EXOSPHERIC POTASSIUM: LABORATORY MEASUREMENT OF TEMPERATURE-DEPENDENT DEPLETION CROSS-SECTIONS FOR POTASSIUM ABSORBED ON ILMENITE. C. Bu[1] , and C.A. Dukes[1]. [1]University of Virginia (Laboratory for Astrophysics and Surface Physics, Materials Science and Engineering, Charlottesville, VA 22904; cb8nw@virginia.edu; car8r@eservices.virginia.edu).

Introduction: Mercury's exosphere shows a fascinating species-dependent variation in abundance and spatial distribution for Na, Mg, and Ca, identified by the Ultraviolet and Visible Spectrometer on the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) spacecraft, and for K based on ground-based observations [1,2]. In particular, measurements of exospheric Na to K abundance vary hugely—from 22 - 400 depending on observation time and location with respect to Mercury's surface [2,3]—and differ significantly from the lunar Na/K ratio of ~6 [4]. The source of this discrepancy is a mystery, but potentially due to differences in regolith composition, production processes and rates, transport mechanisms, and/or loss processes. Temperature variation across the Hermean surface is significant—from 100K on Mercury's darkside and within permanently shadowed regions to 700K within the nearside equatorial regions. Thus, measurement of the thermal-dependence of ejection parameters is of high importance for understanding Mercury's exosphere kinetics, especially with BepiColumbo on the horizon.

In this work, we investigate the effect of regolith temperature on adsorbed potassium ejected from mineral surfaces by solar-wind ions, using X-ray photoelectron spectroscopy (XPS) and 4 keV He^+ to quantify the decrease in surface K concentration as a function of ion fluence. Helium is an important component of the solar wind, due to its larger sputtering yield in comparison to protons [5]. K sputtering cross-sections will be compared with previous measurements for Na [6].

Experimental Methods: Ilmenite, characterized by X-ray powder diffraction, was cut with a diamond saw, then cleaned with acetone and methanol prior to transfer into the ultra-high vacuum chamber (~2 x 10^{-10} Torr). The sections were first characterized with XPS (PHI Versaprobe III) and then sputter cleaned with 4 keV He^+ to remove surface and atmospheric contaminants. Potassium was subsequently evaporated *in situ* on to the clean ilmenite (~29 °C) using a K-metal dispenser from SAES Getters, for 30 minutes at an evaporation current of 6A (the dispenser temperature is ~750 °C). Using a spot size of 200 μm and a pass energy of 140 eV, XPS was used to determine the surface composition before and after potassium evaporation.

The potassium-coated ilmenite was irradiated with 4 keV He^+ at a flux of ~7 x 10^{12} He^+ cm^{-2} s^{-1}, and XPS measurements were performed at different fluences (at

the order of 10^{13} - 10^{17} He^+ cm^{-2}). Reductions in surface potassium concentrations were quantified as a function of fluence (ions cm^{-2}). The ion beam was at 60° incidence with respect to the surface normal, and was rastered across an area of 8mm x 8mm (much larger than the analysis area) to assure uniform irradiation. A low-energy electron flood gun was used during irradiation to mitigate surface charge.

XPS measurements were performed with the detector at 45° with respect to the surface plane, providing quantitative surface compositions within a depth of ~5 nm. To investigate the thermal effects, the sample temperatures during irradiation were held at 110 K, 300 K, and 400 K. Ilmenite sputtering cleaning, K deposition, XPS measurements, ion irradiation were all performed *in-situ* without exposure of the samples to atmosphere.

Results: A representative XPS spectrum for ilmenite shows O, Fe, Ti, and C on the surface along with small amounts Mg, Al, Si and F from sample impurities or substitutions (Fig. 1a). C from atmospheric contamination was removed by sputtering cleaning (Fig. 1b). A thirty minute evaporation resulted in ~30 atomic % of surface potassium (Fig. 1c).
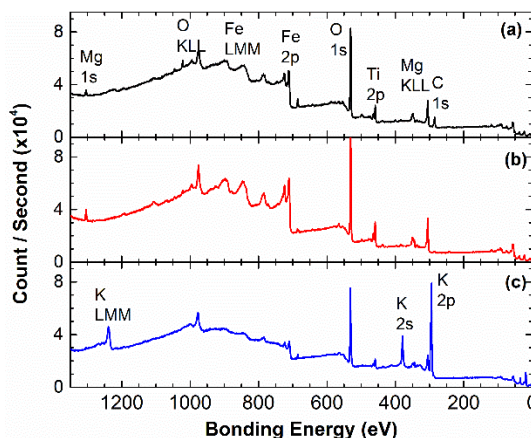

Fig. 1 Representative XPS spectra of ilmenite a) before and b) after sputter cleaning, and c) with K-coated. The photoelectron lines identify the element and the energy of the ejected electron. The Fe-2p3/2 photoelectron peak at a binding energy of 710.5 eV was used to determine the amount of surface iron, while the K-2p photoelectron doublet at ~297 and 294 eV was used to determine the amount of surface potassium. The KLL structures are due to the Auger process following the creation of a K-shell hole.

Fig. 2 shows the ratio of surface potassium to iron (K/Fe) as a function 4 keV He fluence at different temperatures. The variation in ratio is a function of K-deposition, while the exponential slope of the curves can be used to determine the sputtering cross-section and the order of depletion mechanisms. The cross-section can then be used to find the K-yield if the surface coverage is known.
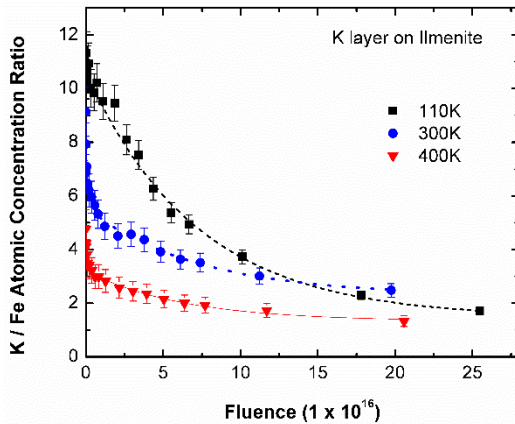
Fig. 2 *Decrease in the surface concentration of evaporated potassium (K) relative to iron (Fe) vs. fluence of 4 keV He$^+$, with samples at different irradiation temperatures. The K was evaporated onto sputtering-cleaned ilmenite thin sections at 300 K, and the K-coated sections were cooled/heated to the desired temperatures prior to irradiation. The dashed-lines are fittings to the data. See Discussion for details.*

Discussion: The dependence of sputtering on sample temperature has been noted previously for alkali halides and condensed gases [7]. For K adsorbed on ilmenite at low temperatures, the concentration curve for 110 K follows a single exponential decay, and provides a depletion cross section (decay constant) of ~1.4 x 10^{-17} cm^2 atom^{-1} (Fig. 2, black-dashed line). Instead of a single exponential decay, results for irradiation at temperatures of 300 K and 400 K can be fitted to a double exponential decay. We find an initial decay constant of ~9.9 x 10^{-16} and 4.3 x 10^{-16} cm^2 atom^{-1} for 400 K and 300 K, respectively, with a second decay constant of 1.6 x 10^{-17} cm^2 atom^{-1} and 1.4 x 10^{-17} cm^2 atom^{-1} for each temperature. The initial decay constant is about two orders of magnitude larger than the second one, and become faster at higher temperature. The second decay constants are similar to that at 110 K. We note that the measured potassium depletion cross sections at 300 K are similar to those for depletion cross sec sections of sodium deposited ion ion-roughened plagioclase (labradorite, albite, and anorthoclase) [6].

Besides sputtering by the ions, other processes may contribute to the measured depletion cross section. Interactions with the He$^+$ result in mixing of the surface potassium with the bulk materials within the ion penetration depth, typically a few hundreds of nm, at the compensation of reduced potassium within the XPS information depth. Diffusion and segregation of potassium - induced by projectiles within the ion range, increasing temperature, etc. – may also play a role.

References: [1] R. J. Vervack, Jr, et al. (2010), *Science* 329(5992), 672-675; [2] A. Doressoundiram et al. (2010), *Icarus* 207(1), 1-8; [3] R. M. Killen et al. (2010), *Icarus* 209(1), 75-87; [4] A. E. Potter and T. H. Morgan (1988), *Icarus* 67(2), 336-340; [5] M. J. Schaible et al. (2017), *JGR: Planets* 122, 1968-1983; [6] C. Dukes, et al. (2011), *Icarus* 212(2) 463-469;[7] R. E. Johnson and R. Evatt (1980), *Radiation Effects* 52, 187-190.