USING ION IMPLANTS TO QUANTIFY HYDROGEN IN NOMINALLY ANHYDROUS MINERALS. A. Distel[1,2], R. Hervig[1], J. Davidson[1,2], M. Wadhwa[1], A. Stephant[3]. [1]School of Earth and Space Exploration, Arizona State University, USA (agdistel@asu.edu). [2]Buseck Center for Meteorite Studies, Arizona State University, USA. [3]Istituto di Astrofisica e Planetologia Spaziali – INAF 00111, Rome, Italy.

Introduction: The primary hydrogen-isotopic ratios (expressed as D/H) of planetary bodies can indicate where in the Solar System their volatile components originated, and allow us to investigate their potential volatile sources ([1] and references therein). Since hydrogen is volatile and thus lost rapidly, determining D/H ratios can also allow us to trace alteration due to geologic and atmospheric processes (e.g., [1–3]). Over the last decade, hydrogen isotope analyses of planetary materials has, therefore, become an important area of study in planetary science [1]. While earlier studies primarily focused on the late-forming mineral apatite, more recent studies have begun to focus on trace H analyses in earlier-formed nominally anhydrous minerals (NAMs) (e.g., [4–7]). The study of hydrogen in NAMs may give us more insight into the primary D/H ratios of planetary bodies and better allow us to understand secondary alteration processes [4].

Trace hydrogen analyses via secondary ion mass spectrometry (SIMS) are challenging, requiring careful sample preparation, standardization and analytical methods (e.g., [8]). Therefore, when conducting SIMS analyses for trace hydrogen and its isotopes in NAMs, there are two important parameters for the analyst to consider for obtaining the most accurate H_2O concentrations and δD values: 1) using matrix-matched standards (e.g., [8–11]); and 2) accurately determining the background signal for H ions during the analysis session (e.g., [12]). This abstract addresses these two issues using hydrous and nominally hydrogen-free samples implanted with ^1H and ^2H (D).

Background: Prior analyses of SIMS standards have provided great insights into analysis procedures, H backgrounds, and sputtering rates (e.g., [8,11,12]). Hauri et al. (2006) [11] quantified changes in sputter yield (atoms ejected/incident primary ion), which is proportional to sputtering rate. Stephant et al. (2014) [12] quantified the effect on the H background signal of increasing the primary Cs^+ current to increase sputter rate.

Approach: MORB glass P1326, Hakone An_{94}, PMR53 clinopyroxene, San Carlos olivine (Fo_{90}), Lake County An_{61}, albite, and Macusani rhyolite glass were all implanted with 10^{15} atoms/cm^2 of both hydrogen and deuterium. SIMS depth profiling analyses (Fig. 1) were performed on the ASU Cameca 6f instrument, using a ~13 nA Cs^+ primary beam rastered over 75 x 75 μm^2, and detection of 5000 eV negative secondary ions from a circular area 15 μm in diameter during three analysis sessions. The sample chamber vacuum ranged from 8.0 x 10^{-10} to 9.4 x 10^{-10} torr. Crater depths were measured using a stylus profilometer. H background was examined using the San Carlos olivine and Lake County plagioclase, both containing << 5 μg/g H_2O [8, 13].
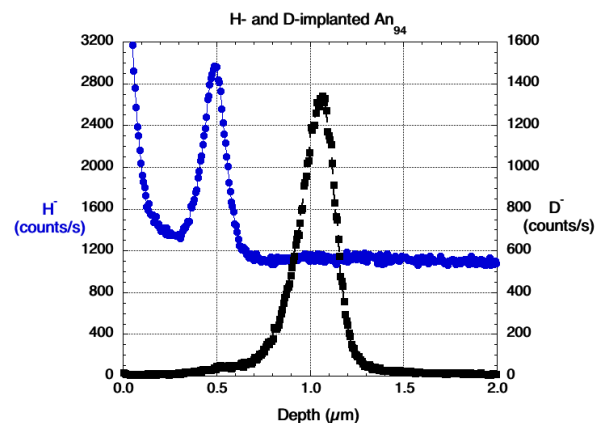

Figure 1: Depth profile showing implanted H (blue) and D (black) in An94. The dose for both isotopes was the same, but the energy of the D implant was twice that of the H. The high H signal at the surface is interpreted to be surficial contamination, and is not considered for this work.

Results: Sputtering rates are relatively low for San Carlos olivine and PMR53 clinopyroxene. Rates increase by 20–30% for An_{61} and An_{94}. MORB glass and crystalline albite sputter rates are 30–40% faster than San Carlos, while rhyolitic glass sputters over 70% faster than the olivine. A single analysis of Durango apatite indicates a rate 50% faster than San Carlos olivine (Fig. 2).

The integrated signal for H (from the implant, after subtracting the background and "native" H) was compared to the integrated signal for D. It is noteworthy that the same amount of the two isotopes was implanted into all phases (such that D/H ratio for these phases should be 1), however, the energy of the D implant was twice that of the H (Fig. 1). The D/H ratios from the implant for San Carlos olivine, PMR53, An_{61}, and An_{94} are shown in Figure 3.
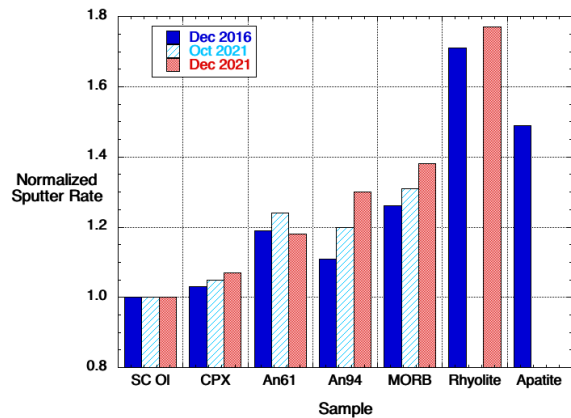
Figure 2: *Sputter rate normalized to that observed on San Carlos olivine in three different analysis sessions.*

Discussion: Variations in sputtering rate are important because the faster surface atoms are removed from a sample, the lower the signal from vacuum-sourced surface-absorbed hydrogen (resulting in a lower H background). High sputtering rates result in lower Cs content in the crater floor, which in turn lowers the ionization probability for H [11]. Thus, high sputtering rates will show lower H signals for two reasons: efficient removal of contaminating H *and* lowered H^- ion yields (Fig. 4). Using the San Carlos H^-/O^- ion ratio as a blank for pyroxene would overestimate the background, and is even less appropriate as a blank for the fast-sputtering plagioclase crystals.
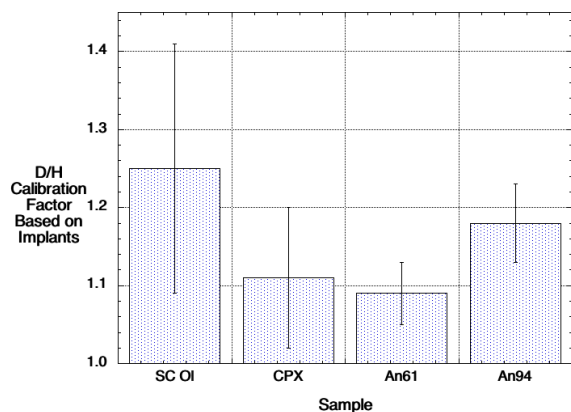

Figure 3: *D/H calibration based on the implanted H and D signals in each sample. All profiles were similar to Fig. 1 except rhyolitic glass, basaltic glass, and the albite, which displayed more pronounced decreases in the H^- ion signal through the implant (leading to greater uncertainties). The errors (1sd) are shown.*

The integrated ratio of D^-/H^- ions from implanted phases represents a calibration factor for δD. All of the crystals shown in Figure 3 show similar calibrations (a bias to higher D/H *ion ratios* by 10 -20%).
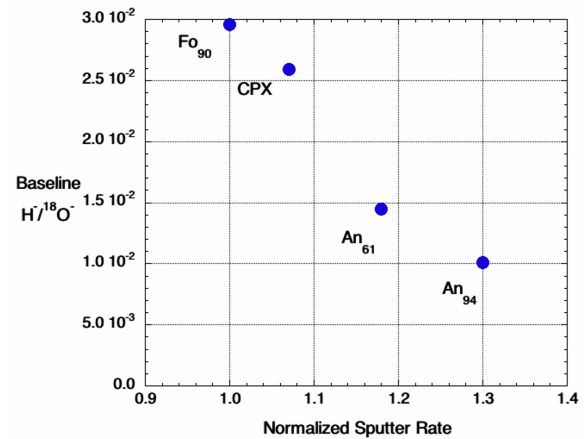

Figure 4: *Relation between sputter rate and the H/O ion ratio. Note the factor of three change in this ratio despite the nearly constant O content and the negligible amount of H_2O in the olivine and the plagioclase samples, while the CPX contains 260 µg/g H_2O.*

Conclusions: The results demonstrate that careful consideration of standards is necessary when measuring trace hydrogen. Specifically, using San Carlos olivine as a blank during trace hydrogen analysis could produce an artificially high H signal due to its slow sputtering rate, while other phases would suggest artificially low H backgrounds.

Future work suggested by these results includes making the H implant deeper to avoid transients, adding different phases, and testing if implanting D/H ratios of <1:1 generate different calibrations.

References: [1] Hallis L. J. (2017) *Phil. Trans. R. Soc. A, 375,* 20150390. [2] Davidson J. et al. (2020) *EPSL, 552,* 116597. [3] Barnes J. J. et al. (2020) *Nat. Geo., 13*, 260–264. [4] Peslier A. H. et al. (2019) *GCA, 266*, 382–415. [5] Davidson J. et al. (2020) *LPS LI*, #1660. [6] Davidson J. et al. (2021) *LPS LII*, #2103. [7] Stephant A. et al. (2021) *GCA, 297*, 203–219. [8] Mosenfelder J. L et al. (2011) *Am. Min. 96,* 1725–1741. [9] Hauri E. et al. (2002) *Chem Geol., 183,* 99–114. [10] Mosenfelder J. L. and Rossman G. R. (2013) *Am. Min, 98,* 1042–1054. [11] Hauri E. et al. (2006) *Chem Geol., 235,* 352–365. [12] Stephant A. et al. (2014) *Chem Geol., 380*, 20–26. [13] Mosenfelder J. L. and Rossman G. R. (2015) *Am. Min, 100,* 1209–1221.