014; Cooper et al., 2016; Klaver et al., 2017)
and exposed arc root complexes (e.g., Dessimoz et al., 2012; Bouilhol et al., 2015). Hence, the exact processes
through which evolved, crystal-poor melts can be generated remain poorly understood. Integrating the insights
from the cumulate record (Klaver et al., 2017) with the geochemical data provided here enables us to put
better constraints on the generation of the HPRD melts.

The early appearance and abundance of amphibole in cumulate fragments entrained in HPRD magmas led
Klaver et al. (2017) to stress the importance of differentiation of primitive, hydrous melts at the base of the
crust (0.5-0.8 GPa). The importance of amphibole in generating calc-alkaline differentiation trends has long
been recognized (e.g., Cawthorn and O'Hara, 1976; Grove and Donnelly-Nolan, 1986; Davidson et al., 2007) and
recent experimental studies directly related a pyroxene-amphibole peritectic reaction to the generation of calc-
alkaline rhyodacites similar to the Nisyros HPRD suite (Blatter et al., 2017; Ulmer et al., 2018). We investigate
whether the HPRD groups represent liquids produced along a peritectic boundary by projecting whole rock
compositions from plagioclase into an olivine-clinopyroxene-quartz pseudo-ternary diagram (Grove, 1993;
Figure 6). The Nisyros LPA and HPRD suites define relatively tight evolution trends. Enclaves in the HPRD suite
that are not affected by significant hybridisation, as gauged from trace element and isotopic constraints, show
a distinct evolutionary trend from the LPA suite, although the two can be derived from a common parental
melt. Both trends are driven by the fractionation of olivine and clinopyroxene and the higher proportion of
clinopyroxene in the HPRD enclaves likely derives from the expanded stability field of pyroxene at higher
pressure (Müntener et al., 2001; Melekhova et al., 2015). The HPRD (rhyo)dacites define a trend with the most
siliceous HPRD group-3 closest to the quartz apex. The clear inflection in the HPRD evolution trend, from the
enclaves to the (rhyo)dacites, suggests a two-stage process for the generation of silicic melts. The first stage is dominated by the fractionation of predominantly clinopyroxene plus minor olivine and plagioclase.

Fractionation of such an assemblage has little influence on the SiO$_2$ content of the derivative melt and produces high-Al basaltic andesites (e.g., Müntener et al., 2001), represented on Nisyros by the quenched enclaves in the HPRD suite (Figure 2). In the second stage, magnetite and amphibole saturate. The evolutionary trend of the HPRD (rhyo)dacites back-projects beyond the clinopyroxene-hornblende tie-line, indicating a peritectic relation in which clinopyroxene is consumed down-temperature to form amphibole (Grove and Donnelly-Nolan, 1986; Blatter et al., 2017; Ulmer et al., 2018). The reaction between amphibole and clinopyroxene is observed directly in hornblende-gabbro cumulates in the Nikia flow (HPRD-3a; Klaver et al., 2017). The net effect of this reaction is the release of SiO$_2$ from clinopyroxene into the melt, driving derivative melts to rhyodacitic compositions over a small decrease in melt fraction (e.g., Cawthorn and O'Hara, 1976; Müntener and Ulmer, 2018). Experimental studies at relevant conditions support the notion of a two-stage evolution and invariably find a marked inflection in major element versus SiO$_2$ trends at the point of amphibole and magnetite saturation (e.g., Grove and Donnelly-Nolan, 1986; Nandedkar et al., 2014; Müntener and Ulmer, 2018; Supplementary Figure S3). Iron and Mg required for the crystallisation of amphibole are provided by resorption of early-formed olivine and clinopyroxene and as a result, FeO*/MgO changes little along the peritectic reaction boundary. Any increase in FeO*/MgO can be further suppressed by the co-precipitation of magnetite. As such, the inferred liquid line of descent for the Nisyros HPRD suite first shows an increase in ASI and FeO*/MgO over a limited range in SiO$_2$ content followed by an increase in SiO$_2$ upon amphibole saturation.

5.2.2. Trace element constraints

The recognition that the HPRD melts are peritectic boundary liquids excludes pure fractional crystallisation as their differentiation mechanism. As we will demonstrate below, trace element systematics also require a more complex differentiation scenario that decouples major- and trace element systematics. We compare trace element behaviour during differentiation of the HPRD suite for a fractional crystallisation model with open-system scenarios. Details on the modelling approach are given in the Supplementary Material. We will outline three arguments against pure equilibrium or fractional crystallisation: i) over-enrichment of highly incompatible elements compared to major element constraints; ii) amphibole-compatible elements such as Y and Yb are too depleted to be caused by crystallisation alone; and iii) compatible elements (Cr, Ni) are enriched by an order of magnitude relative to the most evolved LPA samples and crystallisation models.

Major element mass balance calculations (Supplementary Table S4) indicate that the HPRD-1 to -3 groups represent residual melts after ~60-70 % crystallisation, which agrees with residual melt fractions found in experimental studies (e.g., Müntener and Ulmer, 2018). On this basis, pure equilibrium or fractional crystallisation predicts a maximum enrichment factor of ~4 for a perfectly incompatible element. Highly
incompatible elements such as Rb, Ba and Th are, however, enriched by up to a factor of 6. A similar feature is observed in mid-oceanic ridge basalts as a result of reactive replacement of cumulate crystals in the gabbroic lower crust (e.g., Lissenberg and MacLeod, 2016). These authors envisage reaction replacement as a zone-refining process in which impurities (incompatible trace elements) are stripped from the reacted minerals and liberated into the melt. The peritectic replacement of clinopyroxene with amphibole could thus contribute to the trace element over-enrichment in the HPRD suite.

Low Y and Dy/Yb reflect the presence of residual amphibole (Buettner et al., 2005; Davidson et al., 2007; Zellmer and Turner, 2007; Bachmann et al., 2012). The magnitude of this amphibole signature, as given by Dy/Yb and Y systematics, increases from HPRD groups 1 and 2 to the HPRD-3a group, consistent with the inferred increase in the proportion of residual amphibole with increasing SiO$_2$ content of the derivative melt. We reiterate that, in the absence of amphibole phenocrysts, any form of magma mixing or crystal-melt segregation is unable to explain these trace element variations. Fractional or equilibrium crystallisation of amphibole and plagioclase, the major crystallising phases as indicated by major element constraints and cumulate textures, cannot account for the observed decrease in Y and Yb either: bulk partition coefficients are not high enough to drive a substantial decrease in Y and Yb in derivative melts even if minor apatite crystallisation is considered. Both these elements are highly compatible in garnet, but garnet is unlikely to have been stable during differentiation of the HPRD suite. For example, Ulmer et al. (2018) conclude that garnet saturation is rare at pressures <0.9 GPa where it occurs along the orthopyroxene-amphibole peritectic curve but not along the clinopyroxene-amphibole peritectic (Figure 6). Given the lack of evidence for residual garnet or orthopyroxene in any of the Nisyros cumulates in combination with cumulate pressures of 0.5-0.8 GPa (Klaver et al., 2017), we exclude the possibility of fractionating garnet to generate lower Y and Yb contents. Furthermore, Cr and Ni contents in the rhyodacites are higher than in LPA siliceous andesites and dacites (Figures 2 and 7). This contrasts with a simple crystallisation model but can be accommodated by cumulate resorption (Kelemen, 1986). Although partition coefficients of Cr and Ni in amphibole are poorly constrained, comparison of co-existing amphibole, clinopyroxene and olivine in arc cumulates (Supplementary Figure S2) shows that both Cr and Ni are compatible in amphibole. Crystallisation of amphibole should thus drive a decrease in Cr and Ni in the residual melt as would clinopyroxene and olivine, in clear contrast with the observed high and constant compatible element contents (Figure 7).

Fractional or equilibrium crystallisation are thus incapable of explaining the observed trace element systematics. To incorporate the effects of the peritectic resorption of clinopyroxene and olivine, we follow the approach of Kelemen (1986) and use an assimilation-fractional crystallisation (AFC) model with a clinopyroxene-olivine assimilant (see Supplementary Material for details). The main result is that resorption of low-Y, high-Ni-Cr wehrlites serves to lower Y and Yb contents in derivative melts compared to fractional crystallisation while Ni and Cr contents are buffered at constant, elevated concentrations. The absolute compatible element concentrations depend on those in the assimilant but will quickly reach equilibrium values and remain constant with progressive AFC, mimicking the observed variation in the HPRD suite. As such, a simple cumulate-resorption model approximates the data better than fractional crystallisation alone and we...
stress the importance of the resorption of previously-formed cumulates in generating characteristic signatures such as low Y and high compatible element contents.

Periodic mixing of HPRD-type evolved melts with primitive melts can help to further decrease Y and Yb and elevate compatible element contents. Mixing of 5-10% primitive melt with an evolved amphibole-saturated melt has a significant effect on trace element contents (Figure 7) but need leave no mark on major element systematics. As long as the proportion of primitive melt added to the system is small, the composition of the melt will only move up-temperature along the peritectic boundary without reaching the distributary point (Glazner, 2007). As such, there will be no change in the crystallising phase assemblage and amphibole and plagioclase will continue to crystallise along the peritectic boundary (Figure 6). Mixing will obviously alter the bulk composition of the system (melts plus cumulates) but melt chemistry will be effectively buffered by the volumetrically dominant, low-variance solid residue. In effect, the composition of the multiply-saturated melts is constrained to lie along the peritectic boundary, in contrast with magma mixing in shallow mush systems. Hybridisation of a small proportion of primitive melts with variably evolved, amphibole-saturated melts in a deep crustal cumulate mush (Hildreth and Moorbath, 1988; Solano et al., 2012; Cashman et al., 2017) thus provides an additional mechanism that can contribute towards the decoupling of major- and trace element systematics. In the case of Nisyros, a model with periodic replenishment (AFC+mix in Figure 7) yields a better fit to the data but cannot be unambiguously established given the uncertainties in the trace element modelling. A pure fractional crystallisation scenario is, however, entirely inconsistent with the data. The peritectic relation in a cumulate-dominated deep crustal mush causes decoupling of major- and trace element systematics: the former are effectively buffered along the peritectic, the latter are controlled by the resorption of wehrlitic cumulates, with or without melt replenishment.

5.3. Is extensive assimilation required to generate rhyodacites?

The systematic variation in radiogenic isotope composition of the Nisyros eruptive products indicates some form of open-system differentiation, but not to the extent seen elsewhere in the Aegean arc (e.g., Elburg et al., 2014; Supplementary Figure S1). Although isotopic variation in the most mafic samples to a certain extent reflects the heterogeneous nature of the Aegean mantle wedge (Klaver et al., 2016), correlations between isotopes and SiO₂ content suggest assimilation of arc crust also plays a role (Figure 3; Wyers and Barton, 1989; Buettner et al., 2005; Zellmer and Turner, 2007). The LPA and HPRD suites display separate trends in radiogenic isotope space that are likely caused by contamination with distinct assimilants, plausibly as the result of differentiation and assimilation at different levels in the crust (Figure 3). The HPRD units, including most enclaves, fall on a common trend in Sr-Nd-HF-Pb isotope space that we interpret to reflect contamination with an isotopically homogeneous assimilant. The observation that the KPT magmas fall on the same trend suggests that this assimilant is uniformly present across the Kos-Nisyros-Yali volcanic centre. Zellmer and Turner (2007) propose the assimilation of a young igneous protolith based on Sr-Nd constraints. Indeed, Miocene volcanic rocks from NE Greece and western Anatolia have an Sr-Nd-Pb isotope composition that is in agreement with the observed assimilation trends (Figure 3; Supplementary Figure S1). Hence, enriched mafic melts that
underplate the Aegean arc crust in the Miocene are a good candidate for the contaminant of the HPRD suite, but clearly the exact nature of the assimilant is not well constrained.

Models for the generation of silicic magmas in the deep arc crust commonly attribute a significant role to partial melting of the arc crust (e.g., Hildreth and Moorbath, 1988; Annen et al., 2006; Solano et al., 2012). On average, Nisyros (rhyo)dacites have a more enriched (i.e., higher $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$, lower $^{143}\text{Nd}/^{144}\text{Nd}$) isotope composition than enclaves. Host lavas and enclaves from the oldest HPRD-1 group, however, have strikingly similar isotopic compositions, suggesting that assimilation occurs predominantly during the early, basaltic differentiation stages with little evidence for assimilation at the dacite-rhyodacite stage. Moreover, the amount of assimilation, as gauged from the isotopic composition of the HPRD groups, is not proportional to their SiO$_2$ content, nor is there a temporal trend; the most enriched isotopic signature is found in the least evolved HPRD-1 group. This is in clear contradiction with crustal anatexis as an important driving force in producing (rhyo) dacitic melts (e.g., Annen et al., 2006). Hence, we find evidence for limited assimilation during the first stages of differentiation, but partial melting of the crust has little control on the major element composition of the derivative melts and is not required to generate silicic melts (Melekhova et al., 2013).

5.4. The evolution of the Kos-Nisyros-Yali volcanic system

The geochemical similarity with the KPT suggests that felsic melts in the Kos-Nisyros-Yali volcanic centre are genetically related and were generated through a common process, as also proposed by Bachmann et al. (2012). Our interpretations differ on where the final stage of differentiation to (rhyo)dacites takes place. Bachmann et al. (2012) infer differentiation through crystal-melt segregation from intermediate parental melts in shallow reservoirs, which we find to be inconsistent with the data presented in section 5.1 and arguments outlined below. Based on petrography of the HPRD suite and its cumulates (Klaver et al., 2017) and the geochemical data provided here, we propose that the Nisyros (rhyo)dacites originate as peritectic boundary liquids whose composition is controlled by amphibole crystallisation. The relative volumes of melts and crystal mush constrain the melt compositions to follow peritectics and thus in effect become chemically buffered. Ascent of these volatile-rich, but crystal-poor, melts leads to degassing and crystallisation. The consequent increase in viscosity causes magmas to either stall as mush bodies in the shallow crust or to be erupted directly as crystal-rich domes or lava flows (e.g., Annen et al., 2006; Cashman et al., 2017). The shallow-level crystal assemblage, as recorded by phenocrysts, lacks amphibole, despite the dominant control this mineral exerts on major element compositions of the host magmas. This model is shown schematically in Figure 8. The narrow isotopic ranges of the three HPRD groups suggests that these represent discrete (rhyo)dacitic melt batches extracted from the lower crustal cumulate mush that have not undergone significant assimilation during ascent and shallow storage. Several lines of evidence, however, indicate that the HPRD groups cannot represent individual batches of primitive melt that differentiated to (rhyo)dacitic compositions. Enclaves in the HPRD suite are in U-series disequilibrium with their host rocks: whereas the enclaves display U-excesses typical of primitive arc melts, the hosts are close to secular equilibrium at lower U/Th, requiring significant aging of the felsic protolith in the crust (Zellmer and Turner, 2007). Individual zircon U/Pb dates for HPRD-3 units (Lower Pumice, Nikia flow, Upper Pumice) display ranges >100 kyr (Guillong et al., 2014), thus supporting long crustal
residence times of zircon-bearing, felsic melts. The long-term storage of felsic melts and zircon growth in an upper crustal reservoir is energetically unfavourable and can only be maintained when magma supply rates are high (e.g., Blundy and Annen, 2016; Cashman et al., 2017). If a shallow mush system was assembled beneath the present-day location of Nisyros since ~250 ka (the oldest zircon dates in the HPRD suite; Guillong et al., 2014), this raises the question why no HPRD-like (or any other) magmas erupted prior to the 161 ka KPT eruption. Hence, the zircon and U-series evidence for protracted generation and storage of evolved melt is not compatible with shallow-level differentiation of basaltic melt batches, nor with a dominant role for melting of amphibolitic cumulates (e.g., Annen et al., 2006; Blatter et al., 2017). Long-term accumulation of felsic melt is, however, possible in the lower arc crust, where evolved melts can be stored along grain boundaries until a critical melt fraction for extraction is reached (e.g., Solano et al., 2012). An extensive lower crustal mush zone can be maintained beneath the Kos-Nisyros-Yali volcanic centre, linking the different volcanic edifices to a common source region wherein (rhyo)dacitic melts are generated and stored (Cashman et al., 2017). We conclude that the felsic HPRD melts slowly matured in the lower crust on timescales of at least 10^5 yr before being emplaced at shallower levels or erupted directly.

5.5. Global perspective

Magma mixing is a common process in convergent margin volcanism and is likely one of the main driving forces behind the eruption of volumetrically abundant andesitic and dacitic magmas, despite the scarcity of melts of such compositions (e.g., Eichelberger, 1975; Reubi and Blundy, 2009; Kent, 2014; Blum-Oeste and Wörner, 2016). On Nisyros, truly hybrid magmas, where hand samples lacking obvious enclaves or inclusions nonetheless yield mixed compositions, are restricted to the youngest Profitis Ilias domes (HPRD-3b; Braschi et al., 2012). This suggests that the magmatic system required ca. 100 kyr after the KPT eruption to incubate a shallow mush zone that could be sustained through the repeated injection of rhyodacitic and mafic melts. Hence, Nisyros underwent a temporal evolution from erupting increasingly felsic peritectic boundary melts (HPRD-1 to -3a) to magma mixing in a shallow mush zone, leading to the eruption of the hybrid HPRD-3b (rhyo)dacites. In more mature arc volcanoes, these earliest stages of volcanism are commonly covered by voluminous younger, often homogeneous, hybrid andesites and dacites, making it difficult to determine the composition of the felsic mixing component (Kent, 2014). In order to investigate if peritectic boundary liquids, as found on Nisyros, might be suitable candidates as felsic components in global arc magmas, we have compiled whole rock and melt inclusion data from the GEOROC database for five arc volcanoes whose recent products are dominated by hybrid andesites and dacites (Figure 9). These five volcanoes, which largely overlap with the selection of Kent (2014), vary dramatically in crustal architecture, ranging from thickened oceanic crust (Montserrat) to ~70 km thick continental crust in the Andes (Parinacota). The main selection criterion was the eruption of hybrid magmas, as indicated by abundant textural and geochemical evidence for hybridisation in a shallow mush system, such as bimodal phenocryst populations, presence of quenched enclaves or banded pumices and linear compatible-incompatible element trends.

An important point is that not all intermediate and felsic arc magmas represent hybrids or require the involvement of peritectic amphibole (e.g., Adam et al., 2016). For example, in the Aegean arc, Santorini displays...
an arc tholeiitic differentiation trend, lacks an REE signature indicative of residual amphibole and appears to
have evolved through low-pressure fractional crystallisation of an anhydrous mineral assemblage (e.g., Druitt
et al., 1999), similar to the Nisyros LPA suite. Only the Akrotiri hornblende-bearing dacites resemble hybrid,
calc-alkaline magmas on Santorini (Figure 9). Nevertheless, the five selected volcanoes show clear geochemical
evidence for magma mixing, although we do not imply that magma mixing is the only operative process at
these volcanoes. They define predominantly sub-horizontal trends in the calc-alkaline field in FeO*/MgO versus
SiO$_2$ space, which is inconsistent with fractional crystallisation of a realistic mineral assemblage. Mixing curves,
on the other hand, are concave due to the higher FeO* and MgO contents in the mafic component and display
near-constant FeO*/MgO over a range in SiO$_2$ (Figure 9), thus supporting other geochemical evidence for their
hybrid nature. Several interesting conclusions emerge from Figure 9. First, melt inclusions show largely
unimodal, rhyolitic compositions close to the eutectic minimum. Only melt inclusions from Mount St. Helens
partly overlap with the peritectic boundary liquid evolution curve defined by the Nisyros HPRD suite. Second,
mixing between rhyolitic melt inclusions and mafic enclaves generally results in too low FeO*/MgO at
appropriate SiO$_2$ contents and hence the melt inclusions are not a suitable endmember composition to
generate the hybrid andesites and dacites. Soufrière Hills (Montserrat) represents an exception as a minor
fraction of the magmas appear to fall on a mixing line with rhyolitic glass. Third, dacitic to rhyodacitic peritectic
boundary liquids constitute suitable mixing components in these volcanoes even though magmas of such
composition are absent in their volcanic record. Fourth, the most mafic magmas commonly have elevated
FeO*/MgO compared to primitive melts, most notably for Santorini-Akrotiri, Mount St. Helens and Soufrière
Hills, in agreement with predictions from our two-stage model whose first stage is dominated by olivine and
clinopyroxene fractionation at relatively invariable SiO$_2$ content.

Based on these lines of evidence, we propose that melts generated by the peritectic reaction of
amphibole with ultramafic cumulates in the deep crust represent suitable mixing components to produce
hybrid arc magmas worldwide. Despite the large differences in crustal architecture of the selected volcanoes
and primary melt compositions that range from high-MgO basalt (Lesser Antilles; e.g., Melekhova et al., 2015)
to high-Mg# andesites (Cascades; e.g., Müntener et al., 2001), all ultimately evolve towards a peritectic
reaction involving amphibole (Müntener and Ulmer, 2018). Although we have focussed on the middle- to lower
crust (>0.5 GPa), Smith (2014) argued that high Na$_2$O contents can promote amphibole saturation even in
volcanoes built on thin oceanic crust. Whether amphibole forms at the expense of clinopyroxene or
orthopyroxene and possibly garnet depends on the depth of differentiation, with the latter favoured at
pressures >1.0 GPa (Ulmer et al., 2018). These peritectic boundary melts are, however, elusive and generally
not present in the whole rock or melt inclusion record. An exception is Mount St. Helens, where both magma
and melt inclusion compositions, including the starting composition used in the experiments of Blatter et al.
(2017), trace the peritectic boundary liquid curve defined by the Nisyros HPRD suite. The implication is that
while the compositions of melts generated in the lower crust are likely to track a pseudo-equilibrium
crystallisation evolution path (Lee and Bachmann, 2014), erupted magmas represent hybrids of multiple
mineral and melt components (Kent, 2014; Cashman et al., 2017; Figure 8). Melt inclusions in these hybrid
magmas need not record the composition of melts delivered to a shallow mush reservoir and are often
profoundly affected by in situ crystallisation of phenocrysts (Figures 5 and 8). Why melt inclusions tracing the peritectic boundary liquid curve are exceedingly rare, requires further study.

6. Conclusions

Nisyros hosts a suite of porphyritic (rhyo)dacites that show a progressive increase in SiO\textsubscript{2} content with time. Magma mixing does not become a significant petrogenetic process until the youngest domes while the older (rhyo)dacites are also not affected by crystal-melt segregation. Rather, these (rhyo)dacites appear to approximate melt compositions and thus shed important light on the generation of felsic melts in convergent margin settings. The main conclusions from this study can be summarised as follows:

1) Major element systematics indicate that the Nisyros (rhyo)dacites represent peritectic boundary liquids extracted from a cumulate mush at the base of the crust (deep crustal hot zone). The down-temperature reaction of hydrous melt with (ultra)mafic cumulates stabilises amphibole, leading to a marked increase in SiO\textsubscript{2} content of the derivative melt while FeO*/MgO and ASI increase only slightly, which we regard as a tell-tale characteristic of this process.

2) Although isotope systematics are indicative of open-system differentiation, assimilation of wall-rock is subordinate and not proportional to SiO\textsubscript{2} content, indicating that extensive crustal melting is not required to generate (rhyo)dacitic melts.

3) Trace element systematics are decoupled from major elements and inconsistent with simple fractional crystallisation. Elevated compatible element (e.g., Cr and Ni) contents and over-enrichment of highly incompatible elements preclude simple equilibrium or fractional crystallisation. Instead, cumulate resorption – the logical result of a peritectic relation – is required to impart a strong amphibole signature (low Y and Dy/Yb) and elevated compatible element contents on derivative melts.

4) Silicic melts are generated and stored in the deep crustal hot zone in the Kos-Nisyros-Yali volcanic centre; extracted melts undergo little modification in shallow mush systems apart from in-situ crystallisation. Magma mixing is restricted to the youngest domes on Nisyros. Zircon U-Pb and U-series data (Zellmer and Turner, 2007; Guillong et al., 2014) indicate protracted maturation of the (rhyo)dacites in the deep crustal cumulates with the oldest zircon dates predating the onset of subaerial volcanism.

5) On a global scale, peritectic boundary liquids, as represented by the Nisyros (rhyo)dacites, are suitable felsic mixing components in the generation of voluminous hybrid arc andesites and dacites. These felsic melts are, however, rarely exposed in mature arc volcanoes and are also not tracked by melt inclusion records. The exposure of the earliest evolved magmas in the embryonic Nisyros arc volcano thus contributes to a better understanding of the petrogenesis of intermediate and felsic arc magmas.

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References


Figure captions

Fig. 1. Simplified geological map of Nisyros and its location within the Kos-Nisyros-Yali volcanic centre (inset), modified after Volentik et al. (2005) and Klaver et al. (2017). The volcanic units are grouped into phenocryst-poor andesite (LPA) and phenocryst-rich rhyodacite (HPRD) suites and further subdivided as discussed in the text. Inferred vent locations for the HPRD units are shown, as well as the presumed location of the Kos Plateau Tuff (KPT) caldera to the north of Nisyros.
Fig. 2. Variation of selected major- and trace elements in the Nisyros eruptive products, as sub-divided into phenocryst-poor (LPA) and phenocryst-rich (HPRD) suites. Older literature data that could be identified as a volcanic unit defined by Volentik et al. (2005) are shown as smaller symbols (HPRD suite) and grey squares (LPA suite; data from Vanderkluysen et al., 2005; Zellmer and Turner, 2007; Braschi et al., 2012). Data for the 161 ka Kos Plateau Tuff (KPT; this study and Pe-Piper and Moulton 2008) are included for comparison. All data are shown on a volatile-free basis. The blue line connects the same samples in each panel and illustrates the likely liquid line of descent for the LPA suite. Crosses depict samples that display geochemical evidence for hybridisation between LPA suite melts. The linear mixing model between a post-UP melt and mafic enclaves for the Profitis Ilias domes (HPRD-3b) is adapted from Braschi et al. (2012). Note that the curvature of the mixing line in panel (d) is due to the logarithmic scale.

Fig. 3. Isotopic variation of Nisyros eruptive products. Literature data (smaller symbols) for the Profitis Ilias domes and enclaves (HPRD-3b) and the mixing model between a post-UP melt and enclaves are adapted from Braschi et al. (2012). Symbols as in Figure 2. Assimilation-fractional crystallisation (AFC) trends highlight that the LPA and HPRD suite have been contaminated by distinct assimilants and followed separate crustal differentiation routes. The HPRD units (shaded fields) and the 161 ka Kos Plateau Tuff (KPT) lie on a common AFC trend; the Profitis Ilias domes (HPRD-3b) are affected by 20-40 % mixing with mafic enclaves. Error bars show 2 SD analytical uncertainty. AFC model parameters are given in the online Supplementary Material.

Fig. 4. Major element variation diagrams of Nisyros volcanic rocks showing the distinct differentiation trends of the LPA and HPRD suites: a) FeO*/MgO versus SiO$_2$ diagram with all Fe as FeO* and the tholeiitic (TH) – calc-alkaline (CA) dividing line of Miyashiro (1974); b) Aluminium saturation index (ASI; molar Al$_2$O$_3$/[CaO + Na$_2$O + K$_2$O]) versus SiO$_2$. The calc-alkaline HPRD (rhyo)dacites display limited variation in FeO*/MgO and ASI over a range in SiO$_2$ contents (65-72 wt.% SiO$_2$), whereas the LPA suite rapidly evolves to tholeiitic, peraluminous dacites as shown by the fractional crystallisation (FC) model for the LPA suite; see text for discussion. Symbols and data sources as in Figure 2.

Fig. 5. Ba versus Rb diagram of the Nisyros eruptive suite together with data for Lower- and Upper Pumice glasses (Tomlinson et al., 2012) and plagioclase in the HPRD-3 group (Braschi et al., 2014; Klaver et al., 2017). Plagioclase (An$_{30-40}$) phenocrysts are in trace element equilibrium with Upper Pumice glass (Braschi et al., 2014). The different HPRD groups do not fall on a mixing line between UP or LP glass and plagioclase (the dominant phenocryst phase), indicating that crystal-melt segregation is a not a viable process to explain the difference between the HPRD groups. See text for further discussion.

Fig. 6. Pseudo-ternary olivine (Ol) – clinopyroxene (Cpx) – quartz (Qtz) diagram projected from plagioclase, after Grove (1993), showing the Nisyros whole rock sample groups and mineral compositions in HPRD cumulate xenoliths reported by Klaver et al. (2017). HPRD enclaves have been screened to exclude samples clearly
affected by magma mixing on the basis of major and trace element composition. The blue dashed line illustrates the liquid line of descent for Nisyros while the grey lines show reaction boundaries found in the experimental study by Ulmer et al. (2018) for a basaltic-andesite primary melt. The HPRD enclaves and LPA suite show distinct evolutionary trends away from a common parental magma, likely reflecting variable olivine/clinopyroxene with crystallisation depth. The HPRD groups 1-3 define an inflected trend that projects outside the Cpx-hornblende (Hbl) tie-line. Together with petrographic evidence from the cumulates, this suggests that the HPRD evolutionary trend follows a peritectic reaction boundary where clinopyroxene is consumed to form amphibole. The experimental study of Ulmer et al. (2018) shows a similar inflection at the Hbl-in point; the exact location of the Hbl-in point and direction of the reaction boundaries is dependent on the bulk composition of the system and hence distinct in the Nisyros samples. Samples falling on the orthopyroxene (Opx) – Hbl peritectic boundary are not found on Nisyros, in line with the absence of orthopyroxene in Nisyros cumulates. Note that garnet only appears along the orthopyroxene peritectic. See text for further discussion.

Fig. 7. Trace element evidence for a two-stage process and the peritectic crystallisation of amphibole to generate the Nisyros HPRD suite. Symbols as in previous figures. Stage 1 comprises clinopyroxene, plagioclase and olivine crystallisation and the HPRD suite subsequently follows a differentiation trend dominated by amphibole (stage 2). Three different models for stage 2 are shown: a pure amphibole-plagioclase fractional crystallisation model (FC), a similar FC model combined with assimilation of clinopyroxene-olivine cumulates (AFC) and a model in which such an AFC process is combined with periodic mixing with a primitive melt (AFC+mix). The latter two models provide the best fit to the Nisyros HPRD suite and hence suggest a dominant role for the resorption of cumulates that leads to the stabilisation of amphibole and calc-alkaline derivative melts. See text for more discussion; details on the modelling approach are given in the Supplementary Material. The composition of hornblende in HPRD cumulates (green fields; Klaver et al., 2017) are shown. Note that panel d is scaled to exclude some LPA basaltic andesites and HPRD enclaves with >950 ppm Sr. Subscript “N” denotes chondrite-normalised values (McDonough and Sun, 1995).

Fig. 8. Model for the generation of evolved melts in the lower crust through the peritectic replacement of clinopyroxene and olivine with amphibole – schematic version of the Rb versus Y diagram shown in Figure 7a. The thick grey-white line illustrates the evolution of melt in a deep crustal hot zone (liquid-line-of-descent, LLD). Upon amphibole saturation, Y content decreases, aided by the resorption of low-Y wehrlite cumulates. Replenishment of the mush system with a small amount of primitive melt P (blue arrows) is evident as mixing in trace element space, but major element compositions are chemically buffered to lie along the multiply-saturated peritectic curve. All melts present in this deep crustal reservoir therefore have a composition that is constrained to lie on a pseudo-equilibrium crystallisation trend. Amphibole-saturated derivative melts (L1 to L3) can be extracted to shallower crustal levels or be erupted directly. These melts are crystal-poor but may carry a small crystal load, including zircon and rare cumulate fragments. When emplaced into a shallow reservoir, the extracted melts undergo decompression-induced crystallisation and become a crystal-rich magma consisting of...
melt (G1,2) and solid (phenocryst; S1,2) components. The composition of the glass (quenched melt) in erupted products is controlled by the amount and composition of crystallised solids in the shallow magma and is no longer constrained to lie on the multiply saturated evolution curve. Melt inclusions are likely trapped after some in-situ crystallisation and hence need not represent liquid compositions derived from the deep crustal hot zone. In the case of Nisyros, an amphibole-free phenocryst assemblage (S1) constrains the coexisting glass (G1) to have reasonably high Y and Rb contents. Under different PT conditions, a similar liquid L1 might crystallise hornblende (high Y) and biotite (high Rb) and form a glass composition G2 and phenocryst assemblage S2. Mixing and mingling with primitive melts in the shallow reservoir can lead to extensive hybridisation at the sample scale as attested to by the common presence of mafic enclaves and disequilibrium textures in phenocrysts. Bulk rock samples are therefore mixtures of different mineral and melt components, as indicated by the hatched field. The blue field represents Nisyros hybrid HPRD-3b samples.

**Fig. 9.** Whole rock and melt inclusion FeO*/MgO versus SiO2 diagram for volcanic centres dominated by hybrid andesites and dacites; data compiled from the GEOROC database. All Fe expressed as ferrous (FeO*) on a volatile-free basis. The tholeiitic – calcalkaline dividing line is from Miyashiro (1974). In the Aegean arc, the Nisyros HPRD suite (shaded fields, colours as in previous figures) defines the evolution of melts formed through the peritectic replacement of clinopyroxene and olivine with amphibole. For the other volcanic centres, one or more mixing lines (in black) are fitted through the data using a mafic composition and a peritectic boundary curve melt as endmembers. The grey mixing line reflects mixing of melt inclusions with a mafic composition. For the selected volcanoes, the majority of the intermediate samples have calc-alkaline compositions at low FeO*/MgO, consistent with magma mixing as a dominant control on their composition. Melt inclusions from the same volcanic centre are predominantly rhyolitic and are consistently not a suitable felsic mixing component, whereas peritectic boundary liquids do present appropriate endmember compositions. See text for further discussion.

**Table caption**

**Table 1.** Summary of the main characteristics of the three HPRD groups and the Kos Plateau Tuff. DRE: dense rock equivalent. Notes: A – Volentik et al. (2005); B – Braschi et al. (2012); C – estimated from present-day exposure; D – Tomlinson et al. (2012); E – Longchamp et al. (2011); F – Guillong et al. (2014); G – Smith et al. (1996); H – Allen (2001).