ELECTRON STIMULATED DESORPTION AS A SOURCE MECHANISM FOR IONS IN MERCURY'S SPACE ENVIRONMENT. Thomas M. Orlando[1], Ann L. Sprague[2], Greg A. Grieves[1], David Schriver[3], Pavel M. Trávníček[3,4], Jason L. McLain[1], and Richard D. Starr[5]. [1]School of Chemistry and Biochemistry and School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0400 (Thomas.orlando@chemistry.gatech.edu), [2]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721-9002, [3]Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA, 90024, [4]Astronomical Institute, ASCR, Prague, [5]Physics Department, The Catholic University of America, Washington, DC 20064.

Introduction: An overlooked and perhaps important mechanism for releasing material to Mercury's neutral and ionized exosphere and near- space environment is electron-stimulated desorption (ESD). This is a well known process that involves the excitation (often with ionization) of a surface target followed by charge ejection, bond breaking, and ion expulsion due to the resultant Coulomb repulsion. While considered for the lunar exosphere [1] and mentioned as a possible source process for Mercury's exosphere [2], the role of electron- stimulated desorption processes has not been discussed in the literature with respect to Mercury nor has it been adequately studied or quantified. Impinging energetic electrons that leak through the magnetosphere or reach the surface during flux-tube transfer events (FTEs) may induce significant surface material removal [3]. Given the range of energy of impacting electrons and the wide band-gap nature of the minerals, the departing material may also be primarily ionic. The role of 10 eV – 1 keV electron stimulated desorption and dissociation in "space weathering" the regolith can be significant. We explore the likelihood that the exosphere is derived in part from molecular neutrals and ions released from the regolith by ESD. We describe laboratory ESD experimental and hybrid magnetospheric modeling results that are suggestive of the source mechanism for heavy ions observed by the Fast Imaging Plasma Spectrometer (FIPS) on MESSENGER during the first flyby of Mercury [4]. The wide spectrum of mass-to-charge ratios of the ions measured clearly indicated that not all ions were photoionization products of Mercury's neutral exosphere.

Experimental approach: The ultrahigh vacuum (UHV; base pressure ~5×10^{-10} Torr) system used in this study consists of a load-lock region for sample introduction, a rotatable cryogenically cooled sample mount, a time-of-flight (ToF) mass spectrometer, a quadrupole mass spectrometer (QMS), and a pulsed low-energy electron (LEG) gun [5]. This custom-built UHV system is ideal for investigating nonthermal desorption and material removal processes on heterogeneous surfaces and interfaces under Mercury's conditions. Specifically, we use pulsed (100 ns; 20-100 Hz) low-energy (5 -500 eV) electron beams that typically supply time-averaged fluxes of 10^{10} to 10^{14} electrons/cm^2 s to cryogenically cooled glasses, minerals, or molecular solids targets under very well controlled vacuum and coverage conditions. Since the beam is on the order of a few mm and the number density of surface sites is 10^{15} cm^2, there are 10^{-3} electrons per surface site. The pulsed-beam method provides an electron flux that is low enough to remove any artifacts from surface charging, and there is no heating. Therefore, the desorption events are due solely to electronic transitions. An important aspect of these experiments is that the electron gun energy can be varied from 5 eV to 500 eV. The uncertainty in the beam energy is about 1eV since the substrate work function is not well known for minerals and insulating materials.

The Na-bearing silicate that we used in our first experiments was manufactured from reagent-grade Na_2CO_3 and SiO_2. These were ground in an agate mortar under ethanol and melted in a crucible at 1250 ^oC. The sample was ground to 1 mm thickness, cleaned with methanol and mounted in the UHV chamber. The sample was heated to 385K to drive off surface contaminants and water and this temperature was maintained during the ESD experiments. To characterize the quality and chemical composition of the mounted substrates, we used Fourier transform infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), and optical reflection.

The ions produced and released as a result of electron impact are measured using either a QMS or ToF mass spectrometer. If the ion yield is high enough, the ToF can be operated in a field–free mode to measure directly the departing ion kinetic energies. Time decay curves allow us to measure electron beam-induced removal cross sections and rates directly. The data to be presented are integrated total yields vs. incident electron energy. The ions were collected at a near normal take-off angle. Our estimated detection sensitivity brackets the threshold data to desorption events that have ESD cross sections at or above 10^{-23} cm^2.

Electron Fluxes and Energy Distributions: There are few measurements of the flux and energy distribution of electrons impacting Mercury's surface. Mariner 10 measurements obtained with particle and field instruments indicated high-energy electron impacts on the night side [6]. MESSENGER's X-ray spectrometer (XRS) measured several count-rate spikes before and after the closest approach of each flyby. The spectral signatures in these measurements

are clearly those of electrons interacting in the XRS detector materials [7].

Description and Heritage of Magnetospheric Model: For this study, we use results from a three dimensional (3-D) hybrid model to simulate conditions of the first and second Mercury flybys and to compute electron impact flux and energy distribution. We produce a kinetic description of ions and a fluid model of electrons [8]. The overall structure of Mercury's magnetosphere, upstream bow shock and magnetosheath are qualitatively similar to those of Earth. The model is designed to examine waves and instabilities generated by ion temperature anisotropy and plasma flow. The model predicts several magnetospheric features observed in the MESSENGER magnetospheric measurements [9], two of which are a velocity shear near the magnetopause that can lead to formation of vortex-like structures and a region in the magnetic cavity close to the planet's equatorial plane filled with ions much hotter than the solar wind protons.

Computations for magnetic field conditions during the first flyby indicate that electron precipitation is highly focused into a relatively small region in the northern hemisphere at ~ 60°N latitude near noon. The computed flux is ~ 10^{10} per cm^2 with typical energy of 0.5 keV. Regions where energies are higher, up to 2 keV, are more widespread but with an order of magnitude lower flux (~10^9 per cm^2). For conditions during the second flyby, precipitation occurs predominantly at the equator, around noon to dusk and then with a hot spot near dawn. At those locations the precipitating energies (1-5 keV) are higher than for the first flyby but the flux is about the same ~10^{10} per cm^2.

Results--ESD of H^+, Na^+, and O^+ from Na- and Na_2O- containing silicates: Direct yields of Na^+, O^+, and H^+ from electron irradiated silicates containing Na and trace amounts of water have been determined. Note that Si^+ was also observed above 100 eV excitation energy but was a minor product. The relative ion abundances observed from this sample using 100 eV electrons was $H^+ > O^+ > Na^+ > Si^+$. Na^+ and O^+ data were obtained using an electron flux of 2×10^{14} electrons/cm^2 s, while the much larger H^+ signals allowed data to be obtained at $0.4x10^{14}$ electrons/cm^2 s. The ion yields showed a linear dependence on electron flux implicating a one-electron single collision initial excitation mechanism.

The Na^+ signal intensity as a function of electron energy shows signal onset at ~ 45 eV and a major threshold between 90 and 95 eV. The O^+ signal vs. electron energy shows two thresholds: the initial weak threshold at 18 eV and a second major threshold near 30 eV. The H^+ threshold is at 25-30 eV, and the yield increases monotonically with increasing energy.

Discussion: It is well known that ESD of ions from wide band-gap materials can be initiated by Auger decay of deep valence, shallow core and/or deep core holes. The process generally consists of hole production, Auger decay, reversal of the Madelung potential, and ion expulsion due to the resultant Coulomb repulsion. The major threshold for Na^+ removal near 90 eV can be attributed to ionization of the Si 2p level. This hole is filled via Auger decay using charge density in the oxygen 2p level. Since energy is gained in the Auger decay, an LVV electron is emitted leaving behind an O^+ ion. This reversal of the Madelung potential leaves the Na^+ in the vicinity of an O^+ and Si^+ site. All of these ions can be removed at this energy, but the number of bonds that need to be broken is the least for Na. The primary O^+ thresholds near 30 eV can be attributed to excitation/ionization of the O 2s level in SiO_2. Though we have worked at temperatures where chemisorbed water should not exist, the surface likely contains many terminal hydroxyl groups. Hydroxyl-rich surfaces are known to be unstable to electron-beam irradiation. The H^+ threshold energy at 25 eV is in the correct energy region for O 2S excitation in the terminal OH groups. Excitation in the SiO_2 produces O^+, whereas excitation of the Si-OH produces H^+. We can not rule out some contribution from two-hole excitations localized on Si-H sites.

It is important to note that the Coulomb explosion resulting from the Auger cascading events ejects the ions with kinetic energies typically between 3 and 10 eV. This is the energy necessary to prevent any recapture by the surface and assures that the ions become "injected" into the exospheric environment.

We suggest here, that ESD removal of ionic molecules provides a good explanation for some of the ions observed by FIPS. Also, the high distributions of Ca, and Mg observed from MESSENGER during the flyby observations [10] could result from photoionization of the ionized molecules or neutral counterparts.

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