Species Specific Molar Absorptivity Coefficients for the total water peak (3500 cm^{-1}) determined by the data of Allison et al. 2019 and Shishkina et al. 2010.
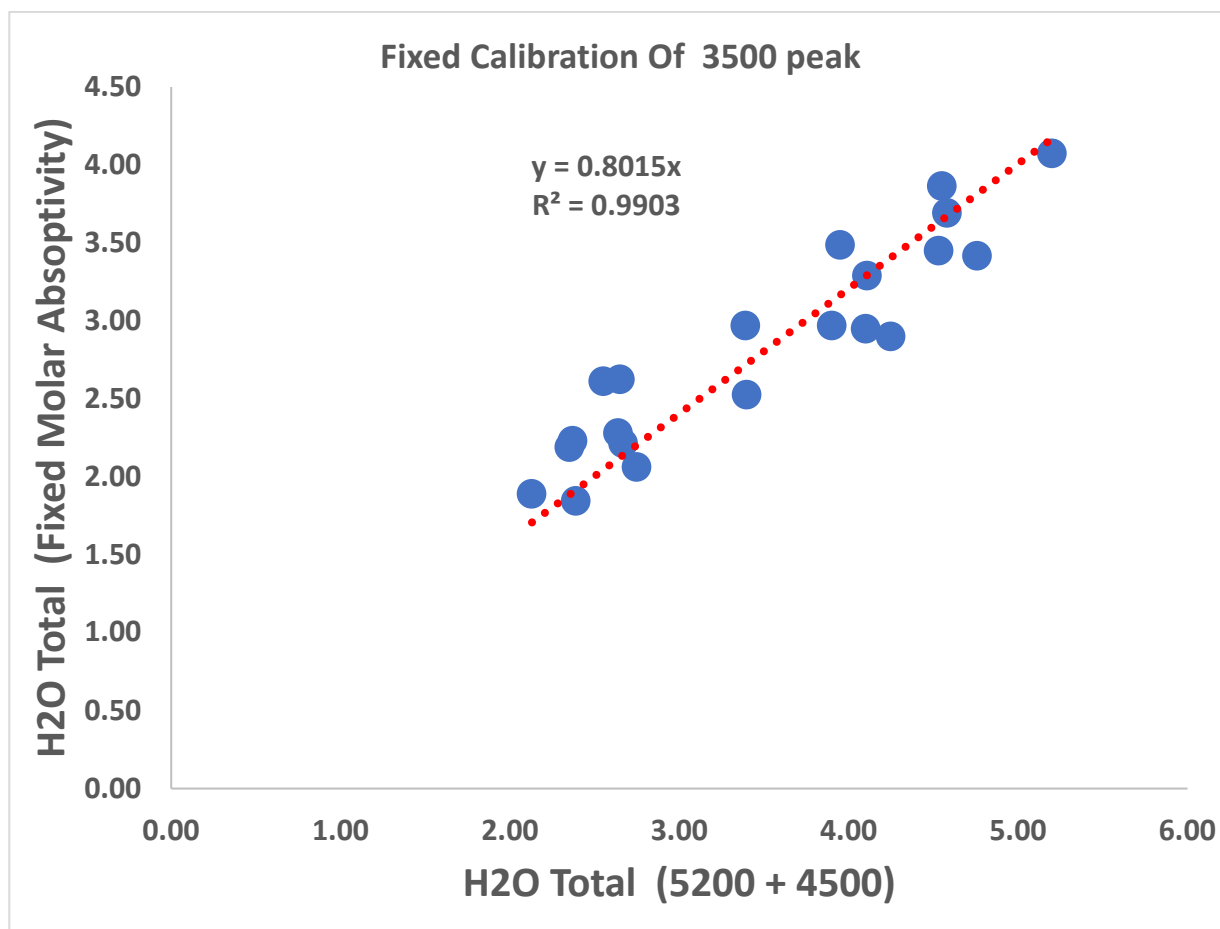

Fixed Calibration Of 3500 peak

y = 0.8015x
R^2 = 0.9903

*Figure 1 Water reported in wt% as calculated from near-IR peaks (5200 cm^{-1} and 4500 cm^{-1}) and the total water peak (3500 cm^{-1}). Molar absorptivity coefficients are from Dixon et al. 1995 (**5200 cm^{-1}: 0.62 mol^{-1} cm^{-1}, 4500 cm^{-1}: 0.67 mol^{-1} cm^{-1}**) and Dixon et al. 1988 (**3500 cm^{-1}: 63 mol^{-1} cm^{-1}**). These are all similar to the coefficients of Shishkina et al. (2010) and Fiege et al. (2015) for the relevant compositions. The concentrations calculated by the two methods differ by 20%. This leads to the conclusion that either the NIR coefficients are generally too low and should be 20% higher or the coefficient for the 3500 cm^{-1} peak should be 20% lower.*
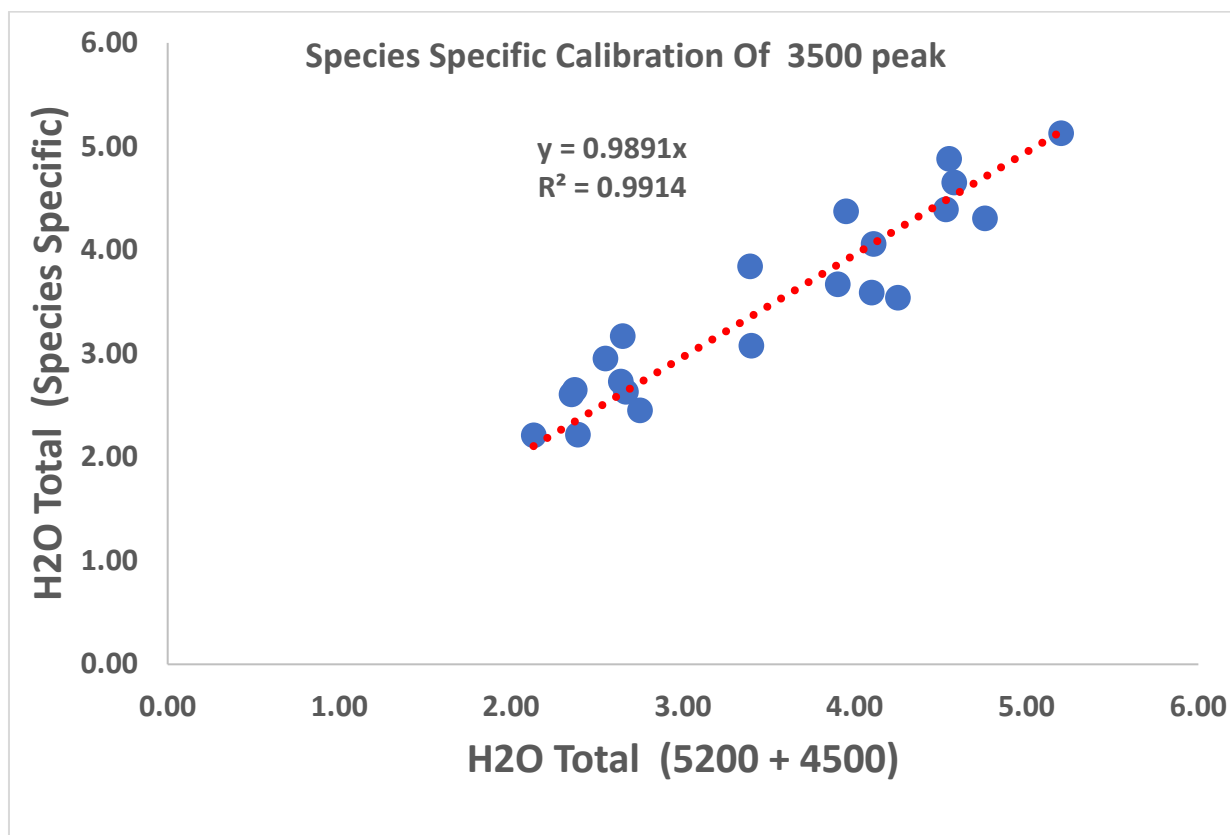
Figure 2 Water reported in wt% as calculated from near-IR peaks (5200 cm^{-1} and 4500 cm^{-1}) and water concentrations determined from species specific molar absorptivity coefficients for the total peak (3500 cm^{-1}). The height of the 3500 cm^{-1} peak was divided into species specific assignments proportionally to the concentration of H_2O and OH^- determined from the near-IR peaks. Species specific molar absorptivity coefficients were determined by minimizing the sum of the squared residuals for total water concentrations calculated from the near-IR peaks and the 3500 cm^{-1} peak. The best fit value are (3500 cm^{-1} H_2O species: **43 mol^{-1} cm^{-1}; 3500 cm^{-1} OH$^-$ species: 57 mol^{-1} cm^{-1}**).
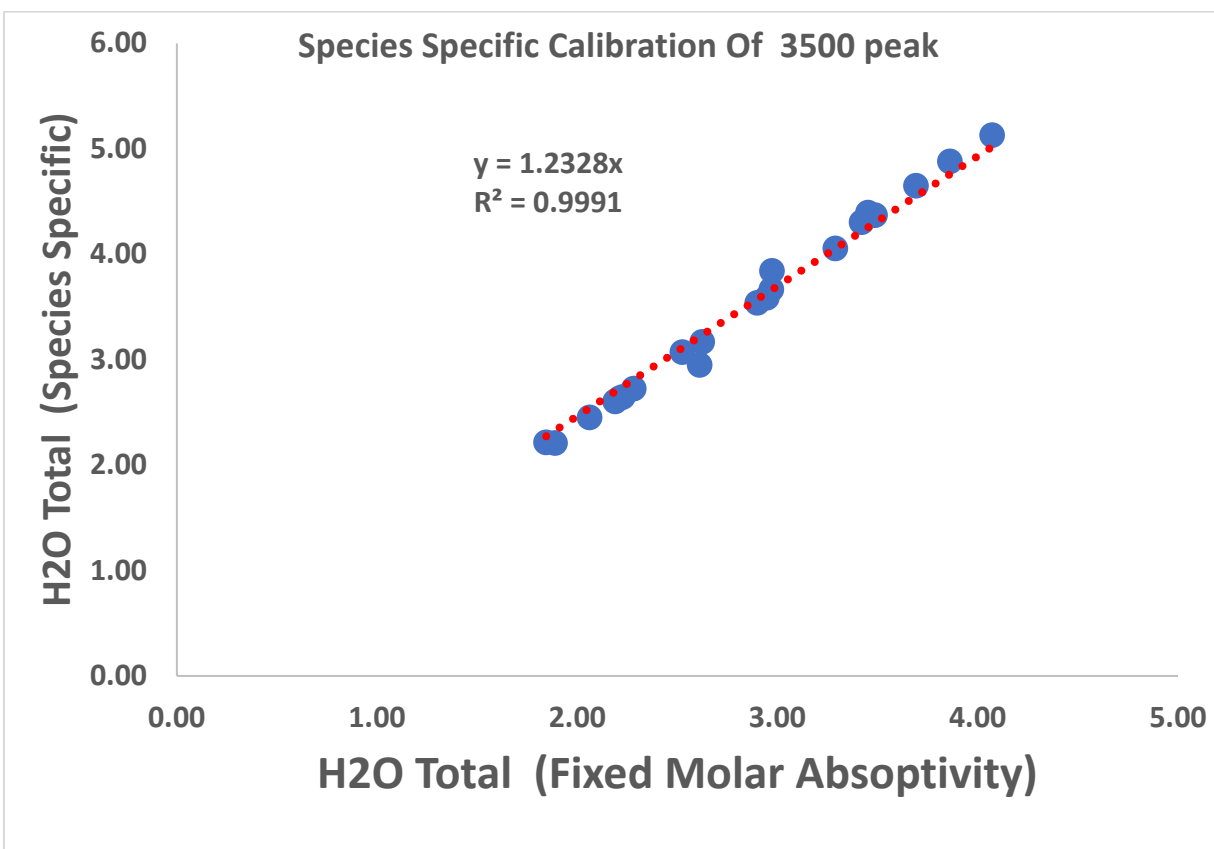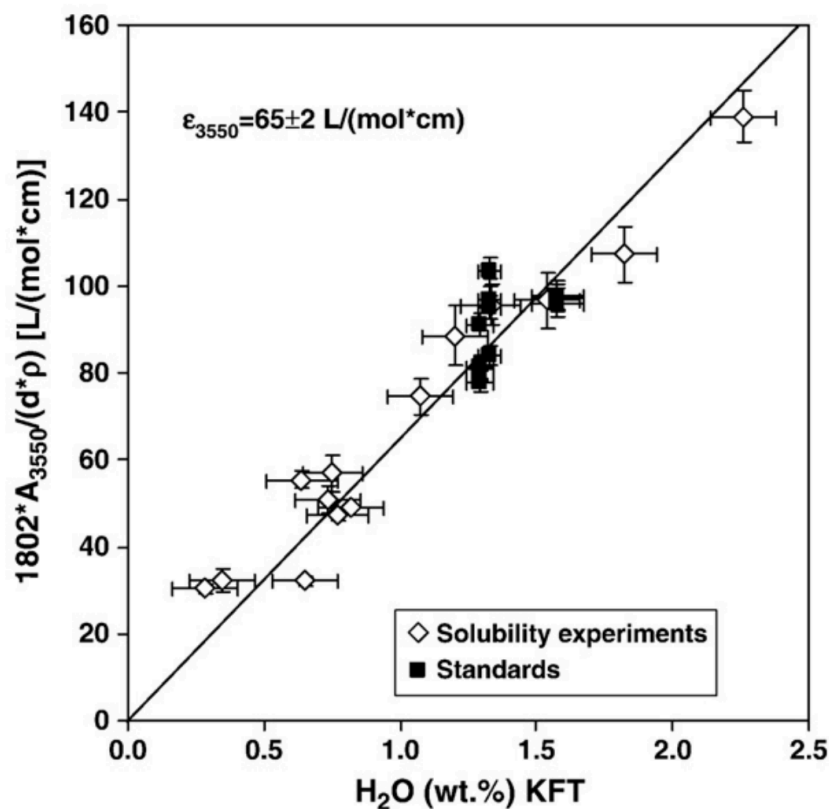
*Figure 3 A comparison between methods of calculating total water concentration for the 3500 cm^{-1} peak using fixed molar absorptivity coefficients of **63 mol^{-1}** cm^{-1} or species-specific coefficients. The species-specific method assumes that the concentrations determined by the near-IR peaks are correct.*

Fig. 2. (a) Calibration plot for the determination of the absorption coefficients for the 4550 cm^{-1} and 5200 cm^{-1} bands. (b) Plot of normalized absorbance of the 3550 cm^{-1} band vs. water concentration in the glasses determined by KFT (see Section 3.2).

Figure 4. From Shishkina et al. 2010. Determining the fixed molar absorptivity of the 3500 cm^{-1} peak. KFT stands for Karl-Fischer Titration.
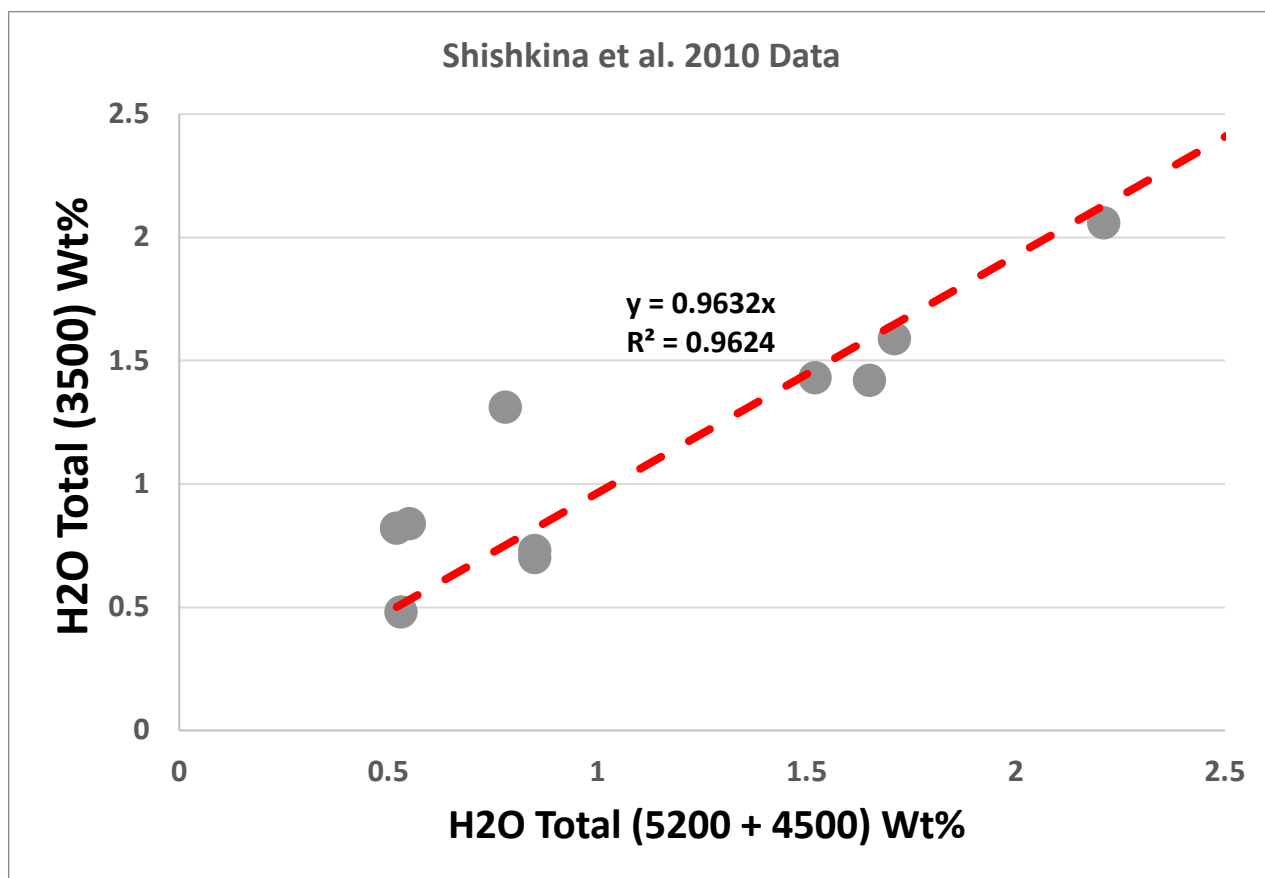
Figure 5 6 Data from Shishkina et al. 2010. Water reported in wt% as calculated from near-IR peaks (5200 cm⁻¹ and 4500 cm⁻¹) and the total water peak (3500 cm⁻¹). Molar absorptivity coefficients were determined by Shishkina et al. 2010 (**5200 cm⁻¹: 0.65 mol⁻¹ cm⁻¹ 4500 cm⁻¹: 0.69 mol⁻¹ cm⁻¹; 3500 cm⁻¹: 68 mol⁻¹ cm⁻¹**). *This plot shows much greater agreement between the near-IR measurements and 3500 cm⁻¹ measurements of total water than the data of Allison et al. 2019 (Fig. 1).*
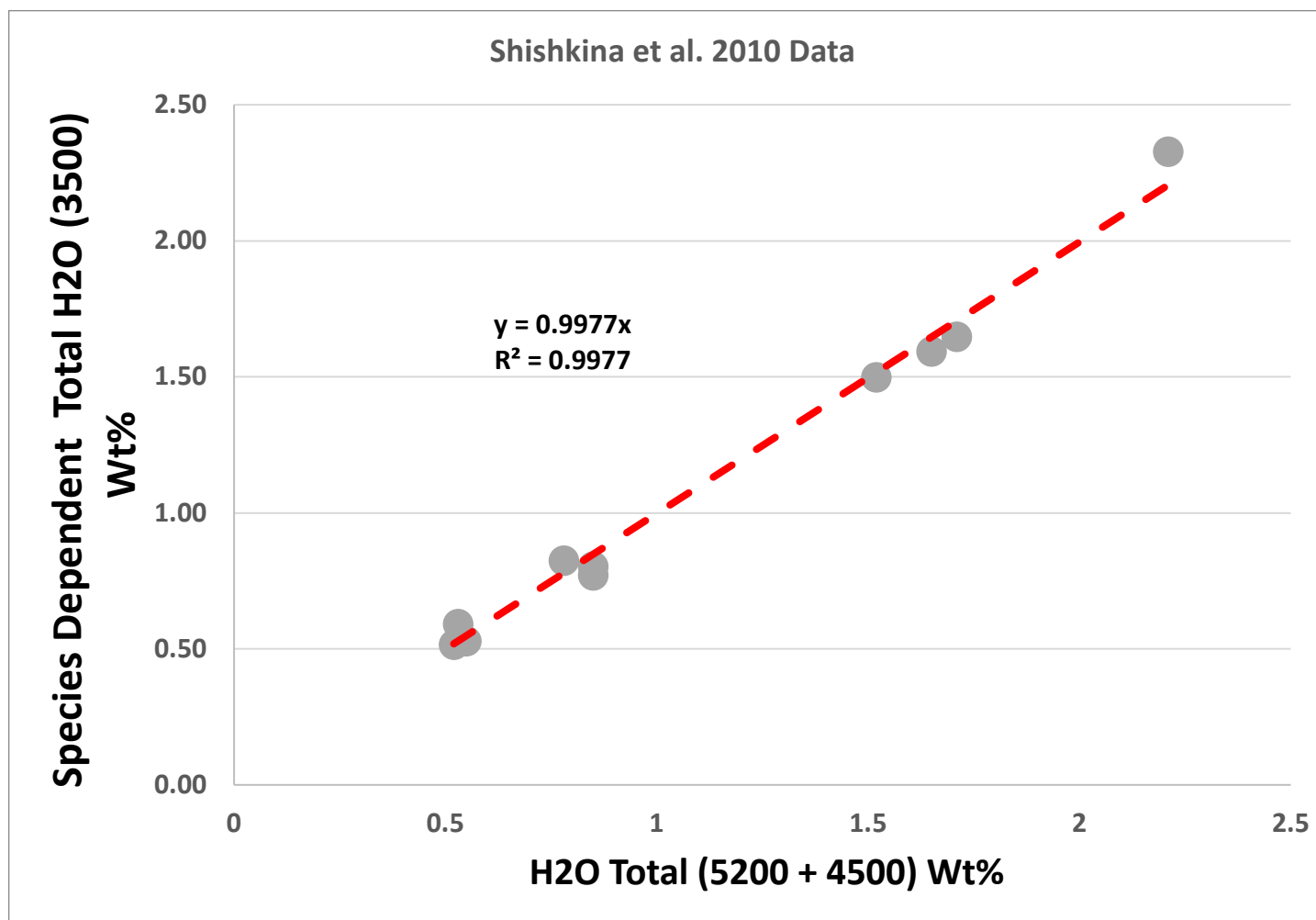
Figure 7 *Data from Shishkina et al. 2010 recalculated to determine species specific molar absorptivity coefficients for the 3500 cm^{-1} peak. Water reported in wt% as calculated from near-IR peaks (5200 cm^{-1} and 4500 cm^{-1}) and the total water peak (3500 cm^{-1}). Methods for determining the peak specific absorptivity coefficients are the same as in figure 2. Coefficients were:* **3500 cm^{-1} H$_2$O species: 38 mol^{-1} cm^{-1}; 3500 cm^{-1} OH$^-$ species: 108 mol^{-1} cm^{-1}.** *The coefficient for OH$^-$ is higher than would be expected for most samples but this has to do with the fact that only a few samples show much variation in the speciation ration of OH$^-$ and H$_2$O as is demonstrated in the next figure.*
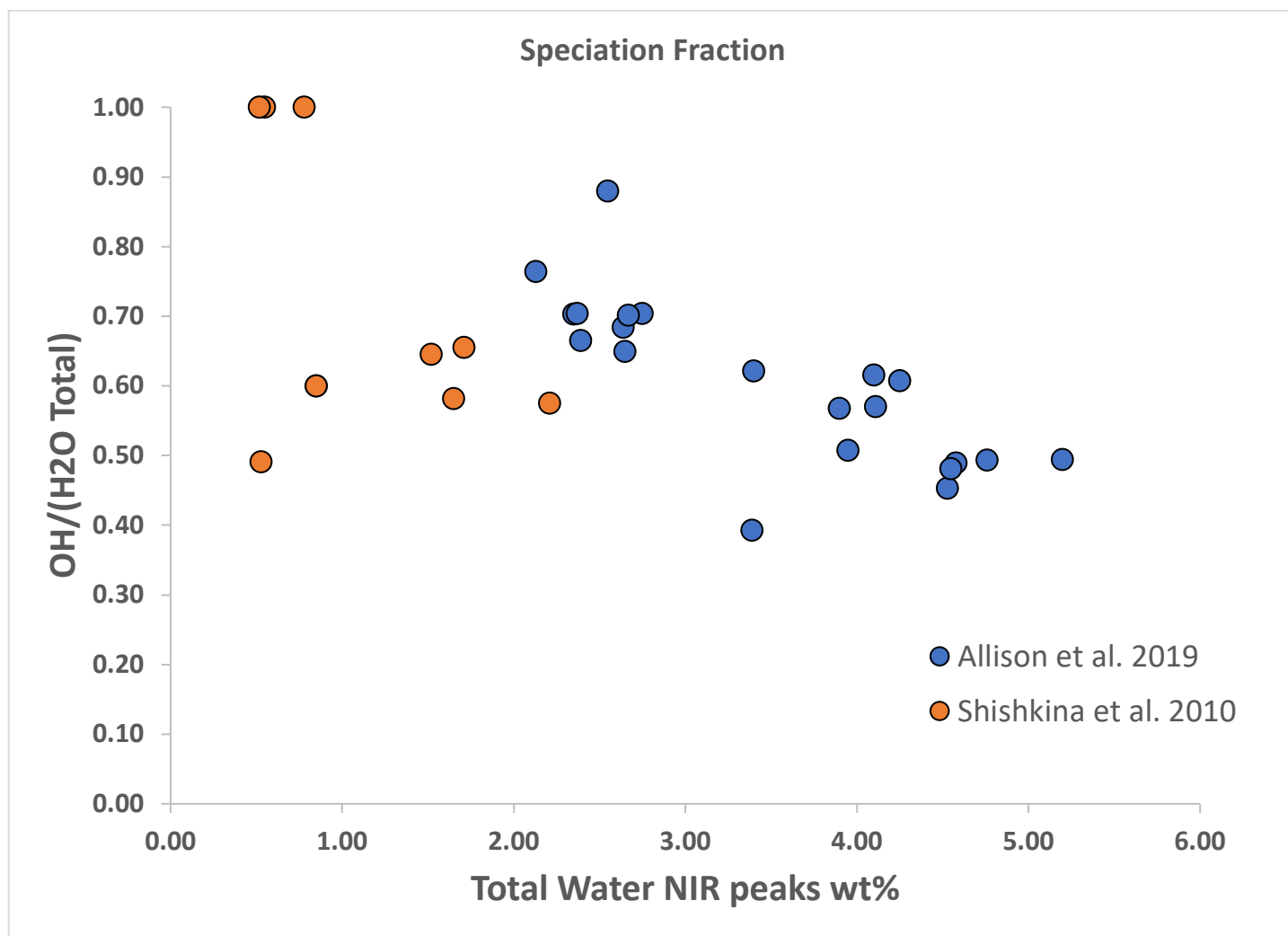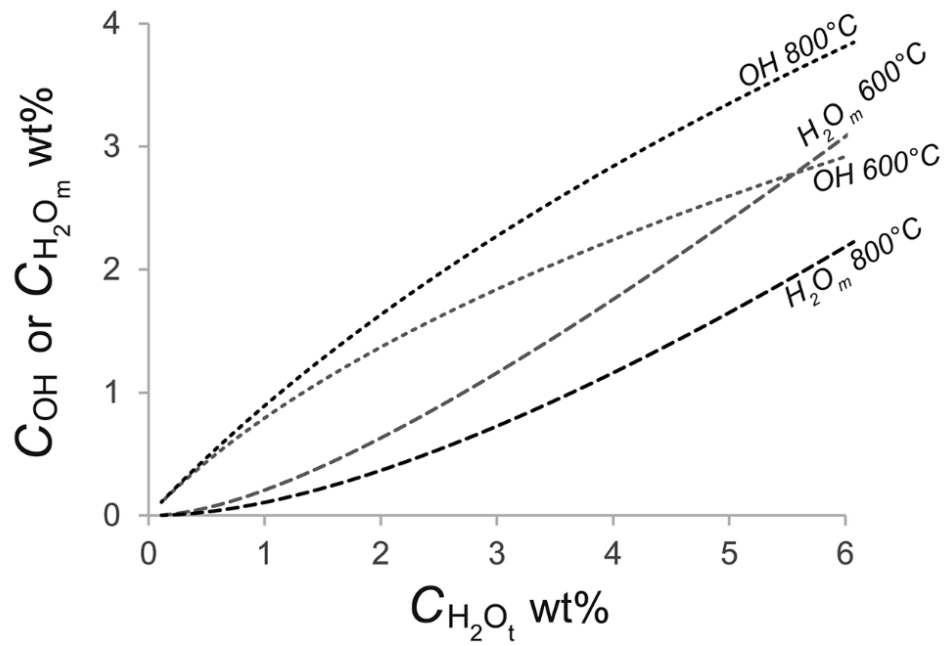
Figure 8 Fraction of OH to Total water as determined by the near-IR peaks. The samples from Shishkina et al. 2010 have less variation than those of Allison et al. 2019. This skews the determination of species-specific molar absorptivity coefficients for the 3500 cm^{-1} peak.
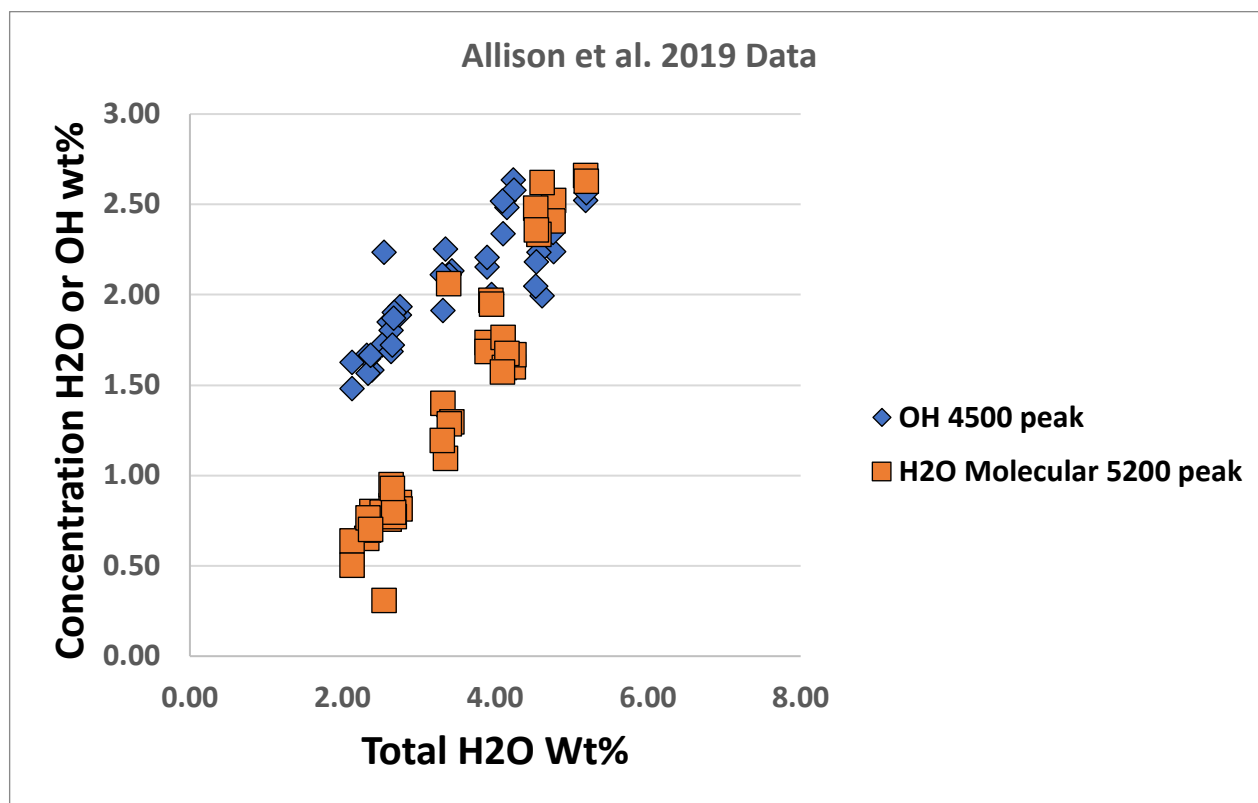
A)

FIGURE 6. Example of experimentally determined water speciation model showing variation in OH and H_2O_m concentration with H_2O_t concentration at different temperatures for haplogranite composition (Nowak and Behrens 2001). OH is the dominant species at low-H_2O_t concentrations and higher temperatures.

B)

Allison et al. 2019 Data
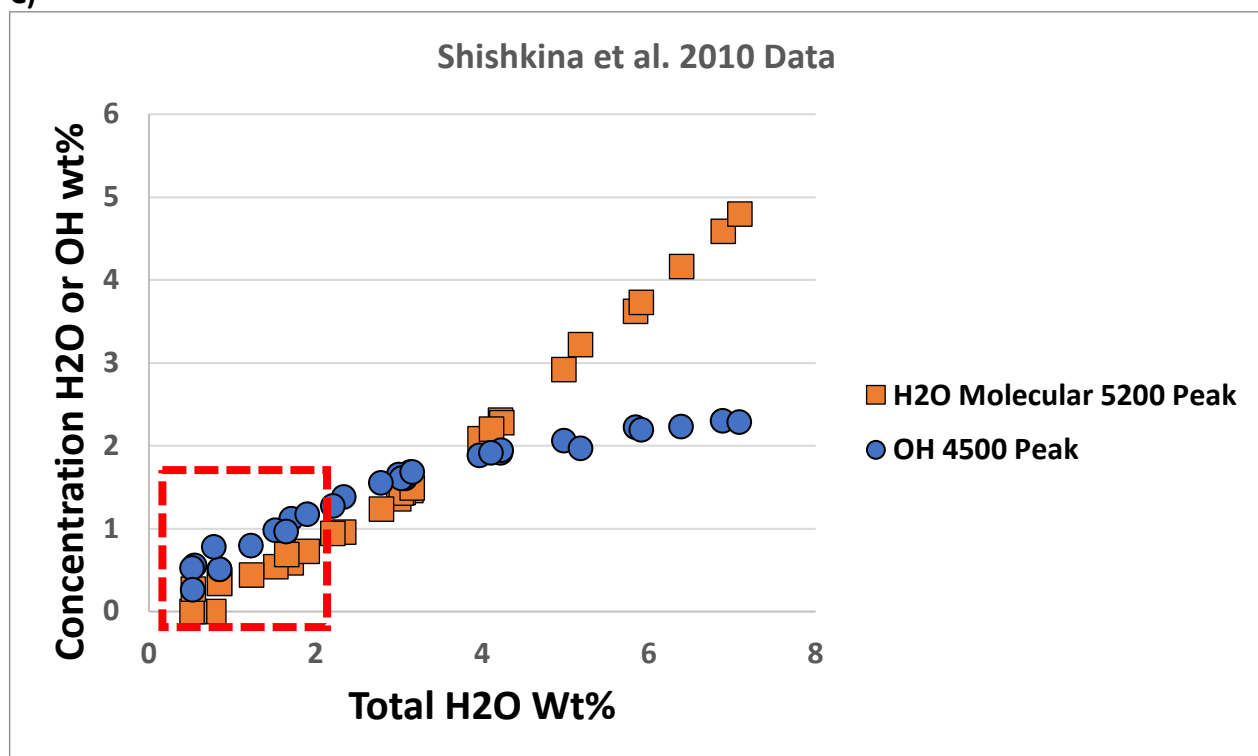
C)

Shishkina et al. 2010 Data

*Figure 9 **A)** Figure from McIntosh et al. 2017 demonstrating water speciation is a function of total water concentration and temperature. For experiments the quench rate will help determine if the speciation at the peak temperature is preserved. **B)** Allison et al. 2019 H_2O and OH^- species in wt% vs Total water. The trends for the different species intersect around 4.5wt% total water. **C)** Shishkina et al. 201o H_2O and OH^- species in wt% vs Total water. The trends for the different species intersect around 3 wt% total water. The red square indicates the range of concentrations for which measurements of the 3500 cm^{-1} peak are available in the Shishkina et al. 2010 experiments.*

Comparing the trends of figure B and C with figure A I am inferring that the experiments of Allison et al. 2019 quenched more rapidly than those of Shishkina et al. 2010. Preserving greater variation in the water speciation.

Allison et al 2019 + Shishkina et al. 2010 Data

y = 0.9873x
R² = 0.9873

- ○ Combined Data
- ◆ Shishkina
- ■ Allison
- - - Linear (Combined Data)

X-axis: **H2O Total (5200 + 4500) Wt%**
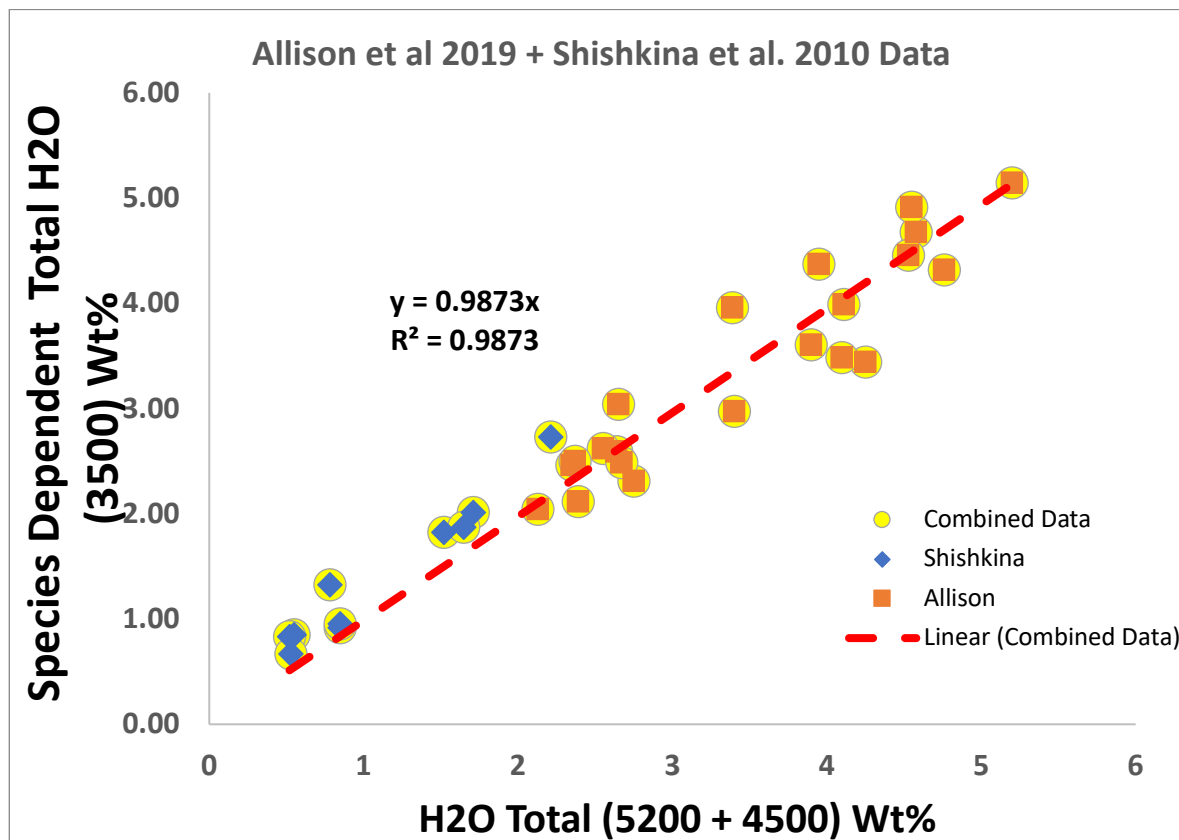Y-axis: **Species Dependent Total H2O (3500) Wt%**

*Figure 10 Combined data from Allison et al. 2019 and Shishkina et al. 2010 recalculated to determine species specific molar absorptivity coefficients for the 3500 cm^{-1} peak. Water reported in wt% as calculated from near-IR peaks (5200 cm^{-1} and 4500 cm^{-1}) and the total water peak (3500 cm^{-1}). Methods for determining the peak specific absorptivity coefficients are the same as in figure 2. Coefficients were: 3500 cm^{-1} H_2O species: **39 mol^{-1} cm^{-1}**; 3500 cm^{-1} OH^- species: **67 mol^{-1} cm^{-1}**.*
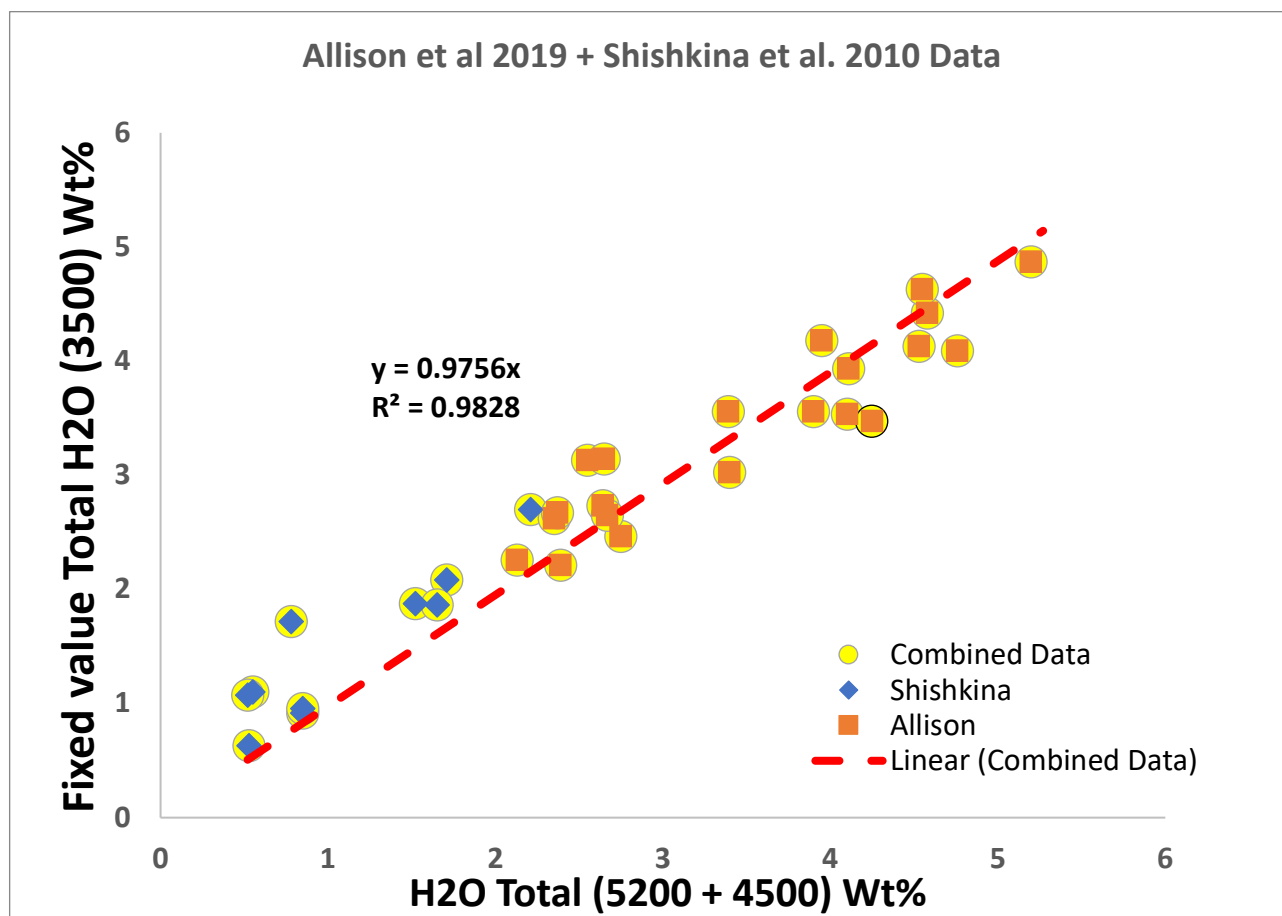
Figure 11 Combined data from Allison et al. 2019 and Shishkina et al. 2010 recalculated to determine a single fixed molar absorptivity coefficient for the 3500 cm^{-1} peak. Water reported in wt% as calculated from near-IR peaks (5200 cm^{-1} and 4500 cm^{-1}) and the total water peak (3500 cm^{-1}). The molar absorptivity coefficient for the 3500 cm^{-1} peak was determined by minimizing the sum of the squared residuals between the total water measured from the near-IR peaks and from the 3500 cm^{-1} peak. The best fit was 3500 **cm^{-1}: 52 mol^{-1} cm^{-1}**