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# The lunar surface-exosphere connection: Measurement of secondary-ions from Apollo soils

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A B S T R A C T

Low energy secondary ions ejected by the solar wind are an important component of tenuous exospheres surrounding airless bodies, since these ions carry information on the planetary surface composition. In this work we examine the dependence of secondary-ion abundance, as a function of energy and mass, on surface composition. The surface compositions of two Apollo soils (10084 and 62231) and a synthetic Corning glass lunar simulant were measured with X-ray photoelectron spectroscopy and correlated with the spectra of secondary-ions ejected from the same soils by 4 keV He ions. XPS spectra for lunar soils show that the surface compositions are similar to the bulk, but enriched in Fe and O, while depleted in Mg and Ca. 4 keV He irradiation on the lunar soils and a glass simulant preferentially removes O and Si, enriching the surface in Al, Ti, Mg, and Ca. Secondary-ion species ejected from the Apollo soils by 4 keV He include: $Na^+$, $Mg^+$, $Al^+$, $Si^+$, $Ca^+$, $Ca^{++}$, $Ti^+$, and $Fe^+$, and molecular species: $NaO^+$, $MgO^+$ and $SiO^+$. Secondary ion energy distributions for lunar soil 10084 and 62231 rise rapidly, reach a maxima at ~5 eV for molecular ions and $Na^+$, ~7.5 eV for $Fe^+$, and ~10 eV for $Mg^+$, $Al^+$, $Si^+$, $Ca^+$ and $Ti^+$, then decrease slowly with energy. We present species-dependent relative conversion factors for the derivation of atomic surface composition from secondary-ion count rates for 4 keV He irradiation of lunar soils 10084 and 62231, as well as the Corning glass lunar simulant.

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## 1. Introduction

The abundance of low energy ions in the tenuous atmospheres near the surface of airless planetary bodies such as the Moon, Mercury, and asteroids should be largely indicative of the planetary surface elemental composition (Johnson and Baragiola, 1991). This is due to the negligible interaction of sputtered particles with other species in an exosphere. For the Moon, the exosphere is defined as the region of space bounded by the lunar surface and reaching an altitude of ~100 km. The atomic density of is so low, $<10^6\ cm^{-3}$, that no physical or chemical interaction can occur between particles which are retained in the lunar envelope by gravity or lost to space, depending on velocity and trajectory. The lunar exosphere is composed primarily of species from the lunar surface: neutrals atoms desorbed by solar photons (PSD) and electrons (ESD), sputtered by solar wind ions, thermally desorbed, ejected during meteoritic impact, and derived from radioactive decay. At this time (prior to LADEE) definitive observations of neutral atoms in the lunar exosphere have been limited to Ar, He, $H_2$, K, Na, O, $^{210}Po$ and $^{222}Rn$ (Hodges, 1973; Hoffman et al., 1973; Potter and Morgan, 1988; Vorburger et al., 2014; Bjorkholm et al., 1973; Gorenstein and Bjorkholm, 1973; Lawson et al., 2005). Recent observations by the Lunar Reconnaissance Orbiter's Lyman-Alpha Mapping Project (LAMP) confirmed the presence of He (Stern et al., 2012; Feldman et al., 2012) and $H_2$ in the lunar exosphere (Stern et al., 2013), while Chandrayaan-1's Energetic Neutral Analyzer (CENA) has reported the first observation of neutral O, presumably sputtered from the lunar surface by the solar wind (Vorburger et al., 2014).

The ionic component of the lunar exosphere is derived from a number of processes: photo-ionization of sputtered or desorbed neutral atoms, solar wind primary ions, and secondary ions generated from solar wind impact. The sputtered ion species are important, as their abundance reflects the lunar surface composition. In addition, sputtered ions may also continue to interact with the lunar surface by charging or neutralizing regions of the regolith and by self-sputtering (Poppe et al., 2013). These ions can be observed locally by mass spectrometers that allow the identification of charged exospheric components. Measurements from AMPTE, WIND, and SELENE have identified $Ar^+$, $Na^+$, $K^+$, $Si^+$, $Al^+$, $C^+$, and $O^+$ plus solar wind ions (Hilchenbach et al., 1993; Stern, 1999; Yokota et al., 2009, 2014). Recent measurements by LADEE of the lunar ion component are expected to add to this list.

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Secondary ion/atom emission by sputtering is a physical process which occurs when energetic (>20 eV) primary ions impact atoms on a surface, transferring energy and momentum such that one (or more) of the surface atoms or molecules are ejected. In the laboratory, mass analysis of secondary ions (positive or negative) ejected by incident energetic (~keV) ions is termed secondary ion mass spectroscopy (SIMS) and is often used to infer surface specific composition. Since secondary ion intensities (ion yields) cannot be simply matched directly to surface composition, but are dependent on primary ion type, atom ionization potential, and the local sample matrix, it is common to use calibration standards of known composition that closely match the sample of interest to enhance the quantitative information that can be extracted from SIMS.

Positive SIMS spectra for keV $H^+$, $He^+$, $Ne^+$ and $Ar^+$ impact on lunar soil *simulants* confirm that many ion species, beyond those identified in the lunar atmosphere, are ejected at significant fluxes and may exist in the lunar exosphere (Elphic et al., 1991). Simulants, however, have very different surface characteristics than lunar soils, which contain grains of different morphology and composition, as many lunar grains have vapor deposited and radiation altered rims. To relate secondary ion emission to surface composition of Apollo soils, we performed experiments using 4 keV $He^+$ on two mature lunar soils where we measured secondary ion mass and energy spectra and correlated to XPS measurements of elemental surface composition in ultrahigh vacuum (UHV).

## 2. Experimental procedure

For this study, two mature lunar soils, Apollo 16 highland 62231 ($I_s$/FeO = 91) and Apollo 11 mare 10084 ($I_s$/FeO = 78), were irradiated with 4 keV $He^+$ in a UHV chamber (<$10^{-9}$ Torr) at room temperature (~295 K). The entire allocated lunar soil size fraction (<1 mm) was used without further sieving in order to provide a particle size distribution analogous to the lunar surface. We note that optical and electron microscope images of the samples show that the larger lunar grains are loosely coated with much smaller grains (<10 μm), enhancing the small size grain fraction in the SIMS and XPS analyses. Highland 62231 soil, collected from the rim of Buster Crater, is compositionally typical of the analyzed highland soils, with a $Al_2O_3$:FeO ratio falling toward the high end of the distribution. Mare 10084, a fine-grained basaltic soil with agglutinate and glassy inclusions, lies in the low $Al_2O_3$:FeO range of the standard mare compositional range for lunar soils. Lunar soil samples were prepared by sprinkling uncompacted soil onto UHV-compatible double-sided carbon tape fixed to a Cu mount. Good coverage (>98%) of the carbon tape was ensured by multiple successive coating of soil onto the tape and subsequent observation under an optical microscope.

A Physical Electronics Inc. (PHI) 04-303 ion gun, with an electron bombardment source, is mounted on the mu-metal lined analysis chamber and directed ions toward the sample at 42° from the sample normal (Fig. 1). However, since the soil surface is topographically irregular, local impact and collection angles varied. Ions were rastered $6 \times 6$ mm$^2$ across the sample surface to cover the entire ion mass-spectrometer entrance aperture, as well as to ensure uniform irradiation across the entire XPS analysis area. Total primary beam current, measured on the sample without bias, was ~4 μA.

Secondary ions, ejected from the outermost 1–2 monolayers (~6 Å) of the sample by the 4 keV primary He ions, were collected at 60° from the sample normal (in the forward direction) and measured by a Hiden Analytical EQS mass spectrometer equipped with a high-transmission 45-degree sector-field ion-energy analyzer (Fig. 1). For this study, positive SIMS spectra were measured at
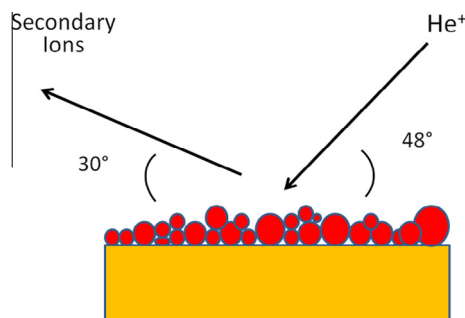


**Fig. 1.** Experimental geometry for secondary ion mass spectrometry with 4 keV He ions. Surface composition (~5 nm) for the same sample region is obtained *in situ* by X-ray photoelectron spectroscopy.

ejected ion energies from 2 to 36 eV, a range where the instrument transmission is expected to be constant as a function of energy. However, quadrupole transmission does vary inversely with mass, passing light mass ions more readily (i.e. Batey, 1987), and requires a correction for absolute measurements. These corrections are not included in the raw spectra presented. The extraction lens voltages were optimized for ions of Mass 27 ($Al^+$) before collecting spectra. Because the lunar soils charged significantly under ion bombardment, the sample surface was charge neutralized during SIMS data collection using low energy (⩽4 eV) electrons. Secondary ion mass spectra were obtained from 0.4 to 100 amu, at a resolution of 0.1 amu. Each spectrum was taken in less than 10 min, and averaged over 10 cycles. Secondary ion energy spectra were collected at masses: 23 ($Na^+$), 24 ($Mg^+$), 27 ($Al^+$), 28 ($Si^+$), 40 ($Ca^+$ or $MgO^+$), 48 ($Ti^+$), 56 ($Fe^+$), and 39 ($NaO^+$ or $K^+$) amu from 0 to 100 eV in steps of 0.2 eV, at a 0.5 s dwell time and averaged over 8 cycles. Surface charge neutrality was maintained with the electron flood gun.

The secondary ion flux was compared with the surface elemental composition of the samples, measured *in situ* using X-ray photoelectron spectroscopy (XPS). This technique provides compositional information from the outermost surface (~1–5 monolayers) of a sample. While the XPS depth sensitivity is slightly less than that for secondary ions, both techniques sample the surface region of the vapor-deposited rims (~60–100 nm) surrounding most lunar grains (Keller and McKay, 1997). By comparing the intensities of the photoelectron peaks, adjusted with empirical instrumental sensitivity factors (Wagner, 1983), the elemental atomic concentrations can be determined with a sensitivity of ~0.1% (atomic percent). Al X-rays (1486.6 eV) eject photoelectrons from sample atoms; their kinetic energy is measured using a PHI 560 double-pass cylindrical electron-energy analyzer (CMA) (Dukes et al., 1999; Loeffler et al., 2008). The spectrometer was operated at a fixed pass energy: 200 eV for survey spectra and 50 eV for high-resolution spectra, providing an instrument energy resolution of 3.2 eV and 0.8 eV, respectively. The measured kinetic energy of the photoelectron is given by the atomic binding energy of the electron, the X-ray energy and the spectrometer work function as: KE = $\gamma$ − BE − $\varphi_s$. Determination of electron binding energy provides both atom identification and chemical bonding information. During the measurements, the electron flood gun was used to suppress positive surface charge due to photoelectron emission. The flood gun parameters employed for XPS measurement were identical to those used for the corresponding secondary ion energy spectra. For all samples XPS analysis was done before and after $He^+$ irradiation.

To calibrate the measurement of secondary ion intensity using the Hiden EQS quadrupole, we use two standards: a Corning glass lunar simulant section and synthetic forsterite powder. The synthetic lunar glass simulant, designed for NASA's Johnson Space