

Electronic Appendix 3

A2.1 Calculation of Dissolved Volatiles in Highly Crystalline Samples

Some highly crystalline samples contained glass pools too small to be analyzed by FTIR but could be analyzed via electron microprobe, and so their dissolved H₂O contents were calculated in two ways: using the “by difference” method of Devine et al. (1995) and by mass balance. In the “by difference” method, the total amount of dissolved volatiles in a sample is taken as 100% minus the major element analytical total from microprobe analysis. Mass balance calculations were performed as follows:

$$H_2O^{melt} (wt\%) = \frac{mH_2O^{initial} - mH_2O^{fluid}}{mH_2O^{initial} - mH_2O^{fluid} + mGlass} \quad (A2.1)$$

where $mH_2O^{initial}$ is the mass of water added to the experimental capsule, mH_2O^{fluid} is an estimate of the mass of H₂O in the fluid post-run (measured using the weight-loss method; see Section 3), and $mGlass$ is the mass of starting material powder, corrected for the crystal content of the sample. In principle, it should be necessary to include a term for water taken up by hydrous phases (i.e. $-mH_2O^{amph}$ in kaersutite-bearing runs). Because of the difficulty in quantifying the precise amount of H₂O contained in experimental kaersutites, due in part to possible oxy-components (see Discussion), and because kaersutites are in few runs and often in low proportion, we have not included this in our calculations. Notably, some H₂O was present in all runs, even those where no liquid water was added to the experimental capsule. Despite the storage of rock powders in a drying oven, H₂O can be introduced to the experimental capsule via remnant water within the starting powder and through H₂O generation during the run via reduction of Fe³⁺. To

account for this excess water, we have added a correction factor of 0.55 mg to the value of mH_2O^{in} (Table 2).

Samples for which FTIR measurements could be obtained (26 AW-82038 samples; 10 KI-04 samples) were used as internal standards to calibrate both the by difference and mass balance methods. For our samples, the “by difference” method proved a very poor estimate of dissolved H₂O. A linear regression of known and calculated H₂O values results in R² values of 0.33 and <0.01 for phonotephrite and basanite experiments, respectively (Figure A2.1). The significant scatter of our data can be attributed to several factors. First, our experiments are characterized by varying ratios of H₂O and CO₂. A comparison of total volatiles calculated by difference and total volatiles calculated by FTIR spectroscopy resulted in a similarly scattered relationship, however the varying H₂O contents of our glasses may contribute non-linearly to varying degrees of Na-migration during microprobe analysis, a common problem for hydrous alkaline glasses. Secondly, microprobe analyses on our samples were performed at three separate laboratories over many analysis sessions. Variations in standardization and beam settings between sessions may also contribute to scatter in these data. We suggest that the “by difference” method may work better for samples with similar XH₂O that are measured during the same microprobe session and when Na-migration is not significant (or can be corrected).

Conversely, there is a better-defined linear relationship between dissolved H₂O concentrations as calculated by mass balance and those measured by FTIR (R²=0.69 for AW-82038 samples; R²=0.84 for KI-04 samples, excluding two outliers; Figure A2.2). For this reason, we have used these mass balance calibrations to calculate H₂O contents

in all samples for which FTIR spectra could not be obtained (see Table 2). The same method was applied to CO₂ contents, which can be calculated by mass balance but not by difference, but a very poor fit was found for both sample groups and so calculated values for dissolved CO₂ contents are not used. The calculation of H₂O by mass balance is preferred here, with an average error of ± 1.0 wt%.

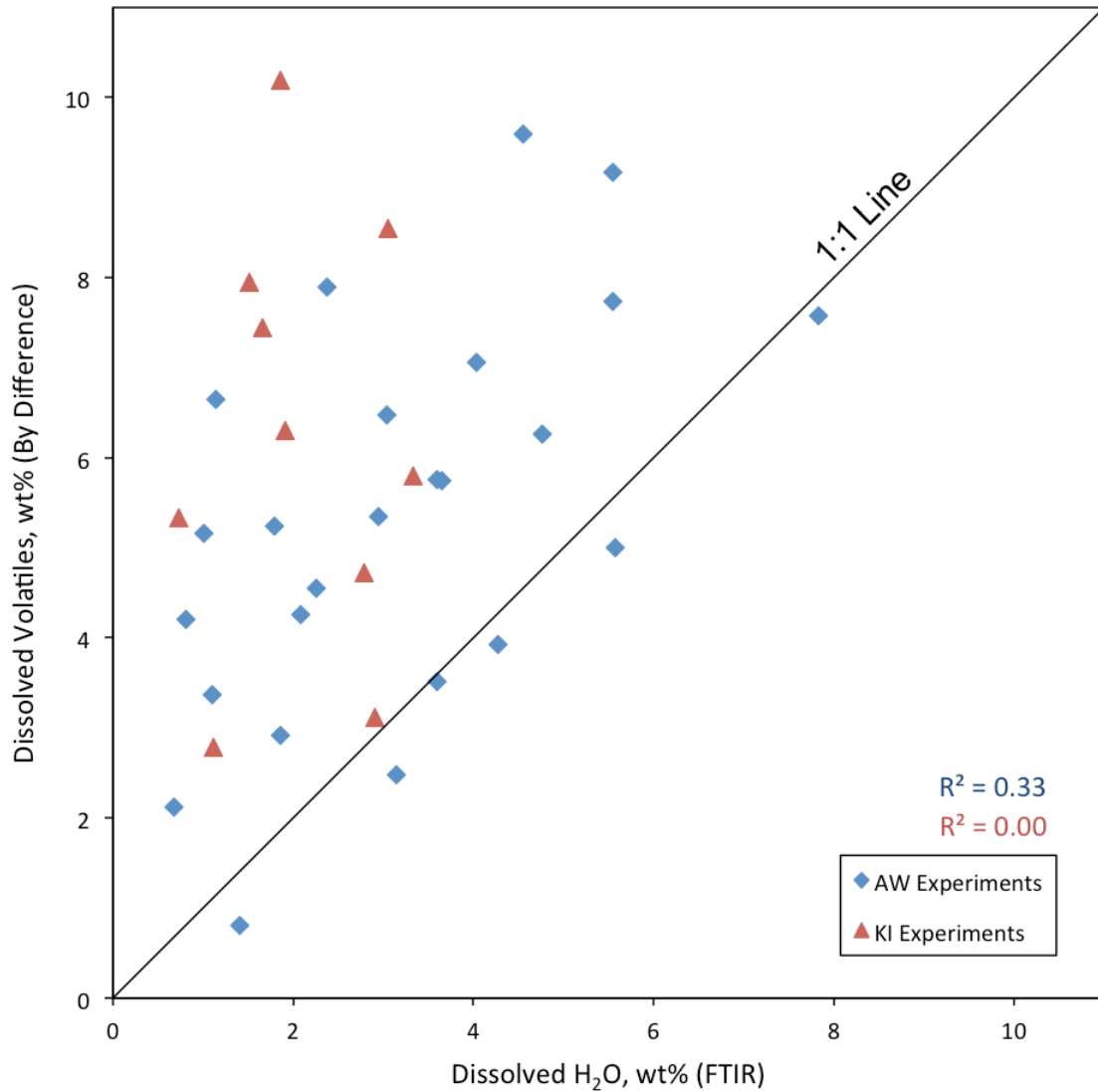


Figure A2.1 Dissolved H₂O contents as measured by FTIR compared to dissolved volatiles calculated by difference in AW (blue) and KI (red) experiments. A 1:1 line is shown in black. Although this technique has been used successfully in similar studies, it is not appropriate in application to our samples, which have varying H₂O/CO₂ and are prone to Na migration during microprobe analysis.

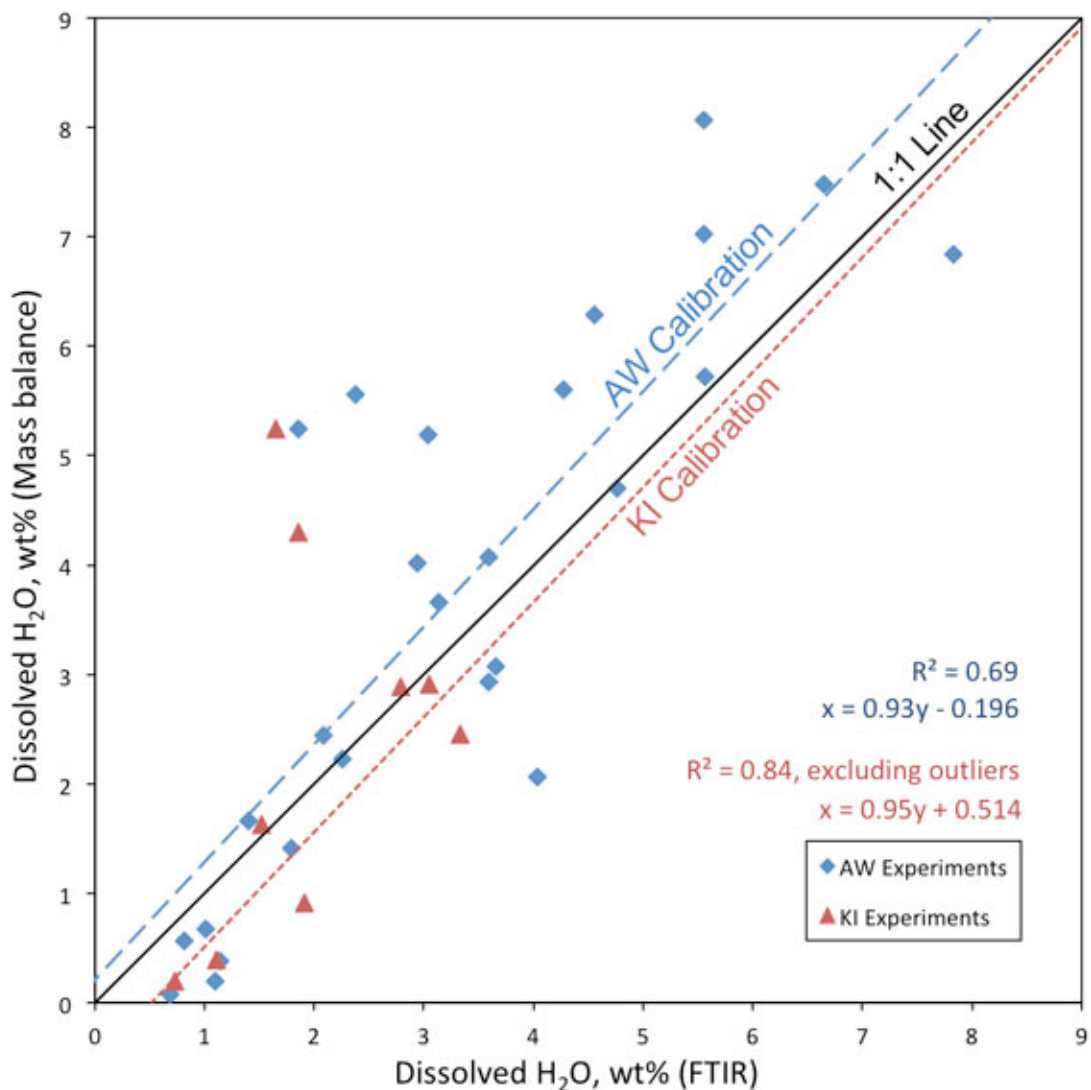


Figure A2.2 Dissolved H₂O concentrations in AW (blue) and KI (red) experiments as measured by FTIR and calculated by mass balance. The best-fit calibration lines and equations for AW (blue dashed line) and KI experiments (red dotted line) are also shown, along with a 1:1 line (black). The mass balance method proved a much better estimate of dissolved H₂O in our experimental samples as compared to the commonly applied “by difference” method. The two outliers excluded from the calibration for KI experiments are samples KI-20 and KI-33. Dissolved CO₂ contents calculated by mass balance showed a very poor correlation with measured values, and so calculated CO₂ contents are not used.