

1 **Analysis of H₂O in silicate glass using attenuated total reflectance**
2 **(ATR) micro-FTIR spectroscopy**

3 **REVISION 1**

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ABSTRACT

24 We present a calibration for Attenuated Total Reflectance (ATR) micro-FTIR for
25 analysis of H₂O in hydrous glass. A Ge ATR accessory was used to measure evanescent
26 wave absorption by H₂O within hydrous rhyolite and other standards. Absorbance at
27 3450 cm⁻¹ (representing H₂O total or H₂O_t) and 1630 cm⁻¹ (molecular H₂O or H₂O_m)
28 showed high correlation with measured H₂O in the glasses as determined by transmission
29 FTIR spectroscopy and manometry. For rhyolite,

30
$$\text{Wt.}\% \text{H}_2\text{O} = 245(\pm 9) * A_{3450} - 0.22(\pm 0.03) \text{ and}$$

31
$$\text{Wt.}\% \text{H}_2\text{O}_m = 235(\pm 11) * A_{1630} - 0.20(\pm 0.03)$$

32 where A_{3450} and A_{1630} represent the ATR absorption at the relevant infrared wavelengths.
33 The calibration permits determination of volatiles in singly polished glass samples with
34 spot size down to ~5 μm (for H₂O-rich samples) and detection limits of ~0.1 wt.% H₂O.
35 Basaltic, basaltic andesite and dacitic glasses of known H₂O concentrations fall along a
36 density-adjusted calibration, indicating that ATR is relatively insensitive to glass
37 composition, at least for calc-alkaline glasses. The following equation allows
38 quantification of H₂O in silicate glasses that range in composition from basalt to rhyolite.

39
$$\text{Wt.}\% \text{H}_2\text{O} = (\omega * A_{3450} / \rho) + b$$

40 where $\omega = 550 \pm 21$, $b = -0.19 \pm 0.03$, ρ = density, in g cm⁻³ and A_{3450} is the ATR
41 absorbance at 3450 cm⁻¹.

42 The ATR micro-FTIR technique is less sensitive than transmission FTIR, but
43 requires only a singly polished sample for quantitative results, thus minimizing time for
44 sample preparation. Compared with specular reflectance, it is more sensitive and better

45 suited for imaging of H₂O variations in heterogeneous samples such as melt inclusions.
46 One drawback is that the technique can damage fragile samples and we therefore
47 recommend mounting of unknowns in epoxy prior to polishing. Our calibration should
48 hold for any Ge ATR crystals with the same incident angle (31°). Use of a different
49 crystal type or geometry would require measurement of several H₂O-bearing standards to
50 provide a crystal-specific calibration.

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56 Key words: IR Spectroscopy, Glass Properties, FTIR, Water, New Technique,
57 Igneous Petrology, ATR, Glass

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INTRODUCTION

63 Numerous methods have been used to quantify H₂O concentrations in natural and
64 experimental silicate glass. Traditional approaches include manometry, loss-on-ignition,
65 and Karl-Fischer titration (as applied to geologic materials by Newman et al., 1986;
66 Westrich, 1987). They are destructive techniques, require large sample size (>100 mg),
67 and are less frequently used in recent years. Later came the development of transmission
68 FTIR spectroscopy (Stolper 1982), a non-destructive and highly reproducible technique
69 that requires calibration to account for variations in the host compositions and preparation
70 of polished wafers of known thickness (Newman et al., 1986; Zhang et al., 1997; Zhang
71 1999). Though the technique remains popular, the difficulty of preparing doubly
72 polished wafers of very small samples such as silicate melt inclusions (MI) has caused
73 many workers to explore other methods for analysis of microscopic glassy samples.

74 Specular reflectance (SR-FTIR) has been successfully used to quantify H₂O in
75 polished glasses (Hervig et al., 2003; King et al., 2004a,b; King and Larsen, in press).
76 The SR technique is less sensitive than transmission FTIR, requiring a larger analysis
77 area to ensure adequate signal, and is challenging for small glass samples such as MI
78 (Hervig et al., 2003; Nichols and Wysoczanski, 2007); nevertheless, SR-FTIR requires
79 only a singly polished sample. The ion microprobe (Hauri et al., 2002) is increasingly
80 popular, but is expensive and requires careful calibration to account for sample matrix
81 effects and high instrumental backgrounds of volatile species (Wright et al., 2012). Laser
82 raman methods have also been successfully developed (Thomas, 2000; Thomas et al.
83 2008) and are increasingly popular, but require relatively sophisticated post-processing
84 (Mercier et al., 2010; LeLosq et al., 2012) and can be subject to sample fluorescence

85 (Zajacz et al., 2005). All these techniques can be used successfully, and the best
86 technique often times will be that which is most accessible and cost effective.

87 This paper describes an alternative FTIR-based technique, attenuated total
88 reflectance (ATR) analysis for H₂O in hydrous glass and compares the technique with
89 SR. The ATR micro-FTIR method utilizes a crystal with high refractive index (an
90 internal reflection element) through which light is passed. When the crystal contacts a
91 sample with lower refractive index, a small amount of light, or evanescent wave, is
92 absorbed at the contact surface (Compton and Compton, 1993). The depth of penetration
93 of light within the sample is typically less than 1-2 μm , and is a function of the refractive
94 indices of the sample and crystal, the angle of incidence inherent to the ATR crystal (Θ),
95 and the specific wavelength of incident light. Magnification (4X) within the ATR crystal
96 permits spatial resolution $< 5 \mu\text{m}$. Most modern FTIR imaging microscopes have a
97 mountable ATR crystal as a relatively inexpensive accessory. Though the technique has
98 been in use for decades to investigate organic compounds, it only rarely has been applied
99 to the study of hydrous glass (e.g., Uchino et al., 1989), and has never been used
100 quantitatively for this purpose.

101 Below we describe methods to use ATR to quantify H₂O concentration in hydrous
102 glass. We find that ATR micro-FTIR is a reliable method to obtain H₂O concentrations in
103 hydrous glasses prepared in epoxy mounts intended for other micro-analytical techniques.
104 The method can be applied successfully to melt inclusions (MI) as small as 15 μm across,
105 and is ideal for rapid mapping of H₂O distributions in heterogeneous materials. Our
106 results indicate that the calibration curve developed for hydrous rhyolites also applies to
107 dacitic, basaltic andesite and basaltic glasses.

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METHODS

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111 **Sample Preparation**

112 Glass chips were prepared first as doubly-polished wafers with parallel sides.

113 Final polishing was done with 0.3 μm Al_2O_3 or 0.1 μm diamond grit. Sample

114 smoothness was comparable to a typical electron-microprobe mount. After transmission

115 FTIR analysis, most free-standing glass chips were then attached to a glass slide with

116 CrystalBondTM for ATR and SR analyses. Others were mounted in a 1-inch epoxy mount

117 and re-polished. A few glass samples were analyzed while remaining embedded in

118 Indium mounts intended for ion microprobe analysis.

119

120 **Transmission FTIR**

121 H_2O concentrations for glass chips were determined by transmission FTIR using

122 established calibrations (Newman et al., 1986; Zhang et al., 1997). Hydrous glass chips

123 from a variety of sources and publications (see Supplementary Methods and

124 Supplementary Table 1) and quartz-hosted melt inclusions were prepared as doubly

125 polished wafers for analysis with a Nicolet iN10 MX infrared imaging microscope with

126 an attached liquid- N_2 -cooled MCT-B detector at the USGS in Menlo Park, CA USA.

127 The iN10 MX is normally purged with low- CO_2 , dry air and is equipped with a collar

128 that, for transmission experiments, can be lowered around the sample stage to maximize

129 purge during sample and reference collection. Samples were placed on a BaF_2 window

130 transparent to both visible and infrared light. The sample surface was brought into focus

131 with reflected light prior to collection of the sample spectrum (S). A reference spectrum
132 (R) was collected through the BaF₂ window away from the hydrous glass sample. We
133 collected sufficient scans to minimize noise (usually 256) at 4 cm⁻¹ resolution. A square
134 aperture, typically sized to 150µm for experimental glass standards, was used to define
135 the precise area of analysis. For melt inclusions, we instead sized the aperture to ensure
136 that the light passed through only the inclusion (as small as 20µm). Measured absorbance
137 (A) was calculated by comparing the detected energy from light passed through the
138 sample compared with a reference spectrum without sample.

139

$$140 \quad A = \log (I_R/I_S) \quad \text{Eq. 1}$$

141

142 where I_R = the radiation transmitted in the reference spectrum and I_S = radiation
143 transmitted through the sample plus reference.

144 Data were collected between 6000 and 700 cm⁻¹. Peak heights at 5200 cm⁻¹
145 (A₅₂₀₀), 4500 cm⁻¹ (A₄₅₀₀), and 1630 (A₁₆₃₀) cm⁻¹ were measured relative to a flexicurve-
146 drawn baseline (Newman et al., 1986; Zhang et al., 1997; Ihinger et al., 1999; Figure 1 in
147 Zhang, 1999). For A₃₅₇₀, a straight baseline was more appropriate. The intensity of the
148 peaks were measured at their maximum height.

149 Concentrations were calculated with Beer's Law following Newman et al. (1986):

150

$$151 \quad \text{wt\% H}_2\text{O} = 1802A/(\epsilon d\rho) \quad \text{Eq. 2}$$

152 where ϵ = the extinction coefficient for the peak in $\text{L mol}\cdot\text{cm}^{-1}$, A is the absorption for the
153 peak of interest, ρ is the density in g L^{-1} , and d is the thickness of the doubly polished
154 sample in cm.

155 Total water (H_2O_t) was calculated with the method of Zhang et al. (1997) where
156 molecular water (H_2O_m) and hydroxyl (OH^-) are quantified by means of the two near-IR
157 (NIR) peaks at 5200 and 4500 cm^{-1} . The required ϵ values change as a function of total
158 H_2O content. For comparison, we also quantified H_2O_m and OH^- with ϵ values from the
159 earlier Newman-Stolper-Epstein (NSE) method that uses fixed ϵ values (Newman et al.
160 1986; Dobson et al. 1989), where $\epsilon_{1630} = 55 \pm 2$; $\epsilon_{3570} = 88 \pm 2$; $\epsilon_{4500} = 1.73 \pm 0.02$; $\epsilon_{5200} =$
161 1.61 ± 0.05 . Basaltic glasses were quantified with fixed ϵ calculated for A_{4500} ($\epsilon = 0.54$)
162 and A_{5200} ($\epsilon = 0.69$) calculated with equations from Dixon et al. (1995) using the basaltic
163 composition and density appropriate for the experimental basaltic glass (D. Blatter,
164 written communication, August 2012). Similarly, we used ϵ of A_{4500} ($\epsilon = 1.24$) and A_{5200}
165 ($\epsilon = 1.41$) for the dacite glasses based on Ohlhorst et al. (2001).

166 Wafer thicknesses were measured with three different techniques depending on
167 sample fragility and thickness: a) a digital pin micrometer, b) interference fringes at the
168 exact spot of analysis as measured with specular reflectance rather than transmission
169 (Wysoczanski and Tani, 2006), and c) a spindle stage mounted on a petrographic
170 microscope with a calibrated reticule. Comparison of thickness measurements made with
171 multiple techniques were typically within a few μm . Uncertainty varies depending on the
172 homogeneity of the wafer and the thickness. For rhyolites, glass densities were
173 calculated with equations in Zhang et al. (1997) assuming anhydrous rhyolite with a
174 density of 2350 g cm^{-3} . For the other compositions, densities were calculated based on

175 Lange and Carmichael (1987) and Ochs and Lange (1999). One-sigma uncertainties for
176 density are 0.02 g cm^{-3} .

177 With the exception of the seven samples measured directly by manometry [the
178 three rhyolite glasses from Newman et al. (1986; 1988) and the four basaltic andesites
179 (M. Mangan et al., in preparation)] all samples were re-analyzed by transmission FTIR
180 for this study and reported concentrations may vary somewhat from values in the original
181 references cited in the Supplementary Methods. Variations can result from a different
182 measured absorption, use of a different ϵ , or a slight variation in the density value used in
183 the calculation. The full data set is reported in Supplementary Table 2.

184

185 **Attenuated Total Reflectance FTIR**

186 We used a Ge crystal with a refractive index of 4.0 that comes as an optional
187 accessory for use with the iN10 MX. The angle of incidence is fixed at 31° and given the
188 index of refraction of natural rhyolitic glass (~ 1.5 ; Hodder, 1978), the incident beam
189 penetrates $0.33 \mu\text{m}$ into the sample at 3450 cm^{-1} and $0.69 \mu\text{m}$ at 1630 cm^{-1} (Compton and
190 Compton, 1993). The ATR crystal has a $350\mu\text{m}$ -diameter circular tip that makes contact
191 with the sample (Figure 1). An optical aperture of was used to define the initial beam
192 size; $100 \times 100 \mu\text{m}$ for hydrous glass chips, and 25 or $30 \mu\text{m}$ for melt inclusions depending
193 on the inclusion size. Because of the magnification within the ATR crystal, this
194 corresponds to a spot size of $25 \times 25 \mu\text{m}$ for the glass chips and $\sim 7 \times 7 \mu\text{m}$ for a typical melt
195 inclusion. A reference spectrum was collected in air after which the sample stage was
196 raised to contact the ATR crystal for sample collection.

197 Typically, 256 scans were collected for each sample with a spectral resolution of
198 8 cm^{-1} . Spectra were collected from 4000 to 1200 cm^{-1} with the same liquid- N_2 -cooled
199 MCT-B detector used for transmission FTIR, and spectra were processed and evaluated
200 as absorbance versus wavenumber. Peak heights in absorbance units were measured at
201 their maximum values near 3450 cm^{-1} (A_{3450}) and 1630 cm^{-1} (A_{1630}), utilizing a straight
202 baseline for 3450 cm^{-1} (Figure 2b) and a flexicurve for 1630 cm^{-1} .

203 Compared with transmission FTIR spectroscopy of hydrous glass, absorbance
204 intensities for a typical ATR spectrum are very low (compare total absorbance in Fig. 2a
205 versus 2c). As a result, atmospheric moisture and CO_2 represent a higher proportion of
206 the signal during both sample and reference spectra, and are therefore more difficult to
207 remove. When needed, peak height was measured after applying a correction to remove
208 interference from atmospheric water vapor, present especially near the 1630 cm^{-1} peak
209 (Figure 2a). The “atmosphere suppression” algorithm is a standard reprocess option in the
210 OMNIC Picta software package that comes with the iN10 MX. The correction aided
211 quantification on samples with low H_2O concentrations, but did not change A_{3450} or A_{1630}
212 peak height and could be performed reproducibly for multiple analyses of the same spot.
213 No other corrections or reprocessing were applied to the data. We also found that noise
214 associated with atmospheric water vapor could be minimized by collecting fewer
215 background and sample scans, and by using lower spectral resolution (16 cm^{-1}). This is
216 because the small measured ATR absorbances are strongly affected by minute variations
217 in atmospheric moisture, such that minimizing the time between sample and background
218 collection can be beneficial. Moreover, IR absorption by H_2O vapor is characterized by
219 much narrower peaks than H_2O dissolved in the glass, so that decreasing the spectral

220 resolution can eliminate the narrow vapor peaks while not affecting A_{3450} or A_{1630} . We
221 did not utilize a different purge gas (e.g., N_2) or a special shroud over the spectrometer to
222 decrease atmospheric gases, though as described below in the Discussion, such
223 techniques are also helpful.

224 Repeated analysis of sample chips confirmed that the chosen aperture size had no
225 effect on peak height for large samples of homogeneous glass (Supplementary Figure 1).
226 We also repeated the ATR measurement at multiple crystal–stage contact pressures and
227 determined a minimum pressure at which the peak height became fixed and reproducible
228 for silicate glass. Though the OMNIC Picta software does not report the actual contact
229 pressure, the relative pressure index was at the low end of the allowable range (setting of
230 12 within a range of 0-100).

231 Typically, spectra for five to ten spots were collected for each rhyolite glass chip.
232 Any rare analysis that was deemed an outlier ($\pm 4\sigma$) was attributed to be the result of a
233 surface impurity (i.e. a scratch or mineral inclusion) or poor surface-crystal contact, and
234 was discarded. The remaining ATR analyses were averaged.

235 Because the sample or aperture cannot be viewed with the ATR in contact with
236 the sample, placement of the ATR crystal on the sample is only approximate (within tens
237 of microns). For the analysis of melt inclusions, maps were collected with a small
238 aperture (8 to 15 μm spot). The stage moves a user-selectable distance, as little as 1 μm ,
239 to create a matrix of analyses, made up of pixels, each associated with a complete
240 spectrum. The maps were framed to ensure that inclusion-free quartz was sampled in the
241 outer pixels, but with a spot size small enough to ensure that the inclusion can be sampled
242 without any overlapping host phase (Figure 3). Between the analysis of each pixel, the

243 stage drops slightly ($\ll 1$ mm) and then moves the user-selected distance. The OMNIC
244 Picta software can automatically calculate baselines and peak heights to map out
245 variations in H₂O (i.e., A_{3450}) within the sampled region. Figure 3 demonstrates an ATR
246 map of a particularly large silicate melt inclusion, and illustrates how inclusions can be
247 mapped with very high spatial precision.

248

249 **Specular Reflectance FTIR**

250 We also quantified H₂O in rhyolitic glasses following the method of Hervig et al.
251 (2003) as clarified by King et al. (2004b). Reference spectra were collected on polished
252 gold. Multiple spectra were collected on each rhyolite chip after careful focusing on a flat
253 sample surface. Spectra were converted to “% reflectance” with the FTIR software. The
254 negative peak ΔR_{3500} and R_{4000} were determined for each sample spectrum and H₂O was
255 quantified via:

256

$$257 \text{ wt\% H}_2\text{O}_t = ((\Delta R_{3500}/R_{4000}) - k_2) / k_1 \quad \text{Eq. 3}$$

258

259 where k_2 and k_1 for rhyolite are 0.007 and 0.021, respectively (King et al., 2004b).

260 ΔR_{3500} is akin to a peak height at 3500 cm⁻¹ and R_{4000} represents the absolute %
261 reflectance at 4000 cm⁻¹. An example of a spectrum and measured ΔR_{3500} and R_{4000} is
262 shown in Supplementary Figure 2.

263

264 **RESULTS**

265 **Calibration of the ATR Micro-FTIR Technique**

266 H₂O concentrations were quantified by transmission FTIR for rhyolite chips from
267 7 samples. Each average analysis represents 3 to 8 separate spots for each chip. Table 1
268 reports means and calculated standard deviations (1 σ), as quantified with extinction
269 coefficients from Zhang (Zhang et al., 1997) and NSE (Newman et al., 1986). Three
270 additional rhyolite standards were obtained that had H₂O quantified by both manometry
271 and FTIR (Newman et al., 1986, 1988).

272 As shown in Figure 4, trends of wt% H₂O vs. A_{3450} (ATR) are linear, with R² of
273 0.99. For rhyolitic glass, total H₂O is predicted by the following equation:

274
$$\text{Wt.\% H}_2\text{O} = (\alpha * A_{3450}) + b \quad \text{Eq.4}$$

275 where α is a correction factor (essentially an inverse-absorption coefficient in units of
276 wt%), A_{3450} is the ATR peak height in absorbance units at $\sim 3450 \text{ cm}^{-1}$, and b is the x
277 intercept of the best fit in Figure 4a.

278 Three samples of dacite (Mangan, 2005) fall close to the rhyolite calibration.
279 Three samples of hydrous basaltic glass and four basaltic andesites plot noticeably above
280 the calibration curve (Figure 4a). However, when normalized by sample density, they
281 plot on top of the rhyolite calibration (Figure 4b). As such, the following equation can be
282 applied to basalts, rhyolite, dacites, andesites and potentially other hydrous glasses:

283

284
$$\text{Wt.\% H}_2\text{O} = (\omega * A_{3450} / \rho) + b \quad \text{Eq.5}$$

285

286 where ω is the density-normalized correction factor (in $\text{wt}\% \cdot \text{cm}^3 \text{g}^{-1}$), ρ is density in g
287 cm^{-3} and b is the x-intercept in wt%. Values of α , ω and b are listed in Table 2 for both
288 A_{3450} and A_{1630} .

289 Similar correlations for A_{1630} versus A_{5230} (Figure 5, Table 2) demonstrate that
290 H_2O_m can be estimated by ATR methods with the 1630 cm^{-1} peak. It is interesting to
291 note that the initial calibration (Figure 5a) appears slightly superior to the density-
292 corrected curve (Figure 5b) for the two basalt samples, such that it may be more accurate
293 to calculate H_2O_m for basalts with Eq. 4 than Eq. 5. We did not attempt to calculate A_{1630}
294 for the basaltic andesites due to the very large carbonate peaks in those particular
295 samples, which interfere with the shape of the background for the 1630 cm^{-1} peak.

296 Subtraction of H_2O_m from H_2O_t , as determined by ATR, allows calculation of
297 OH^- , such that ATR spectra can be used to assess speciation of H_2O within the glass.
298 Table 1 lists calculated OH^- for the rhyolite standards. Values for OH^- via transmission
299 FTIR (using A_{4500}) and ATR are comparable for the rhyolites (and dacites), with an R^2 of
300 0.94 (Supplementary Table 3).

301

302

DISCUSSION

303 The ATR micro-FTIR technique provides an accurate and reproducible means for
304 quantifying both H_2O_m and H_2O_t in hydrous rhyolite glasses. Usable spectra were
305 achieved for spot sizes down to $5\mu m$ on samples with only $\sim 1.5\%$ H_2O . Reproducibility
306 was excellent: for example, nine spectra on dacite F33 produced A_{3450} between 0.0145
307 and 0.0149, yielding variations $< 1.5\%$ around the mean of 0.0147.

308 Because samples were singly polished, the technique offers the capability of determining
309 H_2O concentrations in small pockets of experimental or natural hydrous glasses (i.e., melt
310 inclusions).

311 One drawback of the technique is the potential for cracking or otherwise
312 damaging fragile samples through direct contact of the ATR crystal with the sample
313 surface. Samples that were free-standing wafers or were affixed to glass slides with a
314 thin layer of adhesive were far more likely to be damaged than samples mounted in
315 epoxy. Our experience suggests that samples prepared in epoxy mounts will be ideal
316 candidates for ATR micro-FTIR spectroscopy. For particularly fragile samples, the SR
317 FTIR (Hervig et al., 2003; King and Larsen, 2013) is preferable.

318

319 **Detection limit for H_2O**

320 Both York (York, 1966) and traditional least-squares approaches did not produce
321 fits that passed exactly through the origin. Calculated b values (Table 2) are ~ 0.2 for both
322 A_{3450} and A_{1630} , as well as their density-normalized equivalents (Figs, 3, 4). The
323 prediction of the presence of a small A_{3450} peak even for nominally anhydrous samples
324 could be due to minimal adsorbed water on the outer nanometers of the polished glass

325 surface. The negative x intercept in Figure 4 and 5 also remained when considering only
326 the three samples with H₂O quantified manometrically. Peaks for A₃₄₅₀ were measurable
327 down to H₂O_t concentrations of ~0.13 wt.% (sample MT-3). The practical detection limit
328 of the technique for both H₂O_t and H₂O_m is approximately equal to 0.1 wt%.
329 Reproducible quantification will be difficult for samples with less than 0.2 wt% H₂O.

330

331 **Comparison of ATR with specular reflection**

332 Specular reflectance and ATR can be used to determine H₂O concentrations in
333 singly polished hydrous glass and provide similar results (Table 1). Because sample
334 preparation is facilitated and thickness measurement is unnecessary, both techniques
335 offer significant advantages compared with transmission spectroscopy. Both have similar
336 detection limits and accuracy.

337 One advantage of specular reflectance compared with ATR is the simple analysis
338 setup, which does not require a “plug-in” accessory for the microscope and is less likely
339 to have any lab-to-lab variations due to accessory type or geometry. Moreover, there is
340 no need to touch the sample with a crystal, so that there is no possibility of damaging the
341 hydrous glass sample.

342 ATR, however, does offer some advantages in quantification and reproducibility
343 relative to specular reflectance. First, it yields better sensitivity for a given optical
344 aperture size, especially < 20µm. Moreover, because the ATR spot size is 25% of the
345 aperture diameter, much higher spatial resolution can be achieved. The uncertainty on the
346 ATR analysis is generally less than that for the more complex reflectance analysis. We
347 demonstrated this by analyzing the same sample (IDDP-1) with both methods using a

348 small optical aperture (25x25 μ m). Propagating the uncertainties for peak measurement
349 with specular reflectance results in a relative error of ~55% for an individual spot,
350 relative to an uncertainty of 20% for the same ATR analysis taken with the same number
351 of scans. Moreover, the actual spot size on the sample with ATR is ~6 x 6 μ m, whereas
352 the spot with specular reflectance is the same as the 25 x 25 μ m optical aperture.

353 Also, whereas ATR measures the absorbance solely at the surface of a sample,
354 specular reflectance can be affected by internal reflectance when the incident beam
355 penetrates the sample and bounces off a polished surface or mineral inclusion. For
356 example, when analyzing a singly polished rhyolite glass chip from Iceland (IDDP-1_6),
357 internal reflections caused by cracks and mineral grains were observed with a reflected
358 light microscope. Analysis of such spots can yield apparent concentrations up to double
359 the true concentration. When using specular reflectance, it is important to avoid analysis
360 of doubly polished samples or ones with potential surfaces for additional reflection back
361 to the detector. King and Larsen, (in press) evaluate this problem and provide tips for
362 eliminating internal reflections.

363 Finally, the reflective method (Hervig et al., 2003; King et al., 2004), requires the
364 identification of 3 points along the spectrum (R_{upper} , R_{lower} , and R_{4000}), none of which are
365 associated with a clear peak and associated baseline (Supplementary Figure 2). The ATR
366 method requires only measurement of a single peak height (A_{3450}), making it trivial to
367 program the FTIR software to instantaneously create a profile map (e.g., Figure 3c,d) that
368 directly reflects H₂O concentration of all pixels within a given map (see Della Ventura et
369 al., 2010 for examples of maps made in transmission mode). Such a map would be
370 difficult if not impossible using specular reflectance, at least as an automated product at

371 the time of analysis. A new method (King and Larson, 2013) for obtaining specular
372 reflectance spectra utilizes a Kramers-Kronig transformation that may allow easier
373 automated processing than the method evaluated herein (Hervig et al. 2003).

374 Overall, quantification of H₂O concentrations with the ATR technique is simpler
375 than specular reflectance, more reproducible, more composition-independent, and more
376 suited for imaging of H₂O variations in large areas. Its primary drawbacks are the
377 additional cost of the ATR accessory and the potential for damaging fragile samples.

378

379 **Applications to the study of melt inclusions**

380 ATR techniques offer many potential advantages for the study of silicate melt
381 inclusions. Though it was not a focus of this paper to analyze melt inclusions, Figure 4,
382 shows data from six rhyolitic MI along with the glass standards and calibration curves.
383 Four of the six overlap the calibration (within 2 σ).

384 Heterogeneity of singly polished inclusions can be assessed at spatial scales down
385 to 5 μm through modern FTIR mapping systems. Such maps (Figure 3) are easy to
386 interpret since they are not affected by inclusion thickness or inclusion geometry (curved
387 walls), as is the case for a map created in transmission FTIR. Moreover, the
388 magnification within the ATR crystal permits higher spatial resolution than is obtained
389 with transmission FTIR or a typical ion microprobe. In Figure 3e, a traverse of the
390 inclusion is displayed, and it is evident that the spot size was reduced to a diameter where
391 overlap between the inclusion and host was limited to only a single pixel with stage steps
392 of 8 μm . Even better resolution is possible. It may be possible to use this technique to

393 identify diffusion-related gradients in melt inclusions, volcanic ejecta, and experimental
394 products, especially if a synchrotron source is utilized (Castro et al., 2008).

395 One drawback of any reflection technique is its relative insensitivity to the
396 inevitable low concentrations (<1000 ppm) of CO₂. Currently, we are evaluating the
397 detection threshold for CO₂ in both basaltic and rhyolitic glasses (Lowenstern et al., in
398 preparation). But even without ATR data for CO₂, ATR spectra for H₂O can be
399 combined with transmission data on singly polished inclusions to quantify both H₂O and
400 CO₂. For example, an inclusion-bearing phenocryst can be prepared as a doubly polished
401 wafer, with one side intersecting the inclusion and the other simply a polished surface of
402 the host crystal. A reflectance spectrum can be collected on the side with the exposed
403 inclusion. Collection of a complementary transmission spectrum obtains a usable peak for
404 CO₂ or carbonate and aids calculation of the glass inclusion thickness. Assuming
405 homogeneous H₂O within the sample, a value for which was determined through the
406 reflectance analysis, d (the thickness of host-free inclusion) can be solved through
407 rearranging Eq. 2 and inserting either A_{3570} or A_{5200} plus A_{4500} . Finally, the new
408 calculated thickness of silicate glass can be inserted to Beer's Law to solve for CO₂,
409 using appropriate ϵ values for CO₂ (e.g., Blank et al., 1993).

410 Nichols and Wysoczanski (2007) provided a similar method whereby spectral
411 peaks from olivine were used to calculate the percentage of host mineral in transmission
412 spectra of unexposed MI. Yet another technique was assessed by Befus et al. (2012)
413 where MI thicknesses in unexposed inclusions were estimated from the mean diameters
414 of the inclusions as measured in cross section. Though we have not directly compared
415 our proposed method to the other two, we expect that direct reflectance measurement

416 with ATR- or SR-FTIR combined with transmission FTIR will be a labor-saving and
417 highly quantitative method for measurement of CO₂ and H₂O in silicate melt inclusions.

418

419 **Tips for Sample Preparation**

420 The most critical aspect of obtaining quality ATR spectra of silicate glass is the
421 contact between the ATR crystal and the sample. To ensure proper contact, we
422 recommend the following steps. First, the sample surface should be as horizontal as
423 possible, with minimal slope or surface topography. It is helpful to mount one or
424 multiple samples in epoxy, such that one creates a broad uniformly polished surface.
425 Grains mounted and polished individually may not provide as successful of an ATR
426 spectrum. On the other hand, a few visible scratches on the sample surface will not
427 adversely affect the analysis (e.g., Figure 3). Next, the sample mount should be fixed to
428 the sample stage so that impact of the ATR accessory does not cause the sample to move.
429 For example, an epoxy mount can be affixed with double-stick tape. If the sample
430 moves, or the ATR crystal is otherwise unable to make firm contact, the resulting
431 spectrum will yield low and irregular absorbance intensities. By collecting data on
432 multiple spots, it is relatively straightforward to assess whether the sample geometry has
433 been optimized. Another common problem occurs when the ATR accessory is not
434 inserted fully into its fittings. Usually, this latter problem will be evident in an
435 anomalous shape for the reference spectrum (air), as well as for the sample spectrum.

436

437 **Improving signal/noise and elimination of signals from atmosphere**

438 Ideal spectral peaks for ATR spectroscopy are those that are highly absorbing and
439 difficult to use in transmission FTIR. For example, in Figure 2, the transmission
440 spectrum for a 74- μm -thick glass wafer is over-saturated at A_{3570} , with an absorbance >
441 2.0 (i.e., < 1% of the initial light is transmitted through the sample). This truncated peak
442 cannot be used for quantitative analysis and the sample must be further thinned to allow
443 for collection of a usable spectrum. In contrast, the ATR spectrum has A_{3450} of ~ 0.02 ,
444 regardless of sample thickness. For samples with less than 1% H_2O , A_{3450} becomes very
445 small and it becomes increasingly important to reduce noise to achieve good spectral
446 quality. Though increasing the number of averaged sampled scans is the typical
447 procedure for increasing signal to noise in FTIR spectroscopy, it is of less importance
448 here than removing the effects of atmospheric H_2O vapor and CO_2 , which have
449 considerably greater influence on the small peaks obtained in ATR FTIR compared with
450 transmission spectra. Moreover, placement of the ATR accessory prevents utilization of
451 the purge collar used for transmission and specular reflectance experiments, making it
452 more difficult to exclude atmosphere from the sample area.

453 As discussed above, we commonly reduced spectral resolution to 16 cm^{-1} and
454 decreased sampling time to minimize variations in background water vapor in the room.
455 Alternatively, we found we could post-process with the atmospheric-correction algorithm
456 available through the Omnic software. Though this post-processing is successful for
457 removing water-vapor fringes on A_{3450} and A_{1630} , it also precludes any attempt at
458 quantification of CO_2 . Therefore, we also experimented with placing a shroud over the

459 sample-stage to minimize circulation of external atmosphere near the ATR assembly.
460 With the shroud, we used both our normal dry-air, low-CO₂, purge (CO₂ measured at ~
461 5ppm) and purified-N₂ (< 1 ppm CO₂) from a pressurized tank. We found that the shroud
462 significantly decreased the effect of H₂O vapor, and that the N₂-purge also allowed us to
463 clearly identify the CO₂-peak (2350 cm⁻¹) in some samples. We are currently working to
464 calibrate the ATR-FTIR for analysis of CO₂ in both basaltic and rhyolitic glass
465 (Lowenstern et al., in preparation). Regardless of the quality of the purge, it seems
466 unlikely that usable spectra can be obtained for the weak-absorbing near-IR H₂O peaks at
467 5200 and 4500 cm⁻¹, which will be much too small for quantification.

468

469 **Interlaboratory Comparison and Caveats**

470 Use of the α , ω and b values in Table 2 are likely to be valid as long as the ATR
471 crystal is similar to that used in the present study (Ge with $\Theta = 31^\circ$). When using
472 different ATR crystal types or Ge crystals with a different geometry, calibration values
473 for H₂O could vary from those cited herein. Workers seeking to use ATR micro-FTIR
474 techniques to quantify H₂O in hydrous glasses are recommended to verify our calibration
475 values in Table 2 with several standard glasses. We also recommend against using our
476 values of α , ω and b for alkali-rich samples such as phonolite or nephelinite until it can
477 be verified that those compositions also fall upon this calibration.

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FINAL THOUGHTS

482

483 ATR micro-FTIR is an easy-to-use, easy-to-quantify technique that can be applied toward

484 the study of experimental glasses, obsidians, and melt inclusions. It is best-suited toward

485 samples prepared in epoxy mounts. As with transmission FTIR, reproducibility is

486 excellent and typically ~1% for a given spot, provided that the sample is flat and the ATR

487 crystal makes complete contact. For the compositions studied (calc-alkaline basalts

488 through dacites and rhyolites), a single standardization permits quantification of H₂O,

489 provided that the sample density can be estimated. High-resolution maps of H₂O

490 concentrations within natural and experimental samples can be obtained with spot size

491 down to ~ 5µm. When combined with brighter infrared sources such as synchrotron

492 FTIR (Guilhaumou et al., 2005; Castro et al. 2008), the ATR should be an extremely

493 powerful technique for mapping H₂O variations in natural and experimental samples.

494 There are numerous options for quantitative analysis of H₂O in silicate glass. None are

495 clearly superior in all aspects, and we expect that users will make their preferred

496 analytical choice based on a combination of availability, cost, and the logistics of sample

497 preparation and analysis.

498

499

500

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FIGURE CAPTIONS

625 FIGURE 1. Schematic cross-sectional diagram of the ATR setup. The Ge ATR crystal
626 makes contact with the sample along a 350- μm -diameter spherical interface.
627 Magnification within the crystal provides a spot on the sample that is 4X smaller than
628 the size of the initial optical aperture. Thus, a 40x40 μm beam will sample a 10x10
629 μm area on the sample surface. With the 31° incident angle and Ge crystal, the depth
630 of penetration of the evanescent wave into rhyolite glass is < 1 μm at relevant
631 wavelengths.

632

633 FIGURE 2. Wavenumber vs. absorbance for FTIR spectra of hydrous rhyolite #51 (4.4 wt.
634 % H₂O; Table 1). **(a)** Original spectrum prior to correction. Note negative CO₂
635 doublet ~2350 cm⁻¹ due to slightly higher CO₂ in the reference spectrum and
636 associated abundant H₂O-vapor spikes from 1500 to 1900 cm⁻¹. **(b)** Atmosphere-
637 corrected spectrum from ATR. Dissolved H₂O in the hydrous glass can be quantified
638 through measurement of the height of the peaks at 3450 cm⁻¹ (e.g., A₃₄₅₀) and 1630
639 cm⁻¹, after drawing appropriate baselines. **(c)** Transmission spectrum for a doubly
640 polished wafer of the same sample shows abundant H₂O and dissolved CO₂ (singlet)
641 and far higher absorbances than are achieved with ATR. In this spectrum the peak at
642 3500 cm⁻¹ is truncated due to very high water concentrations and/or excessive
643 thickness and cannot be used to quantify dissolved H₂O.

644

645 FIGURE 3. ATR-generated map of a melt inclusion in quartz (AK48-10 with H₂O_t = 3.5
646 wt.%) from the 1912 eruption at the Valley of Ten Thousand Smokes. **(a)** Reflected

647 light image of melt inclusion in quartz. Some scratches are evident on the sample
648 surface. **(b)** Clarification of outline of melt inclusion in **a**. The letters f, g, and h,
649 represent the figure parts depicting spectra for those regions. The associated pink
650 squares show the approximate spot size of 10 μ m. **(c)** Unsmoothed map depicting A_{3450}
651 of area shown in **a** and **b**. The map is an array of 47x34 pixels, each 8 μ m on a side,
652 each representing a separate analysis; i.e., the stage moves 8 μ m in between analyses.
653 The spot size (10 μ m) is slightly larger than the pixel. Each spectrum averages 8
654 scans, collected in < 1 second. **(d)** Same as **c** but with a spline smoothed representation
655 of the data. Height of A_{3450} and wt.% H₂O_t is shown in color bar pertains to both **c** and
656 **d**. **(e)** Transect from A to B (shown in **c**) that depicts consistency of A_{3450} within the
657 inclusion and the excellent spatial resolution such that only one pixel at the inclusion
658 edge is a mixed spectrum of glass and quartz. The inclusion contains an apparently
659 homogenous glass with ~3.5 wt.% H₂O. **(f)** Representative spectrum of quartz. Each
660 spectrum is the average of 8 scans at 16 cm⁻¹ spectral resolution. **(g)** Spectrum of pixel
661 within glass/melt inclusion. **(h)** Spectrum of pixel at boundary of melt inclusion, thus
662 incorporating absorbance-related peaks from both quartz and glass.

663

664 FIGURE 4. Calibration curves for ATR spectra. All data and errors from Table 1. **(a)** ATR
665 peak height at 3450 cm⁻¹ (A_{3450}) versus H₂O concentration as determined by
666 transmission spectroscopy (Zhang et al., 1997). The best-fit line is based on the
667 rhyolite standards alone and accommodates errors in both variables (York, 1966). **(b)**
668 Normalization for density allows a single correction factor (ω) to accommodate
669 compositions from rhyolite to basaltic glass.

670

671 FIGURE 5. Calibration curves for ATR spectra. All data and errors from Table 1 except for
672 H_2O_m for the three samples from Mono Craters (Newman et al., 1986, 1988). **(a)** ATR
673 peak height at 1630 cm^{-1} (A_{1630}) versus H_2O_m concentration as determined by
674 transmission spectroscopy at 5200 cm^{-1} (Zhang et al., 1997). The best fit is based on
675 the rhyolite standards alone and accommodates errors in both variables (York, 1966).
676 Symbols as in Figure 4. **(b)** Same plot normalized for density. As with A_{3450} , the
677 calibration applies to a variety of natural glass compositions.

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Table 1. FTIR peak heights, calculated concentrations, and associated errors (one sigma) using transmission, ATR and SR techniques.

Sample	Comp*	Type**	Density g/cc	Peakst	Transmission FTIR				ATR-FTIR			Specular Reflectance			
					H ₂ O _m wt% (Zhang)	OH wt% (Zhang)	H ₂ O _t wt% (Zhang)	H ₂ O _t wt% (fixed e)	A ₃₄₅₀	A ₁₆₃₀	wt% H ₂ O _t from A ₃₄₅₀ [§]	wt% H ₂ O _t from A ₁₆₃₀ [§]	wt% OH ⁻ by difference [§]	DR ₃₅₀₀ /R ₄₀₀₀	‡H ₂ O wt%
MT3	Rhy.	Chip	2.35	MID				0.133 (7)	0.0025 (3)	0.0018 (2)	0.39 (8)	0.21 (4)	0.19 (13)	0.0064	0.0 (1)
C10D2	Rhy.	Chip	2.33	NIR				0.69 (7)	0.0057 (8)	0.0020 (3)	1.15 (20)	0.29 (7)	0.86 (27)	0.0199	0.59 (12)
IDDP	Rhy.	Chip	2.31	NIR				1.77 (20)	0.0090(13)	0.0044 (7)	1.94 (33)	0.81 (15)	1.13 (48)	0.0395	1.49 (26)
88YS7_3	Rhy.	Chip	2.27	NIR				3.29 (25)	0.0125 (5)	0.0112 (3)	2.84 (18)	2.39 (14)	0.46 (32)		
EXP2170	Rhy.	Chip	2.21	NIR				7.15 (42)	0.0262 (2)	0.0209 (1)	6.34 (28)	4.77 (23)	1.57 (51)	0.1683	7.62 (18)
EXP51	Rhy.	Chip	2.25	NIR				4.72 (38)	0.0195 (9)	0.0132 (2)	4.57 (40)	2.9 (17)	1.67 (57)	0.1232	5.49 (25)
EXP54	Rhy.	Chip	2.30	NIR				2.07 (33)	0.0094 (3)	0.0035 (1)	2.07 (13)	0.62 (5)	1.45 (18)	0.0580	2.40 (2)
N. Coulee	Rhy.	Chip	2.34	MAN	0.271 (2)				0.0020 (1)	0.0009 (1)	0.28 (5)	0.01 (2)	0.26 (7)		
MC84-df	Rhy.	Chip	2.35	MAN	0.696 (4)				0.0036 (3)	0.0015 (1)	0.65 (8)	0.14 (3)	0.51 (12)		
MC84-t	Rhy.	Chip	2.33	MAN	0.779 (5)				0.0040 (2)	0.0020 (1)	0.76 (8)	0.25 (3)	0.51 (12)		
SB872-4	Bas.	Chip	2.73	NIR				4.66 (40)	0.0229 (7)	0.0084 (3)	4.42 (25)	1.43 (11)	2.99 (35)	0.0737	3.87 (7)
SB872-3	Bas.	Chip	2.81	NIR				1.95 (18)	0.0124 (4)	0.0023 (3)	2.24 (15)	0.24 (5)	2.00 (19)	0.0272	1.55 (4)
SB2329	Bas.	Chip	2.84	NIR				1.05 (10)	0.0094 (6)		1.63 (15)			0.0165	1.02 (6)
88YS7_MI_2	Rhy.	MI	2.27	NIR				3.80 (28)	0.0149 (1)	0.0133 (1)	3.43 (16)	2.89 (15)	0.53 (31)		
88YS7_MI_3	Rhy.	MI	2.27	NIR				3.85 (27)	0.0143 (1)	0.0117 (2)	3.27 (16)	2.52 (14)	0.75 (30)		
PGAF40	Rhy.	MI	2.19	NIR				8.05 (53)	0.0212 (1)	0.0230 (1)	5.13 (23)	5.31 (26)	-0.18 (48)		
PGAF_MI_2	Rhy.	MI	2.19	NIR				7.90 (57)	0.0243 (6)	0.0176 (4)	5.90 (30)	4.02 (22)	1.88 (51)		
LAS1842-3	Rhy.	MI	2.25	NIR				4.68 (24)	0.0163 (2)	0.0122 (2)	3.79 (19)	2.66 (15)	1.14 (34)		
LAS1842-4	Rhy.	MI	2.31	NIR				1.66 (8)	0.0076 (1)	0.0067 (1)	1.61 (10)	1.33 (8)	0.28 (19)		
BA2065	BasAnd.	Chip	2.62	MAN	2.8 (1)				0.0138 (6)		2.70 (18)				
BA2066	BasAnd.	Chip	2.63	MAN	2.5 (1)				0.0143 (5)		2.79 (18)				
BA2068	BasAnd.	Chip	2.59	MAN	3.9 (1)				0.0212 (5)		4.31 (22)				
BA2070	BasAnd.	Chip	2.59	MAN	3.9 (1)				0.0216 (2)		4.40 (20)				
F14	Dac.	Chip	2.45	NIR				1.11 (7)	0.0061 (3)	0.0016 (1)	1.17 (11)	0.15 (3)	1.02 (14)		
F33	Dac.	Chip	2.38	NIR				3.49 (19)	0.0147 (1)	0.0088 (2)	3.21 (16)	1.74 (10)	1.47 (26)		
F40	Dac.	Chip	2.40	NIR				2.71 (15)	0.0136 (2)	0.0075 (2)	2.93 (15)	1.44 (10)	1.49 (24)		

Note: Sample provenance, chemistry, and references provided in Supplementary Methods and Supplementary Table 1.

*Composition: Rhy. = Rhyolite; Bas. = Basalt; BasAnd. = Basaltic Andesite; Dac. = Dacite

**Type: Chip (doubly polished wafer of hydrated experimental or natural glass) or MI (doubly polished melt inclusion)

†MID = NSE using 3570 peak, NIR uses 5200 and 4500 peaks, MAN = manometry

‡Calculated with Eq. 3 and K1 and K2 for rhyolite (and andesite for SB samples) from King et al. (2004b)

§Calculated with Eq. 5 and coefficients in Table 2 (OH⁻ calculated by difference of H₂O_t and H₂O_m).

Table 2. ATR correction factors derived from measured standards.

Peak	Equation 4 Correction Factor			Equation 5 Density-normalized correction factor		
	<i>a</i>	<i>b</i>	R ²	ρ	<i>b</i>	R ²
<i>A</i> ₃₄₅₀	245 ± 9	-0.22 ± 0.03	0.99	550 ± 21	-0.19 ± 0.03	0.99
<i>A</i> ₁₆₃₀	235 ± 11	-0.20 ± 0.02	0.99	525 ± 23	-0.19 ± .02	0.99









