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Quantification of the CO_2 budget and H_2O–CO_2 systematics in subduction-zone magmas through the experimental hydration of melt inclusions in olivine at high H_2O pressure

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ABSTRACT

Reliable evaluation of CO_2 contents in parental arc magmas, which can be preserved in melt inclusions in phenocrysts, is required to verify the proposed efficiency of CO_2 recycling at convergent margins. Quantification of bulk CO_2 concentration in melt inclusions requires their complete homogenization. Using samples from lavas from the Bulochka vent of Klyuchevskoy Volcano (Kamchatka), we applied a novel experimental approach to homogenize and re-equilibrate naturally dehydrated (<1 wt.% H_2O) melt inclusions from high-Fo (85–91 mol.%) olivine. The experiments were performed at temperatures of 1150–1400 °C, pressures of up to 500 MPa, under dry to H_2O-saturated conditions and with oxygen fugacity ranging from CCO to QFM+3.3. No homogenization was achieved at dry conditions. Complete dissolution of fluid bubbles (homogenization) in the melt inclusions was achieved at H_2O pressures of 500 MPa and temperature of 1150 °C, when water content in the melt inclusions reached 4–5 wt.% H_2O. The CO_2 content in the homogenized inclusions is 3800 ± 140 ppm and $CO_2/Nb = 3000 \pm 420$, which are the highest values reported so far for the typical middle-K primitive arc melts and fall within the range of values inferred from the magmatic flux and volcanic gas data for primary arc magma compositions. About 83% of the CO_2 in Klyuchevskoy magmas is likely to be derived from the subducting slab and can be attributed to flux melting with a fluid having a CO_2/H_2O ratio of $\sim$0.06. The H_2O and CO_2 contents in the melt inclusions after hydrous experiments were found to correlate positively with each other and negatively with the volume of fluid bubble, reflecting increasing internal pressure in melt inclusions with increasing melt hydration. Therefore, similar trends observed in some natural sets of melt inclusions can be attributed to a partial dehydration of melts after entrapment, operating simultaneously with or following post-entrapment crystallization. Our study implies that the process of post-entrapment dehydration can be completely reversed under high pressure experimental conditions. If temperature, redox conditions and pressure of melt inclusion entrapment can be independently estimated, then our novel experimental approach (homogenization at high H_2O pressure) can be used to reconstruct the initial CO_2 content and also the entire composition of melt inclusions in olivine, including their initial H_2O content, from any type of volcanic rock. With this approach volatiles in ancient lavas can also be determined, expanding our knowledge of volatile recycling further back in Earth history.

1. Introduction

Magmatic and hydrothermal processes at convergent plate margins represent an important component of the global carbon cycle. At such margins large amounts of CO_2 in sediments and oceanic crust are subducted into the mantle and partially returned to the exosphere by arc volcanism (e.g., Marty and Tolstikhin, 1998; Hilton et al., 2002). The median $CO_2/^3He$ ratio in volcanic arc gases is higher than that in normal mid-ocean-ridge basalt (N-MORB) by a factor of $\sim$8, suggesting that arc magmas are enriched in CO_2 compared to MORB and contain at least 80% recycled slab-derived CO_2 (Marty and Tolstikhin, 1998). C-isotope systematics of volcanic gases indicate an even higher amount of slab-derived

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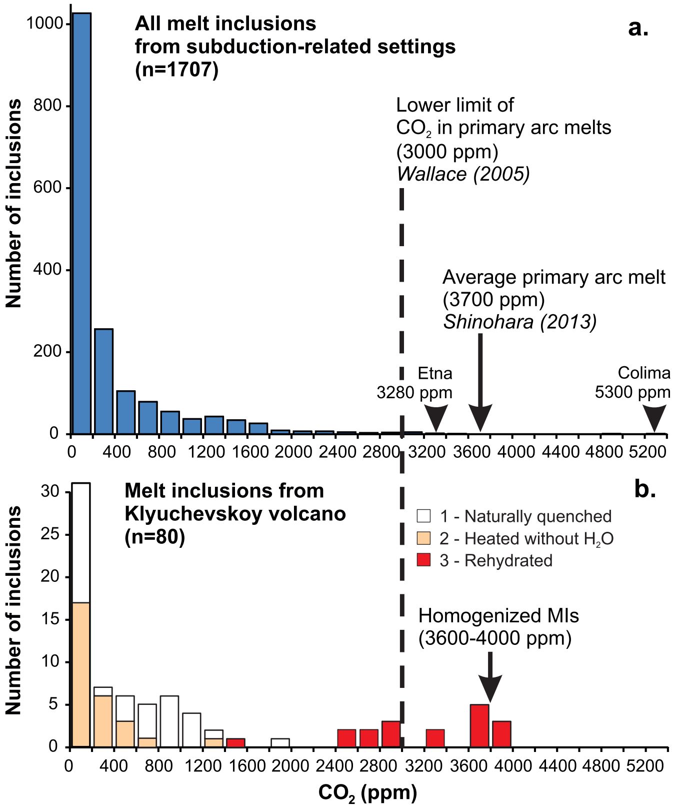

Fig. 1. CO_2 concentrations in arc melt inclusions: (**a**) All melt inclusions from subduction-related settings are from the GEOROC database (GEOROC, 2014). Before this study, the highest CO_2 content was measured in MIs from Etna (Kamenetsky et al., 2007) and Colima (Vigouroux et al., 2008) volcanoes. (**b**) Olivine-hosted melt inclusions from volcanic rocks from Klyuchevskoy Volcano rocks: natural glassy inclusions (Auer et al., 2009; Mironov and Portnyagin, 2011; this study); reheated at 0.1 MPa and 300 MPa without H_2O (Mironov and Portnyagin, 2011; this study); and rehydrated at high H_2O pressure (300–500 MPa, this study). The lowest expected CO_2 concentration in primary arc melts is shown (~3000 ppm after Wallace, 2005). The most recent estimate of CO_2 in primary arc magmas (~3700 ppm) is based on the ^{3}He flux and magmatic emplacement rate estimates at convergent margins (Shinohara, 2013).

CO_2 (88–97% for 7 arcs, including Kamchatka; Hilton et al., 2002). The absolute amounts of CO_2 in parental arc magmas, however, are poorly constrained. The available indirect estimates from CO_2 volcanic gas fluxes and magma emplacement rates in arcs range from 0.3 to 1.3 wt.% CO_2 (Wallace, 2005; Fischer and Marty, 2005; Shinohara, 2013). Independent and reliable evaluation of CO_2 contents in parental arc magmas is required to verify the proposed volatile fluxes, efficiency of CO_2 recycling and crustal growth rates at convergent margins.

Experimental studies demonstrate that solubility of CO_2 in silicate melts decreases strongly with decreasing pressure (e.g., Blank and Brooker, 1994). In addition, CO_2 partitions into the fluid phase as soon as magmas start to degas. Therefore, CO_2 is commonly lost through exsolution into coexisting magmatic fluids during magma ascent and eruption. The only direct approach for quantifying the primary CO_2 content in magmas is to study melt inclusions (MIs) in minerals, which represent small droplets of melt trapped by growing crystals at depth (e.g., Roedder, 1984; Wallace, 2005). The available database of CO_2 content in MIs from subduction-related settings consists of ~1700 analyses (GEOROC, 2014). The CO_2 concentrations range from below the detection limit to 5300 ppm, with about 90% of inclusions having <500 ppm CO_2 (Fig. 1). The highest concentrations of CO_2 in MIs were reported for basalts of Etna Volcano, Italy (≥3280 ppm, Kamenetsky et al., 2007) and for basanites from Colima volcanic complex in Mexico (5300 ppm, Vigouroux et al., 2008). However, the Etna and Colima rocks have major and trace element compositions, which are quite different from middle-K calc-alkaline arc rocks (e.g., Kelemen et al., 2003). None of the published CO_2 contents in MIs from typical arc rocks is consistent with the large CO_2 output from volcanic arcs inferred from volcanic gas data (Wallace, 2005; Shinohara et al., 2013) (Fig. 1).

The majority of studied MIs formed during the late stages of magma evolution at shallow depths and therefore the minerals trapped already strongly degassed melts with low CO_2 contents (e.g., Wallace, 2005). Primitive MIs trapped in high-Fo olivine (Fo>85 mol.%) are rare in the existing database. Such inclusions are usually significantly modified after entrapment during cooling and decompression and always contain a fluid (gas) bubble (e.g., Anderson and Brown, 1993; Danyushevsky et al., 2002). Thermodynamic modeling (Steele-MacInnes et al., 2011) and several studies of natural inclusions (e.g., Anderson and Brown, 1993; Kamenetsky et al., 2002, 2007; Hartley et al., 2014; Wallace et al., 2015; Moore et al., 2015) have demonstrated that the bubbles can comprise a major fraction (80% or more) of the initial CO_2 content in the MIs, explaining the low CO_2 concentrations measured in the coexisting glasses.

Estimation of the bulk CO_2 content in bubble-bearing MIs is possible through two different approaches. According to one approach, the bulk CO_2 content is calculated by mass balance using volume proportions of fluid and glass in MIs and the amount of CO_2 stored in them. The amount of CO_2 in the fluid phase is calculated from the ideal gas equation and saturation pressure at melt–glass transition (Shaw et al., 2010) or from the fluid density measured by cryometry (Naumov et al., 2006) or by Raman spectroscopy (e.g., Hartley et al., 2014; Moore et al., 2015). This approach has a number of uncertainties arising from the determination of the fluid density (e.g., Hartley et al., 2014) and the volume proportions in MIs, which sometimes contain an excessive ("prisoner") fluid phase trapped with melt, and from the common precipitation of carbonates on the bubble wall (e.g., Kamenetsky et al., 2002; Moore et al., 2015). An alternative, direct approach is an experimental homogenization of MIs leading to a complete dissolution of CO_2 back into the melt and enabling the direct analysis of CO_2 concentration in the quenched glass (e.g., Wallace et al., 2015). Although this approach seems to be straightforward and easy, heating experiments with MIs from arc rocks performed at 0.1 MPa often fail to dissolve the fluid bubble completely even during significant overheating (e.g., Danyushevsky et al., 2002).

In this study, we introduce a new experimental approach to homogenize MIs under high H_2O pressure. This approach was successfully applied to homogenize strongly dehydrated inclusions from Klyuchevskoy Volcano, Kamchatka, and to estimate their initial CO_2 content. The results help to understand better MI evolution after entrapment and during experiments and suggest that the entire composition of MIs in olivine, including their initial H_2O and CO_2 contents, can be restored experimentally, if conditions of MI entrapment can be independently estimated.

2. Samples from Klyuchevskoy Volcano

Melt inclusions were studied in olivine phenocrysts from a lava flow (sample K9-N27, 56.1526°N, 160.7939°E, 876 m) and tephra layer comprising 0.5–1 cm lapilli (sample K7-T1-51, 56.1464°N, 160.8241°E), both associated with the ~3 ky old Bulochka cone on the NE slope of Klyuchevskoy Volcano. These rocks are the most primitive from Klyuchevskoy (e.g., Kersting and Arculus, 1994; Khubunaya et al., 1994; Ariskin et al., 1995) (Table 1) and contain up to 10 vol.% olivine phenocrysts with high-Mg ($Fo_{87–91}$) cores and outer 100–200 µm-wide rims of less magnesian olivine (~Fo_{85}) (Fig. 2a).