

Diffusive fractionation of H₂O and CO₂ by vesiculation of rhyolitic melts

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Background

Degassing of magmas during ascent is central to an understanding of dynamics of volcanic eruption. One powerful tool to estimate the degassing processes is volatile systematics. Assuming a closed system in which gas and melt are in chemical equilibrium, concentrations of the volatile components in the melt decrease with decreasing pressure (magma ascent) according to batch fractionation. If the system becomes open, then the concentration decrease would get close to the Rayleigh fractionation. The volatile contents in the volcanic rocks have been traditionally discussed based on this equilibrium relationship (e.g., Newman et al., 1989).

Since vesiculation is a kinetic process, however, gas and melt should not be necessarily equilibrated. Watson (1991) predicted that diffusive fractionation between H₂O and CO₂ should occur during vesiculation as diffusivity of CO₂ is lower than that of H₂O by about one order of magnitude. Gonnermann and Manga (2005) showed, based on a theoretical calculation, that nonequilibrium degassing due to diffusive fractionation could reproduce natural H₂O-CO₂ trend obtained by Newman et al. (1989). The theoretical framework for the kinetic fractionation has thus been developed gradually, but experimental evidence for the fractionation has been scarcely presented.

Present study

We have so far conducted three vesiculation experiments on H₂O and CO₂-saturated rhyolitic melts. Starting materials are natural rhyolitic obsidian slabs. Oxalic acid dihydrate was used as a source of H₂O-CO₂ binary fluid. These are put into a gold capsule with NNO powder, and then the capsule was welded shut. In a cold-seal pressure vessel the capsule was heated to 850 degC and pressurized at 100 MPa for 4 to 7 days to get the melt saturated with the binary fluid. The pressure was then dropped down to 50MPa in a single step within a few seconds, and held for 500 to 5000 sec to promote vesiculation. The vessel was quenched to less than 100 degC by compressed air within 10 minutes.

The bubbles were heterogeneously nucleated on the inner wall of the gold capsule, and no bubble was observed in the interior glasses. Some of the bubbles have coalesced into large bubbles. We found that the concentration profiles of both H₂O and CO₂ across the glasses between bubbles are decreasing toward the bubbles. The obtained profiles were well reproduced by the calculation of diffusion in the melt assuming diffusion in a finite plane and surface equilibrium between melt and coexisting free fluid at the final holding pressure. Due to the smaller diffusivity of CO₂ than of H₂O, the difference in melt concentrations from the equilibrium is much larger for CO₂ than for H₂O. The present experiments clearly show that elemental fractionation had occurred during melt vesiculation.