



Conditions of pinnacle formation and glass hydration in cooling ignimbrite sheets from H and O isotope systematics at Crater Lake and the Valley of Ten Thousand Smokes

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ABSTRACT

Spire-like pinnacles and fins are common features in silicic ignimbrite sheets that represent the fluxing of water through the cooling deposit. Fumarolic pinnacles at Crater Lake, Oregon (Mt. Mazama; 7.7 ka) and in the Valley of Ten Thousand Smokes, Alaska (VTTS; 1912) represent the iconic images of these processes. Glasses within these structures remain fresh despite experiencing high temperatures and extensive water–rock interaction with infiltrating groundwater. These glasses can be used to interrogate the thermal and hydrologic conditions of pinnacle formation, which are not well-understood. Higher diffusivity of water at elevated temperatures facilitates rapid secondary hydration of glass. This allows for δD of pinnacle glasses to be used a “snapshot” proxy for the isotopic composition of the hydrating meteoric water with applications to paleoaltitude and paleoclimate. We present comprehensive H and O isotope data for volcanic glasses from pinnacles in the VTTS and from Crater Lake, which includes bulk $\delta^{18}O_{\text{glass}}$ and $\delta^{17}O_{\text{glass}}$ analyses and a new parameter, $\delta^{18}O$ of water-in-glass ($\delta^{18}O_{\text{wig}}$). The δD and $\delta^{18}O$ values of lake waters from the Katmai region are used to constrain the likely composition of VTTS hydration waters. The VTTS rhyolitic glasses from fumarolic mounds in the uppermost portion of the ignimbrite have depleted δD_{glass} ($\geq -152\text{‰}$) but minimally depleted $\delta^{18}O_{\text{glass}}$ in high H_2O (4.2 wt.%) pumices. These trends are best explained by the simple addition of modern meteoric waters from the Katmai region, thereby providing a snapshot of the meteoric water composition in the years to decades following the 1912 AD Novarupta-Katmai eruption. Glasses from Crater Lake pinnacles are used to estimate the δD and $\delta^{18}O$ of their hydration water shortly following the eruption of Mt. Mazama as well as the temperature conditions of their formation. Mt. Mazama glasses contain a narrow range of 1.6–1.9 wt.% H_2O with depleted δD and $\delta^{18}O_{\text{glass}}$ values as low as -149‰ and 0.95‰ , respectively. All measured δD_{glass} and $\delta^{18}O_{\text{glass}}$ values fall between $75\text{--}100^\circ\text{C}$ based on estimated δD and $\delta^{18}O$ equilibrium fractionation between glass and water, as do $\Delta^{17}O_{\text{glass}}$ compositions. The new $\delta^{18}O_{\text{glass}} - \delta^{18}O_{\text{wig}}$ approach gives a wider range of temperatures up to $\sim 150^\circ\text{C}$, but overall are in good agreement with $\delta^{18}O_{\text{glass}}$ isotope data. These compositions indicate $75\text{--}150^\circ\text{C}$ hydration temperatures and record extensive isotope exchange with meteoric waters. The near-boiling hydration temperatures strongly suggest that cooling ignimbrites remain dry above these temperatures. Cooling ignimbrite sheets likely have enough magmatic vapor overpressure to drive off vapor from ambient hydrosphere surface waters until they approach $\sim 100^\circ\text{C}$, at which point external waters are able to percolate into the deposit. Pinnacles therefore reflect late-stage cooling features rather than vigorous fumaroles. These results are consistent with previous modeling work on cooling ignimbrites that drive water away until sub-boiling temperatures, but contrast with the near-magmatic temperatures previously suggested by depletions in $\delta^{18}O$ in ignimbrite groundmass. Reconstructed δD and $\delta^{18}O$ values of paleo-meteoric waters at Mt. Mazama are -130 and -120‰ and -17.5 and -16.3‰ respectively, notably lighter than modern spring water compositions. This is interpreted to reflect a low- δD and low- $\delta^{18}O$ groundwater source fed by high-altitude glaciers or snowfields that originated from >3 km on the pre-collapse of Mt. Mazama edifice, more than 1 km above the modern lake level.

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1. Introduction

Ignimbrites are globally ubiquitous, and their emplacement can reshape the local landscape and radically affect the biosphere and

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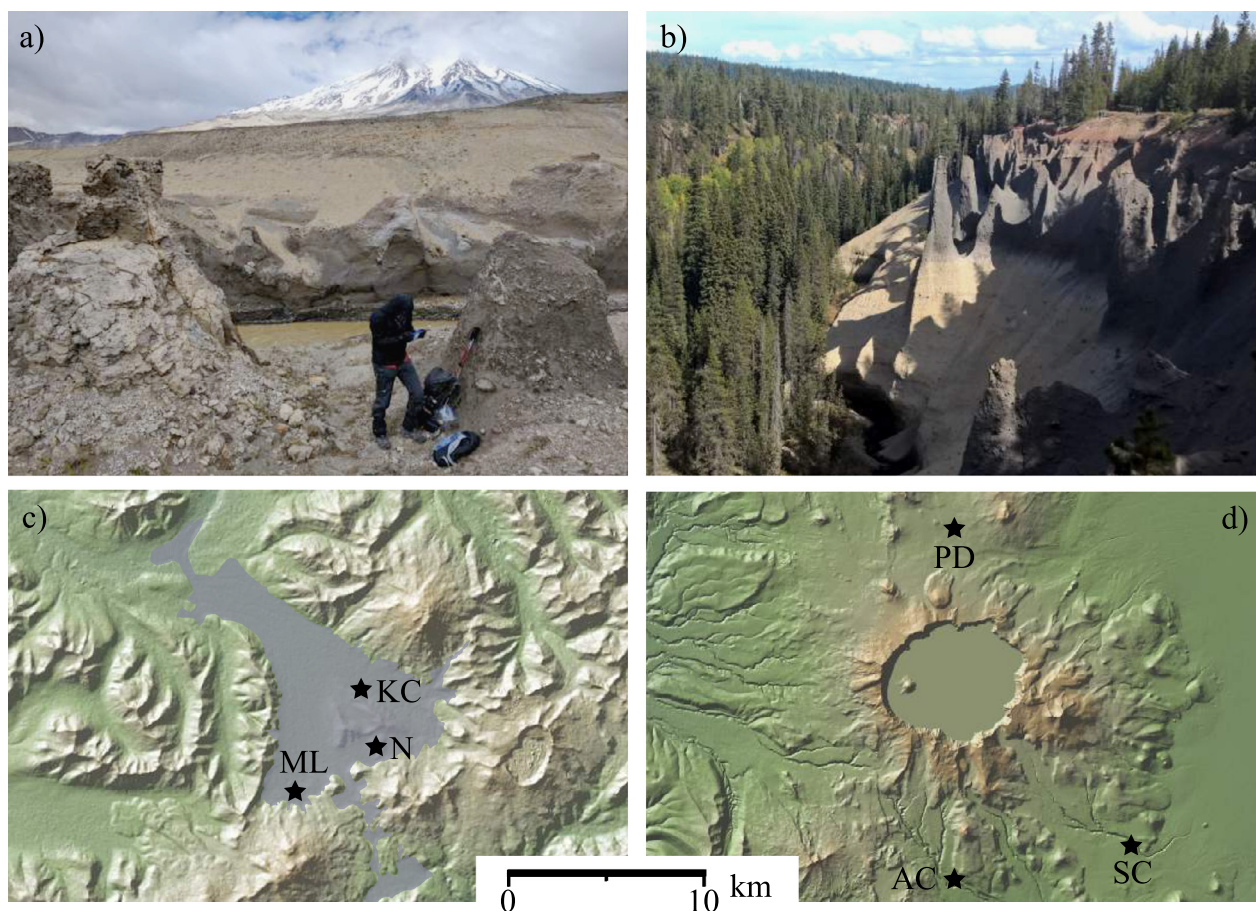


Fig. 1. Ignimbrite–water interaction features and maps investigated in this study. Photos of fumaroles from ignimbrites (a) and (b) and the maps of the field locations (c) and (d). Pumices in ignimbrite-hosted fumarolic pinnacles were sampled at the Valley of Ten Thousand Smokes (VTTS) at Katmai National Park, Alaska (a, c) and in Crater Lake National Park and Winema National Forest, Oregon (b, d). Extinct fumaroles from Knife Creek in the VTTS (a) were sampled. Sand Creek, Oregon samples were collected from downstream of the iconic pinnacles at Crater Lake (b). Sample locations are shown with stars in the VTTS (c) and in the Crater Lake area (d). The mapped extent of the 1912 Novarupta pyroclastic deposits are shown in a purple overlay from Hildreth and Fierstein (2012). KC = Knife Creek; ML = Mageik Lakes; N = Novarupta; PD = Pumice Desert; AC = Annie Creek, SC = Sand Creek. Maps from GeoMapApp (<http://www.geomapp.org>).

hydrosphere. Common cooling structures in almost all eroded ignimbrites include mounds, fan-like columnar jointing, and fumarolic pinnacles (e.g. Sheridan, 1970), spectacular structures that can be tens of meters in height (Fig. 1). These spires and fins are more resistant to erosion than the surrounding tuff because of cementation by hydrothermal mineral precipitation during cooling. Despite being visually striking and common to almost all silicic volcanic systems, their origin and the temperature of formation have not received much attention. This is additionally surprising given that pinnacles record the role water plays in ignimbrite cooling (Keating, 2005). Gazis et al. (1996) and Holt and Taylor (2001, 1998) used gas escape pipes in ignimbrites of Chegem Caldera (Caucasus, Russia) and Long Valley caldera in California to estimate the temperature of $\delta^{18}\text{O}$ depletions in these deposits. Based on low- $\delta^{18}\text{O}$ values observed in groundmass, they inferred that these systems are high temperature ($>500^\circ\text{C}$) and short lived, given the preservation of magmatic $\delta^{18}\text{O}$ major phenocrysts (Holt and Taylor, 1998). Such an interpretation was deemed consistent with high temperatures measured in fumaroles in the Valley of Ten Thousand Smokes, Alaska (VTTS; Griggs, 1922) and following the 1980 eruption of Mount St. Helens (Banks and Hoblitt, 1981). However, Randolph-Flagg et al. (2017) used the stability of mordenite, a cementing hydrothermal zeolite, to estimate that the peak temperature of similar Bishop tuff columnar pinnacle structures did not exceed 130°C .

Both H and O isotopes in pumice glasses from pinnacles at Crater Lake and the VTTS are used to assess the temperature

and timing of pinnacle formation in a cooling ignimbrite and into glass during low T rehydration (also referred to as secondary hydration). For example, with progressive water loss during volcanic degassing, δD_{glass} decreases with decreasing H_2O (e.g. Taylor et al., 1983). Similarly, diffusion of meteoric water into anhydrous glasses at ambient temperature has allowed δD_{glass} to be used as a proxy for paleoclimate (Friedman et al., 1993b; Seligman et al., 2016) or paleoaltitude (Cassel et al., 2009). Yet few people have applied high- T glass hydration features as a paleoclimate tool (e.g. Bindeman and Lowenstern, 2016). There are several advantages and challenges to using this approach. Glass hydration is well studied at ambient atmospheric (e.g. Friedman and Long, 1976) and high T ($>400^\circ\text{C}$; e.g. Zhang and Behrens, 2000), but not over the relevant $100\text{--}400^\circ\text{C}$ range expected in a cooling ignimbrite. Likewise, the fractionation of δD between glass and water is well-constrained at ambient T (Friedman et al., 1993a; Seligman et al., 2016), but unconstrained at hydrothermal temperatures. Combining δD and $\delta^{18}\text{O}$ from glasses in these systems may elucidate how and under what conditions water may play a role in ignimbrite cooling. Where water–rock ratios are higher, discrete alteration haloes (e.g. Holt and Taylor, 1998) or layers within a stratigraphic section (Gazis et al., 1996; Holt and Taylor, 2001) can form.

Three main challenges have prevented wider use of δD for paleoclimate studies. First, hydration of volcanic glass at ambient temperatures is extremely slow (several $\mu\text{m}/1000\text{ yr}$; e.g. Friedman and Long, 1976), and thus D/H in glass provide centuries to mil-

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