Amphibole "sponge" in arc crust?

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ABSTRACT

Pressure-temperature-time paths followed by arc magmas ascending through the lithosphere dictate the phase assemblage that crystallizes, and hence the compositions of liquid fractionates. Here we use La/Yb and Dy/Yb versus SiO_2 relationships from selected volcanoes to show that amphibole is an important mineral during differentiation of arc magma. Production of intermediate and silicic arc magmas occurs as magmas stall and cool in the mid-lower crust, where amphibole is stable. Because amphibole is rarely a phenocryst phase, we term this "cryptic amphibole fractionation." If this process is as widespread as our investigation suggests, then (1) amphibole cumulates may act as an effective filter for water dissolved in mantle-derived magmas; (2) amphibole cumulates may act as a fertile source of intracrustal melts and fluids; and (3) recycling of amphibole cumulates has the potential to return incompatible trace elements and water to the mantle.

Keywords: amphibole, recycling, crustal origin, rare earth elements, magma, basalt, fractionation, arcs.

INTRODUCTION: CONTROLS ON ARC MAGMA DIFFERENTIATION

Magmas produced by subduction represent one of Earth's most significant hazards and provide the primary ingredient for growth of continental crust. Most arc magmas are highly differentiated, and rarely represent primary mantle-derived melts. The compositions of melts that are ultimately emplaced into the crust and their physical properties, such as viscosity and water content, that dictate the hazard potential of erupted magmas are dependent on processes of differentiation, but determining the differentiation pathways remains a challenge.

Mineral assemblages observed in volcanic rocks are typically used to estimate conditions of crystallization, on the basis that given assemblages are stable at particular pressure-temperature conditions. In instances where experiments reproduce observed mineral assemblages, they point to low-pressure crystallization (Pichevant et al., 2002; Sisson and Grove, 1993); however, the minerals found in the rock may not be those that control the evolution of the magma suite. While arc basalts and andesites often carry gabbroic mineral assemblages (plagioclase + pyroxene ± olivine), many arc terranes contain large volumes of amphibole-bearing cumulate rocks such as diorite, amphibolite, and amphibole gabbro (DeBari and Coleman, 1989; Ducea and Saleeby, 1996). Resolving this discrepancy

between the postulated and observed residua of basalt differentiation in arcs is an important step in determining models of crustal growth and water storage in the arc crust.

RARE EARTH ELEMENT CONSTRAINTS ON THE ROLE OF KEY MINERALS AND DEPTH OF FRACTIONATION

We adopt a simple approach of examining trace element trends reflecting the fractionation of pressure-sensitive minerals, specifically amphibole and garnet. We consider trace element trends only for cogenetic suites from single volcanoes. Trace element modeling may have the problem of poorly known distribution coefficients. Therefore we focus on rare earth element (REE) ratios, which define the fundamental shapes of REE patterns; REE ratios are not sensitive to the exact choice of distribution coefficient (Kd; Fig. 1). The gabbroic assemblage widely implicated in the evolution of arc magmas has limited effect on the shapes of REE patterns; only clinopyroxene discriminates significantly among the REE. The effects of clinopyroxene fractionation are broadly similar to those of amphibole, but for a given composition Kd_{REE} clinopyroxene << Kd_{REE} amphibole. Garnet incorporates heavy REEs (Kd_{HREE}>>1) while amphibole preferentially incorporates middle REEs over heavy REEs. As a consequence, while La/Yb increases during garnet and amphibole fractionation, garnet fractionation will simultaneously increase Dy/Yb, but amphibole fractionation will decrease Dy/Yb (Macpherson et al., 2006). Accessory phases such as apatite



Figure 1. Partition coefficients (basaltic compositions) for clinopyroxene (cpx), amphibole (amph), and garnet (gt) plotted against ionic radius (Blundy and Wood, 2003). Curves are fitted by eye for easy comparison and do not imply any lattice strain model solution.

and zircon may significantly affect REE patterns, but they typically crystallize only from more evolved magmas; for the suites in Figure 2, P_2O_5 and Zr contents increase with SiO₂ at least into intermediate compositions (~60% SiO₅).

Trends for each volcano in our compilation (Fig. 2; see the GSA Data Repository Appendix DR11) can be compared with the theoretical effects of clinopyroxene (gabbro) versus garnet versus amphibole fractionation to evaluate which of these minerals is a major fractionating phase. This, in turn, constrains the depths of fractionation. Our compilation effectively rules out gabbro as the main assemblage controlling differentiation of arc magma from basalt to dacite. Although La/Yb correlates positively with SiO₂, fractionation models using experimentally determined equilibrium assemblages also indicate that garnet is rarely a major fractionating phase (Fig. 2A). Most arc volcanoes exhibit trends of decreasing Dy/Yb with differentiation (Fig. 2B); this is consistent with significant amphibole, but not garnet, fractionation.

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¹GSA Data Repository item 2007196, Appendix DR1, data references for Figures 2 and 4, is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



For basaltic compositions, garnet is stable in 16 kbar experiments and amphibole is stable at 8 kbar (Rapp and Watson, 1995). Thus, most arc magma differentiation appears to occur at shallower depths than those of garnet stability.

CRYPTIC AMPHIBOLE FRACTIONATION AS A CONTROL ON ARC MAGMA DIFFERENTIATION

It is likely that differentiation of arc magmas in the mid-deep crust is open-system and the geochemical signature of amphibole might reflect melting of stockpiled basalts with residual amphibole (Barclay and Carmichael, 2004), rather than simply amphibole crystallization from an evolving melt. In some of the suites studied (e.g., Mount Pelée, Salak), isotopic variations correlate with indices of differentiation, attesting to open-system evolution. However, mafic end members in some of the suites have high MgO (>6%) and Ni (>50 ppm), which would require unrealistically large degrees (~100%) of melting. Regardless, amphibole is inferred to be present, either as a directly fractionating phase or as residual in melting, mixing, and contamination processes.

Figure 2. A: La/Yb vs. SiO₂. B: Dy/Yb vs. SiO₂. Data are shown for individual volcanoes (see GSA Data Repository [text footnote 1] for data sources) defining differentiation trends. Color coding illustrates volcanoes from a single arc (e.g., Lesser Antilles, Aleutians, Indonesia) and demonstrates the importance of considering a single volcano rather than combining on an arc-by-arc basis. Schematic inset shows expected fractionation effects. Model fractionation curves are experimental assemblages of Rapp and Watson (1995) (R&W), and a nominal gabbro comprising 20% olivine, 35% clinopyroxene, and 35% plagioclase. Abbreviations: cpxclinopyroxene; am-amphibole; gt-garnet; plg, plag-plagioclase (opx-orthopyroxene, –ilmenite). Partition coefficients as in Figure 1. Vectors for Surigao (Philippines) and Anatahan (Marianas) are included as examples of suites that have fractionated garnet and gabbro, respectively. Note that trends do not back project to a common parent: variation in parent compositions could be due to earlier differentiation (perhaps with garnet) or variable slab-derived components.

Amphibole fractionation is consistent with intermediate crustal depths and with the high water contents that characterize primitive magmas at subduction zones (Fischer and Marty, 2005; Wallace, 2005). Few of the suites shown have significant modal amphibole. Thus amphibole fractionation is cryptic, with the observed (typically gabbroic) silicate phase assemblage representing crystallization in the shallow subvolcanic system, or remobilization of shallow cumulates (Dungan and Davidson, 2004), and having limited leverage on compositions. A significant role for amphibole is borne out by a survey of cumulate xenoliths found in arc lavas that are commonly amphibole bearing. Arculus and Wills (1980) reported amphibole in cumulate nodules from along the arc in the Lesser Antilles, despite its rarity in erupted lavas. Amphibole-magnetite-bearing cumulates are also important components of Alaskan-type ultramafic complexes.

PHASE EQUILIBRIA AND ROCK CHEMISTRY

The REE distributions presented here (Fig. 2) point to a more persistent and widespread role for amphibole fractionation in arc magma evolution than has commonly been suggested. While crystallization of anhydrous phases may be driven by decompression (Annen et al., 2006), the stability curve for amphibole is subparallel to decompression pathways. Crossing this boundary down-pressure will result in resorption, rather than precipitation (Fig. 3). An H₂O-saturated magma arriving from the mantle (Fig. 3, curve 1) will precipitate amphibole as soon as it encounters the amphibole stability curve (1.5–2 GPa; Allen and Boettcher, 1983). Curve 2 (Fig. 3) illustrates how cooling of an undersaturated magma may be a more effective way to precipitate amphibole than decompression. Most studies of individual arc volcanoes reveal trends of decreasing ²²⁶Ra disequilibrium with increasing differentiation. If this reflects decay from the mantle signature (Turner et al., 2001), then time scales of differentiation from mafic to intermediate or silicic compositions are a few thousand years. These time scales are consistent with amphibole crystallization by cooling rather than decompression-degassing crystallization of anhydrous phases, which would be much faster.

Experiments performed by Barclay and Carmichael (2004) showed that amphibole crystallization was prolific when basaltic liquids crossed the amphibole-in phase boundary. The increase in crystallinity when amphibole starts to crystallize may increase magma viscosity, impeding further ascent and/or eruption and trapping magmas in the deep crust. The continuous and apparently cogenetic basalt to dacite geochemical trends observed at many volcanoes (Fig. 2) show that basalts and their derivatives can reach the surface, in which case they have left behind a significant amphibole fractionate, the geochemical signature of which they now carry.

The upper limit of thermal stability for amphibole is typically ~1050 °C, lower than many estimates of equilibrium crystallization temperatures of the minerals commonly observed in subduction-related rocks. This fact has been an argument against significant amphibole fraction-



Figure 3. Schematic phase diagram for H₂Obearing basalt-andesite (after Carmichael, 2002) showing topology of phase boundaries for amphibole and for gabbro (clinopyroxeneplagioclase \pm olivine). Phase boundaries may vary, but it is their basic pressuretemperature (P-T) slopes that are important. Bold line—H₂O-saturated liquidus. Curves 1–2 represent P-T paths of magma ascent (see text for details). Dashed extensions represent possible heating during decompression crystallization (Blundy et al., 2006).

ation during the differentiation of arc magmas. The objection is obviated, however, if we consider the mounting evidence that a significant fraction of so-called phenocrysts in arc magmas are actually recycled "antecrysts" from earlier cumulates (Dungan and Davidson, 2004; Turner et al., 2003; Davidson et al., 2007), which must have reached low temperatures near solidus or subsolidus at some stage in their evolution

The curves in Figure 3 reach Earth's surface outside the amphibole stability field; amphibole is resorbed rapidly near the surface (Rutherford and Hill, 1993). This may, in part, explain why so few volcanic arc rocks contain amphibole, while it is a common phase in cumulate xenoliths hosted in arc rocks and in arc plutons. Opacitization of amphibole on decompression may further impede recycling of amphibole into ascending magmas by increasing the bulk density of the mineral and enhancing gravitycontrolled fractionation processes.

Amphibole may also influence the distinctive major element characteristics of arc lavas. Amphibole contains significantly less SiO_2 and more TiO_2 than basalt, such that fractionation will efficiently drive liquid compositions to higher SiO_2 and lower TiO_2 , typical of arc lavas compared with those of other settings. Simul-



Figure 4. Effect of amphibole-rich cumulates in crust beneath arcs: t_1 represents time early in development of magmatic center, at which amphibole sequesters mantle-derived H₂O. Recycling of amphibole-rich cumulates at this stage returns water and incompatible trace elements (e.g., large ion lithophile elements) into mantle. Lower panel illustrates possible effect of recycling amphibole cumulates; lowering H₂O/Ce while simultaneously raising H₂O content of mantle (key indicates number of data points; see footnote 1 for data sources). With thermal maturation (t_2) (Annen et al., 2006; Petford and Gallagher, 2001), local crustal geotherm sweeps up-temperature and crosses the steep amphibole stability curve. This produces large volumes of hydrous melt that may ascend into upper crust to trigger explosive volcanism or exsolve ore-bearing fluids. MORB—mid-ocean ridge basalt; OIB—ocean island basalt.

taneous fractionation of magnetite, as implied by the modal assemblage of many cumulates, would accentuate this effect and help drive calcalkaline differentiation trends. In contrast, gabbroic assemblages, with similar SiO_2 to primary basalts, can exert little leverage on SiO_2 contents of the liquid (see Fig. 2).

IMPLICATIONS

Mid-deep crust fractionation of amphibole at arcs could have the following consequences:

1. Amphibole could be a filter for water entering the crust from mantle-derived magmas: although the H₂O content of amphibole is modest (generally 1.5–4 wt%), the middle to lower arc crust may constitute a significant reservoir of labile water where amphibole-rich cumulates are abundant. This crust would act as a sponge, incorporating water from melts crystallizing at or below mid-crustal levels. Cumulates with ~50% amphibole would contain ~1% H₂O. Even if water contents of arc magmas reach 5% (Wallace, 2005), and despite the incompatibility of water in all assemblages, that represents removal of ~20% of the mantle-derived water en route to the surface.

2. Amphibole-rich lithologies in the middeep crust could provide a fertile source for melts and fluids: the availability of a substantial, temperature-sensitive water reservoir provides a means to enhance the fertility of the crust as a source of melts, increase the potential explosivity of magmas during differentiation and/or interaction with crustal rocks, and release fluids capable of transporting metal solutes into ore deposits. Amphibole-bearing lithologies have been shown to enhance melt productivity (Rapp and Watson, 1995; Peacock et al., 1994). Thermal maturation of the arc crust, as modeled by recent underplating and intrusion scenarios, would sweep geotherms up-temperature (Fig. 4). The temperature sensitivity of the amphibole stability curve means that it could be crossed suddenly, producing large volumes of intermediate-silicic hydrous melt or hot solute-rich brine.

3. A reservoir to recycle water and incompatible elements into the mantle could be produced. Models of crustal growth that consider the contributions from arc magmatism require a return of cumulate material to the mantle in order to produce andesite bulk crust. If the cumulate is amphibole rich, then it could recycle water into the mantle, and the presence of magnetite may make the assemblage negatively buoyant. Water budgets of the mantle are increasingly constrained with reference to H₂O/Ce ratios. H₂O/Ce ratios in amphibole appear to be low (generally < 120) with respect to the upper mantle (150-250; Fig. 4). Delamination of arc cumulates could provide an alternative to recycling of dehydrated oceanic crust as a source of low H₂O/Ce domains in the upper mantle (Michael, 1995).

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