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Hydrous basalt–limestone interaction at crustal conditions: Implications for generation of ultracalcic melts and outflux of CO$_2$ at volcanic arcs

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A B S T R A C T

High degassing rates for some volcanoes, typically in continental arcs, (e.g., Colli Albani Volcanic District, Etna, Vesuvius, Italy; Merapi, Indonesia; Popocatepetl, Mexico) are thought to be influenced by magma–carbonate interaction in the crust. In order to constrain the nature of reaction and extent of carbonate breakdown, we simulated basalt–limestone wall-rock interactions at 0.5–1.0 GPa, 1100–1200 °C using a piston cylinder and equal mass fractions of calcite (CaCO$_3$) and a hydrous ($\sim$4 wt.% H$_2$O) basalt in a layered geometry contained in AuPd capsules. All experiments produce melt + fluid + calcite ± clinopyroxene ± plagioclase ± calcic-scapolite ± spinel. With increasing T, plagioclase is progressively replaced by scapolite, clinopyroxene becomes CaTs-rich, and fluid proportion, as inferred from vesicle population, increases. At 1.0 GPa, 1200 °C our hydrous basalt is superliquidus, whereas in the presence of calcite, the experiment produces calcite + clinopyroxene + scapolite + melt. With the consumption of calcite with increasing T and decreasing P, melt, on a volatile-free basis, becomes silica-poor (58.1 wt.% at 1.0 GPa, 1100 °C to 34.9 wt.% at 0.5 GPa, 1200 °C) and CaO-rich (6.7 wt.% at 1.0 GPa, 1100 °C to 43.7 wt.% at 0.5 GPa, 1200 °C), whereas Al$_2$O$_3$ drops (e.g., 19.7 at 1100 °C to 12.8 wt.% at 1200 °C at 1.0 GPa) as clinopyroxene becomes more CaTs-rich. High T or low P melt compositions are 'ultracalcic,' potentially presenting a new hypothesis for the origin of ultracalcic melt inclusions in arc lava olivines. Wall-rock calcite consumption is observed to increase with increasing T and decreasing P. At 0.5 GPa, our experiments yield carbonate assimilation from 21.6 to 47.6% between 1100 and 1200 °C. Using measured CO$_2$ outflux rates for Mts. Vesuvius, Merapi, Etna and Popocatepetl over a T variation of 1100 to 1200 °C at 0.5 GPa, we calculate 6–92% of magmatic input estimates undergo this extent of assimilation, suggesting that up to $\sim$3% of the current global arc CO$_2$ flux may be crustally derived. Application of the assimilation extent bracketed in this study to the estimated elevated number of carbonate-assimilating arc magmatic systems active during the late Cretaceous to early Paleogene suggests that magma-induced upper plate decarbonation alone had the potential to contribute up to 2.7×10^{14}–5.6×10^{15} g/y CO$_2$, assuming no dilution and complete gaseous release of all assimilated carbon. Using an estimated assimilation extent averaged from current systems gives a slightly lower though still significant value of $\leq 5.5 \times 10^{14}$ g/y of excess CO$_2$ being released into the atmosphere.

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1. Introduction

Carbon dioxide released through arc volcanoes is conventionally assumed to be mantle-derived with an input from the subducted slab, and a range of carbon transfer mechanisms from the downgoing slab to the overlying mantle wedge has been pro-

posed (e.g., Behn et al., 2011; Dasgupta et al., 2013; Duncan and Dasgupta, 2014, 2015; Shaw et al., 2003; Skora et al., 2015; Tsuno and Dasgupta, 2012; Tsuno et al., 2012). Although this may be dominant for most arc volcanoes situated on oceanic crust, i.e., for island arcs, the scenarios for volcanic degassing of CO$_2$ may be vastly different in arc volcanoes underlain by significant carbonate strata (e.g., Lee et al., 2013). For example, anomalously high CO$_2$ degassing rates currently estimated at several continental arc volcanoes (e.g., Burton et al., 2013; Caliro et al., 2005; Frondini et al., 2004) are thought to be augmented by carbonates in the up-

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per plate. Carbonate assimilation is identified in natural systems not only by heightened emissions, but also by: the presence of skarn xenoliths (e.g., Barnes et al., 2005; Di Rocco et al., 2012; Goff et al., 2001); carbon, strontium, and neodymium isotopes, which can become contaminated with crustal signatures (Barnes et al., 2005; Chadwick et al., 2007; Troll et al., 2012), though sometimes clear evidence is lacking (Halldórsson et al., 2013); and calcium-rich mineralogy typical of endoskarns (Di Rocco et al., 2012; Einaudi and Burt, 1982; Kerrick, 1977). Magma–carbonate interactions are also reflected in compositions of glasses and melt inclusions that become uniquely silica-undersaturated and calcium-enriched (Watkinson and Wyllie, 1964).

The lines of evidence in support of active crustal carbonate assimilation by magmas, predominantly expelled at arc volcanoes, have been well-documented in the field at Mount Merapi, Indonesia (Chadwick et al., 2007; Deegan et al., 2010; Troll et al., 2012); Popocatepetl, Mexico (Goff et al., 2001 and references therein); Pacaya, Guatemala (Goff et al., 2001); Santorini and Nisyros, Greece (Spandler et al., 2012); Etna, Italy (Michaud, 1995); Vesuvius, Italy (Iacono-Marziano et al., 2009, 2008; Jolis et al., 2013); and the Colli Albani Volcanic District (CAVD[1]) in Italy's Roman Province (Di Rocco et al., 2012; Freda et al., 2008; Gaeta et al., 2009; Iacono-Marziano et al., 2007; Mollo and Vona, 2014; Mollo et al., 2010). Decarbonation amplifies the outgassing efficiency in these systems by the general reaction:

$$CaCO_3 \text{ (solid)} \rightarrow CaO \text{ (melt)} + CO_2 \text{ (gas)} \tag{1}$$
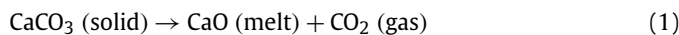
which has the potential to increase explosivity at the vent (e.g., Troll et al., 2012).

Previous experimental studies simulated the natural systems of Italy (Conte et al., 2009; Iacono-Marziano et al., 2009, 2008, 2007; Jolis et al., 2013; Mollo et al., 2010) and central Java, Indonesia (Deegan et al., 2010). Two studies utilized Indonesian and Vesuvian samples in time-series disequilibrium experiments, which determined that the rapidity of the reaction is exceedingly fast (Deegan et al., 2010; Jolis et al., 2013). Using estimated temperatures and pressures of limestone–magma interaction scenarios (e.g., 3–15 km, Roman Province, Freda et al., 1997; 10–15 km, Merapi, Troll et al., 2012), previous experiments kept pressure constant (at ≤ 0.5 GPa) with or without a minor temperature range. Water content and crustal input was varied, though the mass fraction of carbonate added to experiments was limited to <20 wt.%, simulating perhaps a stoped interaction with a limited availability of carbonate. The goal was focused either on using a carbonate quantity that reproduced results matching natural systems, or on following the liquid line of descent (Conte et al., 2009; Freda et al., 2008; Iacono-Marziano et al., 2007). Only some of the experiments discerned pressure–temperature effects (Freda et al., 2008; Iacono-Marziano et al., 2008), but remained at very low pressures (≤ 0.5 GPa) while underthrusted carbonates in e.g., the cretaceous, could have been assimilated at up to 30 km depth (e.g., DeCelles et al., 2009; Lackey et al., 2005).

This study fills the lack in data regarding the effect of pressure (depth within the crust) and temperature (extent of basaltic crystallization, discerned by calcite-free experiments) on limestone–basalt interaction, with conditions astride the basaltic liquidus at mid- to lower-crustal depths, such that results may be applicable to calcite assimilation conditions of various present and past volcanic systems. Furthermore, we simulate the reactive front that forms in natural systems between an intruding magma body and a carbonate wall-rock by layering an excess of pure limestone with

typical near-primary arc basalt. We determine residual mineralogy and melt compositions as a function of reactive crystallization, pressure, and temperature. Our data have implications for ultra-calcic melt inclusions that have been identified in subduction-zone settings and constrain the extent of assimilation and the maximum limit of excess magmatic CO_2 that may be derived from upper plate magma–limestone interactions as a function of depth and temperature.

2. Methods

2.1. Starting materials

To represent the intruding magma, a synthetic primary arc basalt (MgO ~ 6.2 wt.%) was used, similar in composition to natural Strombollian K-basalt used by Iacono-Marziano et al. (2007) and natural Vesuvian shoshonite in the experiments of Jolis et al. (2013), though a characteristic of Italian lavas is an elevated potassium content not reproduced in this study (Supplementary Table 1). Reagent grade oxides and carbonates were first dried by firing SiO_2, TiO_2, Al_2O_3 and MgO overnight at 1000 °C, Fe_2O_3 at 800 °C, MnO_2 at 400 °C, $CaCO_3$ at 250 °C, and K_2CO_3 and Na_2CO_3 at 110 °C. Using a microbalance, these powders were measured out to predetermined portions to generate the basaltic composition desired and combined. The mixture was then ground to a powder and homogenized in an agate mortar under ethanol, after which the ethanol was evaporated off. To reduce the Fe_2O_3 to FeO and drive off CO_2, the mixture was heated to 1000 °C in a $CO–CO_2$ gas mixing furnace at $\log fO_2 \sim$ FMQ-2 for 24 h. Finally, gibbsite [Al(OH)$_3$] was added, contributing 4.03 wt.% water to the hydrous melt and bringing the alumina content up to the desired level. The second starting material representing the intruded crustal carbonate was pure $CaCO_3$ powder. Both starting materials were stored covered at 110 °C to minimize water adsorption.

2.2. Experimental methods

Experiments were performed in a 1/2-inch end-loaded piston cylinder apparatus at Rice University following the standard protocol detailed in Tsuno and Dasgupta (2011). Starting materials were packed in coned Au$_{75}$Pd$_{25}$ capsules in a layered geometry with calcite underlying synthetic basalt, in a 1:1 ratio by weight (with error ≤ 0.1 wt.%). Capsules were weighed before and after being line-welded shut to ensure that volatile loss was negligible. To consider a range of pressures and temperatures relevant for lower- to mid-crustal intrusions, experiments were conducted at three distinct pressures of 0.5 GPa (~ 15 km deep), 0.8 GPa, and 1.0 GPa (~ 35 km deep) and between 1100 and 1200 °C (Table 1). An additional set of calcite-free experiments were also performed at 1.0 GPa to determine the phase compositional evolution along the liquid line of descent of the starting basalt uncontaminated by calcite. Run duration ranged from 3 to 72 h. Initially, the recovered capsules were ground until the edge of the sample was visible before being impregnated with epoxy to prevent sample loss. Final polish was achieved using dry polycrystalline diamond powder (3, 1, 0.25 μm) on nylon and velvet surfaces.

2.3. Analytical techniques

Polished samples were carbon-coated and studied for phase identification and major element phase composition using a Cameca SX100 electron microprobe at NASA Johnson Space Center in Houston, Texas. Analysis was performed using a 15 kV, 10 nA electron beam with spot sizes varied between 10 μm on calcite and glass and a focused 1 μm on silicate grains and smaller melt pools. Peak counting times for Si, Al, Ti, Fe, Mn, and Mg were

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[1] **Abbreviations:** P = pressure, T = temperature, X = composition, F = melt fraction, CAVD = Colli Albani Volcanic District.