

Rhyolitic and basaltic reference materials for TC/EA analysis: Investigation of water extraction and D/H ratios

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ABSTRACT

Increasingly, water and D/H ratios of silicic and basaltic glasses are used to investigate magmatic degassing and secondary hydration, as well as for study these parameters in the mantle and crustal magmas. The advent of the High Temperature Conversion Element Analyzer (TC/EA) continuous flow mass spectrometry made the determination of hydrogen isotopes relatively quick and precise (± 0.04 wt% H₂O and 1–3‰ $\delta^2\text{H}$). Many labs around the world have such systems, thus there is a need to develop both silicic and basaltic volcanic glass reference materials (RMs) that can be used for interlaboratory comparison by bulk and microanalytical methods. Here, we report results of such investigation run against solid RMs (USGS micas) and water RMs (including VSMOW) in three different labs and describe analytical protocols. We report on the effects of glass size fraction, the mass of aliquots measured, and yield dependency for two glasses: UOR (drill cutting of IDDP-1 rhyolite, Iceland) and UOB (an E-MORB basalt from the East Pacific Rise). Proposed RM values are:

UOB rhyolitic glass ($n = 31$):

$$\text{H}_2\text{O} = 1.84 \pm 0.06 \text{ wt\% (1 s.d.)}, \text{ and } \delta^2\text{H} = -115.5 \pm 2.6\text{‰ (1 s.d.)}$$

UOB basaltic glass ($n = 60$):

$$\text{H}_2\text{O} = 0.37 \pm 0.03 \text{ wt\% (1 s.d.)}, \text{ and } \delta^2\text{H} = -82.1 \pm 5.7\text{‰ (1 s.d.)}$$

Glass reference materials are available in 100 mg quantities from the Stable Isotope Laboratory at the University of Oregon for a nominal fee.

1. Introduction

Hydrogen isotopic investigations of hydrous phases are relevant to many fields within the geosciences as water-rock interactions are ubiquitous in sedimentary, igneous, metamorphic, and planetary processes; and therefore, efforts to measure H isotope ratios in rocks accurately and precisely has long been a focus of mass spectrometry development. Conventional analysis of waters or extracted hydrogen

from solid phases (terrestrial and extraterrestrial) for isotope analysis employed native metals like uranium (Bigeleisen et al., 1952; Friedman and Smith, 1958; Godfrey, 1962) and zinc (Friedman, 1953; Coleman et al., 1982; Kendall and Coplen, 1985; Vennemann and O'Neil, 1993) heated to high temperatures. These off-line methods reduced liberated H₂O and converted it into H₂ for measurement before introducing the gas into the mass spectrometer. Additional off-line methods varied slightly and liberated H₂, traditionally converted it to H₂O with CuO,

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and reduced it back to H₂ with hot U (Suzuoki and Epstein, 1976).

Development of online continuous flow isotope ratio mass spectroscopy (CF-IRMS) accelerated experimentation of novel, high temperature conversion (HTC) methods as it greatly reduced the necessary mass of material (e.g., Begley and Scrimgeour, 1996; Burgoyne and Hayes, 1998; Hilkert et al., 1999; Midwood and McGaw, 1999; O'Leary et al., 2007; Sharp et al., 2001). Techniques using chromium (Gehre et al., 1996; Greenwood, 2018), nickel (Begley and Scrimgeour, 1996), manganese (Tanweer and Han, 1996), zinc (Vennemann and O'Neil, 1993) and Pt–Mg (Halas and Jasińska, 1996) have been published, but the implementation of glassy carbon as a catalyst for the pyrolysis reaction of $C + H_2O \rightarrow H_2 + CO$, first used for oxygen and nitrogen in organic materials (Brand et al., 1994), also proved to be useful for hydrogen isotope analyses. The Thermo TC/EA has since become the primary analytical method for hydrous minerals (Sharp et al., 2001) after it became commercialized by the ThermoFisher Corporation with many instruments sold around the world. This has led to the routine analysis of micas and amphiboles (Deering et al., 2012; Underwood et al., 2012; Underwood et al., 2013), clays (e.g. Bauer and Vennemann, 2014), volcanic glasses (e.g. Martin et al., 2017; Seligman et al., 2016), epidotes (Pope et al., 2009; Pope et al., 2014; Zakharov et al., 2019; Zakharov and Bindeman, 2019), apatites (Greenwood, 2018), and even nominally anhydrous minerals like garnet and pyroxene (Gong et al., 2007; Gong et al., 2010).

With multiple techniques applied to such a diversity of materials, we note however that there is growing potential for disagreement between different labs in terms of standardization. A method for sealing water RMs in Ag tubing (Qi et al., 2010) has enabled an inexpensive and widely available common standardization. While a community need remains for phase-specific interlaboratory reference materials (RMs) to minimize matrix effects in the measurement of these phases, and the work herein is part of a broader effort to address this issue. For instance, the recent development of USGS biotite and muscovite RMs on the VSMOW-SLAP scale involved interlaboratory comparisons of several different HTC techniques and mass spectrometers (Qi et al., 2017).

This paper develops two RMs for H₂O and hydrogen isotopes in well-studied natural silicic and mafic volcanic glasses for a growing variety of volcanological and paleoclimate applications. Hydrogen isotopes in volcanic glasses were first measured in the 1950s by Friedman and Smith (1958), but it would take 25 years before these types of measurements were put into context (Taylor et al., 1983). This pioneering work investigated volcanic degassing styles in rhyolitic eruption and was quickly followed by additional research on natural samples and experimental studies (Newman et al., 1988; Anderson and Fink, 1989; Dobson et al., 1989; Taylor, 1991). Non-unique solutions to degassing pathways and relative difficulties of routine analyses limited further development until the advent of CF-IRMS. Applications of hydrogen isotopes to volcanic degassing has been revisited and expanded to interrogate more specific conduit processes (Rust et al., 2004; Mandeville et al., 2009; Castro et al., 2014; Giachetti et al., 2020; Walter and Castro, 2020). Hydrogen isotope ratios of RMs are given in delta notation in units of permille using VSMOW as the normalizing standard (Eq. (1)).

$$\delta^2H = 1000 \times \left(\frac{{}^2H/{}^1H_{\text{sample}}}{{}^2H/{}^1H_{\text{standard}}} - 1 \right) \quad (1)$$

Not all H₂O in volcanic glass is residual magmatic water, however. It has long been recognized that H₂O in the environment slowly diffuses back into glass through time (Friedman and Smith, 1960). Because hydrogen isotopes in precipitation are dependent on local meteoric waters and temperature (Craig, 1961; Dansgaard, 1964) hydrogen isotope compositions of rehydrated volcanic glass were proposed as a paleoclimate proxy (Friedman et al., 1993a; Friedman et al., 1993b). While this requires some effort to disentangle magmatic and meteoric H₂O contribution from the glass (Seligman et al., 2016), sample

preparation (Dettinger and Quade, 2015) and TC/EA methods (Martin et al., 2017) have been developed and widely implemented (Mulch et al., 2008; Cassel et al., 2012; Cassel et al., 2014; Hudak and Bindeman, 2018; Seligman et al., 2018; Jackson et al., 2019).

Here we report results from the investigation of two glasses, a basalt and a rhyolite, that span several years of efforts in the University of Oregon Stable Isotope Lab (UOSIL) employing a TC/EA configured to a Thermo MAT-253 and confirmed in two other labs: USGS Reston Stable Isotope Lab (RSIL) and Slovak Academy of Sciences (SAS). This effort targeting the two most common magma types is important for absolute characterization of water concentrations and D/H ratios in the mantle and extraterrestrial materials (e.g., meteoritic and planetary glasses) on the absolute VSMOW scale.

1.1. Selection of reference materials

Well studied, natural, crystal poor basalt (UOB) and rhyolite (UOR) glasses that were rapidly quenched at elevated pressures of ~0.3–0.5 GPa were chosen to develop glass RMs for H₂O and δ^2H determinations. The UOB volcanic glass RM is an enriched mid-ocean ridge basalt (EMORB) pillow glass from an off-axis pillow mound on the northern East Pacific Rise (Goss et al., 2010; Waters et al., 2011; Perfit et al., 2012) that was quenched at a depth of 2660 m; sufficient to retain its magmatic H₂O of 0.36 wt% measured in this work. Several other EMORB samples were also collected from this pillow mound with the submersible Alvin during dive 2489 and yield H₂O concentration ~ 0.4 wt% (le Roux et al., 2006). The UOR volcanic glass RM is the rhyolite from the famous IDDP-1 drill core at Krafla volcano in northern Iceland, accidentally sampled by drilling in 2009. Quenched in situ upon eruption through a drillhole, UOR has been extensively studied and found to have the expected H₂O content and OH/H₂O ratios for the depth at which it was encountered, ~2100 km (Elders et al., 2011; Zierenberg et al., 2013). Subsets of the most typical bulk material erupted and quenched on 6 June, 2009 at 17:00 GMT were separated to create a more homogenous material. Time series of the IDDP eruption, as well as investigation of D/H and H₂O in diverse clast types were presented in Saubin et al. (2021) but show scatter around average values. Homogeneous natural glasses with elevated H₂O contents are advantageous because they can be processed in large quantities that can be widely and commonly used across laboratories. Chemical analyses of UOR and UOB RMs are provided in Table 1.

2. Methods

Large chunks of clean rhyolite and basaltic glasses were separated under the microscope from minor contamination products (felsite inclusions in rhyolites, and orange Mn-oxide coatings on basalts). Samples were later sonicated in deionized water several times for 15–30 min to remove dust and particulates. Basaltic glasses were additionally soaked in 1.4 N HCl and 30% H₂O₂ mix with 60:40 (v/v) ratio to get rid of any remaining Mn oxides and hydroxides as well as organics and carbonates (Goss et al., 2010). Both rhyolitic and basaltic glasses were, sonicated in deionized water and ethanol to remove dust and particulates, and sieved into size fractions for analysis.

The general methods and conditions for HTC analyses are broadly similar between the three laboratories and differences are described in Table 2. Thermo HTC elemental analyzers (TC/EA) are interfaced with a Thermo MAT-253 isotope ratio mass spectrometer (IRMS) at UOSIL and SAS. A Thermo TC/EA, ConFlo IV coupled with Delta+ XP IRMS are used at USGS RSIL. Approximately 1–31 mg of sample are loaded into Ag capsules depending on H₂O content of the glass and the IRMS, larger for 3 kV Delta instrument. In all cases, samples are dried for at least 1 h, typically overnight, in a hot 130 °C vacuum drying oven. Furnaces in all three HTC systems are operated at ≥1400 °C and gas chromatographs are operated at 70 °C to 90 °C. Samples are dropped from autosamplers into a graphite crucible in the furnace where they are melted to liberate

Table 1

Chemical analysis of reference materials. *Analysis from Waters et al. (2011), depth is below sea level. **Analysis reported in Zierenberg et al. (2013), depth refers to rhyolite intersection by IDDP-1 drillhole.

Standard	Sample	Location description	Depth (m)	Lat (N)	Long (W)	SiO ₂ (wt %)	TiO ₂ (wt %)	Al ₂ O ₃ (wt %)	FeO (wt %)	MnO (wt %)	MgO (wt %)	CaO (wt %)	Na ₂ O (wt %)	K ₂ O (wt %)	P ₂ O ₅ (wt %)	Total (wt %)
ALV	2489-3*	EPR off-axis pillow mound	2664	9.52920	-104.22580	50.97	1.83	14.48	10.71	0.20	6.69	11.03	3.26	0.41	0.28	99.87
UOB		IDDP-1 drillhole,														
UOR	JB2**	Iceland	2100	65.71587	-16.76453	74.93	0.42	11.86	2.96	0.07	0.35	1.65	4.00	2.72	0.07	99.20

Table 2

Instruments, methods, and experimental conditions for HTC analyses.

Laboratory	Instruments	Methods and Conditions
University of Oregon Stable Isotope Laboratory (UOSIL)	Thermo-Finnigan TC/EA with Thermo MAT-253 IRMS and Thermo ConFlo IV gas introduction system	80 mL/min He flow; glassy carbon tube and chips; 1450 °C furnace; 70 °C gas chromatograph (GC) after 300 °C overnight bake out
USGS Reston Stable Isotope Laboratory (RSIL)	Thermo-Finnigan TC/EA with Thermo Scientific Delta Plus XP IRMS and Thermo ConFlo IV gas introduction system	110 mL/min H flow; glassy carbon tube and chips; 1450 °C furnace; 90 °C GC
Slovak Academy of Sciences Laboratory of Isotope and Organic Geochemistry (SAS)	Thermo Scientific Flash 2000 HT Plus with Thermo MAT-253 IRMS and Thermo ConFlo IV gas introduction system	80 mL/min He flow; glassy carbon tube; 1400 °C furnace; 90 °C GC

H₂O and reduced by glassy carbon to convert it to H₂ gas for analysis. Graphite crucibles are removed between analytical sessions to reduce backgrounds and memory effects. Helium carrier gas flushes extracted volatiles to the IRMS at rates of 80–120 mL/min. Reference waters sealed in Ag tubes and micas are run concurrently for H₂O and $\delta^2\text{H}$ calibration.

For spot analysis of H₂O and $\delta^2\text{H}$, glasses were analyzed by secondary ion mass spectrometry (SIMS) with a Cameca IMS 6f at Arizona State University for the purpose of checking any clast-to-clast heterogeneity. We used a primary beam of Cs⁺ accelerated to +10,000 V while the sample was held at -5000 V. The 1–2 nA beam was rastered over a 30 × 30 μm^2 area on the sample, but the transfer optics and field aperture were selected to allow only secondary ions derived from a 15 μm diameter circular area in the center of the sputtered crater into the mass spectrometer. Prior to collecting ion intensities, the sample was “pre-sputtered” with a 35 × 35 μm^2 raster for 4 min. Secondary ions with -5000 ± 20 eV total energy were allowed into the mass spectrometer and were detected by peak switching the magnetic field. A typical analysis involved counting ¹H⁻ for 1 s and ²H⁻ for 10s in each cycle, repeating for ~100 cycles. At the end of the 100 cycles, the secondary ion magnetic field was shifted to detect the matrix species ¹⁶O⁻ for 5 s. Hydrogen and deuterium ions were detected using an electron multiplier, but the ¹⁶O⁻ signal was measured using a Faraday cup. Parameters are summarized in Table 3.

3. Results

3.1. Isotopic and chemical homogeneity at UOSIL

Isotopic homogeneity and chemical homogeneity were evaluated in bulk glasses at the University of Oregon Stable Isotope Laboratory by TC/EA and on small spatial scales within and between individual glass particles at the Arizona State University Secondary Ion Mass

Table 3Analytical conditions for ²H⁻/¹H⁻ and H⁻/O⁻ in glass on the Cameca 6f SIMS at Arizona State University.

Primary beam:	Cs+
Primary source potential:	10 kV
Primary current:	1–2 nA
Primary raster (pre-sputter):	35 × 35 μm^2
Primary raster (analysis):	30 × 30 μm^2
Secondary ion beam:	negative
Sample potential:	-5 kV
Secondary ion energy:	-5000 ± 20 eV
Analyzed diameter:	15 μm
Electron Multiplier:	1H-, 2H-
Faraday cup:	16O-

Spectrometry (SIMS) Laboratory on a Cameca IMS 6f SIMS. All samples were analyzed for bulk H₂O and $\delta^2\text{H}$ at UOSIL. Each individual analysis is plotted in Fig. 1a and means with 1 s.d. are plotted in Fig. 1b. New TC/EA analyses of UOR and UOB and mica RMs are given in Tables 4 and 5, respectively.

3.1.1. Reference materials and standardization

The choice of reference materials can have significant effects on calibrating samples. Ideally, matrix-matched RM should be used when possible. Mica RMs biotite (USGS57, $\delta^2\text{H} = -91\text{‰}$) and muscovite (USGS58, $\delta^2\text{H} = -28\text{‰}$) are used (Qi et al., 2017) along with a low $\delta^2\text{H}$ internal laboratory RM used at the University of Oregon, Butte Montana muscovite (BUD, $\delta^2\text{H} = -151\text{‰}$), for UOR and UOB data. In three analytical sessions for UOB and one for UOR, a combination of water RMs sealed in Ag tubes from the USGS were analyzed as well, including VSMOW, GISP, USGS47, and W62001 (Table 6). Calibration of the UOR and UOB glasses with mica RMs produced neither uniformly higher nor lower $\delta^2\text{H}$ values than a calibration using water RMs (Fig. 2). However, in no analytical run did the mica and water RMs yield glass $\delta^2\text{H}$ results >5‰ different. All results are here on reported normalized to the USGS mica RMs.

3.1.2. Homogeneity of H₂O and $\delta^2\text{H}$ in bulk materials by TC/EA

Analyses of rhyolitic glass, UOR, by TC/EA at UOSIL are highly reproducible for both H₂O and $\delta^2\text{H}$ with $1.83 \pm 0.06 \text{ wt\%}$ (1 s.d.) and $-114.2 \pm 2.4\text{‰}$ (1 s.d., $n = 16$) respectively. These results are comparable to the error on the mica RMs of Qi et al. (2017), for both H₂O and $\delta^2\text{H}$ (Table 7; Fig. 1b). The UOR results represent study of a carefully selected split of IDDP-1 rhyolitic material from 6 June, 2009 at 17:00 GMT. The analyses of this split are compared to the previously published data collected at UOSIL for a time series of the IDDP-1 rhyolite drill core “eruption”, which included the full diversity of glass textures and colors (Saubin et al., 2021). The earlier results are within error of the above-stated H₂O content of UOR glass that represent just one time interval for eruption and include the predominant brown glass but show slightly lower mean H₂O and larger errors for both clear ($1.74 \pm 0.15 \text{ wt\%}$, 1 s.d.) and brown, opaque glasses ($1.80 \pm 0.12 \text{ wt\%}$, 1 s.d.). The $\delta^2\text{H}$ values from Saubin et al. (2021) are higher and also have higher standard deviations: $-110.3 \pm 8.7\text{‰}$ (1 s.d.) for clear glasses and $-108.4 \pm 9.7\text{‰}$ (1 s.d.) for brown glasses. However, because their study investigated how H₂O varied with glass colour and vesicularity, larger variation in measured values is expected relative to the UOR split that has been carefully selected for homogeneity. The 1–3 mm size chunks of glass were purified by picking non-glassy, vesicular, or darker-colored fragments. The resulting ~95% of material is represented by light brown

Table 4

UOR H₂O and δD results from UOSIL. Micas include USGS57 (biotite), USGS58 (muscovite), and an internal laboratory standard, BUD (muscovite), calibrated to the USGS mica reference materials.

Date of analysis	H ₂ O (wt%)	δD (permil)	Size fraction (um)	Mass (mg)	RM type
04-02-2015	1.84	-116.6			
04-02-2015	1.84	-116.5			
04-02-2015	1.92	-114.2			
04-02-2015	1.91	-113.1			
04-02-2015	1.88	-107.0			
04-02-2015	1.80	-112.4			
04-02-2015	1.80	-116.2			
04-02-2015	1.82	-115.4			
21-05-2010	1.68	-115.8			
21-05-2010	1.85	-114.8			
18-10-2019	1.74	-113.4	125–250	2.124	micas VSMOW, USGS47
		-109.4			
18-10-2019	1.82	-115.5	125–250	1.926	micas VSMOW, USGS47
		-111.5			
18-10-2019	1.79	-111.8	50–125	1.811	micas VSMOW, USGS47
		-107.9			
18-10-2019	1.82	-115.6	50–125	2.027	micas VSMOW, USGS47
		-111.6			
18-10-2019	1.84	-114.5	<50	2.278	micas VSMOW, USGS47
		-110.5			
18-10-2019	1.86	-113.8	<50	2.141	micas VSMOW, USGS47
		-109.8			

non-vesicular glass, with <5% particles of slightly darker or lighter colour. This material was crushed to size fraction >43 μm to <250 μm that homogenized it further.

Water contents in UOB are highly reproducible, with means of $0.37 \pm 0.03 \text{ wt\% H}_2\text{O}$ (1 s.d.) with and $\delta^2\text{H}$ of $-79.1 \pm 6.5\text{‰}$ (1 s.d., $n = 42$). However, the scatter in $\delta^2\text{H}$ increases when different size fractions are considered. Size fractions greater than 43 μm yielded H₂O and $\delta^2\text{H}$ means of $0.36 \pm 0.02 \text{ wt\%}$ (1 s.d.) and $-81.0 \pm 4.6\text{‰}$ (1 s.d.), respectively (Fig. 1b). Analyses of UOB without a noted size fraction return values within error of the >43 μm aliquots. With roughly one tenth the H₂O content of the mica RMs (Qi et al., 2017), UOB is expected to have comparable errors for H₂O than the mica RMs but comparatively higher $\delta^2\text{H}$ error as was observed with our previous investigation of water-poorer silicate glasses (Martin et al., 2017). Both RMs have a 1 s.d. of

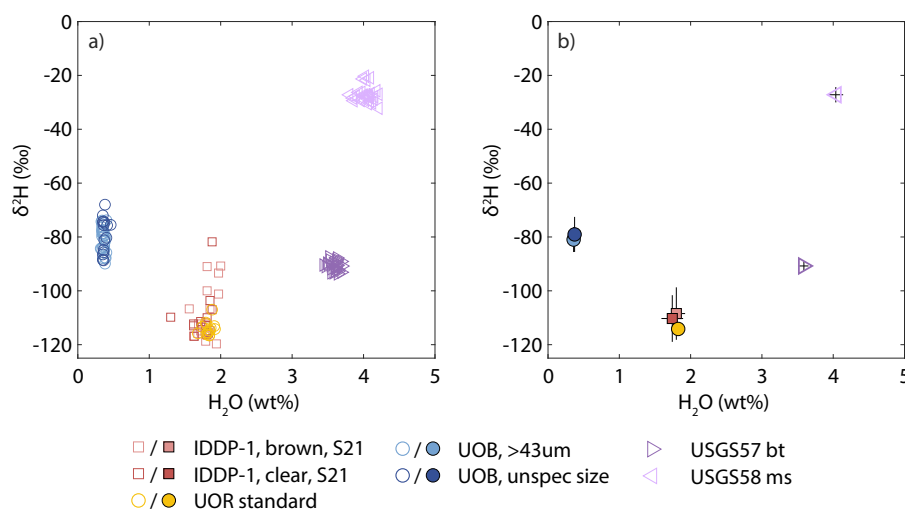


Fig. 1. H₂O and $\delta^2\text{H}$ data analyzed by TC/EA in the UO Stable Isotope Lab. (a) All data for UOR and UOB with data for USGS mica RMs. Brown and clear UOR glasses published in Saubin et al. (2021) were selected to capture the full heterogeneity of IDDP-1 drill cuttings and rhyolite petrology. The material for the UOR RM is more homogenous. UOB is subdivided into analyses 1) with record size fractions in excess of 43 μm and 2) unspecified size fractions. Less than 43 μm size fractions are excluded because they adsorb water and may contain alteration products. (b) Means with 1 s.d. We note the UOR $\delta^2\text{H}$ reproducibility, and UOR and UOB H₂O reproducibility is as good or better than mica RMs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5

UOB H₂O and δ D results from UOSIL. Micas include USGS57 (biotite), USGS58 (muscovite), and an internal laboratory standard, BUD (muscovite), calibrated to the USGS mica reference materials. *Analytical session with only USGS57 and USGS58.

Date fo analysis	H ₂ O (wt%)	δ D (permil)	Size fraction (μ m)	Mass (mg)	RM type
16-08-2018	0.40	−85.8	43–63	4.330	micas
16-08-2018	0.38	−89.9	43–63	6.290	micas
16-08-2018	0.35	−83.7	50–250	4.77	micas
16-08-2018	0.39	−87.8	50–250	5.33	micas
16-08-2018	0.37	−84.8	50–250	11.25	micas
16-08-2018	0.40	−73.8	50–250	0.968	micas
19-06-2020	0.65	−90.4	<43	5.181	micas
19-06-2020	0.63	−92.4	<43	5.581	micas
19-06-2020	0.65	−92.2	<43	5.345	micas
19-06-2020	0.38	−80.6	43–63	4.878	micas
19-06-2020	0.38	−87.7	43–63	6.850	micas
19-06-2020	0.38	−79.3	43–63	5.852	micas
19-06-2020	0.37	−83.0	63–105	7.022	micas
19-06-2020	0.36	−78.7	63–105	5.000	micas
19-06-2020	0.38	−81.7	63–105	6.018	micas
19-06-2020	0.34	−76.4	105–250	3.931	micas
19-06-2020	0.34	−79.8	105–250	5.933	micas
19-06-2020	0.34	−77.5	105–250	8.008	micas
19-06-2020	0.34	−77.7	105–250	10.022	micas
19-06-2020	0.34	−78.7	105–250	12.095	micas
19-06-2020	0.35	−78.6	105–250	9.920	micas
19-06-2020	0.34	−73.9	105–250	7.902	micas
19-06-2020	0.33	−74.3	105–250	5.986	micas
19-06-2020	0.34	−75.2	105–250	3.989	micas
13-10-2020	0.33	−84.4	105–250	8.03	micas VSMOW, USGS47
		−79.4			
13-10-2020	0.32	−84.3	105–250	7.67	micas VSMOW, USGS47
		−79.4			
13-10-2020	0.35	−87.9	250–500	6.25	micas VSMOW, USGS47
		−82.7			
13-10-2020	0.36	−79.7	250–300	5.65	micas VSMOW, USGS47
		−75.1			
13-10-2020	0.91	−100.2	<43	5.82	micas VSMOW, USGS47
		−95.2			
13-10-2020	1.12	−95.7	<43	5.65	micas

Table 5 (continued)

Date fo analysis	H ₂ O (wt%)	δ D (permil)	Size fraction (μ m)	Mass (mg)	RM type
		−90.9			VSMOW, USGS47
13-10-2020	0.36	−77.6	43–63	6.40	micas VSMOW, USGS47
		−74.1			
13-10-2020	0.37	−83.4	43–63	7.53	micas VSMOW, USGS47
		−79.5			
11-06-2018	0.35	−88.5		6.048	micas
11-06-2018	0.38	−68.0		6.061	micas
11-06-2018	0.41	−75.7		6.073	micas
05-07-2018	0.37	−81.2		7.40	micas W62001, USGS47, GISP
		−83.1			
05-07-2018	0.37	−74.7		4.11	micas W62001, USGS47, GISP
		−76.6			
05-07-2018	0.35	−86.5		5.85	micas W62001, USGS47, GISP
		−88.5			
05-07-2018	0.36	−84.8		6.018	micas W62001, USGS47, GISP
		−86.8			
05-07-2018	0.36	−85.7		6.016	micas W62001, USGS47, GISP
		−87.7			
05-07-2018	0.36	−88.7		6.069	micas W62001, USGS47, GISP
		−90.7			
13-09-2018	0.40	−80.3		6.10	micas*
13-09-2018	0.46	−75.5		4.10	micas*
18-10-2019	0.36	−75.6		6.052	micas VSMOW, USGS47
		−74.3			
18-10-2019	0.35	−72.0		5.905	micas VSMOW, USGS47
		−70.9			
18-10-2019	0.35	−74.4		6.143	micas VSMOW, USGS47
		−73.2			
24-10-2019	0.36	−74.2		5.943	micas

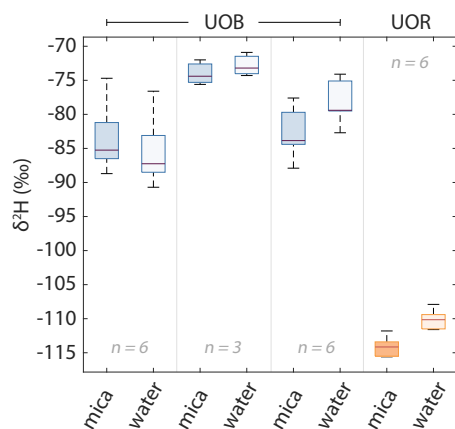
0.10 wt% H₂O and 2.8‰ δ^2 H or less (Table 6; Fig. 1b), which is within the analytical error reported for H₂O for this method at UOSIL, but not for δ^2 H (Martin et al., 2017). That study focused on analyzing rhyolitic glasses and may not reflect the true variance for basaltic compositions analyzed by TC/EA.

We evaluated the effect of grain size and mass on H₂O and δ^2 H in UOB and found that there was no clear trend in samples with size fractions entirely above 43 μ m in diameter (Fig. 3) or with mass of material put for analysis (Fig. 4). Fine sieve fractions of glasses (containing any fraction <43 μ m, including the finest particles hereon referred to as powders) have a median H₂O nearly twice that of the mean in all other samples (Fig. 3a). The size fraction of 105–250 μ m has the

Table 6

Values of mica reference materials used for calibration of UOB and UOB.

USGS57 biotite		USGS58 muscovite	
H ₂ O (wt%)	δD (‰)	H ₂ O (wt%)	δD (‰)
3.52	−87.4	4.02	−20.3
3.64	−92.8	4.04	−21.8
3.61	−91.7	3.99	−21.3
3.64	−93.7	4.09	−20.9
3.53	−88.6	4.10	−26.7
3.64	−92.2	4.12	−30.2
3.63	−87.8	4.08	−28.3
3.60	−91.4	4.14	−28.8
3.54	−90.6	4.04	−27.6
3.69	−89.1	4.04	−27.1
3.58	−93.3	3.96	−29.3
3.55	−91.8	4.09	−29.6
3.62	−89.5	4.02	−29.2
3.60	−91.3	4.00	−27.3
3.60	−91.8	4.07	−27.5
3.63	−90.6	3.97	−26.3
3.55	−93.3	3.86	−29.4
3.47	−91.0	3.89	−27.8
3.50	−90.1	3.85	−28.4
3.49	−89.7	3.93	−26.3
3.57	−89.9	3.80	−27.2
3.44	−90.4	4.21	−27.0
3.69	−93.1	4.21	−32.2
3.61	−90.8	4.18	−25.7
3.70	−90.8	4.15	−27.9
3.59	−89.4	4.06	−30.5
3.62	−88.4	4.00	−27.8
3.62	−88.9	4.07	−27.9
3.60	−92.7	4.07	−28.0

**Fig. 2.** The $\delta^2\text{H}$ results for UOB (blue) and UOR (orange) calibrated with mica and water reference materials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lowest median H₂O of 0.34 wt%. The highest medians were 0.38 wt% H₂O for the 43–63 μm and 50–250 μm size fractions. Similarly, $\delta^2\text{H}$ is notably lower in powders than in any other size fraction with a median of -92.4‰ (Fig. 3b). The slightly higher H₂O size fractions, 43–63 μm and 50–250 μm , have lower medians of -82.0‰ and -84.2‰ , respectively, compared to the lower H₂O 105–250 μm size fraction (-77.7‰). The $\delta^2\text{H}$ variability that gives rise to lower reproducibility is not a simple function of particle size or aliquot mass (Fig. 4). Instead, the subtle correlation between H₂O and $\delta^2\text{H}$ in size fractions in Fig. 3 suggests that a separate process: secondary hydration/adsorption of concentration of secondary alteration products, controls their covariation.

3.1.3. Homogeneity of H₂O and $\delta^2\text{H}$ within glass fragments by SIMS

Fifteen analyses were made on 5 different glass chips of UOR. The

average D/H ion ratio was normalized to the absolute D/H ratio based on bulk analyses showing $\delta^2\text{H}$ of -114‰ , which translates to D/H of 1.381×10^{-4} , assuming D/H of VSMOW is 1.5576×10^{-4} (Fig. 5a; Hagemann et al., 1970). Four of the five chips of glass showed similar values for this normalized D/H ratio, which are referred to as α , of ~ 1.164 and are shown with 2 SE. The 5th chip yielded a uniformly lower α value. However, because we obtained the $^{16}\text{O}^-$ intensity, we can compare the H/O ion ratio (which should be related to the H₂O content as the O contents are unlikely to vary significantly as the structural O contents of the anhydrous glass are unlikely to vary) to the isotope ratio (Fig. 5b). Evidently, four of the measurements sampled H-rich, relatively D/H-poor areas of the glass, concentrated in one of the 5 chips. The three spots on the 5th chip constitute three of the four high H/O ratios and low alpha analyses.

Why would H-rich areas result in low D/H ratios? Does this represent zoning or an artifact of the analytical technique? It is possible that as the H count rate increases, uncertainty in the dead-time correction increases, leading to an under-correction and high D/H. However, the last analysis of the 5th chip of glass was conducted using a reduced primary beam current to decrease the count rate for hydrogen. Because this analysis produced a D/H ratio identical (within error) to the other 2 analyses on this chip, it might be suggested that this particular piece of glass actually contains areas high in H₂O and correspondingly, approximately 30‰ lower in $\delta^2\text{H}$ than most areas of the glass. Hauri et al. (2002) showed that the D/H ion ratio of glasses sputtered (using very similar conditions as here) by Cs⁺ ions gradually decreased with increasing H₂O content. The effect was not as large as indicated here, but the effect of increasing H₂O on decreasing D/H ion ratios was independently observed on the ASU Cameca 6f by Befus et al. (2020), lending support to the idea that the change in the SIMS D/H ion ratio is the result of a small change in the H₂O content of one glass fragment.

Overall, however, the UOR sample is quite homogeneous in its hydrogen isotopic values. Taking the 12 measurements with H/O $< 1.3 \times 10^{-3}$, the average value of alpha is 1.1639 ± 0.0048 (2 SE). This suggests a 4‰ (2 SE) uncertainty in selected measurements of the SIMS ion ratio. If all 15 spot analyses on the 5 chips are used, the 2 SE variation is 8‰. However, calculating standard errors may not be appropriate here, considering the local variation in measured D/H and low numbers of measurements. The homogeneity of the H₂O content is reflected by the variation in the SIMS H/O ion ratio. There are two possible ways of determining this ratio. We can average the H count rate over the ~ 30 min-long analysis and divide by the oxygen ion count rate determined at the end of the analysis or only use the average H count rate over the last ten cycles prior to collecting the O signal. That latter value shows an uncertainty of 2.5%, two standard errors.

Twelve analyses were made on 3 UOB chips of glass. Fig. 6a D/H ion ratios were normalized to the absolute D/H ratio of the basaltic glass ($\delta\text{D} = -82.1\text{‰}$, or D/H = 1.4298×10^{-4}). One of the analyses on the 1st chip is clearly different than the others. In this case, the hydrogen ion signal was significantly lower (by $< 20\%$) than the average of the other eleven analyses (Fig. 6a). The average SIMS value of α , excluding the outlier, is 1.1790 ± 0.0054 (or $\pm 4.7\text{‰}$, 2 SE). Of course, standard errors should be interpreted with caution when n is so small (11). Except for the one outlier, the H₂O content of the basaltic glass (expressed as the H/ $^{16}\text{O}^-$ ion ratio) is homogeneous (Fig. 6b). The average of 11 analyses is $3.91 \pm 0.27 \times 10^{-4}$, 1 s.d. ($\sim 3\%$ scatter).

3.2. Interlaboratory comparison

Having evaluated reproducibility for H₂O and $\delta^2\text{H}$ in UOR and UOB glasses at UOSIL, we compare these results to two sets of data collected by TC/EA in two other laboratories. At the Earth Sciences Institute at the Slovak Academy of Sciences (SAS), like at UOSIL, measurements were made on a Thermo MAT 253 IRMS. Measurements at RSIL were conducted on a Thermo Fisher Delta V Plus IRMS. Results are given in Table 8.

Table 7

Means and standard deviations of UOR and UOB at each laboratory. Weighted means pool all individual analyses from all three laboratories. Unweighted means take the average of the means from each laboratory to weigh results from each laboratory equally. Recommended values are the means of the means from each laboratory. *Heterogeneous IDDP-1 samples from [Saubin et al. \(2021\)](#) are not included in calculations. These data are again presented for only for comparison.

Glass	Laboratory	n =	Median H ₂ O (wt %)	Mean H ₂ O (wt %)	1 s.d. (wt %)	Median $\delta^2\text{H}$ (‰)	Mean $\delta^2\text{H}$ (‰)	1 s.d. (‰)
UOR	UOSIL	16	1.83	1.83	0.06	−114.7	−114.2	2.4
IDDP-1 (clear)*	UOSIL	15	1.80	1.74	0.15	−112.3	−100.3	8.7
IDDP-1 (brown)*	UOSIL	16	1.80	1.80	0.12	−112.9	−108.4	9.7
UOR	SAS	4	1.81	1.79	0.04	−114.4	−114.1	1.8
UOR	RSIL	11	1.89	1.88	0.02	−118.1	−117.9	1.2
UOR weighted mean*	All labs	31	1.84	1.84	0.06	−115.6	−115.5	2.6
UOR unweighted mean*	All labs			1.83			−115.4	
Recommended UOR*		31		1.84	0.06		−115.5	2.6
UOB (unspecified size)	UOSIL	15	0.36	0.36	0.02	−79.8	−81.0	4.6
UOB (>43 μm)	UOSIL	27	0.36	0.37	0.03	−75.7	−79.1	6.5
UOB	SAS	11	0.36	0.37	0.02	−85.4	−84.7	4.2
UOB	RSIL	7	0.40	0.40	0.04	−88.7	−88.9	2.0
UOB weighted mean (without unspecified size data)	All labs	45	0.36	0.37	0.03	−84.3	−83.1	5.1
UOB weighted mean (with unspecified size data)	All labs	60	0.36	0.37	0.03	−83.5	−82.1	5.7
UOB unweighted mean	All labs			0.38			−83.4	
Recommended UOB		60		0.37	0.03		−82.1	5.7

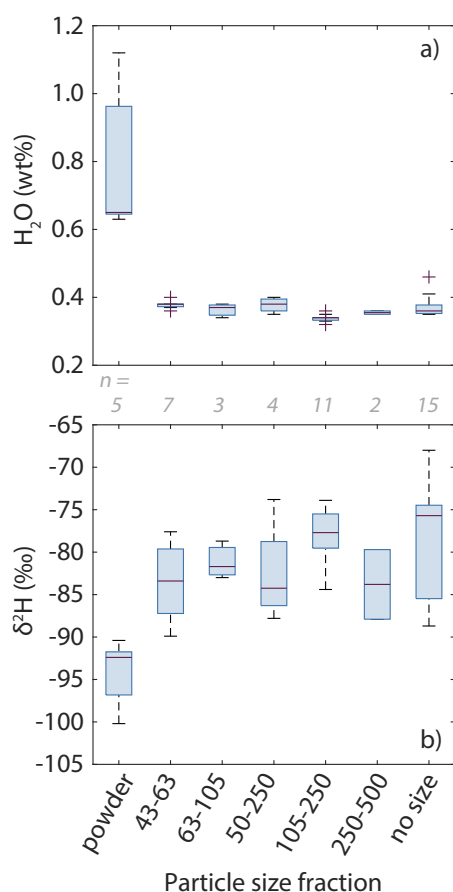


Fig. 3. Box and whisker plot as a function of size fraction for UOB H₂O (a) and $\delta^2\text{H}$ results (b) analyzed at UO. Boxes represent the 25th to 75th percentiles and the central bar represents the median. Whiskers extend to minimum and maximum values not considered outliers, which are shown as crosses. Powders yield high H₂O and low $\delta^2\text{H}$, but size fractions greater than 43 μm largely provide consistent results.

Each measurement made on UOR or UOB is shown with a bar depicting the mean plus or minus 1 s.d. in [Fig. 7](#). For UOB, the mean values are 0.37 ± 0.02 wt% H₂O (1 s.d.) from SAS and 0.44 ± 0.02 wt%

H₂O (1 s.d.) from RSIL ([Fig. 7a](#)). The mean H₂O concentration in UOR from SAS and RSIL are 1.79 ± 0.04 wt% (1 s.d.) and 1.86 ± 0.02 wt% (1 s.d.), respectively ([Fig. 7b](#)). For both glasses, the RSIL measurements (Delta-Plus-TCEA system) yield relatively high H₂O compared to UOSIL and SAS measurements (MAT253-TCEA systems). Total H₂O measurements from UOSIL and SAS are within error for both UOR and UOB, while measurements conducted at RSIL are only within error of UOSIL for UOR.

Similarly, the $\delta^2\text{H}$ measurements from UOSIL and SAS are within error for both UOR and UOB, but RSIL data are only with error of UOSIL for UOR ([Fig. 7b](#)). The mean $\delta^2\text{H}$ values for UOB, are -84.7 ± 4.2 ‰ (1 s.d.) from SAS and -89.7 ± 1.9 ‰ (1 s.d.) from RSIL ([Fig. 7a](#)). Values for UOR are -114.1 ± 1.8 ‰ $\delta^2\text{H}$ (1 s.d.) and -117.2 ± 0.7 ‰ $\delta^2\text{H}$ (1 s.d.) from SAS and RSIL, respectively. Means with 1 s.d. for data from each lab and the IDDP-1 data from [Saubin et al. \(2021\)](#) are shown in [Fig. 7b](#). Again, histograms show the distribution of $\delta^2\text{H}$ from each lab. At first glance, UOB appears bimodal, but analytical sessions with more analyses exert greater influence on the histogram of every analysis and the means and medians of sessions vary. Therefore, we show a second histogram with the mean $\delta^2\text{H}$ values from analytical sessions in which UOB was analyzed at least in triplicate. This histogram of analytical session means reveals that UOB has a wide distribution for $\delta^2\text{H}$ results, but with a peak occurs between -84 ‰ and -82 ‰ $\delta^2\text{H}$, consistent with the preferred values given in [Table 7](#).

4. Discussion

Investigation of these two natural glasses – UOR and UOB – over 10 years at the University of Oregon and additionally in 2 other labs has resulted in overlapping values that make these two materials appropriate as reference materials. [Table 7](#) presents recommended reference material values of $\delta^2\text{H}$ and H₂O that are recommended for use. For UOR we recommend values of 1.84 ± 0.06 wt% H₂O (1 s.d.), and -115.5 ± 2.6 ‰ $\delta^2\text{H}$ (1 s.d.). For UOB we recommend values of 0.37 ± 0.03 wt% H₂O (1 s.d.), and -82.1 ± 5.7 ‰ $\delta^2\text{H}$ (1 s.d.). These recommended values are means of all individual H₂O and $\delta^2\text{H}$ analyses from all three laboratories and are slightly weighted towards the UOSIL means as the most analyses were done there. Unweighted means, which take the averages of the H₂O and $\delta^2\text{H}$ means from each laboratory, are also presented in [Table 7](#). These values are well within 1 s.d. of analytical precision of the preferred values.

There is a weak negative correlation between H₂O and $\delta^2\text{H}$ over the whole suite of UOB samples, anchored by the high H₂O powders. We

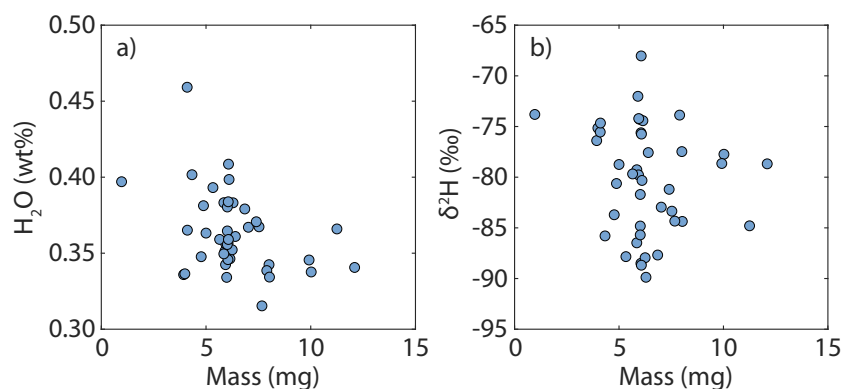


Fig. 4. H_2O (a) and $\delta^2\text{H}$ (b) as a function of the mass of the analyze aliquot of UOB. No systematic trends are observed.

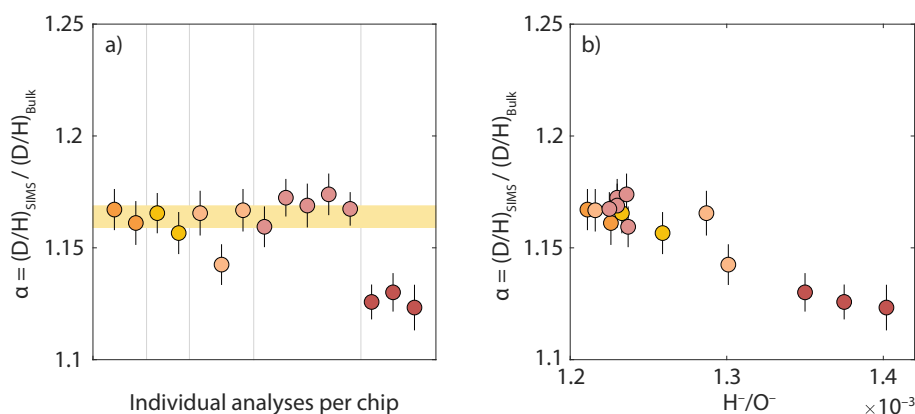


Fig. 5. Raw SIMS D/H measurements divided by mean D/H ratios (α) from UOSIL TC/EA results (a) and H^+/O^- ratios vs. SIMS α values for UOR (b). Each colour represents a separate chip of the volcanic glass RM. The yellow bar in (a) is 2 SE for the first 4 UOR chips. Measurements with higher H/O trend towards lower $\delta^2\text{H}$ values. Error bars show 2 SE of measurement. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

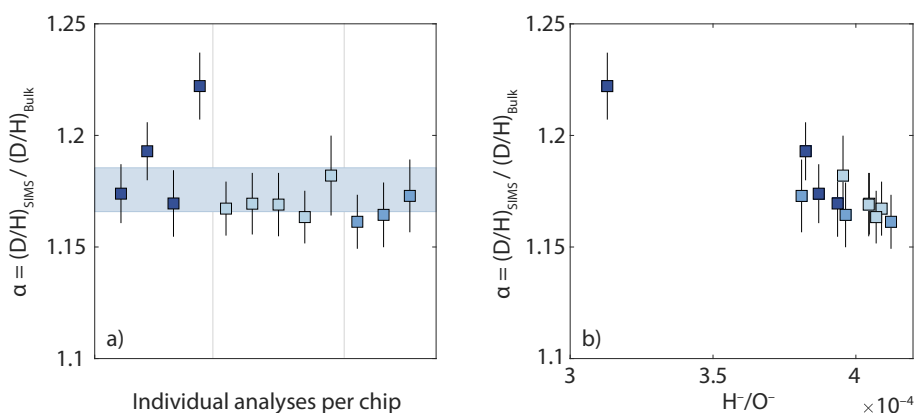


Fig. 6. Raw SIMS D/H measurements divided by mean D/H ratios (α) from UOSIL TC/EA results (a) and H^+/O^- ratios vs. SIMS α values for UOB (b). Error bars show 2 SE of measurement. One outlier with lower H_2O has a higher $\delta^2\text{H}$. The blue bar in (b) is 2 SE for all UOB data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

model two hypotheses that could influence this trend. First, high H_2O measurements in powdered samples are likely affected by adsorbed moisture on particle surfaces, despite overnight drying. Mixing calculations between glass (0.34 wt% H_2O and -77.7‰ $\delta^2\text{H}$) and condensed moisture in Eugene, Oregon (approximated with a $\delta^2\text{H} = -107\text{‰}$) trend in the direction of the powders. Although we dry samples in hot vacuum oven overnight prior to analysis, previous research on smectites demonstrates that minor atmospheric exposure results in rapid water re-adsorption during transfer between the vacuum oven and the sample carousel purged with He (citation). It is also possible that the finest

fraction concentrates hydration and secondary alteration products, including smectite and other clays, of this glass which was emplaced in submarine conditions and resided under water for many thousands of years before collection by the Alvin submersible apparatus. The $\delta^2\text{H}$ composition of condensate/alteration product is likely variable through time, so Fig. 8a simply illustrates that adsorbed moisture is a sufficient possible explanation for low $\delta^2\text{H}$ values in the high H_2O powders. However, it fails to explain the variance in compositions at H_2O below 0.4 wt% (Fig. 8a).

Alternatively, incomplete extraction of H_2O from the glass in the TC/

Table 8

Results of UOR and UOB analyses from RSIL and SAS.

Reference Material	Laboratory	H ₂ O (wt%)	δD (‰)
UOR	RSIL	1.88	−118.1
UOR	RSIL	1.86	−116.8
UOR	RSIL	1.84	−116.7
UOR	RSIL	1.89	−116.8
UOR	RSIL	1.89	−118.4
UOR	RSIL	1.89	−120.1
UOR	RSIL	1.89	−118.5
UOR	RSIL	1.89	−115.9
UOR	RSIL	1.89	−118.4
UOR	RSIL	1.89	−119.2
UOR	RSIL	1.89	−117.7
UOR	SAS	1.74	−113.4
UOR	SAS	1.82	−115.5
UOR	SAS	1.79	−111.8
UOR	SAS	1.82	−115.6
UOB	RSIL	0.44	−89.5
UOB	RSIL	0.41	−88.7
UOB	RSIL	0.45	−92.5
UOB	RSIL	0.45	−88.2
UOB	RSIL	0.36	−87.4
UOB	RSIL	0.36	−90.0
UOB	RSIL	0.36	−86.2
UOB	SAS	0.35	−86.1
UOB	SAS	0.36	−84.5
UOB	SAS	0.36	−85.4
UOB	SAS	0.36	−88.4
UOB	SAS	0.35	−83.8
UOB	SAS	0.39	−87.9
UOB	SAS	0.37	−84.9
UOB	SAS	0.37	−80.9
UOB	SAS	0.36	−74.3
UOB	SAS	0.40	−85.9
UOB	SAS	0.38	−89.9

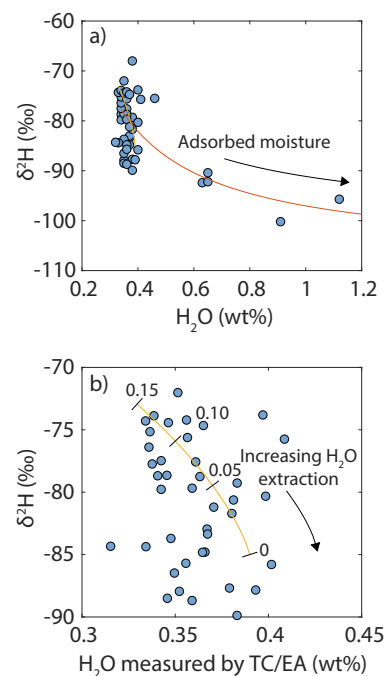


Fig. 8. Two models to explain the variation in H₂O and δ²H results for UOB. High H₂O and low δ²H results can be explained by adsorption of atmospheric moisture (a), but do not explain the variations in δ²H over a narrow range of H₂O content (~0.34–0.38 wt%). The second model treats the liberated and measured gases from the samples as accumulated magmatic vapor in an open system (b). This model shows that small residual fractions (tick marks) of H₂O in a melt can have large isotopic effects, especially for low H₂O samples, such as UOB.

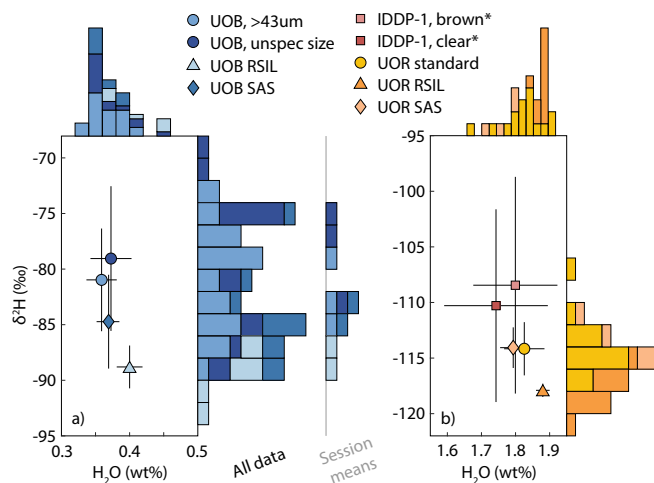


Fig. 7. H₂O and δ²H data for UOB (a) and UOR (b) analyzed by TC/EA at UOSIL, RSIL, and SAS are shown with *IDDP-1 measurements from Saubin et al. (2021) on the scatter plot (but omitted from the histograms). See Fig. 1 caption for detail on samples. Reston data were normalized with H₂O reference materials rather than micas. Histograms show all H₂O and δ²H data from each of the 3 laboratories. Mean δ²H values from each analytical session where UOB was run at least in triplicate are shown as an additional histogram to remove bias towards analytical sessions with many more analyses.

EA could cause subtle differences in δ²H composition. Although our FTIR investigation has found zero remaining water in extracted glasses suggesting complete extraction, we nonetheless entertain this possibility as the melted glass samples remained at high temperature during the entire analytical session. The H₂O and δ²H measured by TC/EA are treated as the accumulated magmatic H₂O in an open system using a

modified basalt degassing model of de De Hoog et al. (2009). Liberated H₂O is rapidly converted to H₂ by a pyrolysis reaction catalyzed by glassy carbon in the reaction chamber and at the front of the GC column before being carried away to CONFLOW open split in front of the mass spectrometer by He gas. If the extraction process likely a of batch nature, so it may be approximated as an open system. If the modeled glass has an initial H₂O of 0.39 wt% and δ²H of −85‰ because incompletely extracted H₂O (hypothetical incomplete degassing) from basaltic melts will yield lower H₂O and higher δ²H values, where a majority of the analyses fall (Fig. 8b). The accumulated magmatic vapor curve is calculated using the Rayleigh equation:

$$\bar{R}_v = R_{l0} \left(\frac{f^\alpha - 1}{f - 1} \right) \quad (2)$$

In Eq. (2), $\bar{R}_v$ is the D/H ratio of the accumulated vapor, R_{l0} is the initial D/H ratio of the melt prior to degassing (converted from −85‰ using the VSMOW reference frame), f is the fraction of H₂O remaining in the melt, and α is the equilibrium fractionation factor between the vapor and the melt, which is given as a constant, 1.040 (~40‰; Dobson et al., 1989; De Hoog et al., 2009). Model results are shown for 0.33 and 0.39 wt% of extracted H₂O, which represents fractions of H₂O remaining in the basaltic melt, ~0.06 wt% or 15% or less. These H₂O contents have a δ²H range from −73‰ to −85‰, roughly equivalent to ±1 s.d. in the δ²H data (Tables 4–5, Fig. 1b). Notably, the extraction of the last 5% (or 0.02 wt%) of the H₂O from the melt to a vapor that is measured by the mass spectrometer results in a change of 5‰ δ²H. While the accumulated magmatic vapor curve cannot explain all the data, it illustrates that incomplete H₂O extraction in low H₂O sample with high liquidus temperature may result in a somewhat greater spread in δ²H, even over narrow H₂O ranges and especially the final few percent of H₂O degassing. However, Fourier transform infrared spectroscopy (FTIR) of a

pure UOB melt collected under normal TC/EA operating conditions yielded undetectable H₂O at the 3500 cm⁻¹ peak (<0.01 wt% in a 840 µm doubly polished wafer; Text E1, Figs. E1–E2). Similarly, there is no correlation in between systematic extension of the ²H₂⁺ and ³H₂⁺ analytical peak tails and resulting δ²H (Text E2). For these reasons, incomplete H₂O extraction from melts may be excluded as a source of analytical uncertainty of the present study.

A harder to quantify, yet more compelling explanation for the variability in δ²H of the UOB basaltic glass is its high Fe content. A comparison of high Fe and low Fe biotite yielded different hydrogen yields by HTC-CF-IRMS using a Delta-Plus mass spectrometer (Qi et al., 2014). These authors posited that high Fe (high metal) concentrations resulted in the formation of metal hydrides, lowering the yield of H₂. The efficiency of H₂ production is likely correlated with the availability of reactive glassy carbon. The TC/EA column is not repacked with new carbon granules after every analytical session, so H₂ production may not be consistent between runs for high Fe samples. The users may also mix glassy carbon particles with the glass inside of Ag capsules (as is the practice in analysis of sulfates to ensure better extraction) and availability of carbon for reduction, especially on Delta-based system requiring greater sample mass.

Formation of iron hydrides and hydroxides (FeH, FeOH, etc.) may retain hydrogen from the melt during the extraction. Hydrides may have large and unknown fractionations with the melt even at high temperatures although it is difficult to test it directly using hydrogen isotopes, but possible to indirectly evaluate it using associated oxygen isotopes and total CO gas produced. Seligman and Bindeman (2019) experimented with dropping FeO, Fe₃O₄, and Fe-silicates together with water RMs in Ag caps to monitor CO gas extracted (i.e. they estimated influence on Fe oxides on degassing of O gas during reduction of Fe). They observed that Fe silicates (even Fe³⁺ bearing) produce little or no O₂ gas, while Fe oxides yielded some O gas. No iron was observed in a metal form during SEM investigation of extracted glass of variable composition as is expected for C-CO buffer conditions in the furnace.

5. Conclusions

Proposed reference materials for rhyolitic (UOR) and basaltic glasses (UOB) are largely homogeneous on small spatial scales and have reproducible bulk H₂O composition within and between laboratories. Hydrogen isotope compositions are also reproducible, although UOB has larger variations in measure δ²H likely owing to its high Fe content, which may cause the formation of iron oxyhydroxides during reduction. We recommend the following values for these reference glasses:

UOR rhyolitic glass:

H₂O = 1.84 ± 0.06 wt%(1 s.d.), and δ²H = -115.5 ± 2.6‰(1 s.d.)

UOB basaltic glass:

H₂O = 0.37 ± 0.03 wt%(1 s.d.), and δ²H = -82.1 ± 5.7‰(1 s.d.)

Samples are available in 100 mg quantities upon request for a nominal fee. Users are encouraged to calibrate their existing standards relative to these ones or develop new standards for day-to-day use. Standards are available in 50–250 µm and 250–500 µm size fractions so the users can select their preferred size.

Declaration of Competing Interest

None.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2021.120486>.

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