



# A chronometric tool for Hawaiian archaeology: the hydration dating of Pu'u Wa'awa'a trachytic glass

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## ABSTRACT

The Pu'u Wa'awa'a trachytic glass deposit located on the Big Island of Hawai'i was a source of lithic tools for much of Hawaiian prehistory. Routinely encountered at habitation sites, the glass has the potential to provide absolute dates based upon the degree of surface hydration. Infrared photoacoustic spectroscopy and secondary ion mass spectrometry were used to monitor the diffusion of water in archaeological and experimental samples. Accelerated laboratory hydration experiments show that water diffusion in trachytic glass containing a structural water content of  $0.16\% \pm 0.03\%$  is linear with time. Application of the calibration to trachytic glass artifacts from the Kahalu'u habitation cave have produced chronometric dates in the 17th–18th centuries. These age estimates are in agreement with radiocarbon dates and artifactual data that bracket the site occupation. However, the glass dates do not correlate well with site stratigraphy and this suggests that slight sample imperfections that retain water may be one factor that results in ages that are too early for later occupation levels.

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## 1. Introduction

The archaeological record of the Hawaiian Islands reflects the emergence of a complex hierarchical chiefdom followed by the development of an archaic state in the 18th century (Kirch, 2010). A late colonization date of approximately AD 1000–AD 1200 is currently accepted for this agro-political system that transformed the landscape of many islands through intensive farming by irrigated pondfield systems (Kirch, 2011) and elaborate dryland field complexes (Ladefoged et al., 2003). One of the main goals in Hawaiian archaeology has been to develop a fine grained chronology for the 600–800 years of pre-contact settlement. This has been a very challenging problem for a number of reasons. A large proportion of prehistoric material culture was perishable. Lithic technology was a core-flake reduction process that exhibited little temporal change. Ceramics are absent and thus technological, stylistic, or luminescent dating studies are not possible. Finally, the late date of occupation can make the use of radiocarbon dating often problematic. Many conventional radiocarbon dates come with multiple intercepts on the calibration curve that are associated with broad (2-sigma) age ranges. Fortunately, thorium/uranium

dating of coral offerings has filled part of this void for the dating of ritual architecture (Kirch and Sharp, 2005; McCoy et al., 2009; Sharp et al., 2010). However, appropriate coral specimens are not routinely abundant and the dating of volcanic glass artifacts through the quantification of surface hydration has been proposed as a complementary dating method.

Natural glasses within the Hawaiian archipelago are basaltic or trachytic in composition. These glasses vary appreciably in both their major constituent silica as well as minor element oxides. This chemical variation can impact overall glass durability and the rate of glass alteration when exposed to natural field conditions. Basaltic glass consists of ~45–53% SiO<sub>2</sub> and may be enriched in alumina (~15%), calcium (~12%), and iron (~10%) (Moberly et al., 2006). Trachytic glass is ~58–69% silica with major oxide contributions from alumina (~18%) and lower amounts of calcium (~0.3–0.6%), iron (~3–4%), and potassium (~4–5%) (Table 1). Both of these materials contain significantly less silica than obsidian (~69–77%). In the course of this discussion all of these glass forms may be referred to as “volcanic glass”.

Trachytic glass is mainly found on the leeward Hawai'i island at the Pu'u Wa'awa'a volcanic trachyte cone (McCoy et al., 2011) where it occurs as nodules within a coarse pumice matrix eroding from the steep northern face of the deposit (Fig. 1). Basaltic glass is much more prevalent within the archipelago and on the island of Hawai'i and occurs as “chill glass” formed on the surface of lava flows.

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**Table 1**

Oxide concentrations and selected trace element concentrations for Pu'u Wa'awa'a trachytic glass and the BHVO-2 analytical standard.

Material	MgO (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	K <sub>2</sub> O (%)	CaO (%)	TiO <sub>2</sub> (%)	Fe (%)	H <sub>2</sub> O <sub>t</sub> (%)	MnO (ppm)
Bonk Pu'u Wa'awa'a 1	0.14	18.3	62.8	4.53	0.3	0.7	4.1	0.53	6729
Bonk Pu'u Wa'awa'a 2	0.60	18.0	63.6	4.33	0.4	0.7	3.6	0.19	6866
Bonk Pu'u Wa'awa'a 3	0.40	17.9	64.2	4.48	0.3	0.7	3.9	0.30	6756
Bonk Pu'u Wa'awa'a 4	0.46	18.4	63.2	4.38	0.6	0.7	4.0	0.26	6730
06 UHH PWW-2	0.19	17.8	63.2	4.60	0.3	0.7	3.9	—	6922
BHVO-2 pellet 10-07.1	7.52	14.0	51.5	0.59	11.3	2.7	9.4	—	1626
BHVO-2 Published	7.23	13.5	49.90	0.52	11.40	2.73	8.63	—	1290

Material	Ni (ppm)	Cu (ppm)	Zn (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Ba (ppm)
Bonk Pu'u Wa'awa'a 1	0	0	173	135	33	61	966	141	421
Bonk Pu'u Wa'awa'a 2	3	12	176	137	34	62	980	143	425
Bonk Pu'u Wa'awa'a 3	0	9	174	140	36	65	976	142	423
Bonk Pu'u Wa'awa'a 4	3	4	180	141	46	64	1010	146	426
06 UHH PWW-2	2	13	179	137	33	62	983	147	472
BHVO-2 pellet 10-07.1	86	107	102	15	409	29	200	20	155
BHVO-2 Published	119	127	103	10	389	26	172	18	130

In this work, we develop a laboratory hydration rate for the Pu'u Wa'awa'a glass and evaluate the ability of the calibration to produce chronometric dates that are in general agreement with accelerator mass spectrometry (AMS) dates on carbonized material from a prehistoric habitation site. In contrast to previous optical dating studies, we use infrared spectroscopy and secondary ion mass spectrometry (SIMS) to measure the developing archaeological hydration layer (Stevenson et al., 2001; Stevenson and Novak, 2011). We begin with a literature review of prior basaltic glass and trachytic glass dating since early attempts incorporated both glass forms and documented similarities in the type of surface alteration.

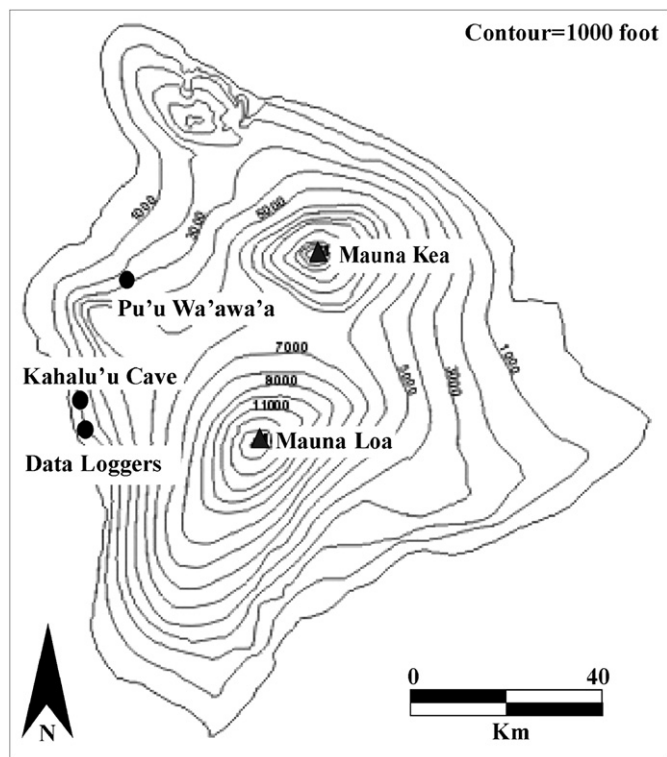
## 2. Background

Basaltic glass dating was introduced into Hawai'i in the mid-1970s (Morgenstein and Riley, 1974; Morgenstein and Rosendahl,

1976) and a small amount of follow-up research occurred after that time (Morgenstein et al., 1999). Optical microscopy was used to measure a slightly birefringent orange–yellow palagonite layer, or alteration layer, formed on the surface of the glass. As proposed at the time, the mechanism of formation entailed the migration of ambient water through numerous micro-channels that promoted additional water diffusion and the mobilization of iron and manganese that crystallized into iron and magnesium hydrates.

The dating method was quickly embraced and applied by archaeologists (Barrera, 1971; Barrera and Kirch, 1973; Hunt, 1976; Kirch, 1975; Tuggle et al., 1978) but came under critical evaluation as the complexities of the alteration process and the impacts of environmental variables became recognized. Strategies in use at the time for obsidian studies, such as the correlation of radiocarbon dates with alteration layer thicknesses to approximate rates of formation (e.g. King, 2004), were difficult to implement (Graves and Ladefoged, 1991). Large uncertainties in radiocarbon assays coupled with archaeological context uncertainties led to unsatisfactory results (Olson, 1983). The lack of data on ground temperature and uncertainties about the compositional variation in glasses and its effect on alteration rates resulted in abandonment of the method (Tuggle, 2010:176–178).

Since the 1980s a good amount of experimental work on basaltic glass has been conducted. Crovisier et al. (2003) summarize the wide variety of experimental designs and reaction media for hydrothermal experiments conducted at less than 100 °C to extract the parameters that govern the formation of palagonite layers. They conclude that palagonization is a post-eruptive phenomenon that occurs at ambient temperatures and that it is not a simple hydration process. They point out that in a static solution (closed system) of pure water the initial dissolution of the glass will consist of selective leaching and exchange with water for mobile ions. No surface alteration layer is formed during this period. At extended time, the entire glass surface undergoes congruent dissolution as the pH of the solution rises to 7.0 and greater. There is sufficient hydroxyl in the solution to break the Si–O–Si bonds that form the glass network. In renewed pure water solutions where the pH is kept below 7.0, or by reaction in saturated vapour, the mechanism does not change to congruent dissolution. Instead, there is a moderate depletion of silica, alumina and calcium and almost total depletion of sodium and potassium alkalis. Water may form up to 30% of the depleted surface layer and secondary mineral phases such as zeolites develop. Over the centuries, the hydration layer increases and the near surface region will convert into a palagonite with a honeycomb like structure (Byers et al., 1985; Stroncik and Schmincke, 2002).



**Fig. 1.** A map of Hawai'i Island showing the location of the Pu'u Wa'awa'a trachyte source and the Kahalu'u habitation cave.

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