THE CONCENTRATION AND SPECIATION OF HYDROGEN IN FELDSPARS FROM $^1$H MAS NMR AND FTIR SPECTROSCOPY. E. A. Johnson and G. R. Rossman, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125 (liz@gps.caltech.edu).

Introduction: Previous studies have established that hydrous species in nominally anhydrous minerals (NAMs) are an important potential reservoir of water in the mantle, but less is known about the role and significance of hydrogen in anhydrous crustal minerals. Trace amounts of hydrogen in feldspars are possibly preserved from original magmatic conditions or result from hydrothermal activity, and may be indicative of thermodynamic variables ($f_{H_2O}$ or $f_{O_2}$) or the amount of water that has passed through a system (water/rock ratio). FTIR spectroscopy is a useful tool for studying hydrogen species in NAMs, but it must be calibrated using a separate method such as $^1$H magic-angle spinning (MAS) NMR to be quantitative. Previous workers [1], [2] have pointed out the difficulties of removing proton signals due to adsorption of water on grain boundaries and onto the NMR probe or rotor. Using careful sample preparation techniques and blanks the concentration and species (OH or H$_2$O) of hydrogen in microcline and three plagioclase feldspars were determined with $^1$H MAS NMR, and FTIR absorption coefficients for these feldspars were calculated.

Experimental Procedures: Feldspar samples used in this study were: microcline from the White Queen Mine pegmatite, CA; albite from Amelia, VA; anorthite from Miyake Island, Japan; and andesine from a tuff near Halloran Springs, CA. Samples free of inclusions were ground and packed into NMR rotors inside a dry box. No liquid was used as a grinding aid. $^1$H MAS NMR spectra were recorded using a Bruker DSX 500 MHz spectrometer and spinning speeds of 6-14 kHz. A $4 \mu$s 90° – $8 \mu$s 180° pulse depth sequence [3] was used to minimize probe background. Dry nitrogen was used for cooling and spinning samples during variable temperature experiments (173 – 373 K). TTMS was used as a chemical shift reference. Analcime from Table Mountain, CO, and ussingite from Ilmamussaq, Greenland, were run as hydrogen concentration standards. Synthetic corundum containing no hydrogen was prepared in the same way as the feldspar samples and was used as a blank. Polarized FTIR spectra were taken on a Nicolet Magna-860 spectrometer at 2 cm$^{-1}$ resolution.

Results: The concentration of hydrogen in the microcline determined by NMR was 1300 ppm H$_2$O by weight, compared to a concentration of 1400 ppm previously measured [4]. The plagioclase feldspars had lower hydrogen concentrations: 350 ppm in the albite, 45 ppm in the anorthite, and 110 ppm in the andesine. Spinning sideband intensities suggested the microcline contains structural hydrogen in the form of isolated H$_2$O molecules, and the plagioclase feldspars contain structural OH. The albite and anorthite OH showed dynamic behavior on the time scale of NMR experiments. The chemical shift (in ppm vs. TTMS) of hydrogen peaks in each sample revealed greater hydrogen bonding and deshielding for ussingite OH groups (13.8, 15.5, and 11.0 ppm) compared to feldspar OH (albite, 4.8 and 5.0 ppm; anorthite, 5.0 ppm; and andesine, 4.8 and 2.1 ppm) and H$_2$O (microcline, 4.7 ppm).

FTIR integrated absorption coefficients ($I'$, in 1/(ppm·cm$^2$)) for the feldspars were calculated with Beer’s law using the hydrogen concentration determined by NMR and the integrated peak area of OH and H$_2$O bands in the 3000-3700 cm$^{-1}$ region of the IR spectra (Fig. 1). The absorption coefficient for all the feldspars in this study, regardless of hydrous species, is 16.13±3.83, determined by fitting a line through the data and the origin in Fig. 1. The albite IR spectra has sharp peaks overlying broad OH bands and might be expected to have different peak absorptivity from the other feldspar samples that only have broad OH bands. If the albite is excluded, an $I'$ = 15.51±0.74 is calculated. Future analysis of other samples will clarify if it is appropriate to use one or more $I'$ to calculate hydrogen concentration in feldspars using FTIR spectra.


Figure 1.