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Variability in Volcanic Glass Preparation Methods: Qualitative Analysis
of Apparent Porosity between Pumiceous and Non-Pumiceous Glass
Shards

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and

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Abstract

Stable isotopes from ancient water have been used extensively to reconstruct paleoclimates and paleoenvironments (e.g. Bershaw et al., 2010, Cyr et al., 2005, Fan et al., 2017, Quade et al., 2011, Rowley and Garzzone, 2007). Volcanic glass found in ash tuffs have been shown to preserve hydrogen (H) isotopes from meteoric water at the time of deposition (Cassel and Breecker, 2017) making it a useful paleowater proxy (e.g. Canavan et al., 2014, Cassel et al., 2009, Friedman et al., 2013, Saylor and Horton, 2014). Carlson (2018) showed differences in δD between two different preparation methods in volcanic glass analysis and suggests that strict grain size filtering and hydrofluoric acid (HF) treatment produce the most reliable results, similar to Cassel and Breecker (2017) findings. Samples were deemed reliable if they contained >99% glass without bubbles. Glass shards with bubbles are less dense and described as pumiceous. Though preparation methods recommend removing pumiceous shards, it is not clear how they affect isotopic results, if at all. I investigate this by comparing pumiceous textures, water concentration, and δD values of different glass samples. Based on the results of this pilot I conclude that; 1) δD and wt. % water are not affected by apparent porosity, 2) The Cassel and Breecker (2017) method effectively removes hydrogen contamination, even in previously discarded pumiceous samples where corrosion is extensive, suggesting pumiceous glass shards can also be used for paleoenvironmental reconstruction. Future work should confirm these results with a more extensive dataset.

Background

Deuterium (D) is the heavy stable isotope of hydrogen. Isotopic ratios of hydrogen (H) to Deuterium are utilized in this study. Deuterium values (δD) are expressed as parts per thousand (‰) deviations from a standard. δD values of meteoric water evolve throughout the hydrologic cycle and are affected significantly by elevation and climate. By analyzing paleowater preserved in proxy material from the rock record, including tuff, researchers are able to reconstruct paleoenvironments.

Volcanic glass varies widely in its permeability, porosity (vesicularity), and surface area to volume ratio. As magma ascends from deep in the Earth, the pressure-dependent solubility of water causes bubbles to form from volatiles exsolving (Fisher and Schmincke, 1984). In addition, bubbles form during the cooling of magma (Williams and McBirney, 1979). After formation, volcanic glass has between 0.1 - 0.5 wt.% magmatic water (Grunder et al., 2015). Over the following 10^4 years, the glass gains up to 10 wt. % water derived from its environment (Cerling et al., 1985; Giachetti et al., 2015; Parruzot et al., 2015). Following hydration, Nolan and Bindeman (2013) concluded that δD in silt sized ($< 70\mu m$) glass shards can continue to change over a short time frame when exposed to highly enriched water (δD values up to 18,205‰). However, Cassel and Breecker (2017) suggest that post-hydration corrosion and alteration is limited to the surface which can be effectively removed with HF acid treatment in 70–150 μm size shards.

Samples from three unique formations are analyzed in this study (Table 1). Sample CVG027 is from the Deschutes Formation, dated between 5.99 and 5.67 Ma. It is a non-welded, fine-grained tuff interpreted to be a fluvially reworked ash-fall deposit (Pitcher et al., 2017). The second, CVG029 is a Quaternary-aged non-welded tuff that overlies a basalt flow and the only ash interpreted to be reworked by aeolian processes. It is dated between 0.055 – 0.007 Ma

(Peterson and Groh, 1970). The third, CVG034 is from the Mascall Formation, dated at 17.6-14 Ma. It is a non-welded fine-grained tuff interpreted to be a fluvially reworked ash-fall deposit (Bestland et al., 2008, Fiebelkorn et al., 1983). Samples are taken in bulk to be processed for δD analysis. All of the samples within each formation were collected at the same outcrop.

To remove impurities in glass samples used for paleoenvironmental reconstruction, many sample prep methods have been used. Two popular examples are described by Cassel and Breecker (2017) and Seligman et al. (2016). Carlson (2018) concluded that the Cassel and Breecker (2017) method produced the most reliable results for paleoenvironmental analysis. Seligman et al. (2016) uses sonicating and rinsing of samples with hydrochloric acid (HCl) and selects samples by hand selection (Carlson, 2018). The Cassel and Breecker (2017) method starts by crushing, sieving, and drying the tuff samples. To remove surface impurities from the glass, all samples are washed twice in 10% HCl for 30 seconds and twice in 8% HF for 30 seconds. Magnetic minerals are removed with repeated passes through a Frantz Isodynamic Separator. In addition, the heavy liquid lithium metatungstate (LMT) is used to create a density gradient of ash constituents. Figure 1 shows the difference between medium density samples and low-density pumiceous samples separated using LMT. On the right are glass shards that contain bubbles, identified as black circles, and on the left is a sample without. Pumiceous shards have a higher surface area per unit volume ratio and so are more likely to have secondary minerals within crevices and surface alteration that may not be fully removed by pre-treatments (Cassel and Breecker, 2017). Figure 2 shows an example of LMT density separation with different layers created. Relatively low density pumiceous glass floats to the top of a funnel and heavier material, containing mineral contaminants, sinks to the bottom. All the pumiceous shards were collected from the A section and glass shards >99% pure were taken from B and used in Carlson (2018).

Figure 1 Sample 034. Images taken from Carlson 2018. Left is non-pumiceous, right is pumiceous. Photo by Tessa Carlson

Hypothesis

Pumiceous samples from the same outcrop as samples without a pumiceous texture will show a significant difference in δD values and water content (weight percent water or wt. % water) suggesting sample porosity is an important consideration when selecting tuff samples for paleoenvironmental reconstruction.

Methods

Each formation has four δD values, two for pumiceous and two for non-pumiceous samples. Non-pumiceous sample results are from Carlson (2018). Pumiceous sample δD results are from previously unpublished. Table 1 contains meta-data related to each individual rock sample, all prepared using the Cassel and Breecker (2017) method.

Name/Formation	ID	Age (MA)	Lat	Long	Welding	Field Notes	Type	Hydration Water	Age/Location Reference
Quaternary Ash	M2-CVG029	0.0550.007	44.54448	-121.25829	Nonwelded	Massive, friable, light beige, overlies ~50 Ka intra-canyon basalt flow	Aeolian reworked ash	Precipitation	Peterson and Groh, 1970
Mascall Formation	M2-CVG034	17.6 – 14a	44.49972	-119.62528	Nonwelded	1-3m beds, fine grained ash, crystal poor, beige (034)	Fluvially reworked ash-fall	Fluvial, Precipitation	Bestland et al., 2008, Fiebelkorn et al., 1983
Deschutes Formation	M2-CVG027	5.99 – 5.67	44.58083	-121.42503	Nonwelded	Massive, beige, fine-grained, crystal-poor ash within crossbedded tuffaceous sediments above and below	Fluvially reworked ash-fall	Fluvial, Precipitation	Pitcher et al., 2017

Table 1: Sample age, location, and source information. Table adapted from Carlson (2018)

To more precisely characterize how pumiceous samples are, photos of sample thin sections were taken under a petrographic microscope. Each image was analyzed with ImageJ, a photo editing software, to characterize specific areas: total area of the image (A_i), area of void space between shards (A_v), area of the glass shards (A_g), area of bubbles of the entire image (A_{bi}), and area of bubbles of the glass shards (A_{bg}). Based on these data, an apparent porosity (θ_a) was calculated with the following equation:

$$\theta_a = \frac{A_{bg}}{A_g} \quad (1)$$

A_i in pixels was calculated in ImageJ by using the measure tool. To estimate A_v , the wand tool was first used to isolate the area of void space in pixels. Clicking with the wand in the void space of the image highlights all pixels of the same color. I continued to click around the glass shards until all the void space was highlighted. Again, the measure tool was used to calculate the area. By subtracting A_v from A_i , A_g was estimated. To measure the area of the bubbles, the black in the images was turned red using the color threshold tool. The measure tool again was used to estimate the red in the image to obtain % area of bubbles within the entire image (A_{bi}). Figure 3 shows an example of using ImageJ to calculate % A_{bi} . This is a percentage

of the picture that is black, not actual pixel area. Next A_g and A_{bg} are calculated with the following equations:

$$A_g = A_i - A_v \quad (2)$$

$$A_{bg} = \frac{A_{bi} * A_i}{A_g} \quad (3)$$

Figure 2: Image of LMT. A is the location where pumiceous shards are collected from, while B is where "pure" glass is collected. C and D contain contaminants that could not be removed with previous steps outlined in Cassel and Breecker (2017). The rainbow color is due to minerals in cross-polarized light, as light will pass through pristine glass without any refraction. They are discarded. Images from Carlson (2018)

Figure 3: Top: ImageJ color threshold processed image. The red was then used to calculate A_{bi} . Bottom: Non-processed image from petrographic microscope. The bubble noted is an artifact from making the slide. It is cropped out before A_{bi} is measured, thus not affecting apparent porosity (θ_a).

It should be noted that process of using ImageJ to estimate the apparent porosity is not as accurate as more established three-dimensional methods (e.g. Add Refs here... do a quick Google Scholar search). ImageJ could not provide the level of detail needed to obtain a more accurate measurement without spending an inordinate amount of time differentiating 2 million pixels. In my analysis, this error would tend to increase θ_a calculations. Image 4 (appendix) is different in color and glass density compared to the other samples due to limited sample size. Also, some error is introduced into the θ_a calculation because of image differences.

Results

Sample ID	Pumiceous	δD	δD Range	% wt. water	% wt. water Range	Phi (a)
M2-CVG027_a	yes	-148.6	-1.2	4.13	0.10%	5.6
M2-CVG027_b	no	-151.8	1.6	3.95	-0.04%	0.1
M2-CVG029_a	yes	-152.9	2.2	3.395	-0.03%	13.3
M2-CVG029_b	no	-151.3	-1.1	3.185	0.19%	0.3
M2-CVG034_a	yes	-163.1	1.9	6.495	0.07%	4.9
M2-CVG034_b	no	-163.3	1.1	5.48	-0.16%	1.7

Table 2: Pumiceous Sample IDs end with an (a) and non-pumiceous shards end in (b). δD and % wt. water Ranges are calculated differences between replicate samples from Carlson (2018).

Figure 4: Graph of θ_a . Pumiceous shards in blue and non-pumiceous shards in orange. Pumiceous shards range from 4.9-13.3 and non-pumiceous shards between 0.1 and 1.7. As expected, pumiceous shards have a significantly higher apparent porosity than non-pumiceous shards.

Figure 5: δD and wt % water graphs. Blue is pumiceous and orange non-pumiceous. Differences in wt. % water and δD are not significant between pumiceous and non-pumiceous samples.

As expected, pumiceous shards have a higher apparent porosity (θ_a) than non-pumiceous shards. Apparent porosity (θ_a) is highly variable between pumiceous and non-pumiceous samples. Pumiceous samples have a range of 8.4% while non-pumiceous samples have a range of only 1.6%. The non-pumiceous shards all have a θ_a less than 2% while pumiceous shards were between just under 5% to just over 13%.

By contrast, wt. % water and δD do not differ significantly between pumiceous and non-pumiceous samples. Pumiceous samples contain between 3 and 7 wt. % water and non-pumiceous between 3 and 6 wt. % water. The largest wt. % water difference between pumiceous and non-pumiceous shards is 1% between samples M2-CVG034 (a) and (b) (Table 2). Among all samples, δD varies between -148.6‰ and 163.3‰, but the difference between pumiceous and non-pumiceous of the same outcrop differ by just over 3.2‰ in samples M2-CVG027 (a) and (b) (Table 2). To confirm the lack of relationship between either δD or wt. % water and apparent porosity (θ_a), scatter plots were created (not shown) and no correlation observed ($R^2 < 0.02$).

Discussion

When comparing θ_a , δD , and % wt. water, no correlations are observed. Despite significant differences in θ_a between a pumiceous and non-pumiceous samples reaching 13%, no significant differences in either δD or % wt. water among samples from the same outcrop are observed. These results are contrary to my hypothesis, and suggest that pumiceous samples with relatively high porosity and variable wt. % water can also be used for paleoenvironmental reconstruction using δD analysis.

As stated, the Cassel and Breecker (2017) method uses several steps to prepare samples for analysis, including HCl, HF, and LMT. During this process, especially during HF treatment, surface contaminants and bubbles are eroded away and the total surface area of individual shards decreases (Carlson, 2018). Previously, pumiceous samples were discarded as they may contain more “contaminants” due to their high surface area to volume ratio and a higher propensity for post-hydration alteration and corrosion. My pilot study suggests that during the sample preparation process, contamination even in highly susceptible pumiceous samples is effectively eliminated, leaving meteoric hydrated glass behind.

Conclusions

Paleoenvironmental interpretation based on volcanic glass δD values is hampered by uncertainties related to a dearth of data across the Pacific Northwest and elsewhere. My results are important as researchers may be able to sample a wider range of volcanic glass textures for paleoenvironmental analysis, particularly where exposure of non-pumiceous, non-welded tuff samples are limited. The amount of usable sample after treatment is often minimal, also limiting the number of results in published studies (Carlson, 2018). Contrary to previous practice, my

results suggest non-pumiceous samples may also be used in analysis, which will potentially add critical datapoints for paleoenvironmental interpretation in future studies.

Future research should confirm these findings using the porosity of volcanic glass samples in three dimensions by measuring porosity using more comprehensive methods (e.g. Add Refs here... do a quick Google Scholar search). More importantly, these results suggest pumiceous samples do faithfully record the dD value of meteoric water at the time of ash deposition. However, the number of samples is limited so conclusions are suggestive in nature. A follow-up study should be conducted that analyzes a larger sample population to confirm my results and interpretations.

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Appendix

A: Initial, unprocessed glass images.

Image 1: Sample 27, pure

Image 2: Sample 29, pure

Image 3: Sample 34, pure

Image 4: Sample 27, pumiceous

Image 5: Sample 29, pumiceous

Image 6: Sample 34, pumiceous

B: Processed Images for %A_b

Image 7: Sample 27, pure, processed for %A_b

Image 8: Sample 29, pure, processed for %A_b

Image 9: Sample 34, pure, processed for %Ab

Image 10: Sample 27, pumiceous, processed for %Ab

Image 11: Sample 29, pumiceous, processed for %A_b

Image 12: Sample 34, pumiceous, processed for %A_b

Image 13: Sample 27, non-pumiceous, Av

Image 4: Sample 34, non-pumiceous, Av

Image 15: Sample 29, pumiceous, Av

Image 16: Sample 34, pumiceous, Av