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

Cin-Ty A. Lee [a,*], Olivier Bachmann [b]

[a] Department of Earth Science, Rice University, 6100 Main St., Houston, TX 77005, USA
[b] Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland

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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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* Corresponding author. Tel.: +1 713 348 5084.
*E-mail address:* ctlee@rice.edu (C.-T.A. Lee).

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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.

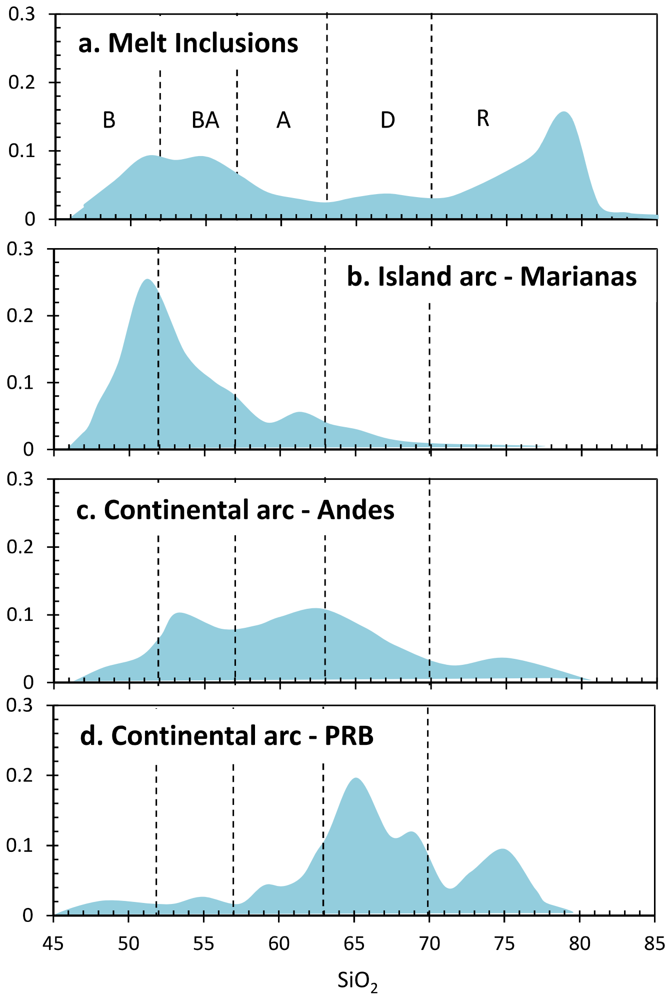

**Fig. 1.** Probability histogram for $SiO_2$ (wt.% on a volatile-free basis) in (a) melt inclusions (gray field), (b) lavas and magmas from the Marianas Island arc, (c) lavas and magmas from the Andean continental arc, and (d) plutonic rocks from the Peninsular Ranges Batholith (PRB) in California (USA). 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)