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Non traditional application of something very traditional: Oxygen and hydrogen isotope ratios in hydrated volcanic glass as paleoclimate proxies

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Over the past decades oxygen and hydrogen stable isotopes have been instrumental in many aspects of paleoenvironmental reconstructions, most importantly in detecting the impact of climate change on the global hydrologic cycle. Here we present two examples of a "non-traditional" application of hydrogen and oxygen isotopes by analyzing the hydrogen (δD) and oxygen (δ^{18}O) isotope ratios in naturally (and experimentally) hydrated silicic volcanic glass by high-temperature combustion (TC-EA) and secondary ion probe mass spectrometry (SIMS), respectively. The aim of this study is to evaluate the potential of hydrated volcanic glass as a proxy for changes in isotopic composition of past hydration water and ultimately rainfall. Applications of such a proxy are manifold and include reconstructions of climate seasonality, atmospheric circulation and continental moisture transport as well as novel approaches to stable isotope paleoaltimetry.

The western United States have been an active center of silicic volcanism over large intervals of the Cenozoic with eruptive centers along the Yellowstone hotspot track and within the Sierran-Cascadian magmatic arc. As a result, volcanic ash deposits characterize large portions of the Miocene-to-recent sedimentary successions in the western United States. Within thousands of years after deposition at the Earth's surface, volcanic glass in these ashes incorporates relatively large amounts of water (3-5 wt.%). This hydration process provides a hydrogen isotope record that reflects paleoclimate and precipitation regimes. Once correctly correlated, widely distributed ashes may serve as excellent paleoclimate and paleoaltimetry proxies as a) deposition and hydration are almost instantaneous on geologic timescales and can be dated with high temporal resolution and b) the chemical composition of the proxy is constant over large areas (100-100,000 km^2) thus eliminating compositional uncertainties related to proxy formation. Hydrogen isotope data from more than 50 volcanic glass samples that cover an age range from 0.4 to 16.0 Ma across the Basin and Range Province delineate a pattern of persistent continental aridity that experienced transient changes in continental moisture recycling. Glass samples from precisely dated ash layers in the Central Valley (CA) with δD $\geq$ -100 ‰ strongly contrast those in the Northern and Central Basin and Range (δD $\leq$ -130 ‰) and systematic spatial variations in δD of volcanic glass document the long-term interplay between regional changes in surface elevation, atmospheric circulation, and changing precipitation patterns.

In contrast, the oxygen isotope ratios of many of the analyzed samples correlate with changes in magmatic source composition over time. The combined δD and δ^{18}O data therefore are consistent with different isotope exchange mechanisms for D/H and ^{18}O/^{16}O that operate under Earth surface conditions. They further support previous claims (Friedman et al. 1993; Mulch et al. 2008) that hydrated volcanic glass carries great potential in serving as a proxy for paleoclimate/ paleohydrological reconstructions in (semi-)arid environments.

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