SINGLE CRYSTALLINE THIN-FILMS AS MODELS FOR WATER EVOLUTION FROM MINEROLOGICALLY RELEVANT PROTONATED AL-O-SI SITES

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Abstract: Chemistry unique to protonated Al-O-Si sites common to feldspars was investigated via temperature programmed desorption (TPD) of water from single crystalline $Al_{0.42}Si_{0.58}O_2$/Ru(0001) bilayer thin-films. Results from this work provide evidence for thermal recombination of hydroxyl groups formed at such sites to produce gas-phase water under conditions expected at the Lunar surface (i.e. two week exposures to $T \leq 400K$ during Lunar days). Importantly, thermal desorption from these sites is distinctly different from analogous thermally driven processes leading to the evolution of water from: (1) both Al-O-Al and Si-O-Si containing interfaces and (2) the same sites present in proximity to different metals presumed to have different capacities for compensating charge imbalances in similar deprotonated films. These differences imply that: (1) quantitatively accurate modeling of the thermal evolution of water from protonated aluminosilicate containing feldspars will require specific rate constants unique to such sites and (2) such rate constants are expected to vary contingent on the concentration and type of charge-balancing ions present throughout the varied minerology of the Lunar surface. Additionally, our work points to the presence of strongly (hydrogen)-bound water molecules on oxides that do not result in lower temperature loss of hydroxyl sites through recombination. From this perspective, mineralogy varying from pure SiO_2 to MgO, TiO_2, Fe-oxide, and/or Al_2O_3 containing minerals (common to the Mare) can be expected to act as relative sinks and sources for molecular water generated through thermal recombination of hydroxyl groups, respectively. By contrast, our results suggest a flexible range of dual modalities for Al-OH-Si sites present in different mineralogical environments. Much of the results to be discussed will come from our recent *Surface Science* publication [1]. Preliminary results comparing our thin-film data to complementary TPD experiments using an Anorthosite Lunar simulant may also be included pending the timeline associated with regionally implemented Coronavirus mitigation strategies.

Figure 1 summarizes the key results associated with our recent publication dedicated to better understanding the fate of Al-OH-Si bridging hydroxyl sites. The study consisted of creating (and characterizing) polymorphically equivalent SiO_2 and $Al_xSi_{(1-x)}O_2$ thin-films, and then conducting identical D_2O TPD experiments from both samples, such that effects unique to the presence of Al-OD-Si sites might be inferred by comparison

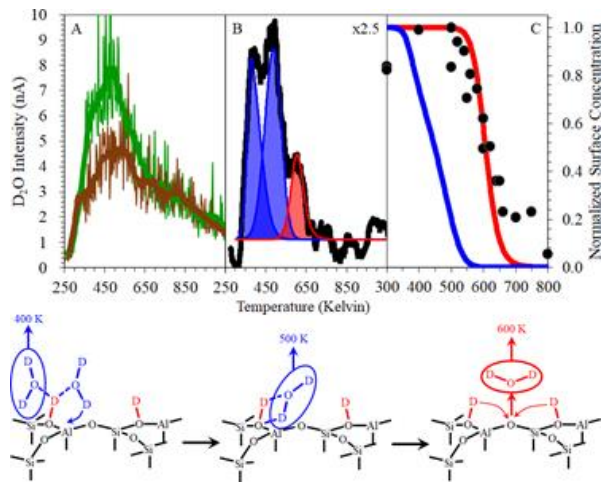

Figure 1. Comparative TPD analysis used to isolate and quantitatively investigate thermally driven Al-OD-Si recombinative desorption processes relevant to water evolution at Lunar interfaces.

(green vs. brown in Fig. 1A). Fig. 1B shows a difference spectrum resulting from subtraction of the SiO2 from the $Al_{0.42}Si_{0.58}O_2$ TPD data. As shown, three peaks emerge, which have been identified as desorption features associated with the loss of hydrogen bound molecular water and recombining OH groups. Additional experiments used to validate this peak assignment and additional quantitative analysis will also be discussed as part of this talk.

Acknowledgement:
This work was directly supported by the NASA Solar System Exploration Research Virtual Institute (SSERVI) under cooperative agreement NNA17BF68A (REVEALS).

Reference:

[1] B. Dhar, J. Pollock, J. Gloria, and W.E. Kaden, *Surface Science* **696**, 12159 (2020).