Hydration and Stability of Natural Glasses on Geologic Timescales

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Records of past topography connect Earth's deep interior to the surface, reflecting the distribution of heat and mass, past crustal structure, and plate interactions. Geodynamic reconstructions depend not only on the magnitude of surface elevation changes, but on the spatial distribution and stability of past high elevations, necessitating quantitative, orogen-scale paleoelevation datasets. Silicate glasses record the hydrogen isotope compositions (δD) of meteoric water shortly after deposition, providing a proxy for ancient precipitation and thus past elevations. As with any stable isotope proxy, glasses must resist alteration on geologic timescales to be useful paleoelevation indicators. Precipitation percolating through ignimbrite deposits replaces mobile cations in the glass, followed by the development of an impermeable, high-density silicate gel layer near the glass surface (in ~5-10 ky) that resists subsequent hydrogen exchange. To test gel layer stability and permeability, we placed natural glass samples of 7 kya to 34 Mya in a DHO solution of 800‰ at 22°C, 40°C, and 60°C for 280 days. DHO solution treatments resulted in no change within analytical error ($\pm 3\%$) in δD values of glass in comparison to untreated samples for all older units. Samples from the 7.7 ky Mazama ash show deuterium enrichment in interacted samples, suggesting that more than 7.7 ky is necessary to completely hydrate glass and form a silicate gel layer. Older glasses record δD values that reflect their depositional environments; lacustrine deposited samples had highly enriched δD values that reflect hydration by evaporative waters, while fluvial samples record depleted values reflecting precipitation. We also tested the use of acid abrasion, as the outer glass surface may partially recrystallize to secondary phyllosilicate phases after hydration. Short term hydrofluoric acid abrasion results in effective removal of these secondary phases. Samples that have not been acid abraded consistently show significantly higher δD values and less variability between samples from various geographic locations, likely reflecting the interaction of modern waters with the glass surface (outside of the gel layer). Ignimbrite glasses are especially well-suited for paleoaltimetry, as hydrated glass gel layers remain impermeable on geologic time-scales, faithfully recording the δD values of ancient meteoric water.