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# How important is the role of crystal fractionation in making intermediate magmas? Insights from Zr and P systematics

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## ABSTRACT

Most magmatism on Earth forms by direct melting of the mantle, generating basalts at the low silica end of the terrestrial compositional spectrum. However, most subduction zone magmas erupted or sampled at the surface are basalt-andesitic to andesitic and hence have higher Si contents. Endmember hypotheses for the origin of andesites are: (1) direct melting of the mantle at water-saturated conditions, (2) partial re-melting of altered basaltic crust, (3) crystal fractionation of arc basalts in crustal magma chambers, and (4) mixing of mafic magmas with high Si crust or magmas, e.g., dacite–rhyolite. Here, we explore the possibility of using Zr and P systematics to evaluate the importance of some of these processes. Direct melting of the mantle generates magmas with low Zr ($<50$ ppm) and $P_2O_5$ ($<0.2$ wt.%). Crystal–liquid segregation should drive an increase in P and Zr in the residual magma because the magma is initially undersaturated in zircon and apatite. With further cooling and crystallization, apatite followed by zircon will saturate, causing P and Zr to decrease so that most rhyolites and granites will have low P and Zr (high temperature rhyolites may never saturate in zircon and will maintain high Zr contents). Mixing of basalts with rhyolites having low P and Zr should generate coupled decreases in Zr and P with increasing $SiO_2$. Here, we show that Zr ($>100$ ppm) and $P_2O_5$ ($>0.2$ wt.%) in island- and continental-arc magmas initially increase to levels higher than what can be achieved if andesites form by direct mantle melting. As Si increases, both Zr and P decrease with Zr decreasing at higher Si, and hence lagging the decrease in P. These systematics, particularly the decoupled decrease in Zr and P, cannot be explained by mixing, and instead, are more easily explained if andesites are dominantly formed by crystal–liquid segregation from moderately hydrous basalt, wherein P and Zr are controlled, respectively, by early and later saturation in apatite and zircon. Although there is clear isotopic and outcrop (enclaves) evidence for mixing in magmatic systems, crystal–liquid segregation appears to be the dominant process in generating intermediate magmas, with mixing playing a secondary role.

Finally, recent studies have suggested that the abundance of certain magma compositions in a given volcanic setting may be dictated by the optimal crystallinity window for efficient crystal–liquid separation (50–70 vol%). We show that the $SiO_2$ content of the residual liquid in this crystallinity window increases with increasing water content. We thus speculate that high water contents ($>2$ wt.% $H_2O$) may favor extraction of andesitic and dacitic liquids while lower water contents favor extraction of more basaltic magmas. If continental arc magmas tend to be more andesitic, as often believed, it follows that they may begin more water-rich than island arc magmas, which are basaltic. In any case, if intermediate arc magmas are formed dominantly by crystal–liquid fractionation, large volumes of complementary mafic cumulates must be generated during the formation of andesitic magmas, as is seen in well-exposed crustal sections.

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## 1. Introduction

### *1.1. The andesite problem*

It is well-known that Earth's continental crust is andesitic and that andesites are predominantly found at subduction zones (Taylor and McLennan, 1985). Understanding how andesites form is thus critical for understanding why the Earth has continents. There are many ways to make andesites (Gill, 1981; Carmichael, 2002), but whether any mechanism dominates is unclear. For example, making andesites by direct hydrous melting of the mantle was motivated by experimental studies showing that andesitic melt can be generated by water-saturated melting of the upper mantle (Kawamoto and Holloway, 1997; Carmichael, 2002; Grove et al., 2012) and very likely explains the origin of boninites (Falloon and Danyushevsky, 2000). However, it is unclear whether such high water contents can be sustained in the mantle wedge at all subduction zones, particularly in regions where hot and young oceanic crust is being subducted and much of the slab dehydration may occur before the magmatic arc front (e.g., Cascadia subduction zone; Syracuse et al., 2010). Making andesites by slab melting is another possibility, but requires hot slab surface temperatures (Yogodzinski and Kelemen, 1998; Rapp et al., 1999; Yogodzinski et al., 2001; Rapp et al., 2003) that may not be achieved in all subduction zones. Making andesites by re-melting of basaltic lower crust has been shown to be energetically unfavorable (Dufek and Bergantz, 2005). Generating andesites by crystal–liquid segregation (Gill, 1981; Jagoutz et al., 2009; Dessimoz et al., 2012), while energetically simpler, is faced with the problem of how to efficiently separate such viscous liquids from the crystals. Finally, a mixing origin for andesites is motivated by isotopic signatures of crustal contamination (Hildreth and Moorbath, 1988; Dungan and Davidson, 2004), the presence of mafic enclaves (Eichelberger, 1975; Furman and Spera, 1985; Wiebe et al., 1997; Clynne, 1999), and a reported lack of intermediate melt inclusion compositions (Reubi and Blundy, 2009; Kent et al., 2010; Özdemir et al., 2011) (Fig. 1a). However, gaps in melt composition are not observed everywhere (Straub, 2003). It is also unclear whether mixing of mafic magmas into felsic magmatic systems is efficient because mafic magmas, owing to their higher solidus and liquidus temperatures, are likely to solidify upon contact with felsic melts, decreasing the efficiency of mixing (Sparks and Marshall, 1986; Paterson et al., 2004; Caricchi et al., 2012).

### *1.2. Potential insights from elements that are controlled by accessory minerals*

Distinguishing between the above mechanisms of forming andesites using major elements is challenging. Major elements are buffered by temperature, pressure and the dominant mineral phases in the crystallizing assemblage. If the composition of the bulk crystallizing assemblage does not change fundamentally during differentiation, major element fractionation trends will generate linear arrays in Harker variation diagrams, making it difficult to distinguish from mixing, which also generates linear arrays. Only when a fundamentally different crystallizing phase appears, will differentiation trends become nonlinear and distinguishable from simple mixing. For example, saturation of an oxide phase like magnetite results in a sudden decline in total Fe in the residual magma. The appearance of magnetite in the crystallization sequence manifests itself as a distinct kink in $FeO_T$ versus MgO variation diagrams. However, because magnetite saturation occurs before or even drives the initial Si enrichment of the basalt, Fe and other major elements turn out to be not particularly diagnostic in evaluating the mechanisms by which Si is further enriched to make andesites.

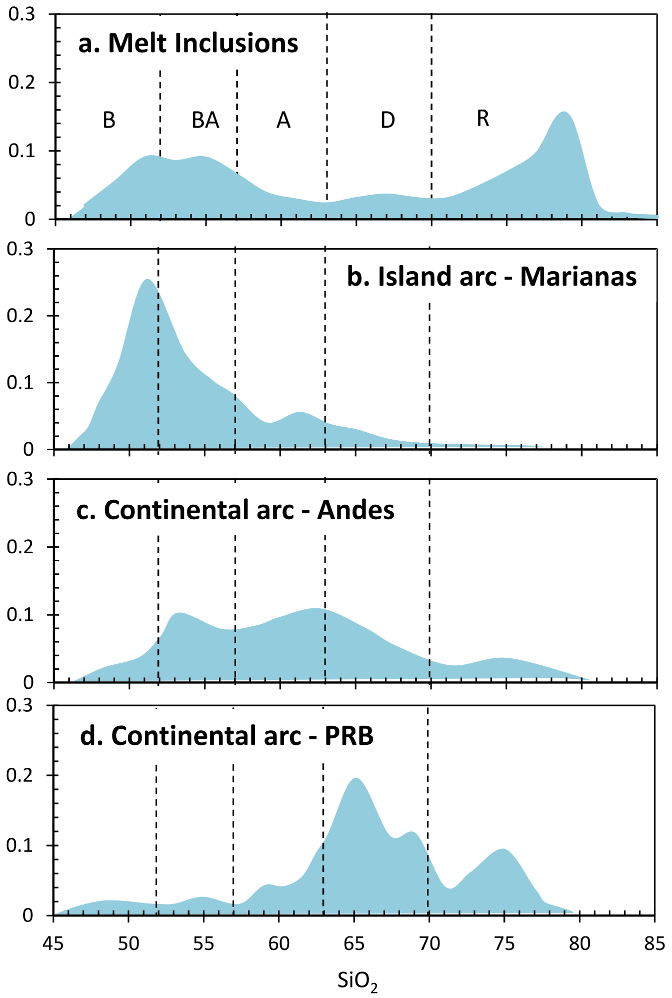

**Fig. 1.** Probability histogram for $SiO_2$ (wt.% on a volatile-free basis) in (a) melt inclusions (gray field), (b) lavas and magmas from the Marianas Island arc, (c) lavas and magmas from the Andean continental arc, and (d) plutonic rocks from the Peninsular Ranges Batholith (PRB) in California (USA). Fields of basalt (B), basaltic-andesite (BA), andesite (A), dacite (D), and rhyolite (R) are shown in (a).

Isotopes are powerful tracers for evaluating mixing between crustal and mantle components. For example, there is no doubt that crustal assimilation or remelting is important in the formation of evolved rocks with radiogenic and stable (e.g., oxygen) isotopic compositions distinct from more primitive endmembers in a differentiation suite (Hildreth and Moorbath, 1988; Kistler, 1990; Chappell et al., 1992; Zeck and Williams, 2002). In other cases, isotopes alone may not resolve the andesite problem. There are examples in which radiogenic isotopes remain relatively constant over $SiO_2$ contents ranging from basalt to rhyolite (Coleman et al., 1992; Francalanci et al., 1995; Lee et al., 2007; Deering et al., 2011) because the mafic and felsic endmembers are isotopically similar or because crustal contamination occurred early in the magmatic differentiation process.

Trace elements, such as Zr and P, which are controlled by the appearance of accessory phases, such as zircon and apatite, may provide an additional tool for distinguishing between some of the above scenarios. When the magma is not saturated in these phases, Zr and P do not partition significantly into the solid phases and thus, their concentrations increase in the liquid with progressive crystal segregation (Fig. 2). When the liquid saturates in zircon and apatite, Zr and P in the liquid become buffered at levels controlled by temperature and the major element composition of the liquid (Watson and Harrison, 1983; Harrison and Watson, 1984)

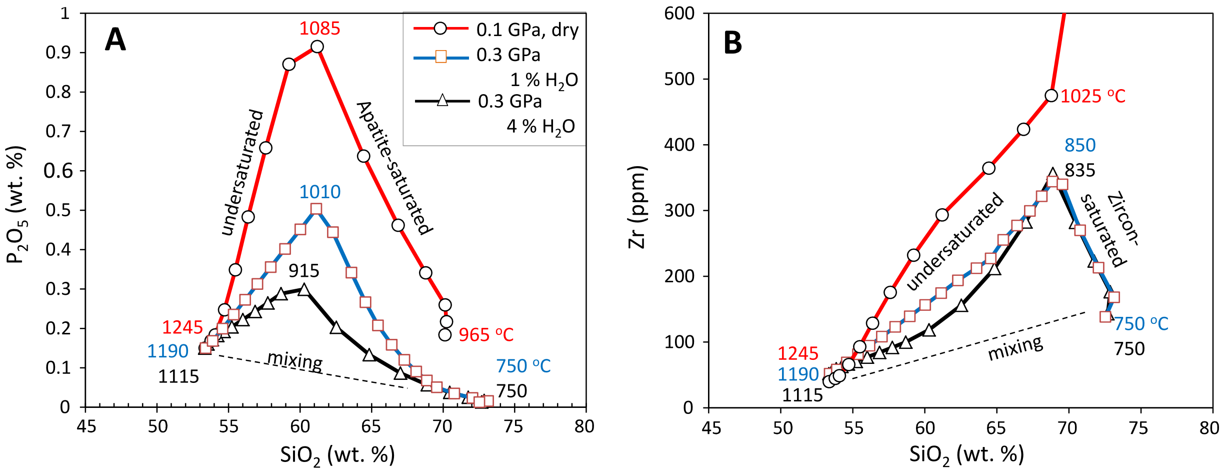

**Fig. 2.** Modeled residual liquids formed by equilibrium crystallization of dry and hydrous parental basalts using Rhyolite-Melts (Gualda et al., 2012). $P_2O_5$ (wt.%) and Zr (ppm) are plotted against $SiO_2$ (wt.%) in (a) and (b), respectively. Elemental concentrations have been normalized to a volatile-free system. Temperatures at the liquidus, point of saturation in apatite or zircon, and the solidus are shown for reference. Dashed straight line in (a) and (b) are hypothetical mixing lines.

such that Zr and P decrease with further crystallization. Importantly, zircon typically saturates at higher Si than apatite with the delay between zircon and apatite saturation controlled by crystallizing temperatures, phase assemblages and melt composition, all of which in turn depend on water content. Under dry and hot crystallization, zircon solubility is suppressed so that Zr peaks at higher Si than under wet and cooler crystallization. Crystal–liquid segregation therefore results in out-of-phase kinks in Zr and P differentiation arrays. This contrasts with mechanical mixing, which generates linear arrays in elemental variation diagrams (Fig. 2). In this regard, Zr and P are useful because Si-enriching differentiation trends generated by mixing and crystal–liquid fractionation are relatively linear for major elements. Zr and P contents are also useful in evaluating the importance of the mantle in generating andesites because the mantle is poor in Zr and P and should therefore generate melts with low Zr and P.

## 2. Methods, data compilation, and reference crystallization models

Arc melt inclusion and magma compositions were compiled for the Marianas island arc, Peninsular Ranges batholith (PRB) in California, the southern Andes, and the Agean arc in Europe. Global melt Inclusion data ($n = 7382$) were obtained from pre-compiled files from the Georoc database (http://georoc.mpch-mainz.gwdg.de/georoc/). This is the same database used in Reubi and Blundy (2009), which allows us to reproduce their results. Data for the Peninsular Ranges Batholith ($n = 289$) are from Lee et al. (2007). Data for Marianas Island arc ($n = 507$ for Zr and 538 for P) are from Earthchem (http://www.earthchem.org). For the Andes, we used only the southern Andean arc in Chile ($n = 1974$ for Zr and 2304 for P). For the Aegean arc, we used pre-compiled files from the Georoc database ($n = 1056$ for Zr and 1367 for P). Data were filtered to exclude rocks that were obviously cumulates (e.g., olivine gabbros), but not all cumulates, especially those with intermediate compositions, could be excluded due to the difficulty in distinguishing cumulates from magmas based on major elements alone. Thus, some primitive samples (low $SiO_2$) with high $P_2O_5$ most likely represent cumulates and should be ignored in Figs. 3 and 4. Finally, basaltic andesites or andesites (55–56 wt.% $SiO_2$) with high Mg# were identified. These high Mg# rocks include boninites. To identify these rocks, we used the following criteria $\mathrm{Mg\#} \geqslant 0.00294\mathrm{SiO}_2^2 - 0.3697\mathrm{SiO}_2 + 11.953$ (where Mg# = atomic Mg/(Mg + $Fe_T$) and $Fe_T$ represents total Fe) (Fig. 5). Although our criterion for identifying high Mg# samples is rather arbitrary, we are consistent in its application in all figures.

Residual liquid compositions were calculated using the Rhyolite-MELTS thermodynamic programs (Gualda et al., 2012) (Fig. 2). Calculations were done for closed-system batch crystallization beginning from the liquidus and cooling at 20 °C temperature intervals at constant pressure. A starting composition equivalent to an evolved basalt/gabbro in the Peninsular Ranges Batholith, California was assumed (52.1 wt.% $SiO_2$, 0.68 $TiO_2$, 18.3 $Al_2O_3$, 7.24 $FeO_T$, 5.55 MgO, 10.5 CaO, 2.6 $Na_2O$ and 0.38 $K_2O$), though the differentiation trends are not particularly sensitive to the starting composition so long as it is basaltic. Oxygen fugacity was buffered at the fayalite–magnetite–quartz buffer. Three scenarios were modeled: (1) 0.1 GPa crystallization at anhydrous conditions, (2) 0.3 GPa crystallization with bulk $H_2O$ of 1 wt.%, and (3) 0.3 GPa crystallization with bulk $H_2O$ of 4 wt.%. Crystallization paths involving higher water contents progress to lower final temperatures due to solidus depression. Zr and P were modeled by post-processing the MELTS output. MELTS may slightly under-estimate $SiO_2$ content of extreme residual liquids, but this does not change overall behavior. Initial Zr and $P_2O_5$ contents of the parental basalt was assumed to be 52 ppm and 0.15 wt.%, respectively, to match natural rocks of this $SiO_2$ content. Zr and P at zircon and apatite saturation were calculated using established solubility models (Watson and Harrison, 1983; Harrison and Watson, 1984). As a first approximation, Zr and P were assumed to be perfectly incompatible in all crystallizing phases except, of course, for zircon and apatite.

## 3. Results: Zr and P systematics of arc magmas

We examined the Zr and P systematics of arc magmas and melt inclusions, respectively representing liquid–crystal mixtures in volcanic/plutonic rocks and homogeneous liquids trapped in phenocrysts (Figs. 3 and 4). The Marianas arc is used as an example of an island arc (Fig. 3c, d), while the southern Andes (Chile), the Peninsular Ranges batholith in southern California (USA), and the Aegean arc are used as examples of continental arcs (Fig. 4).

For most magmas, Zr rises from ~50 to ~100–150 ppm and $P_2O_5$ rises from 0.1 to 0.3 wt.% as $SiO_2$ increases. Zr and P then

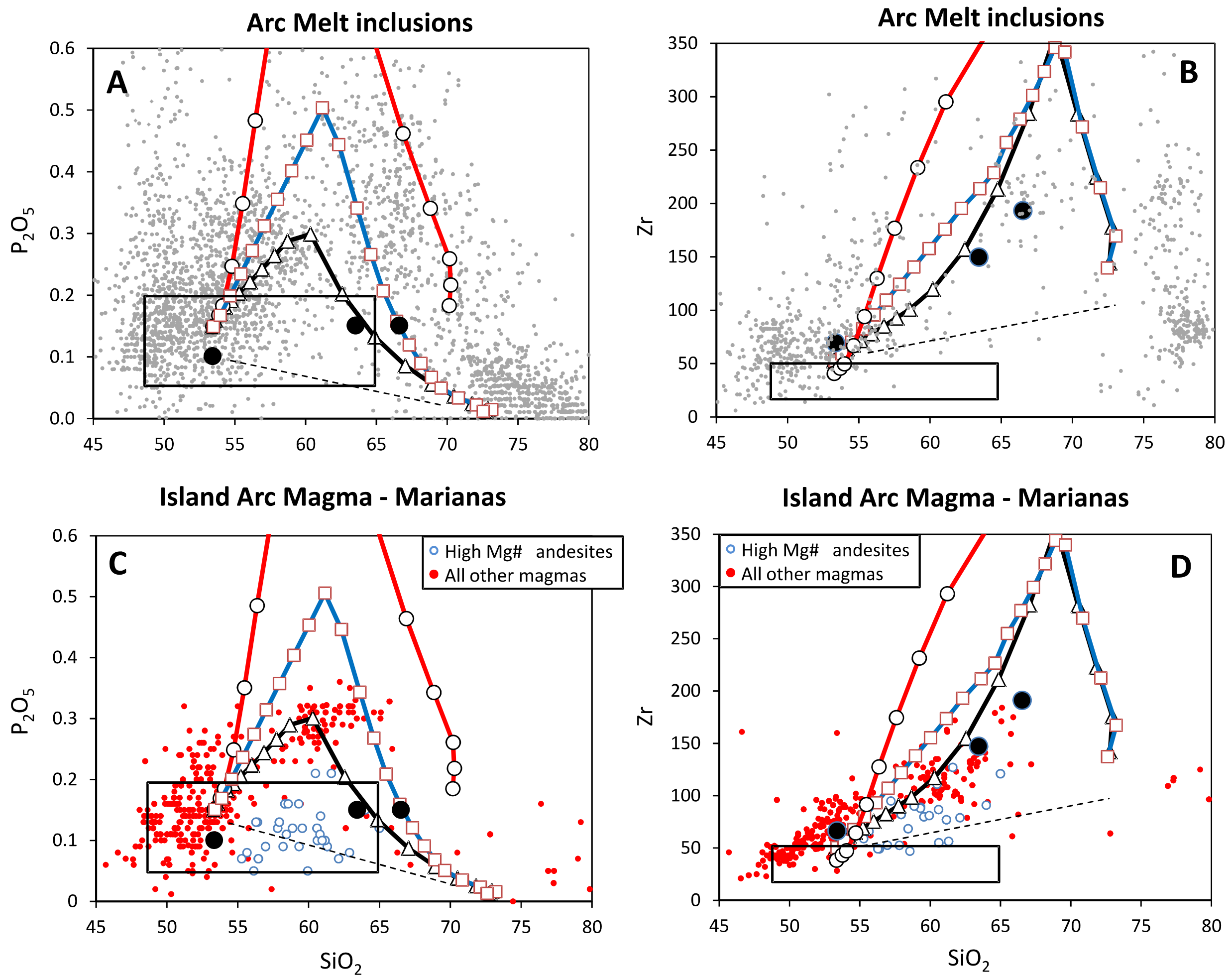

**Fig. 3.** Plots of $P_2O_5$ (wt.%) and Zr (ppm) versus $SiO_2$ for arc melt inclusions in (a) and (b) and Marianas island arc lavas in (c) and (d). Melt inclusion data include the following arcs: Sulawesi, New Zealand, New Hebrides, Mexico, Marianas, Luzon, Lesser Antilles, Kuriltes, Kermadec, Kamchatka, Central America, Cascades, Andes and Aleutians. Boxes in each panel refer to estimated $P_2O_5$ and Zr contents of mantle-derived magmas, such as basalts and boninites. High Mg# andesites and basaltic-andesites, which would include boninites, in the Marianas arc lava dataset (c and d) are defined here as magmas with $SiO_2$ between 55–65 wt.% and $Mg\# \geqslant 0.00294SiO_2^2 - 0.3697SiO_2 + 11.953$ where $Mg\# =$ atomic $Mg/(Mg + Fe)$ and $SiO_2$ (see Fig. 5). Large solid black circles represents model compositions for lower, middle and upper continental crust in order of increasing $SiO_2$ content (Rudnick and Gao, 2003). Straight dashed lines in each panel represent hypothetical mixing line between low Si (basaltic) and high Si (rhyolitic) endmembers.

peak at ∼65 and ∼60 wt.% $SiO_2$, respectively, followed by rapid declines with further increase in $SiO_2$, generating a kink in the Zr- and P–$SiO_2$ arrays that are broadly consistent with the modeled crystallization trends for hydrous basalt. However, a small fraction of the data, particularly for continental arcs, fall below the kink, approaching the linear array predicted for binary mixing between basalt and rhyolite. It can also be seen that those andesites identified to have high Mg#s have the lowest Zr and P contents in our compilation.

For melt inclusions (Fig. 3a), intermediate compositions appear to be scarcer than in magmas, which Reubi and Blundy (2009) have used to argue that melt inclusions represent real liquids and magmas are crystal + liquid mixtures of mafic and felsic endmembers. The overall Zr- and P–$SiO_2$ systematics of the melt inclusions nevertheless outline the overall rise and fall of Zr and P as seen in the magmas. This suggests that the dearth of intermediate *melt* compositions may be a sampling bias introduced in the global database (most melt inclusions are sampled from olivine and quartz hosts, leading to an over-representation of mafic and silicic melt) rather than a robust geological observation (see also melt inclusion data from Avachinsky volcano in Kamchatka and volcanoes from the Izu Bonin-Marianas arc (Straub, 2003; Krasheninnikov and Portnyagin, 2011)), which supports the inference of a biased sampling in the global melt inclusion database.

## 4. Discussion

### 4.1. On making primary mantle-derived andesites

The high Zr and P at intermediate $SiO_2$ are not easily explained by direct derivation of the mantle. For example, 10–20% melting of an upper mantle with 5 ppm Zr and 0.019 wt.% $P_2O_5$, equivalent to that estimated for depleted mid-ocean ridge basalt mantle (Workman and Hart, 2005), yields primary liquids with 25–50 ppm Zr and 0.1–0.2 wt.% $P_2O_5$ (these are upper bounds because sub-arc mantle may be more depleted than ambient mantle). These levels are lower than the majority of andesites shown in Fig. 4. The only intermediate magmas that have sufficiently low Zr and P to be consistent with a direct mantle origin are those basaltic andesites and andesites we identified as having high Mg# (Fig. 5), which would include boninites (Figs. 3 and 4). Boninites, indeed, are thought to represent the products of hydrous flux melting of highly depleted peridotite (Falloon and Danyushevsky, 2000), but the scarcity of intermediate rocks with low Zr and P suggests that direct mantle melting is not the dominant mechanism for making andesites globally.

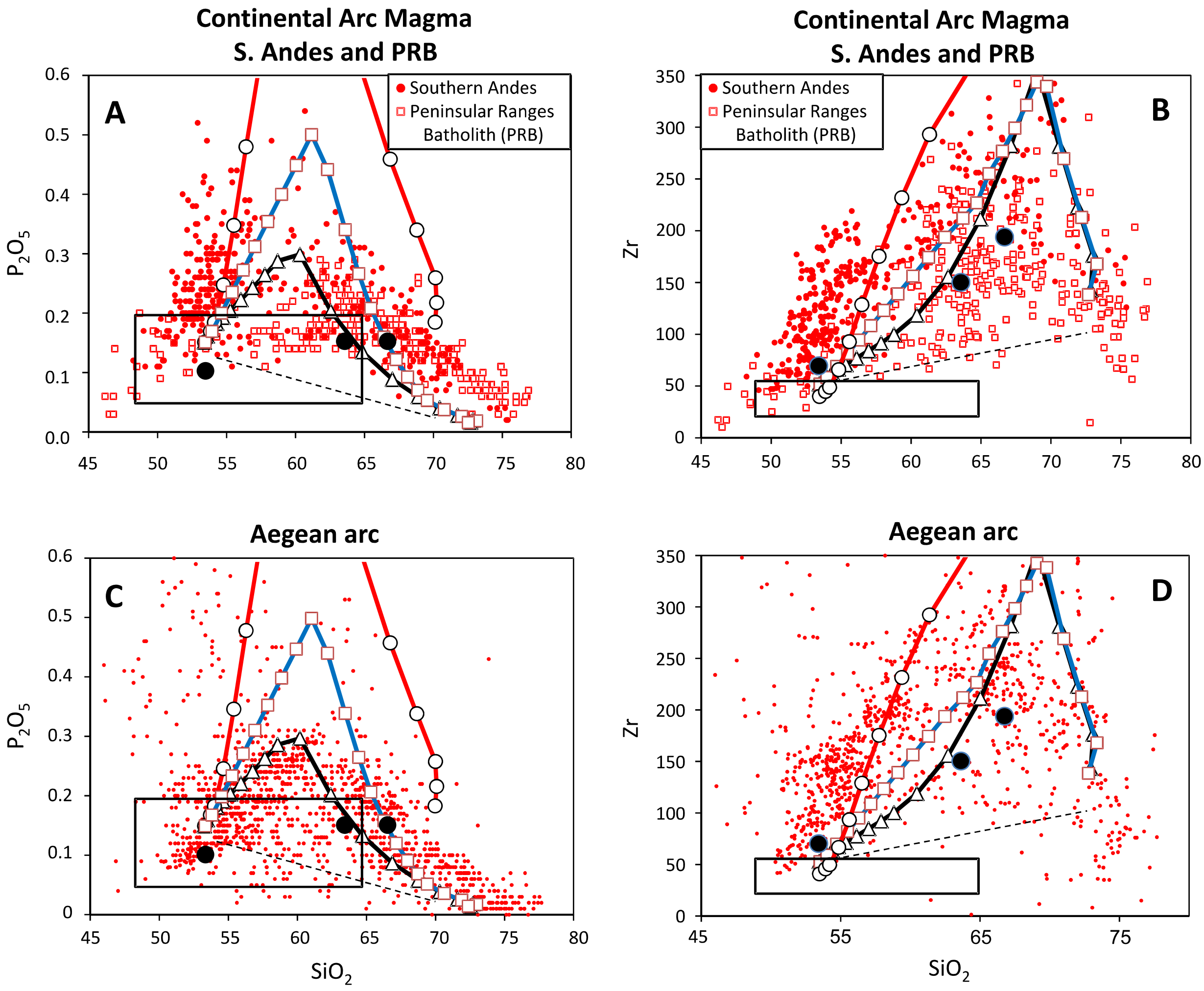

**Fig. 4.** Same as in Fig. 3, but (a) and (b) show continental arc lavas and plutons from the southern Andes and Peninsular Ranges Batholith (USA) and (c) and (d) show Aegean arc magmas (reference sources in text). Symbols as in Fig. 3.

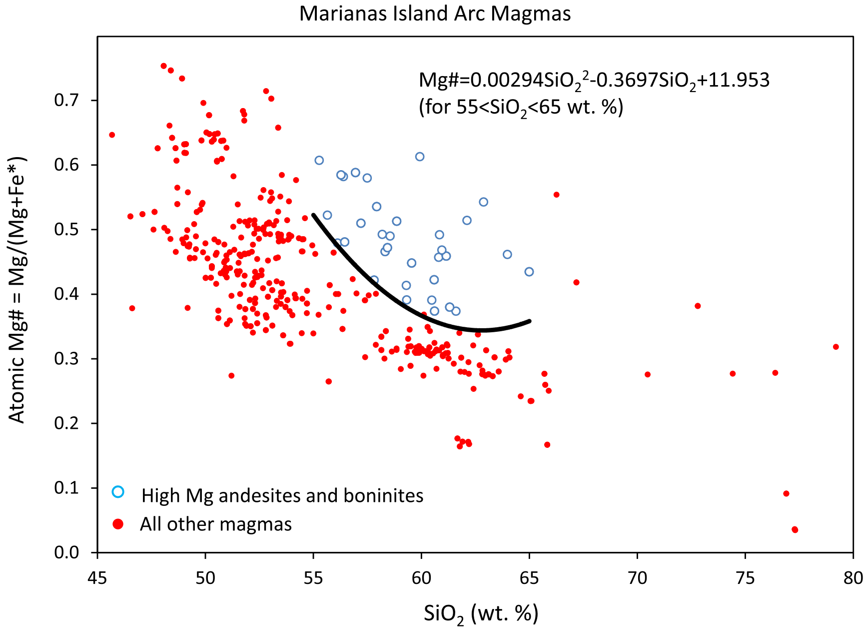

**Fig. 5.** Mg# versus $SiO_2$ (wt.%) in Marianas Island arc magmas as in Figs. 3c and 3d in main text. Mg# is equal to Mg/(Mg + Fe*) in atomic proportions, where Fe* corresponds to total Fe. Basaltic andesites and andesites with anomalously high Mg# may be direct mantle melts under hydrous conditions. We have defined those magmas between 55–65 wt.% $SiO_2$ with $Mg\# \geqslant 0.00294SiO_2^2 - 0.3697SiO_2 + 11.953$ to be anomalously high in Mg#. This criterion was adopted for Figs. 3b and 3c in the main text.

### 4.2. On making andesites by mixing basalt with high silica endmembers

The switch in the overall behavior of Zr and P, combined with the fact that the Zr peak lags the P peak in terms of $SiO_2$ as a differentiation index, cannot be explained solely by mixing of a basalt with any silicic endmember, such as a dacite or rhyolite, because such a process would generate linear mixing arrays and require that Zr and P decrease at the same $SiO_2$. As noted above, some intermediate samples (57—68 wt.% $SiO_2$), particularly in continental arcs, fall below the Zr and P peaks, suggesting some involvement of mixing. However, for the examples studied here, no more than ∼20% of intermediate continental arc and none of the island arcs (excluding high Mg# andesites) fall on pure endmember mixing arrays between basalt and rhyolite, indicating that generating andesites and dacites by mixing basalts with rhyolites is not the dominant process. The role of mixing is primarily to blur the crystal fractionation signature as multiple parcels of magmas at different stages of evolution interact during the incremental growth of magma reservoirs. Our observations are broadly consistent with the studies of Özdemir et al. (2011) and Kent et al. (2010), who show that magmatic series at given volcanoes can be cogenetic, generated by down-temperature crystallization, albeit sometimes overwhelmed by a mixing signal introduced just before eruption (Kent et al., 2010). Similarly, recent studies show that the mixing of mafic enclaves into felsic host plutons may be rate-limited by chemical reaction between the enclave and host pluton, which may occur late in the lifespan of the magma chamber (Farner et al., 2014).

### 4.3. On making andesites by direct melting of subducted sediments

There is ample evidence that fluids and partial melts from subducted sediments contribute to the trace element signature of arc magmas, including arc basalts (Johnson and Plank, 1999; Plank, 2005; Tollstrup and Gill, 2005). However, partial melts of sediments are generally rhyolitic (Patino Douce and Johnston, 1991), so sediment melts are not likely to be dominant producers of andesites in arc systems, unless these sediment melts mix with basalt (which we showed above to be rather limited). Furthermore, He isotopic systematics of most of the circum-Pacific island arc volcanoes are indistinguishable from mantle values, arguing against an origin by slab or sediment melting (Poreda and Craig, 1989). Nevertheless, it is worth evaluating the possibility of a sediment origin for arc andesites in the context of Zr and P systematics. A key feature of greywacke and pelitic sediments is that they have Zr and P concentrations much higher than mantle peridotite and primary mantle-derived basalts owing to the presence of zircon of detrital origin and apatite of detrital and/or biogenic origin (Plank and Langmuir, 1998). Thus, partial melts of sediments would generally be expected to be saturated in zircon and apatite, and consequently, their Zr and P concentrations should follow the saturation curves. As can be seen from Figs. 2–4, this would predict andesitic magmas with Zr contents much higher than andesites derived from fractionation of basalt, which would be zircon undersaturated. Thus, although the influence of sediment melts to the trace element signature of arc magmas is undisputed, it seems unlikely that sediment melts are volumetrically important enough to be the dominant producers of andesites or arc crust in general.

### 4.4. On making andesites by direct melting of pre-existing mafic rocks

Making andesites by partial melting of pre-existing mafic rocks cannot be ruled out from Zr and P systematics alone. In terms of geochemistry, equilibrium melting and equilibrium crystallization are identical. However, generating the entire spectrum of arc magma compositions via melting of mafic crust would require partial melting fractions to range from low degrees (generating rhyolite) to complete melting (generating basalt). In addition, generating large volumes of basalt by re-melting mafic rocks is energetically inefficient. In magmatically active areas, the heat for melting pre-existing rock comes from heat advected in by magmatic intrusions, but a significant component of such heat is consumed by first heating the country rock up to the solidus before any country rock melting can occur (e.g., see discussions as early as in Bowen (1928)). Various models have shown that crustal melting of refractory, sub-solidus mafic lithologies is inefficient in producing large volumes of silicic melts (Barboza and Bergantz, 2000; Dufek and Bergantz, 2005; Annen et al., 2006; Gelman et al., 2013).

### 4.5. On making andesites to rhyolites by crystal–liquid segregation

The simplest explanation for the Zr and P systematics of arc magmas with intermediate silica content (andesites – dacites) is that andesites are formed by crystal fractionation from mafic parents, in which zircon and apatite join the crystallizing assemblage at intermediate but different $SiO_2$. The observation that Zr peaks at dacitic rather than rhyolitic compositions suggests that crystallization occurs dominantly under hydrous and cool conditions rather than dry and hot conditions because the latter would suppress zircon saturation until the magma reaches near-solidus temperature (see also differentiation in alkaline series in which zircon never reach saturation, e.g. Wiesmaier et al., 2012). These hydrous conditions are consistent with the low Zr contents of dacites and rhyolites, which imply crystallization temperatures between 700–800 °C (Figs. 2 and 3), well below the dry solidus of rhyolite and dacite. Finally, as shown in Fig. 1, rhyolites are volumetrically limited in arc magmatic suites (e.g., Hildreth, 2007), consistent with rhyolites being formed as extreme, late stage residual liquids in the upper crust (Fowler and Spera, 2010; Gualda and Ghiorso, 2013). We thus suggest that silica enrichment in arc magmas, all the way to rhyolites, is dominantly produced by down-temperature crystallization from hydrous basaltic parents. This has petrogenetically been shown to be plausible (Dessimoz et al., 2012; Jagoutz and Schmidt, 2012).

Our conclusion that silica enrichment is dominantly controlled by crystal fractionation may seem at odds with the observation that andesites and their plutonic equivalents, particularly in continental arc environments, often have evolved radiogenic isotopic compositions or non-mantle like oxygen isotopes, requiring incorporation of old crustal components (Lipman et al., 1978; Francis et al., 1980; Taylor, 1980). This apparent inconsistency is reconciled if contamination by crustal components occurs concurrently or before the magmatic system has undergone significant increase in $SiO_2$. One possibility is that hydrous mantle-derived basalts first pond in the deep crust, where they undergo simultaneous crystallization, assimilation of mafic lower crust, and magmatic recharge (Hildreth and Moorbath, 1988; Annen et al., 2006; Lee et al., 2013), generating an evolved basalt with inherited crustal isotopic signatures (Fig. 4). Residual melts generated in this deep crustal staging and blending zone then rise upwards and subsequently differentiate into magmas with an extended range of silica contents (Fig. 4). Such a scenario explains how some volcanic and plutonic suites can be diverse in major element composition and, at the same time, have relatively uniform, but crustal contaminated isotopic compositions (e.g, Coleman et al., 1992; Deering et al., 2011). Some crustal contamination can also occur in the mid- to upper crust, as magmas have reached more evolved compositions (e.g., Boroughs et al., 2005; Bindeman et al., 2008; McCurry and Rodgers, 2009; Mollo et al., 2009; Reubi et al., 2011). However in most cases, incorporation of cold crust into differentiated magmas is likely to be volumetrically limited (Thompson et al., 2002).

### *4.6. Why do intermediate compositions dominate in arc magmas?*

An outstanding question is why do intermediate magmas dominate arc magmatic suites, and, in detail, why are continental arcs andesitic and island arcs basaltic to basalt-andesitic (Fig. 1)? Previous studies suggested that true intermediate liquids are actually quite rare because of strong nonlinearities in how $SiO_2$ varies with temperature in fractionating magmas (Grove et al., 1997; Reubi and Blundy, 2009; Melekhova et al., 2013). This has led to the suggestion that the abundance of andesitic *magmas* (liquid + crystals) is the result of mixing mafic and silicic liquids (Reubi and Blundy, 2009; Melekhova et al., 2013). Mass balance considerations require that such mixing involves roughly equal volumes of basalt and rhyolite, followed by efficient mixing to generate andesites. However, Figs. 1b–d (plus abundant field data in well-characterized arcs (Hildreth, 2007) and hot spots and mid-ocean ridges (Thordarson and Höskuldsson, 2008)) show that exposures of rhyolites are volumetrically minor in every tectonic environment (but particularly so in island arcs). In the context of the mixing hypothesis, the paucity of rhyolitic magmas would imply that most of the rhyolitic liquids have already been mixed to form andesites, leaving little evidence of rhyolitic magmas other than in melt inclusions.

An equally robust alternative to mixing is crystal–liquid fractionation. Crystal–liquid separation in magmatic systems is expected to be inefficient at low crystallinity because convection is vigorous enough to keep stirring the reservoir and re-entraining settling crystals (Dufek and Bachmann, 2010). Once a critical crystal fraction is reached, the strength of convective re-entrainment subsides, allowing crystal–liquid separation to happen most efficiently by processes ranging from hindered settling to compaction (Miller et al., 1988; Petford, 2003; Bachmann and Bergantz, 2004). The optimal crystallinity window for physical separation of crystals and liquids has been theoretically shown to be between 50–70 vol% because convective stirring is hampered but the mushy reservoir is not completely clogged by crystals to prevent liquid segregation altogether (McKenzie, 1985; Dufek and Bachmann, 2010).

The composition of the residual liquid at the optimum crystallinity window for melt extraction is thus of interest. As seen in Fig. 6, Rhyolite-MELTS simulations predict $SiO_2$ content of initially dry magmas expelled at 50–70% crystal fraction to be basaltic (∼54–57 wt.%). However, for hydrous conditions (3–5 wt.% $H_2O$), the expelled magmas at the same crystallinity window would be andesitic to dacitic (∼57–65 wt.% $SiO_2$). This is because the effect of water is to expand the temperature interval over which crystallization occurs and to increase the $SiO_2$ activity of the residual liquid. We thus speculate that because island arcs are more basaltic and continental arcs more andesitic (Fig. 1), the initial water content of parental basalts in island arcs is lower than that of parental basalts in continental arcs. This inference may not be unreasonable in light of the general observation that island arcs follow Fe-enriching differentiation paths and continental arcs and mature island arcs follow Fe-depleting paths (Miyashiro, 1974) due to early crystallization of Fe–Ti oxides. Specifically, magnetite saturation is thought to be controlled by water and oxygen fugacity (Berndt et al., 2005; Zimmer and Plank, 2006). Under wet conditions, magnetite saturates early, driving early Fe depletion. Under dry conditions, magnetite fractionation is delayed, allowing Fe to enrich in the residual magma. Exactly why continental arc magmas are wetter and island arc magmas dryer is unclear. Possibilities include differences in the composition of the sub-arc mantle or subducting slab, in the thermal state of the mantle wedge, or in the nature of magmatic differentiation within the crust.

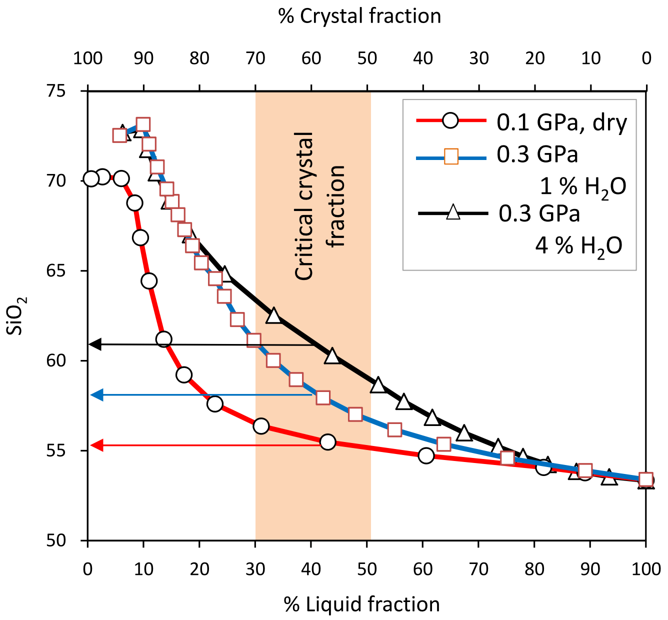

**Fig. 6.** Crystal fraction versus residual liquid fraction estimated from thermodynamic modeling of equilibrium crystallization of dry and hydrous evolved basalts. Critical crystal fraction for efficient liquid segregation from a crystalline mush is denoted by the vertical orange bar (Dufek and Bachmann, 2010). Intersection of this bar with the model crystal fraction-$SiO_2$ curves denotes the $SiO_2$ content of the residual liquid at the point of most efficient segregation. For typical arc magmas, this occurs at 60–65 wt.%, generating andesites and dacites.

## 5. Summary words on andesite formation

Zr and P systematics in magmatic series imply that high pressure crystal fractionation of hydrous basalts, coupled with some lower crustal assimilation early (prior to silica enrichment) in the differentiation process, is a fundamental mechanism by which arc magmas today evolve towards intermediate to silicic compositions (Fig. 7). Mixing between different magma endmembers undoubtedly occurs, as shown by many textural observations (e.g., presence of enclaves, zoning patterns in phenocrysts in erupted lavas (Larsen et al., 1938; Pe-Piper and Moulton, 2008; Kent et al., 2010; Özdemir et al., 2011)), but mixing alone is not central to the magmatic distillation that is generating the Earth's continental crust. Formation of andesites by direct mantle melting explains the origin of boninites, but is unlikely to be a dominant process in making the vast volumes of andesites in island and continental arcs.

A consequence of a crystal fractionation-dominated differentiation scheme is the formation of large volumes of mafic and ultramafic cumulates. Evolved basalts to dacites are produced in deep crustal reservoirs by extraction of interstitial melt from partially crystallized mush zones (Dessimoz et al., 2012). If deep enough, plagioclase-free cumulates are left behind in the lower crust and may eventually founder back into the mantle (Herzberg et al., 1983; DeBari and Sleep, 1991; Ducea and Saleeby, 1996, 1998; Greene et al., 2006; Lee et al., 2006, 2007; Jagoutz et al., 2009; Jagoutz and Schmidt, 2012; Lee, 2014). If the pressures in the lower crust are not high enough, plagioclase-bearing cumulates will form (Blatter et al., 2013), but such cumulates would be difficult to founder owing to their low densities. In both cases, we speculate that rhyolites also form dominantly by crystal fractionation (± some crustal assimilation), but from evolved parental magmas that have ascended into the upper crust, (Bachl et al., 2001; Deering and Bachmann, 2010). Such a model is consistent with

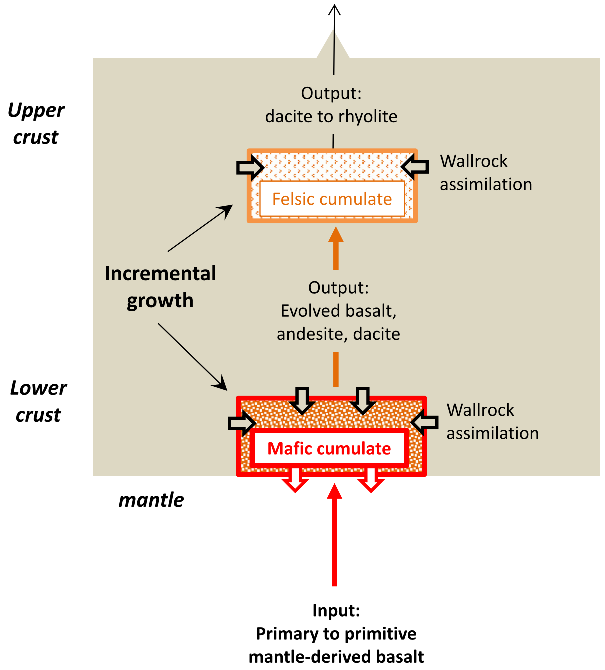

**Fig. 7.** Cartoon showing polybaric multi-stage differentiation history of magmas. Primary, mantle derived basalts rise from the mantle and stall in or below the deep crust, resulting in cooling, crustal assimilation and crystal fractionation. This generates a range of compositions from evolved basalts to dacites, depending on conditions, such as water content. Andesites dominate in continental arc settings. Such melts then rises into the middle and upper crust, where they differentiate by crystal–liquid segregation to form rhyolitic liquids. Mixing can occur anywhere along this path due to the incremental growth of reservoirs, but is not crucial to the generation of intermediate magmas.

the few crustal cross-sections sampled at the surface of our planet (Ducea and Saleeby, 1998; Lee et al., 2006; Jagoutz et al., 2009; Jagoutz and Schmidt, 2012; Greene et al., 2006; Otamendi et al., 2012). Quantifying the relative proportions of high and low pressure crystal fractionation would go far in furthering our understanding of how arc magmas differentiate.

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