

Isotopic signatures of magmatic fluids and seawater within silicic submarine volcanic deposits

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Abstract

Addressing questions of magma ascent, volcanic eruption dynamics, and volatile fluxes requires accurate measurement of magmatic water concentrations in volcanic glass. Glass in volcanic rocks in the deep-sea environment can experience rehydration (addition of external water) across a range of temperatures, and from different sources (e.g., seawater and hydrothermal fluids), which can lead to overestimation of magmatic-H₂O. This study used H and O isotopes (δD and $\delta^{18}\text{O}$) to identify sources of rehydration in pumice and lava from the deep-sea 2012 volcanic eruption of Havre volcano, Kermadec Arc, and from a variety of older (tens to thousands of years) silicic submarine deposits across the Izu-Bonin Arc and Lau Basin. We find that old seafloor pumices were rehydrated up to 6 wt.% H₂O by the diffusion of cold seawater over 100s to 1000s of years, and thus, enriched in δD , bulk- $\delta^{18}\text{O}$, and water-in-glass (wig) $\delta^{18}\text{O}$ up to -30‰ , $+9\text{‰}$ and -5‰ respectively. By contrast, the young Havre deposits exhibit a much wider range of both isotopic enrichment and depletion with $\delta\text{D} = -50$ to -120‰ , $\delta^{18}\text{O}_{\text{bulk}} = +5.7$ to $+6.2\text{‰}$, and $\delta^{18}\text{O}_{\text{wig}} = -10$ to $+4\text{‰}$, depending on the eruptive units. Using magmatic degassing and vapor δD -H₂O modeling, a volatile-melt $\delta^{18}\text{O}$ -geothermometer, and previous textural studies of Havre 2012 deposits, we identify multiple high-temperature rehydration sources, timescales, and mechanisms. δD -depleted pumices were likely rehydrated by vapor co-existing in bubbles and vesicles at temperatures around and below the glass transition (320–670 °C) over timescales of a few minutes during clast cooling above the eruptive vent. Conversely, δD -enriched Havre pumice and lava from different deposits were most likely rehydrated by heated, δD -enriched seawater at glass temperatures > 100 °C. These results provide a natural confirmation of recent experimental findings, which tackle the fundamentals of H and O diffusion and isotope exchange in silicate materials at temperatures of 100–400 °C. Addressing the effects of rehydration, and thus accuracy of H₂O measurements, in volcanic glasses and crystals is important for improving our understanding of conduit processes during volcanic eruptions, and the kinetics of glass hydration and alteration.

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1. INTRODUCTION

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As magma rises to the surface during a volcanic eruption, water (H₂O) dissolved within the melt diffuse out of

the magma and form a vapor phase (Sparks, 1978; Eichelberger and Westrich, 1981; Cashman and Sparks, 2013). Upon eruption, melt forms a glass if quenched rapidly to prevent significant crystallization, and residual dissolved magmatic water concentrations in glass can be used to determine key parameters for understanding dynamics of volcanism (Gardner et al., 1995; Wallace, 2005; Collins et al., 2009; Burgisser et al., 2010; Owen et al., 2013; Schipper et al., 2013). These include initial depth of magma storage, erupted magma viscosity, and where and when magma quenches (above or within a volcanic vent) (Bottinga and Weill, 1972; Eichelberger and Westrich, 1981; Holtz et al., 1995; Lowenstern, 1995; Zhang 1999; Hauri, 2002; Giordano et al., 2004; Zhang et al., 2007; Giordano et al., 2008). Additionally, H₂O concentrations in glass can be used to quantify the outgassing and fluxes of magmatic volatile species from subsurface to the ocean and atmosphere. For eruptions with few, or no, direct observations (e.g., volcanoes under deep bodies of water), understanding and correctly interpreting historic geochemical records is essential for advances in physical volcanology, petrology, and geodynamics (Garcia et al., 1979; Allen et al., 2010; Schipper et al., 2010; Soule et al., 2012; Gardner et al., 2016; Jones et al., 2018).

1.1. Silicate glass rehydration by external H₂O

Measurements of H₂O in silicate glasses are a cornerstone of geochemical and physical volcanology and have been applied in broader geochemical research and archaeological dating for many decades (Friedman and Long, 1976; Taylor et al., 1983; Devine et al., 1995; Hauri et al., 2002; Hauri, 2002; Anovitz et al., 2006; Liritzis and Laskaris, 2011; Stevenson and Novak, 2011; Le Losq et al., 2012; von Aulock et al., 2014; Martin et al., 2017). However, these geochemical records can become contaminated when external H₂O diffuses into volcanic glass after eruption and/or quenching, on annual to millennial timescales (Denton et al., 2009; Giachetti and Gonnermann, 2013; Nolan and Bindeman, 2013; von Aulock et al., 2013; Giachetti et al., 2015; Seligman et al., 2016; Cassel and Breecker, 2017; Martin et al., 2017; Seligman et al., 2018; Giachetti et al., 2020). Accuracy of magmatic H₂O measurements in volcanic glasses and crystals is vital for furthering understanding volatiles budgets and cycling within hydrous tectonic settings such as subduction zones and volcanic arcs (Stern, 2002; van Keken et al., 2011; Plank et al., 2013).

The addition of external water to volcanic glass, predominantly as molecular H₂O (H₂O_m) (or H⁺) – and not OH, is a process known as “rehydration” or “secondary hydration” (Giachetti and Gonnermann, 2013; Sessegolo et al., 2021); the rate of diffusion of H₂O_m is several orders greater than that of OH (Zhang et al., 2007). Rehydration can obscure the magmatic H₂O concentration and signature, causing overestimates of H₂O in glass resulting in misinterpretations of eruptive processes (Mitchell et al., 2018), inaccuracies in obsidian artifact dating (Anovitz et al., 1999), and miscalculation of magma storage depths (Bucholz et al., 2013; Myers et al., 2019).

Many studies of rehydration focus on slow H₂O diffusion, of cold meteoric water (precipitation, rivers, lakes) into matrix glasses, such as in pyroclasts and lava flows, which may occur on the order of tens to thousands of years with diffusion coefficients (D_{H_2O}) on the order of $10^{-23(\pm 1)}$ m²/s (Friedman and Long, 1976; Giachetti and Gonnermann, 2013; Giachetti et al., 2015). However, fewer studies have explored rehydration rates at hydrothermal or magmatic temperatures, e.g., syn-eruptive, or immediately post-eruptive, settings such as lavas and hot pyroclastic deposits (Friedman and Long, 1976; Mazer et al., 1991; Seligman et al., 2018; Hudak and Bindeman, 2020; Hudak et al., 2021). This work set out to identify the sources, timescales, and mechanisms of proposed rapid rehydration within subaqueous silicic volcanic deposits.

A unique example of potential rehydration by water of known composition (seawater) is provided by the well-studied 2012 submarine eruption of Havre volcano in the Kermadec Arc (Carey et al., 2018; Mitchell et al., 2018). Rehydration signatures (higher than anticipated H₂O concentrations) observed in these very recent deep-sea pumice deposits could not be explained by cold seawater rehydration due to insufficient time for observed H₂O diffusion length scales (Mitchell et al., 2018). In the deep-sea environment, rehydration by seawater is common in silicic pumice deposits (Fig. 1) due to thin glass walls between vesicles, long ocean residence time (up to tens of thousands of years old), and an ready supply of external H₂O (Giachetti and Gonnermann, 2013; Martin et al., 2017). However, Mitchell et al. (2018) concluded that hotter, rapid rehydration was required to produce the observed Havre rehydration signatures, inferring that rehydration occurred at 300–400 °C, over timescales of minutes while pumice remained hot within a large submarine volcanic plume or during oceanic settling. The method used to identify this rapid rehydration (FTIR – Fourier-transform infrared spectroscopy) could not identify the *source* of H₂O contamination; the H₂O species that are measured by FTIR (hydroxyl OH groups and molecular H₂O_m; H₂O_t (total) = OH + H₂O_m) do not record the origin of water in glass, and FTIR does not measure their isotopic values (Stolper, 1982; Newman et al., 1986; McIntosh et al., 2014; McIntosh et al., 2017). Here, we use recently developed isotopic methods to determine the source of rapid rehydration within the Havre deposits.

1.2. Hydrogen and oxygen isotopes in magma

Stable isotope ratios of elements that comprise volatiles, such as hydrogen (H) and oxygen (O), within magmas are reliable indicators for tracking magmatic degassing and interactions between melts and coexisting or external fluids (Taylor et al., 1983; Dobson et al., 1989; Mandeville et al., 2009; Giachetti et al., 2020). Characterization of hydrogen and oxygen isotope compositions (δD and $\delta^{18}O$, respectively) with H₂O in glass are used to model degassing of water from silicate melts (Fig. 2). Delta notation expresses ratios of isotopes of an element normalized to the isotope ratio of a standard (e.g., VSMOW – Vienna Standard Mean Ocean Water). Here, we express variations in deuterium,

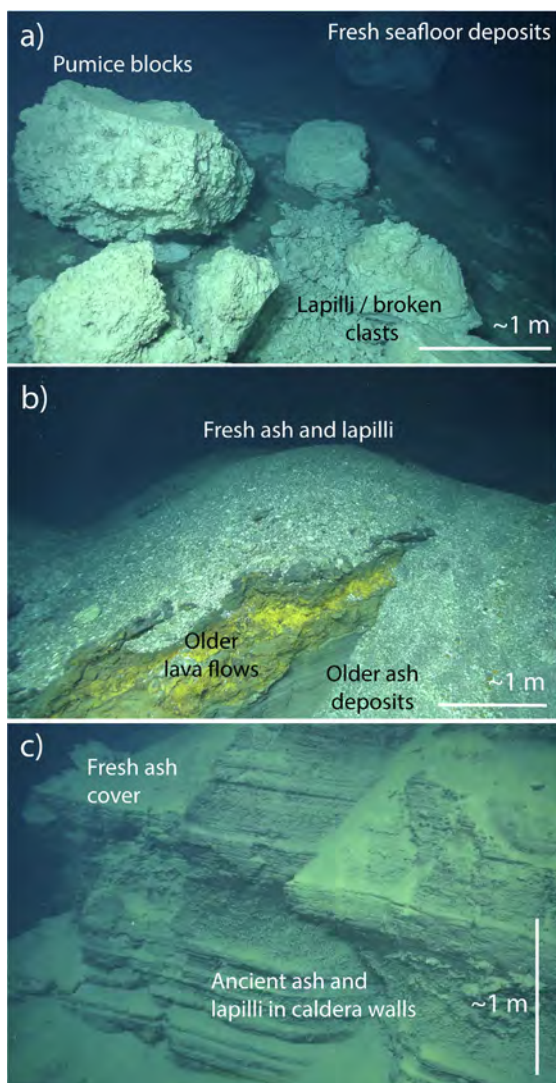


Fig. 1. Images taken from a Remotely Operated Vehicle in April 2015: a) fresh pumice deposits from the 2012 submarine Havre eruption – giant pumice blocks; b) fresh ash and lapilli deposits (Havre 2012) overlying older lava flows and pyroclastic stratigraphy – age unknown; c) ancient stratified tephra fall deposits in the Havre caldera walls (300 meters down from the caldera wall rim).

D (or ^2H), to hydrogen, H, as δD (Eq. (1)) and variations of ^{16}O and ^{18}O as $\delta^{18}\text{O}$ (Eq. (2)).

$$\delta\text{D}(\text{‰}) = 1000 \left(\frac{\frac{D}{H_{\text{sample}}}}{\frac{D}{H_{\text{VMSOW}}}} - 1 \right) \quad (1)$$

$$\delta^{18}\text{O}(\text{‰}) = 1000 \left(\frac{\frac{^{18}\text{O}}{^{16}\text{O}_{\text{sample}}}}{\frac{^{18}\text{O}}{^{16}\text{O}_{\text{VMSOW}}}} - 1 \right) \quad (2)$$

Trends that deviate from the well-established degassing models are used to identify mixing of magmatic water in glass with external sources of water, such as seawater, hydrothermal fluids, and discrete magmatic fluids (Taylor,

1991; Castro et al., 2014; Seligman et al., 2016; Giachetti et al., 2020; Walter and Castro, 2020). External sources of H_2O have distinct δD and $\delta^{18}\text{O}$ signatures dependent on the source (meteoric H_2O , seawater, hydrothermal fluids, or magmatic H_2O), physical state (vapor vs. liquid), pressure, and temperature (Lécuyer et al., 1998). We can use our existing knowledge of these isotopic signatures to assess rehydration (and dehydration) of glasses/melts by magmatic, meteoric, oceanic, or hydrothermal fluids, and the temperatures at which these occur (Fig. 2).

During volcanic degassing, exsolved vapor is enriched in the heavier D and ^{18}O isotopes (e.g., Taylor et al., 1983; Dobson et al., 1989). These isotopic variations arise due to the changes in H_2O solubility and speciation with decreasing pressure; at a given temperature, dissolved magmatic H_2O undergoes disproportionation as $\text{H}_2\text{O}_{\text{m}}$ exsolves into the vapor phase, where OH^- becomes the more dominant species over $\text{H}_2\text{O}_{\text{m}}$ at lower pressure (Stolper, 1982; Newman et al., 1986). The lighter isotopes are preferentially partitioned into OH, so as $\text{H}_2\text{O}_{\text{m}}$ exsolves the melt becomes depleted in δD . Pressure, H_2O speciation in melt, and style of degassing (open or closed) are primary controls on δD isotopic composition of the coexisting and accumulated magmatic vapor at given depth within a volcanic conduit (Fig. 2a). As a result, δD in the melt/glass can record volcanic processes and features such as degassing, quenching, and volatile resorption (Castro et al., 2014; Seligman et al., 2016; Giachetti et al., 2020).

The behavior of $\delta^{18}\text{O}_{\text{wig}}$ (water in glass) during degassing is not as well established as δD , as the mass fractionation between ^{18}O and ^{16}O is much smaller than between D and H, and because oxygen is the dominant element in main silicate and OH structure (Seligman and Bindeman, 2019); $\delta^{18}\text{O}_{\text{wig}}$ variations will have a small effect on, and will always be offset from, bulk $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{bulk}}$). $\delta^{18}\text{O}_{\text{bulk}}$ values are better constrained than $\delta^{18}\text{O}_{\text{wig}}$, e.g., 5–7‰ in rhyolitic melts (Bindeman, 2008). $\delta^{18}\text{O}_{\text{wig}}$ is hypothesized to decrease during degassing because the exsolving $\text{H}_2\text{O}_{\text{m}}$ phase is enriched in D and ^{18}O (Fig. 2b; Seligman and Bindeman, 2019). Additionally, hydration experiments between water and glass at 100 and 400 °C by Hudak and Bindeman (2020) find that the offset (fractionation) between $\delta^{18}\text{O}_{\text{bulk}}$ and $\delta^{18}\text{O}_{\text{wig}}$ varies as a function of temperature, which can be applied as a hydration thermometer. In a magmatic degassing trend, we would expect to see coupled depletion of δD and $\delta^{18}\text{O}_{\text{wig}}$ with decreasing $\text{H}_2\text{O}_{\text{t}}$ content (Fig. 2b).

In this study, we used δD and $\text{H}_2\text{O}_{\text{t}}$ measurements to resolve possible sources for rapid rehydration signatures in pumice and lava from the 2012 submarine Havre eruption detailed by Mitchell et al. (2018) (Fig. 1a, b). The offset between $\delta^{18}\text{O}_{\text{wig}}$ and $\delta^{18}\text{O}_{\text{bulk}}$ was used as an intra-glass rehydration thermometer. Our isotopic data also provides a natural validation of experimentally-determined H_2O diffusivity and oxygen isotope fractionation (Hudak and Bindeman, 2018, 2020) in silicic glasses at elevated temperatures (100–400 °C). For an endmember comparison, we also measured H and O isotopes and $\text{H}_2\text{O}_{\text{t}}$ of much older (tens to thousands of years) silicic submarine lavas and pumice clasts from other submarine arc volcanoes (Fig. 1c).

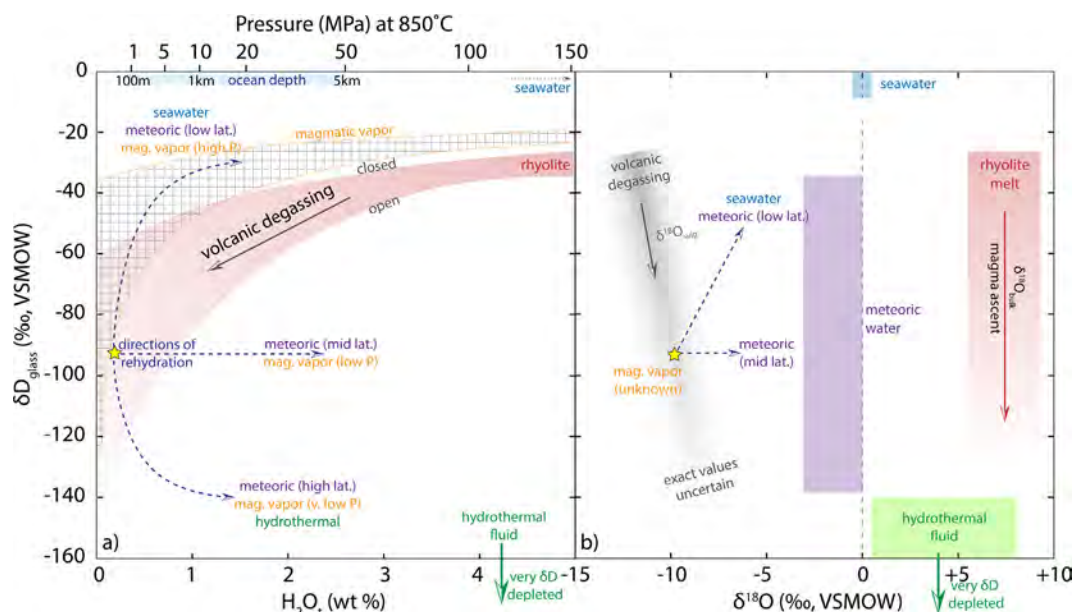


Fig. 2. Schematic degassing and rehydration trends shown as a) δD - H_2O and b) δD - $\delta^{18}\text{O}$: general expected open and closed degassing of silicic volcanic melt and resulting magmatic vapor composition (Taylor, 1991; Giachetti et al., 2020), potential directions of rehydration (dashed arrows) for a single degassed data point (star) – a common value for highly degassed magma (Castro et al., 2014), and possible mixing sources for rehydration within their isotopic signature fields (colored words). Mixing sources of H_2O extrapolate to 100 wt.%. Equilibrium H_2O solubility (pressure) is calculated at 850 °C for a silicic melt (Newman and Lowenstern, 2002) and hydrostatic-pressure-equivalent ocean depth is given. In b), an expected degassing trend is shown for $\delta^{18}\text{O}$ of water in melt ($\delta^{18}\text{O}_{\text{wig}}$), although exact values with δD and for that of magmatic vapor are not well established. A magma ascent path is shown for $\delta^{18}\text{O}$ of a bulk rhyolitic magma ($\delta^{18}\text{O}_{\text{bulk}}$). Magmatic vapor has a large isotopic range at low H_2O due to large vapor-liquid fractionation changes with pressure and temperature (Giachetti et al., 2020). Meteoric water isotopic signatures change with latitude (Seligman et al., 2016).

2. SAMPLING AND METHODS

The Havre 2012 samples analyzed within this study were identical (i.e., fragments from the same cm-sized clasts) to those characterized by Mitchell et al. (2018) using FTIR spot and mapping analysis to allow direct comparison of water speciation with isotope signatures (supplements 1, 2). These included samples from rafted pumice, exterior fragments from giant (>1m) pumice (Fig. 1a; supplement 1), lapilli within tephra layers (ALB) (Fig. 1b), dense lapilli tube pumice (from the Lava G lapilli; Mitchell et al., 2018), and lava-dome talus (Carey et al., 2018; Ikegami et al., 2018; Mitchell et al., 2019; Murch et al., 2019). The Havre samples were collected from 650 to 1000 m deep in 2015 (just three years of cold seawater exposure), subsequently heated and dried, and then subject to analysis in 2018. Raft pumice, giant pumice and ALB lapilli are all assumed to have erupted from the same vent at 900 m deep (~9 MPa), and the dense tube pumice are a clastic deposit associated within a single Lava flow (Lava G) (Carey et al., 2018). All Havre 2012 samples have a rhyolitic composition with 71–73 wt.% SiO_2 and a limited crystallinity range of 5–13 vol.%, the highest found in dome talus samples; crystals identified are anhydrous phases of plagioclase, pyroxene, and Fe-Ti oxides. (Carey et al., 2018; Knafelc et al., 2020).

The older silicic submarine samples from other volcanoes (as follows) span a range of ages, textures, eruption styles, and eruptive depths. All samples have rhyolitic composition (>70 wt.% SiO_2) except for a series of high silica

dacitic lavas (65–68 wt.% SiO_2) from the Lau Basin (Embley and Rubin, 2018). All samples are either aphyric or have low crystallinity. They are:

- (1) Dense (avesicular) obsidian dacitic lava flow exteriors from lava flow fields NE of the Niuatahi caldera in the Lau Basin, thought to be < 100 years old (Embley and Rubin, 2018).
- (2) High-vesicularity lapilli clasts settled on top of the Lau Basin dacite flows < 100 years old (Embley and Rubin, 2018).
- (3) Highly-vesicular lava knoll samples from the very shallow (<120 m deep) Oomurodash volcano in the Izu Arc south of Japan, thought to be many thousands of years old.
- (4) High vesicularity pumices from the Myojin Knoll and Kurose Nishi volcanoes considered to be < 1000 years old, Izu Arc.
- (5) High vesicularity pumice and dome carapaces from the Sumisu Domes Complex on the Izu Arc likely to be thousands of years old.

Due to the variety of different conditions within these pre-2012 silicic samples, we simply refer to these collectively as “older submarine pumice (or lava)” to act as the seawater-control-group for the rest of the study. We do not make any interpretations of the eruptive mechanisms of these varying older samples, as Havre is the primary interpretive focus of the study. Further details on all Havre and non-Havre sampling locations, depths, and compositions are given in supplements 1 and 2.

2.1. Analytical methods

A MAT 253, isotope ratio mass spectrometer (IRMS) and a high temperature conversion elemental analyzer (TC/EA) at the University of Oregon were used to measure H and O isotope ratios and $\text{H}_2\text{O}_\text{t}$ concentration in glass; the isotope results are presented as δD and $\delta^{18}\text{O}$ (Eq. (1) and (2)). For complete TC/EA methodologies for δD and $\text{H}_2\text{O}_\text{t}$ see Martin et al. (2017), and for $\delta^{18}\text{O}$ of water-in-glass ($\delta^{18}\text{O}_\text{wig}$) see Seligman and Bindeman (2019). A CO_2 laser fluorination line was utilized to determine the bulk $\delta^{18}\text{O}$ of select, glassy samples (Bindeman et al., 2012). With both bulk and water-in-glass $\delta^{18}\text{O}$ components, we apply O isotope thermometry (O'Neil and Taylor, 1967; Clayton et al., 1972; Bindeman and Lowenstern, 2016; Sharp et al., 2016). Powdered samples used for TC/EA and laser fluorination analysis were taken from crushing a few mg of the same clast analyzed by FTIR, so we are making direct data comparisons within individual clasts with multiple FTIR measurements.

The TC/EA measurements were made on 1–4 mg of material with 0.4 to 5.6 wt.% $\text{H}_2\text{O}_\text{t}$ content (from preliminary FTIR analyses) and carry 1 s.d. analytical uncertainties on the order of $\pm 2\text{‰}$ for δD and 0.05 wt.% on $\text{H}_2\text{O}_\text{t}$ (Martin et al., 2017). For Havre samples, the duplicates were reproducible within 10‰ δD , 0.1 wt.% $\text{H}_2\text{O}_\text{t}$ at high H_2O contents and 1.0‰ $\delta^{18}\text{O}_\text{wig}$ at low H_2O content. Greater variations in the samples, as compared to standards, are expected in this case due to some geochemical heterogeneity in natural glasses (Rubin et al., 2001; von Aulock et al., 2013; Castro et al., 2014), including the spatial extent of rehydration and vesicle texture – discussed later in the discussion. We also make the reasonable assumption that all H is held up in $\text{H}_2\text{O}_\text{t}$ ($\text{H}_2\text{O}_\text{m}$ and OH) and not in H_2 , which is found to be negligible ($\ll 100$ ppm) in hydrous silicic arc magmas – especially at low pressure and higher oxygen fugacities typical of silicic arc magmas (e.g. FMQ>+1) (Robie et al., 1978; Hirschmann et al., 2012; Moine et al., 2020).

A JEOL JXA-8500F microprobe analyzer at the University of Hawai'i at Mānoa was used to acquire backscattered secondary electron (BSE) images of 2D clast textures to potentially identify rehydrated vesicle rims, such as observed by McIntosh et al. (2014). Clast porosity (volume % void space) was determined by dry and wet weight ballast method as per Houghton and Wilson (1989). Further details on sample selection, techniques used, and analytical conditions are found within supplements 1–3.

3. TEXTURAL IMAGES: IDENTIFIED REHYDRATION RIMS

A variety of Havre juvenile products were studied with the following vesicularities: lava dome talus fragments have clast porosities of 23–42%, giant pumice block fragments (GP): 66–83%, tube pumice (Lava G lapilli): 40–65%, raft pumice (RP): 69–91%, and pumice lapilli within a poorly-sorted ash and block layer (ALB): 67–87% porosity (supplement 2). BSE images of Havre pumice and lava show that higher vesicularity samples have very thin vesicle walls

(Fig. 3). In ALB lapilli and giant pumice samples, many vesicles are coalesced, i.e., their vesicle walls were breached and thus vesicles are highly connected in 3D pore space (Fig. 3d–f). Prior studies of Havre 2012 pumice show that giant pumice, ALB lapilli and raft pumice have highly connected vesicle networks (Manga et al., 2018a; Mitchell et al., 2021). Older non-Havre submarine lavas (high silica dacites and rhyolites) are glassy, acrySTALLINE, and have negligible vesicularity, and older non-Havre silicic pumices analyzed have high porosities ($>65\%$).

Evidence of rehydration in lower-porosity glasses with thick vesicle walls can be identified as rims around vesicles within BSE images of talus from Dome OP erupted in 2012 at the Havre volcano (Fig. 4). The darker-backscatter rims correspond to a larger mass proportion of relatively low-mass H_2O present within the glass. H_2O diffusion profiles were acquired from these rims (up to 10 μm thick) by Mitchell et al. (2018), confirming the rims had increased in H_2O up to 4.5 wt.% from 0.5–1.0 wt.%. We note that not *all* vesicles exhibit rehydration rims; more isolated and smaller vesicles tend *not* to have rims whereas large, interconnected vesicles have rims that can extend up to 20 μm from the vesicle edge (Fig. 4a,b). In pumice of high vesicularity, the vesicle walls are too thin to identify distinct boundaries between areas with or without significant rehydration, and BSE charging right at the vesicle edge could obscure rehydration rims.

4. GEOCHEMICAL RESULTS

4.1. $\text{H}_2\text{O}_\text{t}$ and δD TC/EA analyses

The TC/EA analyses show that older submarine pumice and lava samples from multiple locations have an isotopically heavier (i.e. enriched) and consistently narrower δD range (-29‰ to -65‰) than the 2012 Havre samples (-48‰ to -116‰) over 0.9 to 5.6 wt.% $\text{H}_2\text{O}_\text{t}$. As expected, these signatures are highly indicative of the presence of seawater-derived excess $\text{H}_2\text{O}_\text{m}$ in older volcanic glass (Fig. 5). Heavier δD values around -30‰ and higher $\text{H}_2\text{O}_\text{t}$ of up to 6 wt.% are consistent with complete rehydration by seawater (up to maximum H_2O solubility in glass; Denton et al., 2009). In these samples, either the glass has re-equilibrated or the seawater has overwhelmed the small amount of residual magmatic H_2O . The δD fractionation between glass and water ($\Delta\text{D}_\text{glass-H}_2\text{O}$) is known to be $\sim -33\text{‰}$ for Earth surface temperature (Friedman et al., 1993; Seligman et al., 2016), so glasses fully rehydrated by seawater ($\delta\text{D} \sim 0\text{‰}$) are not expected to exhibit $\delta\text{D} > -30\text{‰}$. However, submarine samples are likely to retain more magmatic H_2O upon quenching than subaerial samples because of hydrostatic pressure effects on H_2O solubility (Fig. 2). Therefore, lighter δD values likely result from a mixture of seawater and magmatic water where residual, non-replaced, magmatic H_2O is present in higher proportions than in the heavier δD samples.

The older submarine lavas have lower porosity and therefore reduced interfacial area between glass and seawater and lower susceptibility to rehydration and as a result, they have lower $\text{H}_2\text{O}_\text{t}$ values than most of the older

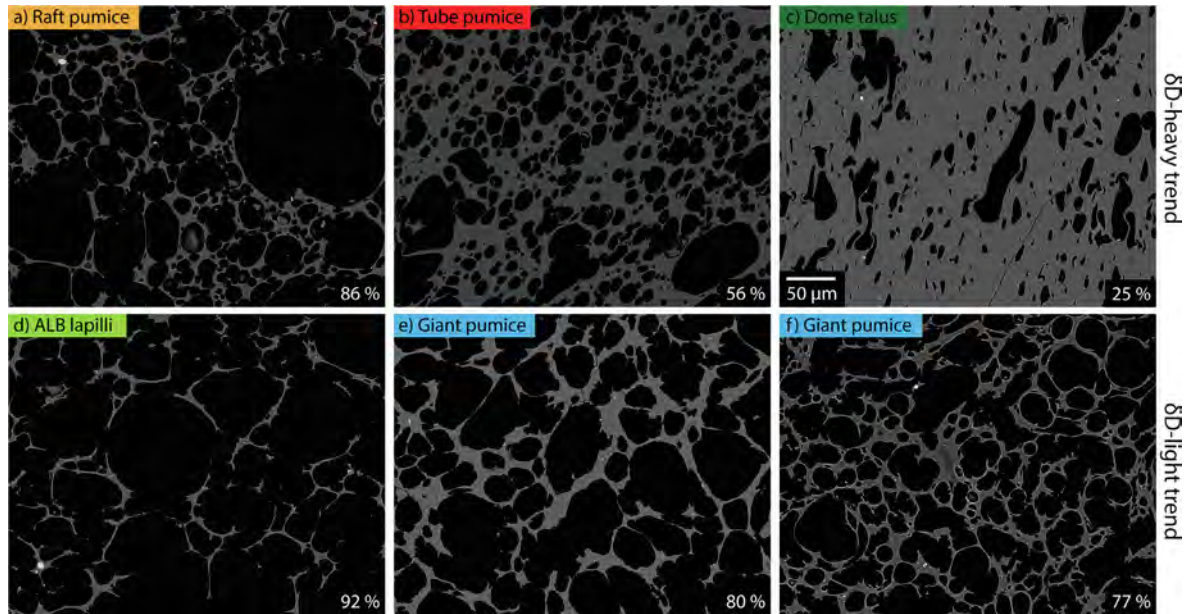


Fig. 3. Backscattered electron images (at 250 $\times$ magnification) of representative vesicle microtextures within clasts from each of the 2012 Havre eruption units along the δ D-heavy (raft pumice, dense tube pumice and dome talus) and δ D-light trend (giant pumice and ALB lapilli). The scale-bar is equal for each image. Vesicles shown in black; glass and microlites in greyscale. 2D image porosity given in %.

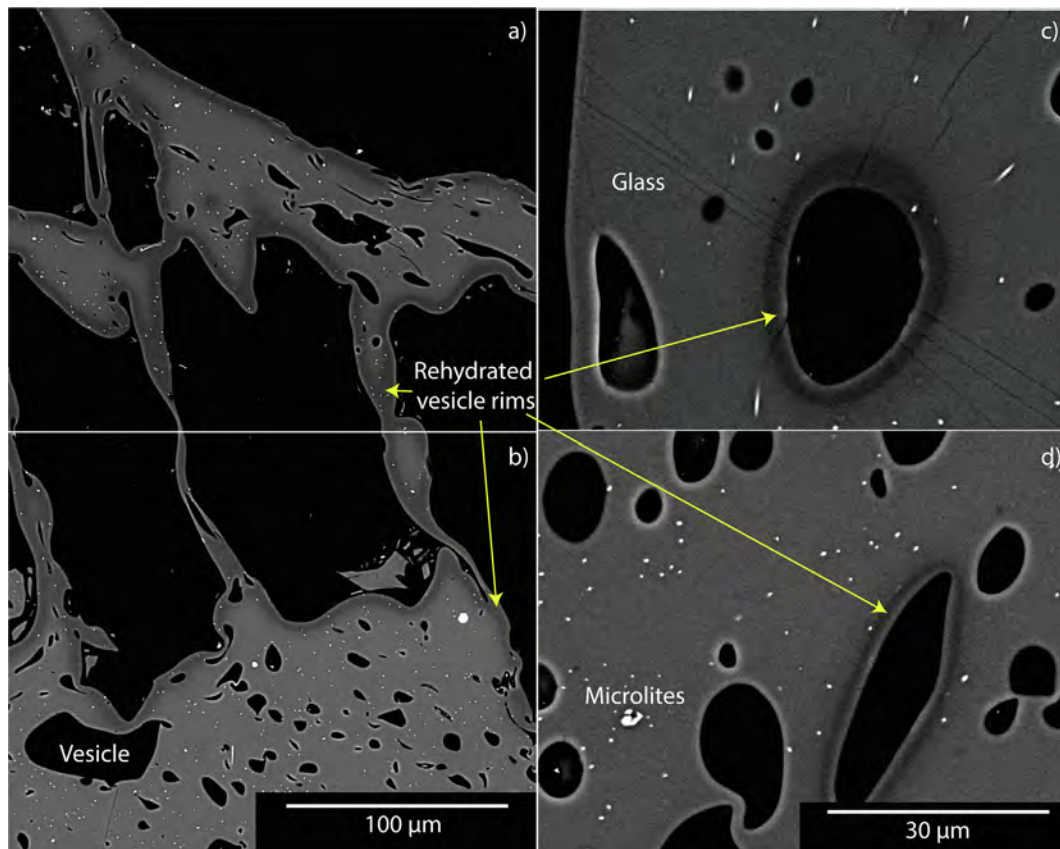


Fig. 4. Backscattered electron images of H₂O-enrichments around vesicle rims in volcanic glass (black = vesicles, grey = glass, white = crystals). Glass greyscale value corresponds to water content; darker glass is enriched in H₂O relative to lighter glass. Samples were taken from the talus of the 2012 Havre Dome OP erupted at 900 mbsl. Thin vesicle walls between large vesicles are completely rehydrated, but smaller isolated vesicles show no rehydration. Note that very thin bright rims around vesicles are ‘edge effect’ artifacts caused by the boundary between glass and void- or resin-filled space. Images c) and d) have the same magnification and scale.

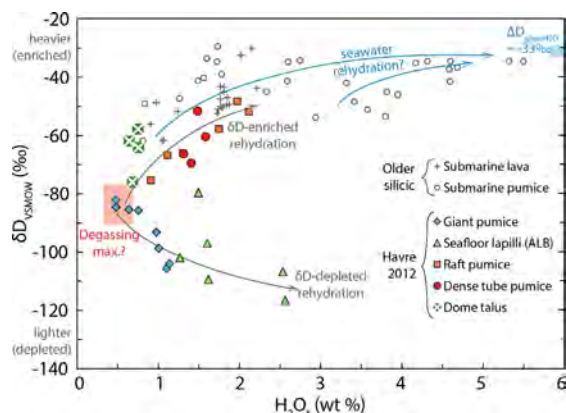


Fig. 5. δD vs. H_2O_t results given relative to VSMOW ($\delta D = 0$) for all Havre and non-Havre samples. Analyses have precisions of $\delta D = 2\text{‰}$, and $< 0.1 \text{ wt.\% } H_2O_t$. Potential rehydration trends (deviation from degassing trend in Fig. 2) are given by the arrows. The orange box represents a likely δD and H_2O_t range for samples that experienced the most degassing at Havre; rehydration trends begin at this point. The δD fractionation between glass and water ($\Delta D_{\text{glass-H}_2O}$) is given as $\sim 33\text{‰}$ and is likely mixing endmember for samples rehydrated by seawater. Older samples include Mohutahi, Niuatahi, Kurose Nishi, Myojin Knoll, Oomurodash and Sumisu Domes; breakdown of the older silicic data is given in supplement 4.

Izu-Bonin pumices, but yield δD values that are relatively consistent (primarily -30‰ to -50‰) with the pumices (Fig. 5). In particular, the vesicular dacite lavas from the Lau Basin Niuatahi cone field have a very narrow H_2O_t and δD range ($1.7\text{--}1.9 \text{ wt.\% } H_2O_t$; -43‰ to -52‰ δD), indicating that they likely experienced relatively uniform, less extensive rehydration and rapid quenching near their eruptive depths; this is consistent also with the interpretation that they are less than 100 years old (Embley and Rubin, 2018). The Niuatahi H_2O_t range is also consistent with the expected water contents (at equilibrium H_2O solubility) from their eruptive pressure of $25\text{--}29 \text{ MPa}$ (Newman and Lowenstern, 2002) further supporting that these lavas experienced little rehydration.

The lowest H_2O_t samples from the 2012 Havre eruption are $\sim 0.5 \text{ wt.\%}$ with δD of ~ -80 to -90‰ . This represents a maximally degassed glass composition close to expected for the hydrostatic quench pressure at the vent (Fig. 5). With increasing H_2O_t , the data form two diverging δD trends: giant pumice (GP) and ALB seafloor lapilli in the isotopically-light (depleted) trend ($\delta D = -82\text{‰}$ to -119‰) with ALB exhibiting the lightest values; and raft pumice, dense tube pumice and dome talus in the enriched trend ($\delta D = -78\text{‰}$ up to -48‰); both trends reach up to $2.6 \text{ wt.\% } H_2O_t$. The δD -depleted values plateau towards $\delta D = -115\text{‰}$ to -125‰ . Mitchell et al. (2018) also identified GP and ALB samples (the δD -depleted trend) as samples with the “greatest relative extent of rehydration” due to their anomalously high H_2O_m/OH values at low $[H_2O_t]$ from FTIR analysis (Table 1). This correlation suggests that GP and ALB samples underwent a different rehydration process to the other samples analyzed

(raft pumice, tube pumice and dome talus). We will use δD - H_2O degassing modelling in the next section to identify H_2O rehydration sources for the Havre juvenile material.

4.2. $\delta^{18}O$ and $\Delta^{18}O_{\text{bulk-wig}}$ fractionation

The δD -depleted trend corresponds directly to a $\delta^{18}O_{\text{wig}}$ -enriched trend where the lowest δD values (down to -116‰) have the highest $\delta^{18}O_{\text{wig}}$ (up to $+3.4\text{‰}$) (Fig. 6a). H_2O_t increases along two $\delta^{18}O_{\text{wig}}$ trends away from $\delta^{18}O_{\text{wig}} \sim -4\text{‰}$ (Fig. 6b). The δD -enriched trend sits within most of the older submarine samples and near values consistent with expected $\delta^{18}O_{\text{wig}}$ values of non-rehydrated volcanic glass of -12 to -9‰ (Seligman and Bindeman, 2019). Older silicic pumices with very high H_2O_t (up to $6 \text{ wt.\%}$) show an increase in $\delta^{18}O_{\text{wig}}$ from -10 to -5‰ and in δD (Fig. 6a, b). This increase in $\delta^{18}O_{\text{wig}}$, δD and H_2O_t of older submarine pumice also corresponds to a significant increase in bulk $\delta^{18}O$ up to $+9.8\text{‰}$; an increase in $\delta^{18}O_{\text{bulk}}$ is not observed in older lavas or any of the Havre 2012 samples (Fig. 6c, d). The Havre $\delta^{18}O_{\text{bulk}}$ values plot in a narrow band ($+5.7$ to $+6.2\text{‰}$) at all δD values – a $\delta^{18}O$ range expected for rhyolites derived by fractionation from mantle melt along subduction zones (e.g. Taylor, 1968; Bindeman, 2008).

Samples with high $\delta^{18}O_{\text{wig}}$ values (up to $+3.4\text{‰}$) have correspondingly small $\Delta^{18}O_{\text{bulk-wig}}$ values (Fig. 6e, f), where $\Delta^{18}O_{\text{bulk-wig}} = \delta^{18}O_{\text{bulk}} - \delta^{18}O_{\text{wig}}$. The depleted δD Havre trend (giant pumice and ALB lapilli) has a relatively low $\Delta^{18}O_{\text{bulk-wig}}$ values of $+2.4$ to $+10.3\text{‰}$ (Fig. 6e, f) – indicative of a higher temperature process. The raft pumice, dense tube pumice and all older samples show greater fluid-melt $\Delta^{18}O_{\text{bulk-wig}}$ fractionations of $+12.8$ to $+17.6\text{‰}$ – this is likely indicative of rehydration setting(s) with temperatures lower than the glass transition temperature ($< 400 \text{ °C}$) (Hudak and Bindeman, 2018; Hudak and Bindeman, 2020). The $\Delta^{18}O_{\text{bulk-wig}}$ results will be important for considering the mechanism, temperature, and timing of diffusive O isotope exchange and fractionation within these samples, whereas the δD - H_2O_t results will point to potential sources of rehydration. All isotopic results from Havre pumice and corresponding FTIR H_2O speciation and porosity data from Mitchell et al. (2018) are given in Table 1 and presented later in the discussion: Section 7.2; all isotope results from older samples can be found in supplement 4.

5. δD - H_2O DEGASSING AND VAPOR MODELING

In this section, we determine the likely rehydration sources for the Havre 2012 samples using degassing modeling. The older submarine pumices and lavas were undoubtedly rehydrated by seawater over long timescales, so degassing and vapor modeling is not required for these samples.

We use the degassing model of Taylor et al. (1991) to determine closed (vapor exsolves, remains within bubbles, and the melt re-equilibrates with the enclosed vapor) and open (vapor exsolves from the melt and leaves the system) degassing pathways for Havre magma (Fig. 7). A combined “closed-open” degassing model is also calculated using a

Table 1

Comparison of textural and analytical data from 2012 Havre pumice using FTIR and TC/EA techniques. *Denotes data taken from Mitchell et al. (2018).

Unit (Havre 2012)	Sample #	Porosity (%)	$\delta^{18}\text{O}_{(\text{sil})}$ (‰)	$\delta^{18}\text{O}_{(\text{blk})}$ (‰)	$\delta^{18}\text{O}_{(\text{wig})}$ (‰)	$\Delta^{18}\text{O}_{(\text{blk-wig})}$ (‰)	δD (‰)	TC/EA H_2O_t (wt.%)	*FTIR H_2O_t (wt.%)	*FTIR OH (wt.%)	*FTIR $\text{H}_2\text{O}_m / \text{OH}$	*Estimated quenching P (MPa)
Dome talus	db-007	42.1	–	–	–5.37	–	–61.88	0.64	0.52	0.31	0.68	0.8–1.4
	hvr-dbv	23.9	–	–	–5.65	–	–64.12	0.76	1.18	0.42	1.81	1.5–3.6
	db-vh	23.9	–	–	–5.65	–	–57.75	0.75	1.18	0.42	1.81	“
Giant pumice	db-007	42.1	–	–	–	–	–75.98	0.68	0.52	0.31	0.68	0.8–1.4
	gpx-231	82.6	–	–	–	–	–85.72	0.75	0.38	0.22	0.73	0.4–0.6
	gpx-270	66.4	6.06	6.11	–4.2	10.31	–84.62	0.48	0.27	0.13	1.08	0.14–0.19
	gpx-290	72.0	6.07	6.13	–0.11	6.24	–98.67	1.01	0.36	0.16	1.25	0.21–0.28
	gpx-290 g	72.6	–	–	1.24	–	–105.66	1.10	0.43	0.19	1.26	0.3–0.4
	gpx-290w	72.6	–	–	1.27	–	–103.97	1.14	0.29	0.17	0.71	0.6–0.9
	gpi-290	80.0	5.77	5.82	–1.34	7.16	–85.42	0.64	0.27	0.15	0.80	0.19–0.26
	gpx-270	66.4	–	–	–	–	–82.12	0.48	0.27	0.13	1.08	0.14–0.19
	gpx-290	72.0	–	–	–0.11	–	–93.19	0.98	0.36	0.16	1.25	0.21–0.28
Seafloor lapilli	albl-1893	78.3	5.70	5.76	3.39	2.37	–116.56	2.56	0.28	0.14	1.00	0.22–0.30
	albm-246	78.3	6.04	6.12	1.38	4.74	–109.33	1.62	0.37	0.19	0.95	0.31–0.44
	albh-120	66.9	–	–	–3.66	–	–79.62	1.49	0.45	0.28	0.61	0.8–1.3
	alb-m	78.3	–	–	1.38	–	–96.95	1.60	0.37	0.19	0.95	0.31–0.44
	alb-l2	78.3	–	–	2.45	–	–106.64	2.53	0.28	0.14	1.00	0.22–0.30
	hvr-albl	86.8	–	–	–	–	–101.90	1.27	0.18	0.10	0.80	0.09–0.12
Dense tube pumice	lgll-158	64.7	–	–	–7.43	–	–66.29	1.31	0.65	0.41	0.59	1.4–2.7
	lgll-11b	40.8	6.00	6.19	–7.25	13.44	–69.42	1.41	0.9	0.53	0.70	2.5–5.5
	hvr-lglm	57.3	–	–	–7.58	–	–60.36	1.58	0.78	0.58	0.34	3.0–7.1
	lgl-m	57.3	–	–	–	–	–51.61	1.48	0.78	0.58	0.34	“
Raft pumice	rp-aus	76.1	5.52	5.77	–8.39	14.16	–57.73	1.75	0.52	0.30	0.73	0.75–1.2
	rp-fjl	90.5	–	–	–	–	–75.32	0.91	–	–	–	–
	rp-fjm152	79.7	–	–	–6.97	–	–66.65	1.12	–	–	–	–
	rp-fjm-155	80.2	–	–	–7.15	–	–65.98	1.31	–	–	–	–
	rp-fjh	69.4	–	–	–	–	–51.76	2.11	–	–	–	–

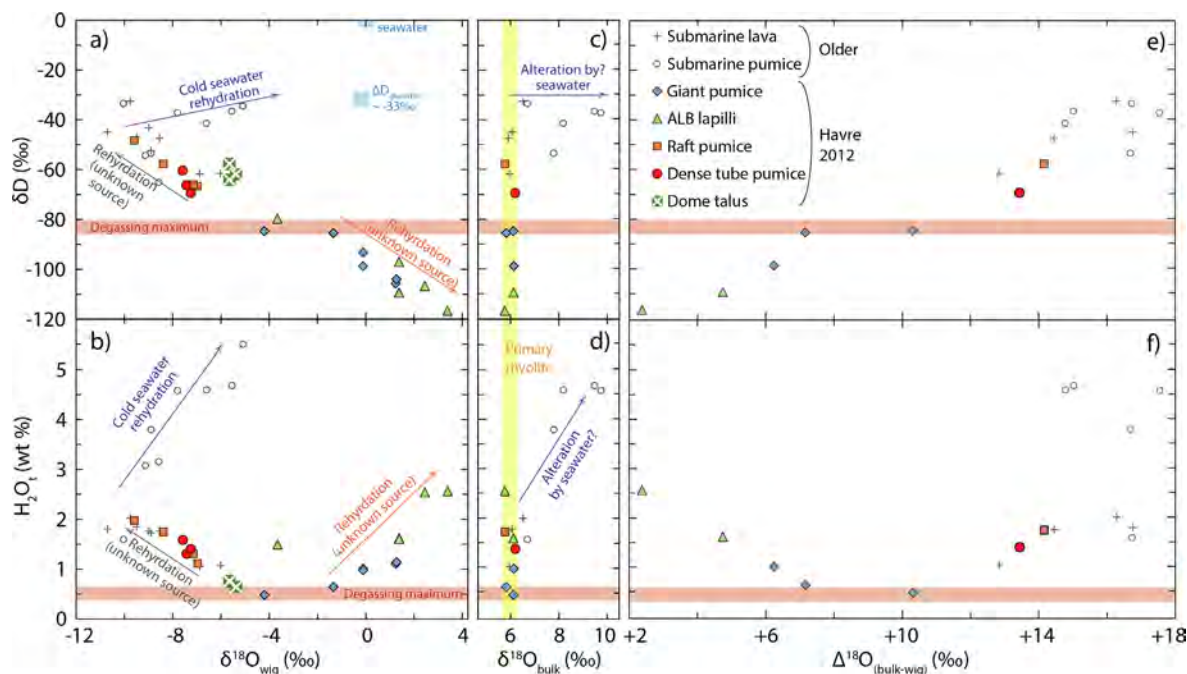


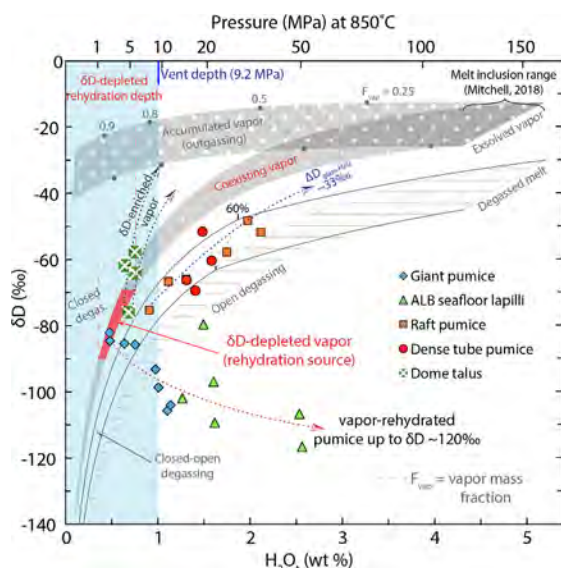
Fig. 6. Analysis of $\delta^{18}\text{O}$ data and $\Delta^{18}\text{O}_{\text{bulk-wig}}$ fractionation: plots of δD and H_2O_t , against $\delta^{18}\text{O}_{\text{wig}}$, $\delta^{18}\text{O}_{\text{bulk}}$ and $\Delta^{18}\text{O}_{\text{bulk-wig}}$. $\delta^{18}\text{O}$ analyses have precisions of 0.4‰ . Seawater is given at VMSOW- $\delta\text{D} = \delta^{18}\text{O}_{\text{wig}}$ at $\sim 0\text{‰}$. Possible trends are identified for: rehydration by cold seawater (older samples), rehydration by unknown fluid sources (Havre 2012), and alteration of bulk $\delta^{18}\text{O}$ seawater (older samples). The yellow box defines the very narrow $\delta^{18}\text{O}_{\text{bulk}}$ range for the Havre 2012 magma despite rehydration, and the orange box reflects the δD composition at maximum degassing identified in Fig. 5 for Havre samples. The δD fractionation between glass and water ($\Delta\text{D}_{\text{glass-H}_2\text{O}}$) is given as $\sim 33\text{‰}$ at $\delta^{18}\text{O}_{\text{wig}} \sim 0\text{‰}$.

percolation threshold value of 60% vesicularity for a rhyolitic melt (Colombier et al., 2017; Giachetti et al., 2020). Initial melt conditions used are a δD range of -30 to -45‰ (hydrous, silicic, cold subduction zone fluids; Shaw et al., 2008; Syracuse et al., 2010; Dixon et al., 2017; Befus et al., 2020) and 4.3 to 5.2 wt.% H_2O (from quartz-hosted melt inclusions; Mitchell, 2018). Equilibrium H_2O melt solubility (pressure) was calculated at 850 °C (eruption temperature from Manga et al., 2018a and consistent with prior speciation calculations) for a silicic melt, using VolatileCalc (Newman and Lowenstern, 2002). Mass fraction and isotopic composition of the exsolved vapor phase was calculated following Giachetti et al. (2020). Exsolved vapor is calculated as (i) coexisting vapor (new, exsolved vapor in bubbles at a given exsolution pressure through, mostly, closed degassing), and (ii) accumulated vapor (vapor accumulated from degassing at depth and propagating through a permeable, magmatic bubble network during open-system degassing). Fractionation between melt and vapor ($\Delta\text{D}_{\text{liquid-vapor}}$) is speciation dependent, as per calculation by Giachetti et al. (2020), where H_2O speciation was calculated using Zhang (1997) and vapor-OH fractionation values from Dobson et al. (1989). Full details and equations for degassing and vapor modeling are given in supplement 5.

5.1. A degassing trend or glass rehydration?

Degassing melt is expected to follow a trend of δD -depletion as H_2O_t in melt decreases and exsolves into the

vapor phase – as shown in Fig. 2. This degassing trend should be best represented by the “closed-open” degassing model (Fig. 7). However, the subsequent δD -depletion of Havre giant pumice and ALB lapilli with increasing H_2O_t is characteristic of rehydration and not degassing (Fig. 7). The δD -enriched Havre trend (raft pumice, tube pumice, and some dome talus) is closer to the expected degassing trend for Havre magma, however, this is more likely a rehydration trend and not reflective of degassing based on the following knowledge of H_2O degassing in rhyolitic system. While dense obsidian pyroclasts have been utilized in previous studies to demonstrate degassing trends and behavior in magma (Castro et al., 2014; Giachetti et al., 2020), pumice clasts are highly degassed upon eruption and therefore have very low H_2O remnant glass prior to rehydration. Raft and tube pumice porosities up to 90 and 65% respectively (Fig. 7), and the very low OH contents of Havre pumices (Table 1 Mitchell et al., 2018) indicate that the H_2O in these glasses is mostly excess (H_2O_m) and not due to a degassing pathway. OH values from dome talus are closer to the expected equilibrium value of eruptive lava depth, and thus the expected pre-rehydration H_2O speciation at magmatic temperatures (Zhang et al., 2007; Mitchell et al., 2018). Furthermore, H_2O_t values up to 2 wt.% would require clast quenching up to 40 MPa, assuming solubility at eruptive temperature, which is unrealistic given the eruptive vent pressure of $\sim 9\text{ MPa}$, and the unlikelihood of disequilibrium degassing as determined from magma ascent modeling by Manga et al. (2018a and



2018b). Instead, the raft and tube pumice samples were rehydrated by a δD -enriched source more consistent with the seawater-rehydrated older silicic samples (Fig. 5).

5.2. Rehydration by magmatic vapor

Even though the exsolving vapor phase is initially heavier in δD than the melt, as magma ascends, the vapor becomes increasingly depleted in δD , particularly at low pressure (Fig. 7). The vapor modeling demonstrates that newly-exsolved coexisting vapor in Havre magma can reach δD values lower than -60‰ at pressures < 9 MPa (equivalent to erupted vent depth of 900 m; Carey et al., 2018). More specifically, vapor with δD in the desired rehydration range of -70 to -90‰ would be exsolving from the melt at pressures of 2–8 MPa, i.e., above the eruptive vent during clast ascent. Mitchell et al. (2018) determined that giant pumice blocks and ALB lapilli must have continued to degas during ascent, due to their very low OH contents reflective of extremely shallow quenching pressures (< 5 MPa) (Table 1). Low OH contents imply that significant degassing was still occurring at shallow pressures above the vent, and therefore there would have been large volumes of newly-degassed vapor available to rehydrate cooling melt/glass within large clasts interiors. However, for rehydration by magmatic vapor to occur, there must have been sufficient time and temperature for molecular diffusion to occur prior to full clast quenching. The following section utilizes the $\delta^{18}O$ data to determine likely temperatures and timescales for rehydration within Havre samples and the older submarine samples as a reliable endmember for rehydration by cold seawater over hundreds to thousands of years.

6. TEMPERATURES AND TIMESCALES OF REHYDRATION

6.1. Estimating rehydration temperatures using oxygen isotope fractionation

Oxygen isotope analysis identified a large range in $\Delta^{18}\text{O}_{\text{bulk-wig}}$ fractionation values of Havre pumice from +2.4 to +14.2‰, and a higher, narrower range in older silicic samples (+12.8 to +17.6‰) averaging around +17‰ (Fig. 6e, f). Recent hydration experiments, and pumices from hydrothermal features in cooling ignimbrites, have shown how $\Delta^{18}\text{O}_{\text{bulk-wig}}$ fractionation increases with decreasing temperature from 375 to 100 °C (Bindeman and Lowenstern, 2016; Hudak and Bindeman, 2018; Seligman and Bindeman, 2019; Hudak and Bindeman, 2020). We use our $\Delta^{18}\text{O}_{\text{bulk-wig}}$ value of +17.6‰ from the old silicic lavas (grey crosses tightly clustered in Fig. 5) to anchor this temperature-fractionation relationship at ambient seawater temperature (~4–20 °C). These values are chosen as the anchor given their apparent lack of rehydration, obsidian nature from the lava exterior (more instant quenching), relatively young age, and tightly constrained H_2O_t values close to expected eruptive H_2O solubility (Fig. 5; Embley and Rubin, 2018). From this, and previous experimental work, we determine a logarithmic relationship ($1000\ln(\alpha_{\text{bulk-wig}}) = A \cdot \ln[T^{-2}] + B$), where A and B are constants and $1000\ln(\alpha_{\text{bulk-wig}})$ is $\sim \Delta^{18}\text{O}_{\text{bulk-wig}}$, to estimate rehydration temperatures (T_{reh}) within our silicic seafloor samples, assuming equilibrium fractionation between vapor and silicate (Fig. 8a). We note that equilibrium fractionation may not apply at the highest magmatic temperatures

when diffusion may occur on timescales of seconds. Varying the low temperature anchor of $\Delta^{18}\text{O}_{\text{bulk-wig}}$ value = +16 to +17.6‰ makes negligible difference to T_{reh} calculations around magmatic temperatures (Fig. 8a). We also note that these calculated temperatures provide an estimate and will likely vary for between and within individual clasts (particularly for larger clasts, where rehydration temperature will vary throughout the clast diameter, or clasts in voluminous hot deposits).

Calculated T_{reh} values for the recent Havre samples range from ~108 to 852 °C (Fig. 8b, c). The highest T_{reh} value determined (1204 °C for an ALB clast) is unrealistic, given eruption temperature estimates of 850–900 °C (Manga et al., 2018a; Knafelc et al., 2020); this value is attributed to a rapid $\Delta^{18}\text{O}_{\text{bulk-wig}}$ disequilibrium process (discussed in supplement 6). It is possible the temperature model may not be sufficient for interpretation at eruptive temperatures due to the possibility of rapid disequilibrium isotopic exchange. Samples with the lowest $\Delta^{18}\text{O}_{\text{bulk-wig}}$ fractionation exhibit the highest estimated rehydration temperatures (Table 2). Giant pumice show T_{reh} values from ~321 to 679 °C with an ALB lapilli sample at ~852 °C. Although, these values can sit within a wide range given the complex eruptive conditions. For the δD -enriched units, raft pumice T_{reh} is estimated around ~108 °C and dense tube pumice at ~141 °C. We can also estimate T_{reh} values for Dome samples, which exhibited $\delta^{18}\text{O}_{\text{wig}}$ values of –5.4 and –5.7‰, if we assume Havre $\delta^{18}\text{O}_{\text{bulk}}$ remains consistent across all samples (+5.7 to +6.2‰) as seen in Fig. 6c, d. Using the same $T^{-2}-1000\ln(\alpha_{\text{bulk-wig}})$ relationship, we obtain Dome T_{reh} values of ~220–270 °C; these values are consistent with textural and previous geochemical interpretations (Mitchell et al., 2018). T_{reh} values of giant pumice (~321–679 °C) conform well with estimates of glass transition temperatures (T_g) from Mitchell et al. (2018) and lower cooling rates within subaqueous giant pumice blocks from modeling by Fauria and Manga (2018). These T_{reh} values support that rehydration in giant pumice and ALB lapilli (that may originate from GP fragments; Mitchell et al., 2021) was occurring during clast cooling and ascent through the water column. The lower T_{reh} values for raft and tube pumice (100 to 140 °C) would indicate a faster cooling process and lower temperature setting for rehydration, as reflected in the different nature of the rehydration trend (Figs. 5, 7). This could possibly due to smaller clast size, lack of trapped exsolving volatiles, or residence time within the hotter portions of the eruptive column.

By using a $\Delta^{18}\text{O}_{\text{bulk-wig}}$ = +17.6‰ as an endmember, the other older silicic submarine samples exhibit estimated T_{reh} values closer to that of ambient seawater (mostly 0–20 °C) (Fig. 8b). Divergence in the $T^{-2}-1000\ln(\alpha_{\text{bulk-wig}})$ relationship at $T < 100$ °C may account for some uncertainty in lower T_{reh} values (Fig. 8a). Nevertheless, these low rehydration temperatures – as well as the highly enriched δD and $\delta^{18}\text{O}_{\text{wig}}$ values and matrix glass H_2O_t contents up to 6 wt. % (Figs. 5, 6) – strongly support the interpretation of cold rehydration by surrounding seawater for the older samples (Fig. 8b, c). More certainty on the best temperature estimates would be served by obtaining larger datasets using this method and by verifying it within more experimental

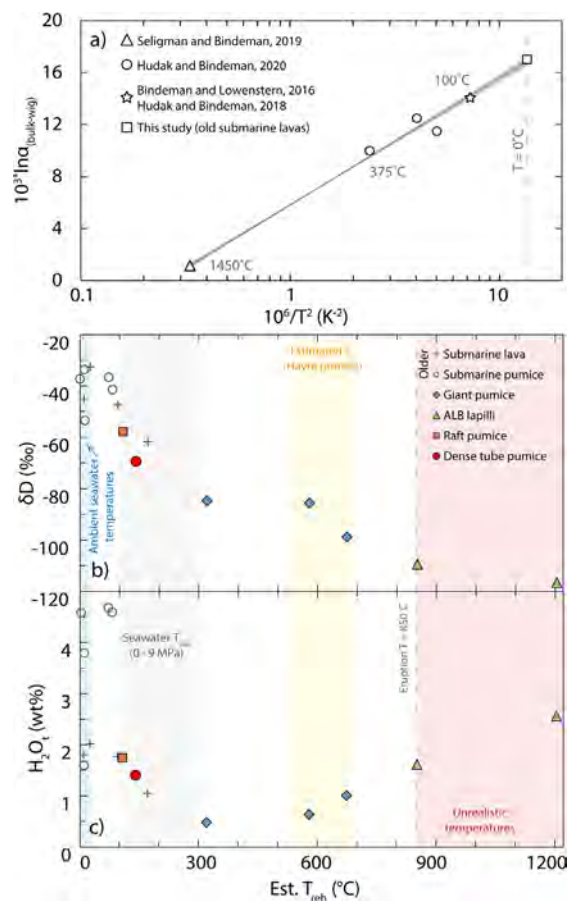


Fig. 8. a) Relationship between bulk-wig oxygen isotope fractionation ($1000\ln\alpha = \Delta^{18}\text{O}$) with temperature of rehydration (expressed as $10^6/T^2$) from experimental studies (Seligman and Bindeman, 2019; Hudak and Bindeman, 2020) and well-constrained natural samples (Bindeman and Lowenstern, 2016; Hudak and Bindeman, 2018; this study). The grey range defines using $1000\ln\alpha(T=0^\circ\text{C}) = +16 - +17.6\text{‰}$ and $1000\ln\alpha(T=0^\circ\text{C}) = +17\text{‰}$ for the black line; b) and c) estimated rehydration temperature (T_{reh}) of analyzed samples using $1000\ln\alpha(T=0^\circ\text{C}) = +17.6\text{‰}$ vs. δD and H_2O_t . Important temperature ranges are shown: seawater temperatures (0–20 °C); seawater evaporation temperatures at 0.1–9.2 MPa ($T_{\text{vap}} = 100\text{--}307$ °C); estimated glass transition temperature range ($T_g = 550\text{--}700$ °C) for Havre 2012 pumice (Mitchell et al., 2018); and calculated eruption temperature (850 °C) for Havre magma (Manga et al., 2018a).

literature and other analytical techniques (e.g., differential scanning calorimetry). Our hope is that this dataset shows the potential value of the technique by temperature range estimates consistent with previously known analytical data and observations.

6.2. Estimated timescales of rehydration

We then used the estimates of rehydration temperature (T_{reh}) from $\Delta^{18}\text{O}_{\text{bulk-wig}}$ fractionation (Fig. 8) and the temperature-diffusivity relationship from Zhang and Behrens (2000) (Eq. (3)) to determine the estimated timescales of rehydration (t_{reh}) using the diffusivity-length and timescale relationship (Eq. (4)).

Table 2

Estimates of rehydration temperature (T_{reh}) and timescale (t_{reh}) using oxygen isotope fractionation ($\Delta^{18}\text{O}_{\text{blk-wig}}$) and diffusivity ($D_{\text{H}_2\text{O}_t}$) calculations, and all corresponding TC/EA δD and H_2O_t measurements. Timescale in seconds and (other units) is calculated for a diffusion half-length (L) of 1–10 μm . *denotes a likely disequilibrium sample from a > eruption temperature estimate.

Sample	$\delta^{18}\text{O}_{\text{blk}}$ (‰)	$\delta^{18}\text{O}_{\text{wig}}$ (‰)	$\Delta^{18}\text{O}_{\text{blk-wig}}$ (‰)	δD (‰)	H_2O_t (wt.%)	Est. T_{reh} (°C)	$\log [D_{\text{H}_2\text{O}_t}]$ ($\text{cm}^2 \text{s}^{-1}$)	Est. t_{reh} (s)	Est. t_{reh} (app.)
Giant pumice	6.11	-4.2	10.31	-84.6	0.48	321	-11.7	$4.5 \times 10^{3-5}$	1–124 h
	6.13	-0.11	6.24	-98.7	1.01	674	-8.7	$5.5 \times 10^{0-2}$	0.08–9 min
	5.82	-1.34	7.16	-85.4	0.64	579	-9.3	$1.9 \times 10^{1-3}$	0.3–32 min
Seafloor lapilli (ALB)	5.76	3.39	2.37	-116.6	2.56	*1204	-7.0	n/a	n/a
	6.12	1.38	4.74	-109.3	1.62	852	-8.0	$9.2 \times 10^{1-1}$	0.9–92 s
Tube pumice	6.19	-7.25	13.44	-69.4	1.41	141	-15.0	$1.1 \times 10^{7-9}$	0.3–34 yr
Raft pumice	5.77	-8.39	14.16	-57.7	1.75	108	-16.0	$9.9 \times 10^{7-9}$	3–312 yr
Submarine lavas (pre-2012)	5.91	-8.54	14.45	-47.4	1.76	96	-16.4	$2.5 \times 10^{8-10}$	8–806 yr
	6.06	-10.7	16.76	-45.0	1.81	10	-20.2	$1.7 \times 10^{12-14}$	53–5280 kyr
	5.95	-6.88	12.83	-61.7	1.05	171	-14.3	$1.9 \times 10^{6-8}$	0.1–5.9 yr
Submarine pumice (pre-2012)	6.52	-9.76	16.28	-32.5	2.02	26	-19.3	$2.2 \times 10^{11-13}$	7–699 kyr
	9.74	-7.8	17.54	-37.2	4.58	0	-20.8	$6.6 \times 10^{12-14}$	0.2–20.8 Myr
	9.47	-5.55	15.02	-36.6	4.68	73	-17.3	$1.8 \times 10^{9-11}$	0.06–5.7 kyr
	8.18	-6.6	14.78	-41.4	4.59	82	-16.9	$7.8 \times 10^{8-10}$	0.02–2.5 kyr
	7.79	-8.9	16.69	-53.4	3.80	12	-20.1	$1.2 \times 10^{12-14}$	39–3904 kyr
	6.69	-10.04	16.73	-33.5	1.60	11	-20.2	$1.5 \times 10^{12-14}$	46–4638 kyr

$$D_{\text{H}_2\text{O}_t} = \frac{C_x}{C_0} \exp \left(10.49 - \frac{10661}{T_{reh}} - \frac{1.772P}{T_{reh}} \right) \quad (3)$$

$$L_{diff} = \sqrt{D_{\text{H}_2\text{O}_t} * t_{reh}} \quad (4)$$

where $D_{\text{H}_2\text{O}_t}$ is the diffusivity coefficient of H_2O_t in rhyolitic glass ($\mu\text{m}^2 \text{s}^{-1}$), C_x is the initial concentration of H_2O_t in glass (used 0.4 wt.% based on convergence of data points in Fig. 5), C_0 is 1.0 wt.% (as per Zhang and Behrens (2000)), P is a pressure of 9 MPa (eruptive vent depth – assumed initiation of rehydration processes), T_{reh} is the estimated rehydration temperature (K) and t_{reh} is the timescale of H_2O diffusion (s). As reconstruction of magmatic H_2O_t pre-rehydration is challenging (Mitchell et al., 2018) and $D_{\text{H}_2\text{O}_t}$ varies over many orders of magnitude as a function of $\exp(T^{-1})$, any natural variations in C_x/C_0 per individual sample will have little effect on the final $D_{\text{H}_2\text{O}_t}$ calculation, so we keep C_x/C_0 constant.

We estimated the timescale of rehydration over a diffusion half-length (L_{diff} , concentration mid-point of a diffusion profile; McIntosh et al., 2014) of 1–10 μm which is the approximate range of vesicle wall thickness and range of observed rehydration rims within Havre pumice and lava (Figs. 3, 4). Zhang and Behrens (2000) only determined this relationship from 400 to 1000 °C, however, lower $D_{\text{H}_2\text{O}_t}$ values were constrained by Hudak and Bindeman (2020) down to 175 °C (Fig. 9, Table 2). As with temperature estimates, these calculations serve to determine an approximate timescale “order” as opposed to absolute values, given the compounded uncertainty from temperature estimates, and individual sample variations in P , L_{diff} and C_x/C_0 within calculation of $D_{\text{H}_2\text{O}_t}$ (Eq. (1), 2). Nevertheless, determining orders of magnitude in timescale is valuable for interpreting the physical sources, processes, and mechanisms of rehydration.

Estimates of rehydration timescale (t_{reh}) for giant pumice range from minutes to hours over ~670–320 °C consistent with previous modeling for clast ascent and cooling rates of a few minutes for larger clasts (Fauria and Manga, 2018), and the ALB lapilli at ~852 °C is estimated to have rehydrated over 0.9–92 s (Fig. 9Table 2). These values would have depended on clast size, and clast residence time within a heated submarine plume, i.e., on timescales of saturation and clast cooling (Mitchell et al., 2018). The lower rehydration temperatures and δD -enriched trend (Figs. 5, 8) of raft pumice (~100 °C) and dense tube pumice (~150 °C) result in rehydration timescales on the order of months to years, due to the limit of 3 years residence time of these samples, the lower end is the more likely, indicating smaller diffusion lengthscales (L_{diff}) of a few microns. The Havre Dome T_{reh} estimates (~220–270 °C) would result in rehydration timescales on the order of hours to days after the eruption, consistent with slower submarine dome cooling. The older submarine glasses, rehydrated by seawater, exhibit diffusion timescales on the order of hundreds to thousands of years (Fig. 9), as expected for cold, secondary hydration, and consistent with their isotopic signatures up to $\delta\text{D} \sim 30\text{‰}$ (Seligman et al., 2016). This may be with the exception of very little rehydration in the Lau Basin dacite lava flows, which display tightly constrained δD - H_2O data and estimated rehydration time-

scales on the order of 1–100 years (Fig. 5). These lavas were interpreted to be < 100 years old from *in-situ* observations by Embley and Rubin (2018).

6.2.1. Comparing timescale estimates with modeling, experiments, and observations

Our data suggests that rehydration in giant pumice occurred around the glass transition during late-stage degassing on a timescale of minutes to tens of minutes during clast ascent. These timescales were confirmed in experimental work and numerical modeling by Fauria and Manga (2018) where they showed that buoyant pumice clasts (0.5–2 m in diameter) may take 3–10 min to ascend 900 m in the water column. Their pyroclast cooling model (Fauria and Manga, 2018) also confirmed that magmatic clasts submerged in water underwent a multi-stage cooling process; larger clasts with initial magmatic temperatures had the potential to remain at internal temperatures of > 200 °C for up to a couple of minutes after initial submergence. Mitchell et al. (2018) further validated this proposed slower cooling process by identifying the low OH contents, and thus shallow quenching, of Havre pumice clasts (Table 1).

H₂O diffusion profiles from vesicle rims in Havre dome glasses fit a temperature of 400 °C at diffusion timescales on the order of a few minutes (Fig. 4); a shift down to 300 °C may increase this up to hours (Mitchell et al., 2018). Diffusivity values (Log D_{H_2O} ; cm² s⁻¹), obtained from the profiles from Mitchell et al. (2018) are –11.7 to –12.9 for modelled temperatures of 400–500 °C. These values are comparable to values from Zhang and Behrens (2000) for hydration experiments of relatively anhydrous (<0.8 wt.% H₂O) glass at 300–500 °C (Log D_{H_2O} = –11

to –12), and significantly less than more hydrous hydration experiments (glass containing 0.5–3 wt.% H₂O) from Hudak and Bindeman (2020) at similar temperatures (Log D_{H_2O} = –9 and –11 at 375 °C and 275 °C respectively). These D_{H_2O} estimates clarify that rehydration likely occurred post-degassing in relatively “dry” dome glass and at temperatures > 400 °C for the depleted δD trend where initial water contents were estimated at ~0.6–1.0 wt.% H₂O_t (Fig. 5; Mitchell et al., 2018).

For the dense Lava-G-lapilli tube pumice, the T_{reh} values conform well to the higher seawater evaporation temperature (T_{vap}) at increased hydrostatic pressure (Fig. 8c). At 0.1 MPa (sea level) T_{vap} ~100 °C, and at 9.2 MPa (900 m deep – equivalent to Havre vent depth; Mitchell et al., 2018) T_{vap} ~307 °C (Driesner and Heinrich, 2007). This, along with δD -enrichments that correlate with heated seawater isotopic signatures, would suggest that the dense tube pumice was rehydrated by geothermally/hydrothermally heated seawater in the days after eruption. The tube pumice was collected from a deposit on the side of the east-west oriented fissure that fed the eruption of an adjacent lava (Murch et al., 2020), and it is highly likely these pumices in contact with superheated seawater (>100 °C) sourced from around this fissure after their deposition. We note there are many unknowns about the timescale of the lava and associated clast production of this deposit, so complete interpretations are challenging. Ikegami et al. (2018) and Murch et al. (2020) explored Lava G and the associated ash deposits in more detail.

For the raft pumice T_{reh} estimate of ~100 °C, it is likely that this pumice was rehydrated by heated (below T_{vap}) δD -enriched seawater within the submarine eruption plume. Rehydration temperatures < 100 °C could have occurred if pumice remained proximal to the powerful submarine (and subaerial) plume existent during the raft phase (~2 days) of the Havre eruption (Carey et al., 2014; Mitchell et al., 2018; Cahalan and Dufek, 2021). Satellite and particle dispersion modeling show large portions of the Havre pumice raft may have been close above the eruptive vent at the sea surface for several days (Jutzeler et al., 2014). Thermal signatures (of 35 °C) identified in MODIS data (at 1 km spatial resolution) at the sea surface directly above the vent identified also suggest that significant heat was present within and surrounding the raft pumice (Carey et al., 2014; Jutzeler et al., 2014). Larger raft blocks above the sea surface may also have taken more time to cool. Manga et al. (2018b) further showed that the vent-centered dome (Dome OP) remained hot and grew for a long time after the raft phase was erupted. The high H₂O_m/OH values of dome talus could also support the hot flux of volatiles through the pore space over months following the eruption (Mitchell et al., 2018). The elevated temperatures of seawater and residence time of pumice proximal to the eruption plume may have been sufficient to produce the δD signatures identified in Fig. 7. As seawater is heated, the liquid-vapor fractionation of D/H increases (Horita and Wesolowski, 1994), and thus, we do not expect the δD values within raft pumice (up to –40‰) to be as enriched as the older silicic pumice (up to –30‰) domi-

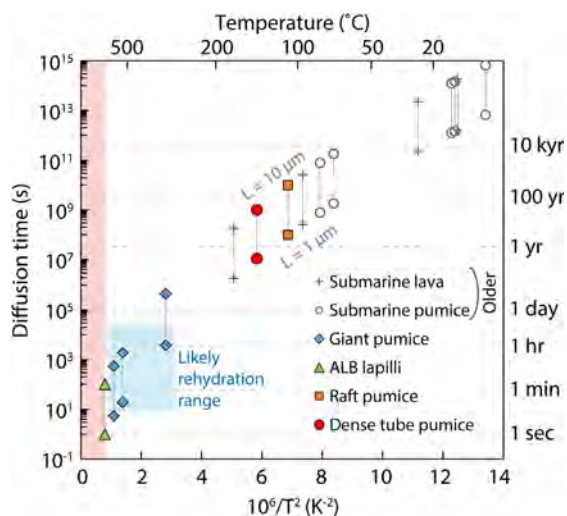


Fig. 9. Estimated temperatures (T_{reh}) and timescales (t_{reh}) of rehydration. Upper and lower values denote H₂O diffusion timescales calculated using a diffusion half-length of 1 and 10 μm respectively. Time scales calculated using the D_{H_2O} - T relationship from Zhang and Behrens (2000) and an initial H₂O_t concentration of 0.5 wt.%. The blue box denotes the estimated temperature range (300–700 °C) and timescale range (minutes to hours) from previous studies and isotopic evidence.

nantly rehydrated by cold seawater over long timescales (Figs. 5, 9).

7. DISCUSSION

7.1. Unlikely sources for rehydration in δD -depleted trends

Before arriving at coexisting magmatic vapor as the δD -depleted trend rehydration source for the giant pumices and ALB lapilli, we examined all other possible H_2O sources that could have produced the observed signatures:

- Cold liquid seawater was ruled out as the trend does not conform to the δD isotopic signatures required, as observed in older silicic deposits (Figs. 5, 6), and temperatures are too low and diffusion timescales too high.
- Meteoric H_2O sources are also ruled out as these samples never left the ocean; in any case, seawater should dominate any “ambient” external isotopic signature (Fig. 2), and, again, temperatures are insufficient.
- Supercritical fluids present in the water column are excluded as seawater and pure H_2O only become supercritical at 29.8 MPa and 407 °C (Bischoff and Rosenbauer, 1984), and 22.1 MPa and 374 °C respectively (Driesner and Heinrich, 2007), far above 9 MPa.
- Seawater vapor is an unlikely endmember, as the vapor-liquid fractionation required for seawater vapor to reach δD values of at least -80‰ (with a low temperature $\Delta D_{H_2O-glass}$ fractionation of $+33\text{‰}$ to achieve a glass δD value of at least -115‰) would require vapor temperatures of < 25 °C (Horita and Wesolowski, 1994). This is too cold for H_2O to exist as a vapor at atmospheric or higher pressure (0.1–9 MPa).
- Hydrothermal fluids are also ruled out, as isotope studies of hydrothermal fluids from black smokers in seawater show that these δD -depletions are insufficient for our mixing requirement ($\delta D = -70\text{‰}$ to -90‰ , and $\delta^{18}O$ close to rock values; $> +5\text{‰}$) (Figs. 2, 6) (Bowers, 1989; Konn et al., 2015; Zakharov et al., 2020).

Another proposed mechanism to explain the coupled δD -depleted and $\delta^{18}O_{wig}$ -enriched trend for Havre pumice is rehydration by thermal diffusion; as it is known that isotope diffusion favors light isotopes at the hotter end of a thermal gradient (Kyser et al., 1998). Experiments by Bindeman et al. (2013) reported isotope profiles in water-saturated high-silica experiments held between 350 and 930 °C where the warmer end experienced δD depletions down to -170‰ . However, these experiments did not show coupled $\delta^{18}O$ -enrichments and δD -depletion; the hydrated “cold” end of the experiment showed both $\delta^{18}O$ and δD enrichment, and the experimental thermal gradient was persistent for many days over a 15 mm profile (Bindeman et al., 2013). These isotopic signatures, lengths and time-scales are inconsistent with our samples and data.

7.2. Reconciling TC/EA versus FTIR H_2O differences

Differences between FTIR and TC/EA H_2O_t measurements show how data from spot vs. bulk techniques can

be affected by sample heterogeneity, making them powerful mutually complementary tools (Fig. 10; Table 1). Previous studies found near 1:1 correlation of FTIR- and TC/EA-acquired H_2O_t in homogeneous, vesicle-depleted experimental glasses or slowly quenched glasses (Dixon et al., 2017; Martin et al., 2017). These samples had little, or no, crystallization, and there was no spatial variation in H_2O_t across the sample, unlike incompletely hydrated (or degassed) natural samples with spatial H_2O speciation heterogeneities (e.g. Giachetti et al., 2020). Differences between analytical techniques measuring H_2O can be explained by assessing sample porosity, crystal content, and the measurement volume (Devine et al., 1995; von Aulock et al., 2014; Mitchell et al., 2018). However, crystal content in the Havre magma is not considered a major control due to a limited range of vesicularity across the pumices and dome talus of 5–13% (Carey et al., 2018; Knafelc et al., 2020). Fig. 10a shows that TC/EA identified higher H_2O_t contents than FTIR measurements within almost all Havre clasts; this deviation was most apparent in the very vesicular ALB clasts with the greatest δD depletion (Fig. 10b,d). The reverse for the dome samples may reflect where FTIR spots were taken within the thick rehydration rims (Fig. 4) where FTIR analysis of vesicle edges was possible. However, low vesicularity of these samples would still mean that large volumes of glass remained unrehydrated (as seen in the FTIR results – Fig. 5).

For transmission FTIR analyses, the data correspond to an analytical volume defined by the area of the spot and the thickness of the glass. Low porosity samples can provide large areas of glass for spot or mapping analysis. For high porosity samples, the bubble walls are too thin for reliable FTIR spot analysis (< 5 μm thick); FTIR spectra from curved, tapering vesicle edges in shards or wafers can be highly distorted at low wavenumber (Wysoczanski and Tani, 2006; McIntosh et al., 2014; Mitchell et al., 2018). Accordingly, FTIR analyses are preferable within regions further away from vesicle edges, and thus analyses may underestimate the extent of rehydration. Nevertheless, obtaining H_2O speciation data from FTIR spectra is extremely useful for identifying the presence of excess molecular H_2O (H_2O_m). Mitchell et al. (2018) used the speciation ratio of H_2O_m/OH as a potential proxy for the extent of rehydration in glass (Table 1). When compared against TC/EA data, we can see that this holds for the ALB-lapilli and giant pumice data (Fig. 10e, f); this was also observed in Owen et al. (2012). Further examination of H_2O_m/OH data can be found in supplement 8 and full speciation plots vs. magmatic temperature are found in Mitchell et al. (2018). The extent of rehydration will also be governed by the surface area of connected porosity available for external H_2O diffusion into melt/glass; Mitchell et al. (2021) showed how GP and ALB clasts had almost completely connected porosity, whereas raft pumice had large volumes of isolated porosity, so the extent of rehydration would be considered less.

Conversely, TC/EA is a bulk method that captures H_2O contents in all the thinnest bubble walls. High porosity samples (with high surface area in connected porosity) analyzed by TC/EA may therefore show much higher H_2O_t val-

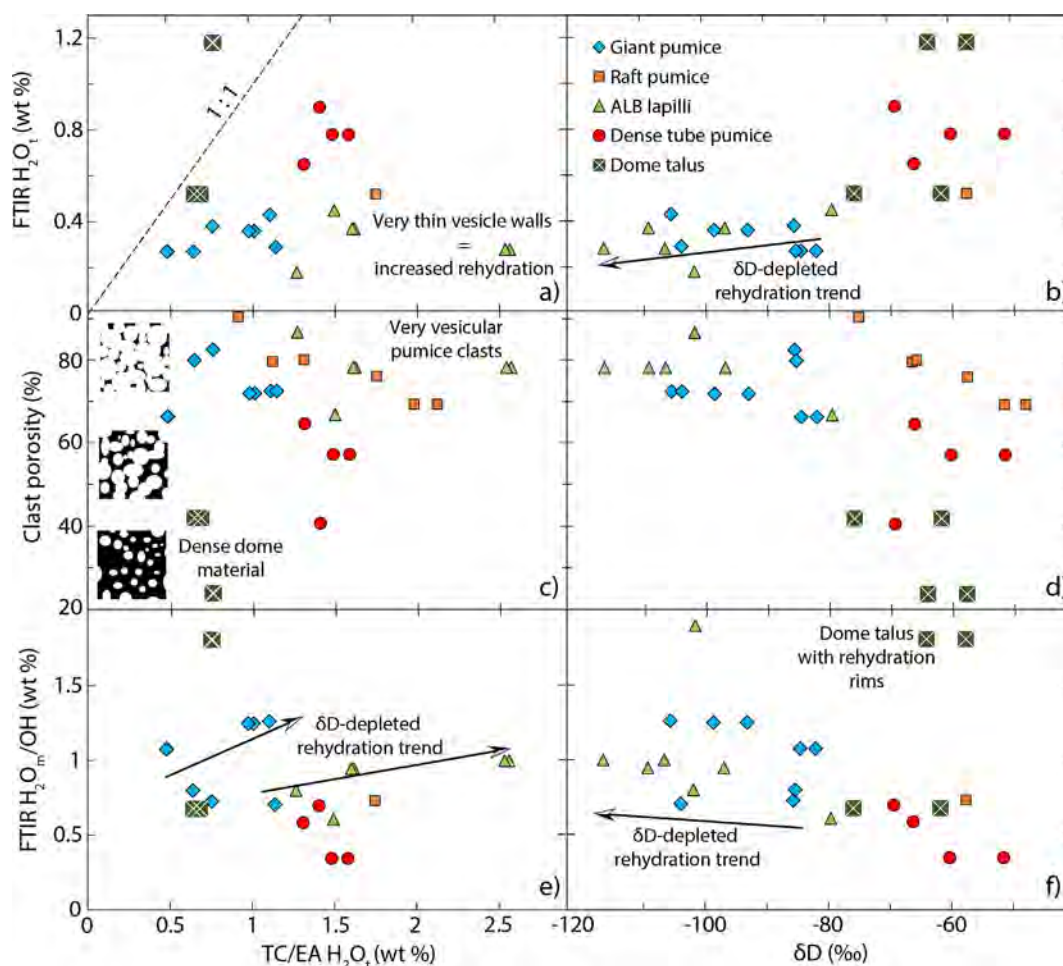


Fig. 10. Relationships between clast texture (porosity), FTIR water speciation (H_2O_t , OH, H_2O_m) from Mitchell et al. (2018), and TC/EA H_2O_t and δD from this study for Havre 2012 samples. The dotted line in (a) denotes a 1:1 relationship between FTIR and TC/EA H_2O_t measurements. Schematic porosity binary images (vesicles in white, glass in black) illustrate schematic variation in porosity through samples. The δD -depleted trend for ALB and GP is shown in b), e) and f). Dome samples with observed rehydration rims from Fig. 3 are identified in f).

ues than measured by FTIR (Martin et al., 2017; Hudak and Bindeman, 2020; Hudak et al., 2021). TC/EA will also capture any δD and H_2O enrichments or depletions present in microlite crystal phases too small to remove prior to analysis. A significant mass of hydrous microlites and microphenocrysts in TC/EA samples could result in apparent overestimates of H_2O remaining in the glass (Martin et al., 2017); anhydrous crystals would also enrich H_2O in the glass. This problem can be resolved by prior assessment of crystal content through micro-analysis. BSE images of Havre pumice (and prior studies – Carey et al., 2018; Mitchell et al., 2019) show that the glasses are mostly aphyric (Fig. 3), and only the dense dome talus samples have numerous, but very small, anhydrous oxide and pyroxene microlites (Fig. 3d, 4). We therefore assume the H_2O (and δD and $\delta^{18}\text{O}_{\text{wig}}$) contribution by microlite crystals to be negligible in our analyses. However, we emphasize that hydrous crystal content needs to be considered during TC/EA sample preparation and analysis.

Increases in clast porosity correlate with δD -depletion and H_2O_t increases in pumiceous samples: giant pumice and seafloor ALB lapilli (Fig. 10c, d). As vesicle walls become thinner, i.e., bubble size increases and connected porosity increases, the diffusion of H_2O into glass dominates a larger “volume” of the sample and thus the effects of rehydration become more significant by mass fraction. The reverse trend in raft pumice may reflect the addition of more isolated porosity (as seen in Mitchell et al., 2021). Table 1 shows that δD depletion in Havre samples correlates well with lower OH contents and thus, shallower estimated quenching pressure ranges (Mitchell et al., 2018), reaffirming that rehydration with δD -depletion occurs somewhere above the vent. We highlighted here that we required knowledge of vesicle textures, spatially obtained H_2O_t and speciation, and bulk isotope measurements to fully assess our analytical measurements of rehydration in glasses. Ideally, high-resolution spatial mapping of H_2O speciation, and δD and $\delta^{18}\text{O}_{\text{wig}}$ in sample transects through

coupled FTIR and NanoSIMS analysis would provide the most comprehensive assessment of these processes. Detailed measurements of connected porosity related to rehydration measurements will also be very informative for assessing the extent of rehydration in samples. Applying other techniques such as differential scanning calorimetry geospeedometry could also be used to explore cooling rates and glass transition temperatures of rehydrated samples.

7.3. Implications for interpreting water contents in submarine volcanic glasses

Now that the process and sources of more rapid, sub-magmatic-temperature rehydration are clearly recognized and defined in their composition (but less so in timescales), not considering the impacts could lead researchers to over-estimate juvenile water content and mis-interpret water isotopic composition in glasses. Rehydration by magmatic vapor during the early syn- and post-eruption stages in the deep-sea environment may later be masked by cold seawater rehydration signatures over long periods of time. This study identifies unique processes occurring during and immediately after a submarine eruption, which may be applicable to many other fresh, subaqueous eruptive deposits and the likely mechanisms that are responsible for, initially, very diverse δD and $\delta^{18}O$ values.

On a wider scale, glass rehydration can occur across all environmental settings where there is water and/or vapor present, and over timescales of minutes to thousands of years (Giachetti and Gonnermann, 2013; Giachetti et al., 2015). Research to date has identified rehydration in: sub-aerial and sublacustrine deposits by meteoric water (Denton et al., 2009; Giachetti and Gonnermann, 2013; Bindeman and Lowenstern, 2016; Seligman et al., 2016) and/or hydrothermal vapor (Randolph-Flagg et al., 2017; Hudak and Bindeman, 2018); and submarine deposits by seawater and magmatic fluids (this study; Martin et al., 2017; Mitchell et al., 2018). The process of rehydration is also not exclusive to volcanic rocks. Studies across mineralogy, petrology, and archaeology are reliant on accurate interpretation of water and H content in glass and crystals. H_2O molecules and H isotopes have the ability to diffuse through minerals and silicate structures given sufficient time, temperature, and source of external water (Sharp, 1990; Zheng, 1993; Hauri, 2002; Underwood et al., 2013; Martin et al., 2017; Roskosz et al., 2018; Moine et al., 2020).

A particularly important consideration is how rehydration may affect glass within crystal-hosted melt inclusions; H_2O measurements from melt inclusions are imperative for our understanding of volatile cycling, particularly along volcanic arcs (Hauri et al., 2002; Wallace, 2005; Plank et al., 2013; Dixon et al., 2017). Many of the world's volcanic arcs and their edifices are mostly submarine (Izu-Bonin, Kermadec, Marianas). By recognizing the isotopic signatures of seawater rehydration and silicate alteration in glass, future studies of melt inclusions from old submarine arc deposits (of which there are currently very few) will be better informed to interpret volatile budgets and cycling along subduction zones.

8. SUMMARY

Our study presents the first detailed suite of H and O isotopic data, coupled with H_2O content and speciation, for submarine silicic volcanic glasses with a range of clasts textures, eruptive depths and styles, and seconds to millennial timescales. Analysis of older submarine glasses provides a clear endmember isotopic composition (δD and $\delta^{18}O$) for rehydration of glasses by cold seawater over hundreds to thousands of years. The model presented requires more detailed scrutiny for individual deposits and eruptions, however, these datasets over a range of deposits highlight the potential use of the model for determining temperatures and timescales of rehydration and cooling process in subaqueous volcanoclastic material.

This knowledge can be applied to subsequent studies of glasses sampled from the seafloor to better understand volatile budgets and eruption dynamics along volcanic arcs. We also reiterate that crystals and pore space textures (such as vesicles, fractures, and voids) are a key control on the extent and distribution of rehydration within silicate glass. Geochemical analytical studies of rehydration must carefully consider the microtextures of samples analyzed and the technique(s) used to assess rehydration.

By combining the δD - H_2O degassing/vapor modeling, $\Delta^{18}O$ -geothermometer, timescale estimates, and work from previous studies, we can explain the obtained isotopic data for all our analyzed submarine volcanic glasses:

1. Giant pumice blocks (Havre 2012) were rehydrated by newly-exsolving magmatic vapor at temperatures of ~ 300 – 670 °C on the order of minutes during clast ascent in the water column; ALB lapilli may have been rehydrated quicker at higher temperature.
2. Raft pumice clasts (Havre 2012) were rehydrated by heated seawater in the days following the eruption if clasts retained heat and remained proximal to the waters above the eruptive vent before oceanic dispersal.
3. Dense tube pumice (Havre 2012) deposited proximal to a fissure were rehydrated by superheated seawater heated by a dyke at depth in the days to weeks following lava effusion.
4. Dome talus fragments (Havre 2012) were most likely rehydrated by δD -enriched outgassing magmatic vapors through the porous network around temperatures of 200 – 300 °C in the hours to days following dome effusion.
5. Much older submarine silicic pumices and lavas (Izu-Bonin arc and Lau Basin) can exhibit clear signatures of ambient seawater rehydration (δD -enrichments up to -30‰ , and up to 6 wt.% H_2O) no matter the eruptive style, depth, age, or texture.

The multiple mechanisms and sources of glass rehydration identified within this study demonstrate the range of temperature and timescales that H_2O diffusion occurs over, and how this can reflect cooling rates, availability of external water, or eruptive dynamics, i.e., residence time of clasts within a submarine plume and the pressure-temperature-phase conditions of this environment. In particular, our data provide natural confirmation of rehydration processes

occurring at temperature below the glass transition (100–400 °C), for which recent experimental studies has shown should occur (Hudak and Bindeman, 2020). The estimates of temperature and timescales from isotopic compositions also validate modeled timescales of clast ascent and cooling, and hydrothermal temperatures hypothesized through previous speciation analysis. Rehydration is a process being more recognized across a range of volcanic environments, and that requires careful consideration when interpreting volcanic processes based on H₂O measurements.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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AUTHOR CONTRIBUTIONS

SJM and MRH conducted the analysis and subsequent data processing and interpretation. RJC and IMM provided samples from the Izu Arc and KHR provided samples from the Lau Basin. All authors provided edits, comments, and feedback to several manuscript iterations, including revisions and final approval of the submitted version.

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gca.2022.03.022>.

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