

Appendix 1 – Water analysis with Raman spectroscopy

In order to determine the water concentration of glasses and to avoid analyzing powders, which quickly adsorb water from ambient atmosphere, we treated the Raman spectra of glasses with a protocol similar to that described in Le Losq et al. (2012). Slight modifications were made to account for the slightly different OH stretching signal in Raman spectra of silicate glasses compared to that of the aluminosilicate glasses analyzed in Le Losq et al. (2012). The OH stretch signal below 3000 cm^{-1} in silicate glasses is intense and cannot be neglected, as Le Losq et al. (2012) did for aluminosilicate glasses. We modified the baseline definition accordingly, as shown in Figure S1. The corrected spectra were normalized to their total area between 350 and 4000 cm^{-1} . The area A_w under the OH-stretching signal between 2000 and 4000 cm^{-1} was measured (Figure S1). Such measurement on area-normalized spectra is equivalent to measuring the ratio between the area of silicate bands and that of the OH stretch band on non-normalized spectra. The water concentrations in NS4 glasses determined through FTIR analysis have been used to standardize the A_w vs. total water concentration relationship. The remaining question was whether Raman cross-sections of the different OH signals observed near 3600 , 2800 , and even 2300 cm^{-1} , in silicate glasses (Figure S1) are equal. The cross-section of the Raman signals from individual species in the 3000 - 4000 cm^{-1} range is independent of glass chemistry (Le Losq et al., 2012). The good agreement between the Raman-measured water concentrations, the nominal ones, and those determined by Loss On Ignition (Table 2) indicates that the O-H stretching Raman cross-section is not significantly

dependent on the type of alkali element present in the glass. We conclude, therefore, that the OH stretching Raman cross-sections are not affected by the glass chemical composition. This may be results from the fact that the OH stretching frequency is mostly controlled by one parameter, the O...O distances, and in agreement the OH stretching Raman cross-section at a given frequency must mostly depend on this parameter in silicate materials. The values in Table 2 are affected by a global error estimated from deviations between the NS4 FTIR and Raman values and from numerical errors inherent to the baseline subtraction and the calculation of OH stretching band area. Because we do not have a large quantity of standards for performing the calibration and refining the standard deviation of the technic, we preferred providing an error representing an upper limit, and equal to 0.30 wt% at the 2σ confidence interval.

Figure S1: Raman spectra of the NS4 + 17.6 mol% H₂O glass. A) Raw spectrum (dark) with the spline cubic baseline (blue) constrained at 1400, 2000 and 3900 cm⁻¹; B) Baseline-subtracted spectrum. Peaks at ~490 and ~1100 results from intertetrahedral bending and intratetrahedral stretching of SiO₄ units respectively, while the ~800 cm⁻¹ band results from SiO₄ rocking motions. The sharp band near 1630 cm⁻¹ results from H₂O_{mol} bending, and the 2300, 2800 and 3600 cm⁻¹ bands results from OH stretching in OH and H₂O_{mol} units in the glass ([Zotov and Keppler, 1998](#)). See also Le Losq et al. ([2012](#)), Le Losq et al. ([2014](#)) and references therein for details on Raman spectra of anhydrous and hydrous glasses. The spectrum

presented in B) is used for measuring the area of the signal assigned to OH stretching (in red). Intensities of the spectrum have been previously normalized to the total area of the spectrum, which is now equal to 1 (theoretical value of the sum of the vibrational density of state).