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Water in volcanic glass: From volcanic degassing to secondary hydration

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Abstract

Volcanic glass is deposited with trace amounts (0.1–0.6 wt.%) of undegassed magmatic water dissolved in the glass. After deposition, meteoric water penetrates into the glass structure mostly as molecular H_2O. Due to the lower δD (‰) values of non-tropical meteoric waters and the ~30‰ offset between volcanic glass and environmental water during hydration, secondary water imparts lighter hydrogen isotopic values during secondary hydration up to a saturation concentration of 3–4 wt.% H_2O. We analyzed compositionally and globally diverse volcanic glass from 0 to 10 ka for their δD and H_2O_t across different climatic zones, and thus different δD of precipitation, on a thermal conversion elemental analyzer (TCEA) furnace attached to a mass spectrometer. We find that tephrachronologically coeval rhyolite glass is hydrated faster than basaltic glass, and in the majority of glasses an increase in age and total water content leads to a decrease in δD (‰), while a few equatorial glasses have little change in δD (‰). We compute a magmatic water correction based on our non-hydrated glasses, and calculate an average $10^3\ln\alpha_{glass\text{-}water}$ for our hydrated felsic glasses of −33‰, which is similar to the $10^3\ln\alpha_{glass\text{-}water}$ determined by Friedman et al. (1993a) of −34‰. We also determine a smaller average $10^3\ln\alpha_{glass\text{-}water}$ for all our mafic glasses of −23‰. We compare the δD values of water extracted from our glasses to local meteoric waters following the inclusion of a −33‰ $10^3\ln\alpha_{glass\text{-}water}$. We find that, following a correction for residual magmatic water based on an average δD and wt.% H_2O_t of recently erupted ashes from our study, the δD value of water extracted from hydrated volcanic glass is, on average, within 4‰ of local meteoric water. To better understand the difference in hydration rates of mafic and felsic glasses, we imaged 6 tephra clasts ranging in age and chemical composition with BSE (by FEI SEM) down to a submicron resolution. Mafic tephra have more bubbles per unit area (25–77 mm^{-2}) than felsic tephra (736 mm^{-2}) and thicker average bubble walls (0.07 mm) than felsic tephra (0.02 mm). We use a simplified diffusion model to quantify the hydration rate of vesicular glass as a function of the diffusivity of water and the average bubble wall thickness. Based on fits to our hydration rate data, we estimate the initial low-temperature diffusivity at 0.1 wt.% H_2O_t in volcanic glass (mafic and felsic) to be on the order of 10^{-3} to 10^{-4} μm^2/year and find that differences in hydration rates between mafic and felsic tephra can be attributed primarily to differences in vesicularity, although slightly slower hydration of basalt cannot be precluded. We also observe no consistent temporal difference in secondary meteoric water uptake in wet versus dry and hot versus cold climates.
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1. INTRODUCTION

Volcanic glass is widely used for paleoclimate studies due to its uptake of meteoric water following deposition (Friedman et al., 1993b). This process is also known as secondary hydration or 'rehydration'. The presence of environmental waters in volcanic glass has been used as a tracer of the δD of local precipitation at the time of deposition (e.g. Riciputi et al., 2002; Mulch et al., 2007; Cassel et al., 2014; Canavan et al., 2014), and the extent of hydration by meteoric waters has been used to estimate the age of obsidian artifacts (e.g. Friedman et al., 1966; Anovitz et al., 2004). However, volcanic glass can be deposited with unknown quantities of primary magmatic water, which varies as a consequence of magmatic degassing processes (Newman et al., 1988; Dobson et al., 1989; Castro et al., 2014). Both magmatic and meteoric water can have distinct δD values (e.g. DeGroat-Nelson et al., 2001; Tuffen et al., 2010), depending on the δD value of the meteoric water that is diffusing into the glass, the degree of volcanic degassing that has occurred, and the original δD of the parental undegassed magma (Figs. 1 and 2). Therefore, these two types of water can obscure each other in δD-H_2O space when they are both present in volcanic glass, even though they could both provide useful information if the properties of one can be known or constrained. Furthermore, the details of secondary hydration are not well understood, and it is still unknown how long it takes for mafic and felsic glass to become secondarily hydrated at surface temperature and pressure.

1.1. Secondary hydration of volcanic glass

Rehydration of degassed (primarily water-free) silicate glass is a complex process of interface kinetics, water in-diffusion, and possibly minor re-speciation of hydrogen between dissolved molecular water and hydroxyl groups (e.g. Zhang, 1999; Anovitz et al., 2008; Nolan and Bindeman, 2013). The proposed models for rehydration range from a simple linear increase to a square root of time dependence (e.g. Friedman et al., 1966; Nolan and Bindeman, 2013 and references therein). Since the diffusion coefficients of water in glass are a strong function of water concentration (Zhang and Behrens, 2000), hydration proceeds with a 'hydration front' that has a relatively sharp interface, which is possible to observe under a microscope (Ross and Smith, 1955; Friedman et al., 1966) and has therefore been used as a chronometer for dating. Riciputi et al. (2002) used microscopic observations and SIMS depth profiling of ancient obsidian artifacts of known age to quantify the distance of the hydration front 'X' into volcanic glass and determined that this distance (X) is proportional to the sum of linear and square root terms evaluated at time (t) (e.g. Friedman et al., 1966; Anovitz et al., 2004):

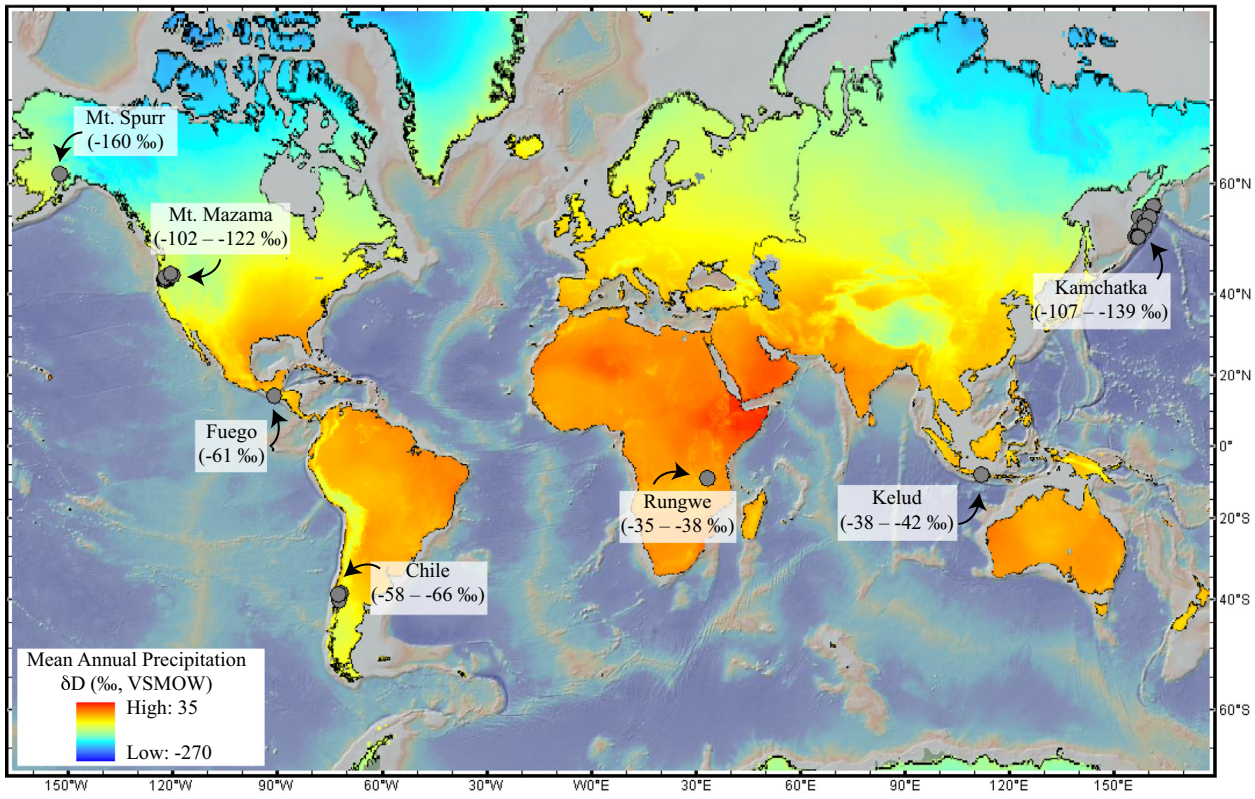

Fig. 1. Sample locations along with local δD of precipitation range in ‰ plotted on a world map with an overlay of δD values (‰) of current precipitation (Bowen and Revenaugh, 2003; Bowen, 2015). The map was created using GeoMapApp as the underlying base map (the Global Multi-Resolution Topography (GMRT) synthesis). GPS coordinates and local δD (‰) of precipitation values for sample locations can be found in Table 1.

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